Waste Management 200 (2025) 114767

Contents lists available at ScienceDirect

Waste Management

journal homepage: www.elsevier.com/locate/wasman

Research Paper

The fingerprint of pesticides in agricultural used polyethylene

Gabriela Castro [a,*], Victoria Fernández-Fernández [a], Miguel Cobo-Golpe [a], María Ramil [a], Enrique Blázquez-Blázquez [b], María L. Cerrada [b], I. Bernabé [c], J. Martínez Urreaga [c,e], M.U. de la Orden [d,e], Isaac Rodriguez [a]

[a] Department of Analytical Chemistry, Nutrition and Food Sciences. Aquatic One Health Research Center (ARCUS). Universidade de Santiago de Compostela 15782 Santiago de Compostela, Spain
[b] Institute of Polymer Science and Technology (ICTP-CSIC), Juan de la Cierva 3, 28006 Madrid, Spain
[c] Department of Industrial and Environmental Chemical Engineering, E.T.S.I. Industriales, Universidad Politécnica de Madrid, Spain
[d] Department of Organic Chemistry, Facultad de Óptica y Optometría, Universidad Complutense de Madrid, Spain
[e] Research Group "Polímeros: Caracterización y Aplicaciones" (U. A. del ICTP-CSIC), E.T.S.I. Industriales, Universidad Politécnica de Madrid, Madrid, Spain

ARTICLE INFO

Keywords:
Agricultural plastic waste
Polyethylene
Pesticides
Recycling
Leaching
Thermal degradation

ABSTRACT

The widespread use of polyethylene (PE) materials in agriculture through mulch films, tunnels, greenhouse covers, irrigation pipes and tying tapes has been instrumental in increasing crop productivity and reducing water demand. However, it raised concerns regarding the interaction between PE and pesticides sprayed on crops. This research strives to study the fingerprint of pesticides in agricultural PE by analyzing new items, end-of-life agricultural plastics and a range of samples corresponding to the recycling of aged PE, from sized and washed flakes to second-hand pellets and plant protection tubes elaborated from recycled plastic. Total concentrations determined for a selection of fungicides and insecticides in the abovementioned materials varied between 4.7 ng g^{-1} and 4179 ng g^{-1}, with the fungicides cyprodinil and difenoconazole showing the highest concentrations. Furthermore, transformation products of pesticides phased out more than 40 years ago, e.g., *p,p'*-DDE, were found in some PE items. The survival of pesticides at temperatures above the melting point of this polymer was confirmed in laboratory-scale melting experiments, as well as through the analysis of second-hand pellets. Experiments carried out using pesticide-polluted dripline pipes confirmed the migration of these compounds from PE to flowing water.

1. Introduction

Plastic wastes are recognized as a significant hazard to environmental biodiversity and ecosystem function (Boughattas et al., 2021; Huang et al., 2021; Lwanga et al., 2023). Debris generated from the degradation of polymeric materials in the environment leads to the formation of meso-, micro- and nanoplastics, which can act as both a sink and a source of different chemicals. In the first case, these substances are concentrated by plastic debris from the surrounding environment, particularly within the aquatic system (Atugoda et al., 2021; Santana-Viera et al., 2021). In the latter case, plastics might leach the additives employed in their initial formulation and manufacturing, as well as the species absorbed during their lifespan (Li et al., 2016). In general, identifying the source of organic pollutants associated with microplastics collected from the environment remains a complex challenge (Elseblani et al., 2023).

Agriculture, particularly horticulture, employs huge amounts of various types of plastics, from mulching and greenhouse films to irrigation pipes and a variety of small size items (e.g., tying tape, synthetic raffia, and trellising clips) (FAO, 2021). Polyethylene (PE) type polymers represent more than 80 % of the plastic employed in horticulture (Castillo-Díaz et al., 2021; Ramos et al., 2015). For instance, between 70 and 80 Kg of PE mulching film are employed per ha of farmland annually (Huang et al., 2020) and their mean lifetime stays around 6–8 months (Ramos et al., 2015). In intensive agricultural regions, such as the Southeast of Spain, plastic waste generation exceeds 1 tonne per ha and year (Castillo-Díaz et al., 2021), with the majority of the waste generated being low-density polyethylene (LDPE).

During their lifespan, agricultural plastics are directly in contact with pesticides applied to crops (e.g., greenhouse covers), as well as with

* Corresponding author at: Department of Analytical Chemistry, Nutrition and Food Sciences. Aquatic One Health Research Center (ARCUS). Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Spain.
E-mail address: gabriela.c.varela@usc.es (G. Castro).

https://doi.org/10.1016/j.wasman.2025.114767
Received 6 December 2024; Received in revised form 21 March 2025; Accepted 22 March 2025
Available online 29 March 2025

those present in the topsoil, which is the case of mulching films (Nerín et al., 1996). Batch experiments have demonstrated the higher affinity of PE, compared to other polymers, to concentrate moderate polar and non-polar pesticides not only from aqueous samples (Lan et al., 2021; Wang et al., 2020b), but also from soil (Wu et al., 2022). Sorption of pesticides in PE increases their persistence, slowing down the rate of key degradation routes and controlling their dissipation in other environmental compartments (Nerín et al., 1996; Ramos et al., 2015). Moreover, interaction between some pesticides sprayed on crops and PE films shortens the useful life of this material under outdoor conditions (Picuno et al., 2022), and thus, increasing the annual consumption of PE in agriculture.

The collection and disposal of aged plastics at recovery centers is the first step to prevent their fragmentation in agricultural fields. Apart from landfilling and incineration, PE wastes can be employed as a source of energy and biochar, through co-pyrolysis with biomass (Seah et al., 2023); or recycled and used as raw material to produce new goods, either to be employed in agriculture or in other applications, such as building materials (Cascone & Gagliano, 2022; Madrid et al., 2022; Martínez Urreaga et al., 2020). Recycling of PE, and in general any other thermoplastic, arises as the most convenient choice attending to environmental sustainability and operational costs. The process involves mechanical sizing, washing, and extrusion, resulting in the production of second-hand pellets. Currently, the behavior of pesticides associated to end-of-life PE during production of second-hand pellets, and their potential transfer to new materials formulated from these pellets remain largely unknown.

In this context, the aim of the current research was to investigate the fingerprint of pesticides in PE items employed in agriculture. To this purpose, different types of samples were analyzed for pesticide residues, including commercially available mulching films, tying tapes and irrigation pipes, before being used in agricultural fields; washed PE flakes obtained from end-of-life agriculture films before extrusion; and second-hand PE pellets obtained by extrusion of the flakes. Additionally, the concentration of selected pesticides in ad-hoc items (plant protection tubes), elaborated from thermal extrusion of virgin and second-hand PE pellets was assessed. The stability of pesticides during the thermal treatment of second-hand PE pellets, and their release from irrigation pipes to water were also studied through laboratory-scale experiments.

2. Materials and methods

2.1. Standards and solvents

Analytical standards of 41 pesticides, including fungicides and insecticides, were acquired from Sigma-Aldrich (Milwaukee, WI, USA) and Dr. Ehrenstorfer GmbH (Augsburg, Germany). Isotopically labelled standards (SSs, either deuterated or ^{13}C species) were obtained from Sigma-Aldrich and Toronto Research Chemicals (North York, Canada). Selection of target compounds was based on information obtained from farmers, consumption data provided by the Spanish Ministry of Agriculture, and previous publications (Cobo-Golpe et al., 2024). Table S1 summarizes the information of the target analytes considered in the current study.

Dichloromethane (DCM, 99.8 %), hexane (Hex) and *iso*octane were purchased from VWR chemicals (Radnor, PA, USA). LC-MS grade methanol (MeOH, 99.9 %), acetonitrile (ACN, 99.9 %) and LC-MS grade formic acid (FA) were acquired by Fisher Chemical (Madrid, Spain). Ultrapure water (18.2 mΩ cm^{-1}) was obtained from a Rephile Bioscience Genie equipment (Acton, MA, USA).

2.2. Sample collection and handling

Plastic debris were collected from different fields located in Galicia (Northwestern Spain), Murcia and Almería (Southeastern Spain) between 2023 and 2024. The residues collected were entirely agricultural plastics that had reached the end of their useful life, either as tying tapes, drip hoses, tunnels, transparent greenhouse covers and black mulching film. Information related to the type of sample, use and state is summarized in Table 1. The largest plastics, such as hoses and greenhouse covers were subsampled from the aged item, while plastic debris from tying tape or small pieces of aged black agricultural plastic were recovered from the cultivars. All samples were collected in HDPE jars

Table 1
Summary of polyethylene (PE) samples considered in this study.

Code	Type	Color	Use	State	Source
Film-1	Film	Transparent	Greenhouse cover	Aged	Murcia
Film-2	Film	Transparent	Greenhouse cover	Aged	Murcia
Film-3	Film	Transparent	Greenhouse cover	Aged	Galicia
Film-4	Film	Transparent	Greenhouse cover	Aged	Galicia
Film-5	Film	Transparent	Tunnel cover	Aged	Murcia
Film-6	Film	Black	Mulching	Aged	Almería
Film-7	Film	Transparent	Mulching	Aged	Almería
Film-8	Film	Transparent	Mulching	Aged	Almería
Tying tape-1	Tape	Green	Canopy holder	Aged	Galicia
Tying tape-2	Tape	Green	Canopy holder	Aged	Galicia
Tying tape-3	Tape	Green	Canopy holder	Aged	Galicia
Tying tape-4	Tape	Green	Canopy holder	Aged	Galicia
Tying tape-5	Tape	Green	Canopy holder	Aged	Galicia
Tying tape-6	Tape	Green	Canopy holder	Aged	Galicia
Tying tape-7	Tape	Green	Canopy holder	New	Retail market
Tying tape-8	Tape	Green	Canopy holder	New	Retail market
Film-9	Film	Black	Mulching	New	Retail market
Film-10	Film	Black	Mulching	New	Retail market
Irrigation-1	Pipe	Black	Irrigation	New	Retail market
Irrigation-2	Pipe	Black	Irrigation	New	Retail market
Drip hose-1	Pipe	Black	Irrigation	New	Retail market
Drip hose-2	Pipe	Black	Irrigation	New	Retail market
Drip hose-3	Pipe	Black	Irrigation	New	Retail market
Drip hose-4	Pipe	Brown	Irrigation	New	Retail market
Flakes	Film	Transparent	Source for second-hand pellets	Aged	Recycling plant
Pellet-1	Pellets	Black	Second-hand raw material	New	Recycling plant
Pellet-2	Pellets	Grey	Second-hand raw material	New	Recycling plant
Pellet-3	Pellets	Grey	Second-hand raw material	New	Recycling plant
Tube-1	Guard tube	Transparent		New	Ad-hoc prepared item
Tube-2	25 % recycled PE	Grey		New	Ad-hoc prepared item
Tube-3	50 % recycled PE	Grey		New	Ad-hoc prepared item
Tube-4	100 % recycled PE	Grey		New	Ad-hoc prepared item

using nitrile gloves.

Samples of different kinds of agricultural plastics, not exposed to the environment or agricultural fields, were acquired from local distributors (Table 1). Furthermore, in order to assess the potential transfer of pesticide residues from second-hand pellets to new PE articles, a private company, whose name has been anonymized, provided us with PE protection tubes made of different percentages of recycled pellets (25 %, 50 % and 100 %).

Once in the laboratory, aged and new materials were rinsed with ultrapure water to remove particles of soil and dust attached to the surface of the material. Then, samples were allowed to dry in a hood at room temperature, and finally sample size was reduced to improve their homogeneity. Samples of plastics in a film format (tying tape, mulching and greenhouse covers) were cut with scissors in pieces of 1 cm x 1 cm. Pellets and flakes, obtained from PE recycling plants, were employed as received. Irrigation pipes were cut in sections with a length of 5 mm. Ad-hoc PE guard tubes, produced from virgin and second-hand PE pellets, were cut in pieces of 5 mm x 5 mm before extraction. Samples were stored in glass tubes with Teflon-lined caps.

2.3. Sample preparation

The sample preparation for the extraction of 41 pesticides from PE plastic was optimized. For this purpose, two extraction techniques, ultrasound-assisted extraction (UAE) and Soxhlet, were tested. UAE was carried out with 0.5 g of sample and 10 mL of a mixture of DCM:Hex (50:50, v/v) and then subjected to ultrasound extraction during different periods of time (15 min and 8 h). After soaking, the supernatant was recovered, and the extraction was repeated using a fresh fraction of solvent. The combined extract was concentrated to almost dryness under a N_2 stream and reconstituted in 2 mL of MeOH:ACN. In the case of Soxhlet extraction, a representative sample of PE plastic ($\approx$ 4.0 g of ground plastic) was weighed out and placed into a cellulose thimble and subjected to Soxhlet extraction with 80 mL of a mixture of DCM:Hex (50:50, v/v), during 24 h. The obtained extract was concentrated to 10 mL under a gentle N_2 stream (at 35 °C). Thereafter, a 2 mL fraction of the extract was fortified with 25 ng mL^{-1} of a mixture of SSs and concentrated to near dryness under N_2. The final extract was reconstituted in 2 mL of MeOH:ACN (50:50, v/v) before analysis by UHPLC-MS/MS. Determination of *p,p'*-DDE was carried out by GC–MS, using a second fraction of Soxhlet extracts previously exchanged to *iso*octane. The deuterated analogue of the insecticide transformation product (*p,p'*-DDE-d_8) was used as SS. In both cases, UAE and Soxhlet, extraction experiments were carried out in triplicates.

2.4. Instrumental analysis

2.4.1. UHPLC-MS/MS

Determination of pesticides was performed by UHPLC-MS/MS with a Xevo TQD triple quadrupole mass spectrometer, containing a Z spray ESI source, and connected to an Acquity UPLC system, both acquired from Waters (Milford, MA, USA). Chromatographic separations were carried out in a Zorbax Eclipse Plus C_{18} rapid resolution column (2.1 × 50 mm, 1.8 μm) connected to C_{18} 2.1 mm i.d. Security Guard™ ultra-cartridge, supplied by Agilent and Phenomenex (Torrance, CA, USA), respectively. Ultrapure water (A) and ACN (B), both containing 0.1 % v/v FA, comprised the mobile phase, and were maintained at a constant flow rate of 400 μL min^{-1}. The UHPLC column and precolumn were kept at 40 °C. The mobile phase gradient was step-programmed as follows: Initial, 2 % B; 1.3–2.8 min, 50 % B; 6.4–7.5 min, 100 % B; 7.6–10 min, 2 % B. The injection volume was 1 μL.

The analytes were ionized under positive ionization mode (ESI +), apart from fludioxonil (FLU) that was ionized in ESI(−). Two MRM (Multiple Reaction Monitoring) transitions per chemical were monitored, being the most intense one (higher S/N ratio) considered as the quantification transition (Q1) and the second in intensity as the confirmation transition (Q2). Both transitions (Table S1) were monitored within a window of 60 s around the retention time of the analyte. The dwell time per transition was adjusted to obtain 12 points per peak, assuming an average baseline peak width of 4 s. Nitrogen was used as drying gas at the ionization source (450 °C at 1000 L $hour^{-1}$). Capillary voltage and collision energies were also optimized. Optimal values were achieved when the capillary voltage was maintained at + 1.50 kV and the cone voltage at 50 V.

2.4.2. GC-Q-MS

Quantification of *p,p'*-DDE was performed by GC-EI-MS using an Agilent 7890A gas chromatograph coupled to a quadrupole mass spectrometer (Agilent MS 5975C) operating in the single ion monitoring mode (SIM). Separations were carried out in a DB-5HT capillary column (15 m × 250 μm x 0.1 μm) acquired from Agilent operating at a constant carrier gas flow of 1.2 mL min^{-1} of Helium (99.999 %). The temperature of the GC oven was as follows: 80 °C (1 min), rate at 15 °C min^{-1} to 300 °C (12 min). The electron impact source (EI) and the quadrupole mass analyzer were set at 230 °C and 150 °C, respectively. One μL of extracts, previously exchanged to *iso*octane, and standards were injected in splitless mode with the injector temperature at 280 °C. The transfer line between the GC and the MS was also set at 280 °C. Quantification ions for DDE and DDE-d_8 were 318 and 326, respectively.

2.5. Plastic characterization using ATR-FT-IR

Plastic characterization was performed according to Castro et al. (Castro et al., 2024). Briefly, the identification of the type of plastic material was determined by infrared spectroscopy (IR) in the attenuated total reflectance mode (ATR). ATR-IR experiments were carried out in a Fourier transform (FT-IR) imaging system (Varian 670-FT-IR spectrometer), operating in transmittance mode (wavelength range 400–4000 cm^{-1}, 32 scans per spectra and resolution 4 cm^{-1}).

2.6. Thermal treatment and recycled materials elaboration

Mechanical recycling stands as the best alternative to dispose plastic wastes (Gu et al., 2017; Schade et al., 2024). The main steps of this process include washing, sorting, shredding, melting, and conversion into secondary raw materials, such as pellets, that can be used to produce new items (Schade et al., 2024). In this case, mixtures of agricultural PE waste, including greenhouse cover, tunnels, mulching film, and other minor products such as cable ties, were shredded and washed with water. The main polymer in this waste is LDPE, with minor amounts of linear LDPE (LLDPE) and traces of other polymers, such as polypropylene (PP) and ethylene–vinyl acetate (EVA) copolymer. The nature of this kind of materials has been previously described by Martínez Urreaga et al. (Martínez Urreaga et al., 2020). To evaluate the incomplete removal of pesticides during handling of end-of-life PE items, a set of samples (coded as recycling plant source in Table 1) were obtained from an anonymized recycling plant and analyzed. Recycled PE pellets were obtained by extrusion from the washed flakes. Guard tubes were obtained by extrusion from different mixtures of recycled PE and virgin LDPE (ALCUDIA® 2203F, supplied by Repsol YPF S.A., Spain). Additionally, to evaluate the removal efficiency of pesticides during the melting process, laboratory-scale tests were performed using the sample containing the highest pesticide concentrations (Pellet-2). For this purpose, 4 g of sample were wrapped in aluminum foil and heated in an oven at two different temperatures (150 and 200 °C) until complete melting, which occurred after 5 h.

2.7. Leaching experiments

The potential migration of pesticides from agricultural products to the surrounding environment was initially assessed through laboratory-scale batch experiments. For this, 4 g of the sample coded as Irrigation-1

(Table 1) were submerged in 40 mL of ultrapure water in a pre-cleaned glass vessel and subjected to continuous agitation using an end-over-end rotator for 5 days. Water samples (1-mL aliquots) were collected at different time intervals (24 h, 90 h, and 120 h), filtered through a 0.22 μm hydrophilic filter, fortified with the SS mixture, and ready for analysis.

Additionally, field experiments were carried out using a dripline pipe (10 m x 16 mm i.d., Drip hose-1, Table 1) connected to a water outlet allowing a continuous flow rate of 0.5 L h^{-1}. Pesticide leaching was investigated by collecting water aliquots from the outlet stream of the pipe at different times from 0.5 h to 24 h. One mL of the aliquots was filtered (0.22 μm hydrophilic filter), fortified with the mixture of SS, and ready for analysis. Series of leaching experiments were repeated in two different seasons (winter and summer of 2024) to assess the impact of temperature on pesticide leaching.

Levels of pesticides in water samples were determined by solid-phase extraction (SPE) on-line connected with the LC-QqQ-MS using the conditions reported elsewhere (Fernández-Fernández et al., 2023). Analysis of water samples generated in the above experiments covers the full set of pre-selected pesticides amenable to LC-ESI-MS analysis, but fludioxonil (FLU).

2.8. Quality assurance and quality control (QA/QC)

QA/QC proceedings were implemented during sample preparation and analysis to avoid contamination problems and to guarantee the accuracy of the data obtained during analysis of PE samples. To that aim, QA/QC involved: i) the use of glassware, previously rinsed with water and MeOH, during both the sample preparation and the storage of the final extracts; ii) the analysis of procedural blanks; iii) sample fortification with SSs to account for any losses during analysis; iv) all samples were analyzed in duplicate for analytical method performance purposes; v) solvent blanks and a standard of 25 ng mL^{-1} were analyzed every 15 samples to check for carry-over effects and instrumental sensitivity deviations, respectively.

3. Results and discussion

3.1. Characterization of plastic degradation

Plastic characterization was performed by ATR-IR to identify the type of polymer and to assess the degradation degree of the plastic, as well as the presence of inorganic contamination. The spectra of new and aged PE items are presented in Fig. 1. To better show the differences, the spectra have not been normalized and the individual spectra obtained for each item are presented in Fig. S1. All the samples considered in the present study were identified as PE. They exhibited the characteristic peak vibration bands at 2915 cm^{-1} attributed to $–CH_2$- asymmetric stretching, 2846 cm^{-1} ($–CH_2$- symmetric stretching), 1463 cm^{-1} ($–CH_2$- scissor bending), and 717 cm^{-1} ($–CH_2$- rocking) (da Silva & Wiebeck, 2022) remarked in green in Fig. 1. Spectra of aged PE (codes Film-2, Film-5, and Film-6), reveal the appearance of new absorption bands at bands at 3100–3600, 1720, 1640, 1020, 874, 524 and 466 cm^{-1} (remarked in brown, Fig. 1), which can be related to degradation processes (De La Orden et al., 2015; Gardette et al., 2013) and contamination. The weak and broad absorption appearing above 3000 cm^{-1} is assigned to hydroxyl and hydroperoxide groups. The bands centered at 1720 and 1640 cm^{-1} are usually assigned to carbonyl compounds (ketones, carboxylic acids, esters and lactones) and unsaturated compounds, respectively. Band centered at 1020 cm^{-1} reveals the presence of silicates, such as talc or kaolin, coming from the soil or from greenhouse covers, where they are used as additives for improving the greenhouse effect (Martínez Urreaga et al., 2020). The contribution of silicates from the soil to this band is important, which explains why the band is intense in aged PE items such as Film-2, Film-5, and Film-6, while it is weak in items that have not been exposed in the field such as Tube-1 and Irrigation-1. In the case of double-walled materials, such as plant protection tubes, separate analysis of the inner and outer surfaces might reveal a significantly higher band intensity at 1020 cm^{-1} on the outer layer, indicating more substantial contamination. Regarding the elimination of this inorganic contamination, it must be taken into account that silicates coming from the soil are located on the surface of the plastic waste, so they can be largely eliminated by means of demanding washing stages during the recycling process. However, particles firmly embedded in the surface cracks as well as those from additives present in the original plastics, which are found inside the material, cannot be effectively eliminated by washing processes. Nevertheless, the latter type of particles can be at least partially retained and eliminated by the extruder filter during the recycling process. Some weak bands observed between 1000 and 800 cm^{-1} can be assigned to unsaturated groups such as vinylidene (884 cm^{-1}). Absorption bands at lower wavenumbers, such as 524 cm^{-1} and 466 cm^{-1}, are attributed to

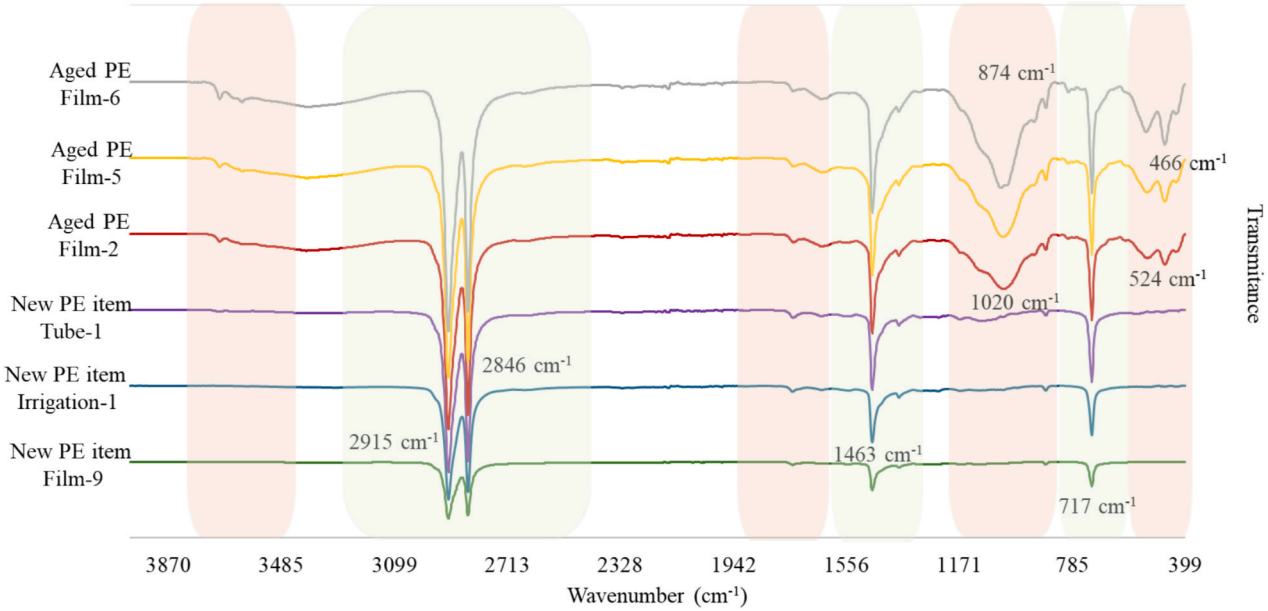

Fig. 1. ATR-IR spectra of new and aged PE items.

inorganic pigments present in the PE items, particularly amber yellow, which is commonly found in kaolin (Vahur et al., 2010).

Finally, it is important to note that some new items, such as Tube-1 (Fig. S1), also show a weak absorption band at 1020 cm^{-1}, even though they have not been exposed in the field. In these cases, silicates are not acting as pollutants, which appear to indicate that recycled plastic of agricultural origin could have been used in the manufacture of these products.

3.2. Performance of extraction protocol

In a previous study from our group, it was demonstrated that the yield of pesticides extraction from PE films requires the use of solvents capable of swelling the polymer (Cobo-Golpe et al., 2024). Consequently, the combination of Hex and DCM performed better than MeOH and ACN, as the latter mixture only released compounds adsorbed on the surface, without affecting those absorbed inside the material (Cobo-Golpe et al., 2024). Therefore, the diffusion of the compounds to the interface with the solvent plays a relevant role in the extraction efficiency. This process becomes especially relevant when the thickness of PE samples increases from μm (i.e., mulching films and tunnels) to mm (i.e., pellets and irrigation pipes). Herein, to select the most suitable methodology for sample preparation (that yielding the highest number of compounds and the highest concentration recovered from the PE items), two different protocols were tested: ultrasound assisted extraction (UAE) and Soxhlet (*section 2.3.*). Fig. 2 compares the concentrations with their standard deviation (SD) and the number of compounds recovered from 3 different types of samples, representing different PE thickness (i.e., pellets, protection tubes and irrigation pipes) obtained in UAE (15-minute extraction) and Soxhlet, as described in *section 2.3.*. According to the obtained results, Soxhlet performed better than UAE, being able to recover between 16 and 18 substances above their LOQs, whereas UAE extracted a maximum of 14 compounds (Fig. 2). As for concentrations, Soxhlet extracted between 4 and 70 % higher concentrations than UAE. To further evaluate the effectiveness of UAE, additional experiments were conducted at a higher temperature (40 °C) and longer extraction time (8 h) (Text S1 and Fig. S2). However, Soxhlet still demonstrated higher efficiency, yielding higher total concentrations and a larger number of extracted compounds. Therefore, Soxhlet was selected as sample preparation technique.

3.3. Pesticide residues in end-of-life PE items

PE items at the end of their useful life were recovered from agricultural fields in several points of Spain. These items showed different visible degrees of degradation, but accurate age and duration in the fields are unknown. End-of-life samples were analyzed for a set of 41 pesticides, 40 of which were detected using the multiresidue UHPLC-MS/MS methodology, while *p,p'*-DDE was quantified via GC-Q-MS (*section 2.4.*). Of the 41 pesticides, 31 were detected in the aged plastic (Table S2). The analyzed end-of-life PE items contained residues of, at least, one pesticide up to 15 compounds above their LOQs. Total pesticide concentrations ranged from 4.69 ng g^{-1} to 3410 ng g^{-1}, corresponding to Film-8 (mulching film) and Film-2 (greenhouse plastic), respectively (Fig. 3). Concentrations for each individual compound are presented in Supplementary material, Table S2.

Four pesticides demonstrated detection frequencies (DF) above 40 %, namely penconazole (PEN, DF 50 %), difenoconazole (DIF, 57 %), cyprodinil (CYP, 71 %), and metalaxyl (MET, 79 %). Among these, DIF and CYP exhibited the highest median concentrations, 172 ng g^{-1} and 119 ng g^{-1}, respectively. Zoxamide (ZOX) was predominant in tying tape samples, being detected only in that type of item, but presenting the highest median concentrations (298.5 ng g^{-1}). A similar trend was reported by Cobo-Golpe et al. in aged PP plastic used in agriculture (Cobo-Golpe et al., 2024). A study conducted in farmlands in the North of China assessed the presence of pesticides in mulching films. The authors reported mean total concentrations of 3463 ng g^{-1} in the collected plastics, which are in the same range of magnitude as the films considered in the present study. The authors also claimed the high variability among the different samples (Guo et al., 2020), following the same trend reported here.

The absorption of pesticides on agricultural PE plastics is well-documented and has been described for numerous pesticides in literature (Cobo-Golpe et al., 2024; Nerín et al., 1996; Sahai et al., 2024; Wang et al., 2020b). However, as Wang et al. highlighted, these studies primarily focus on virgin plastic rather than aged materials, which would be more in line with actual field conditions (Wang et al., 2020a). The presence of pesticide residues in agricultural plastic depends on several factors, including type and amount of pesticide application, meteorological conditions, plastic degradation degree and duration in the field. Antunes et al. investigated the absorption of persistent organic pollutants, such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and DDT in pellets recovered from beaches

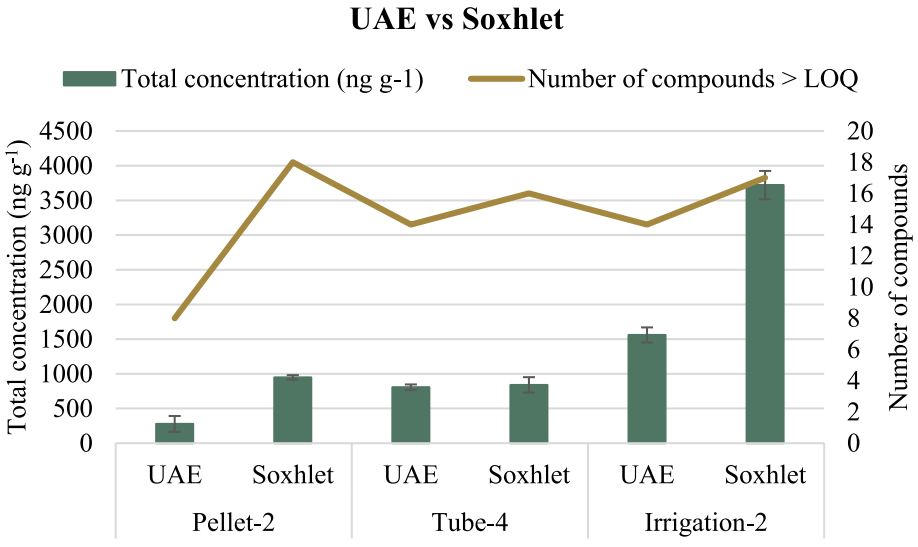

Fig. 2. Comparative of total concentration and number of compounds recovered from different PE items under different sample preparation techniques. Average values for triplicate extractions.

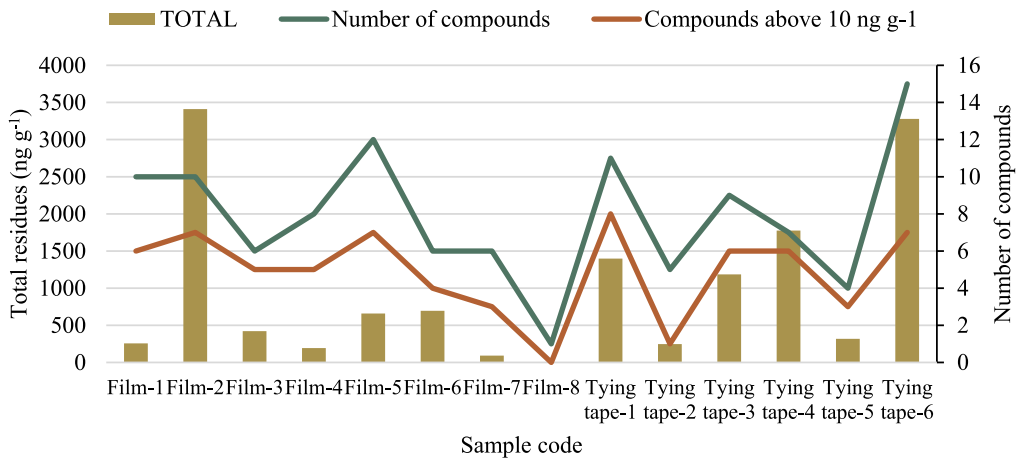

Fig. 3. Total pesticide concentrations (ng g^{-1}) in aged plastic collected from different locations. Average values for duplicate extractions.

in the Portuguese coast (Antunes et al., 2013). The authors detected higher concentrations in aged pellets than in the virgin material, which can be attributed to the presence of oxygen-containing functional groups (−OH) in the aged plastics, which likely increased the adsorption capacity (Liu et al., 2019). This O/C ratio in plastics played a significant role in the adsorption capacities of PE polymers (Liu et al., 2019).

3.4. Residues in new PE items for agricultural uses

New PE goods commonly used in agriculture were acquired from the retail market. Thus, 10 new items, including tying tapes, mulching films, drip hoses, and irrigation pipes that had never been exposed to sunlight, nor exposed to pesticides in agricultural fields, were selected and prepared in the laboratory for analysis (Table 1).

Total pesticide concentration ranged from 9.04 ng g^{-1} to 4179 ng g^{-1} corresponding to samples of tying tapes of different colors, light and dark green, respectively (Fig. 4). Among the different samples, the number of compounds detected varied between 9 and 18 out of the 41 considered in the study. Fourteen compounds presented DF above 40 %, with CYP and metrafenone (METRA) noticed in eight out of the ten new PE-made items (Table S2).

The samples labeled as Irrigation-2 and Tying tape-7 presented the highest total pesticide concentrations, 3740 ng g^{-1} and 4179 ng g^{-1}, respectively. According to the label issued by the retailer, these samples were made from LDPE derived from recycled or substandard material. CYP was the dominant pesticide in Irrigation-2 (1963 ng g^{-1}), while METRA presented the highest concentration in Tying tape-7 (4144 ng g^{-1}). Both substances remain stable up to 270 °C and 250 °C, respectively (Table S3), and thus, they might survive the mechanical recycling process applied at the facilities. As for drip hose-2 and drip hose-3, also produced from recycled PE, presented total pesticide concentration below 500 ng g^{-1}, suggesting that the presence of pesticides in the final product, made from recycled PE, mainly depend on the raw material. In addition to the above discussed compounds, presence of residues of *p,p'*-DDE were noticed in 50 % of new PE items, with concentrations ranging from 17 ng g^{-1} to 46 ng g^{-1}.

3.5. Behavior of pesticides during PE agricultural waste recycling

Data on the occurrence of pesticide residues in PE wastes from agricultural applications, along with the detection of certain compounds in newly manufactured items, suggest that, at least, a portion of these compounds may persist through the steps involved in recycling of PE waste into secondary raw materials (e.g., pellets). These recycled materials are subsequently used in the production of new goods and thus, those substances that are not eliminated during recycling could be detected in new items. To investigate this hypothesis, a series of experiments were conducted under conditions designed to simulate the recycling processes (*Section 2.6.*).

Evidence of incomplete pesticide removal during handling of end-of-life PE items was assessed by analyzing washed, crushed materials (flakes, Table 1), as well as three different batches of recycled pellets (Table 1). Despite these four samples were not related, all of them contained residues of, at least, one of the pesticides determined in the current study (Fig. 5).

According to the obtained results, analyzed raw materials presented total concentrations ranging from 43.0 to 823 ng g^{-1}, corresponding to Pellet-1 (black pellet) and Pellet-2 (grey pellet), respectively. In

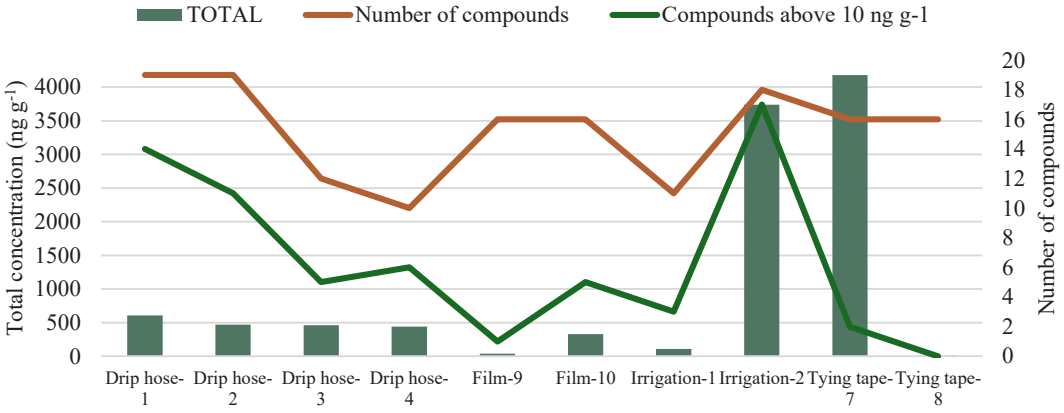

Fig. 4. Total pesticide concentration in new PE items. Average values for duplicate extractions.

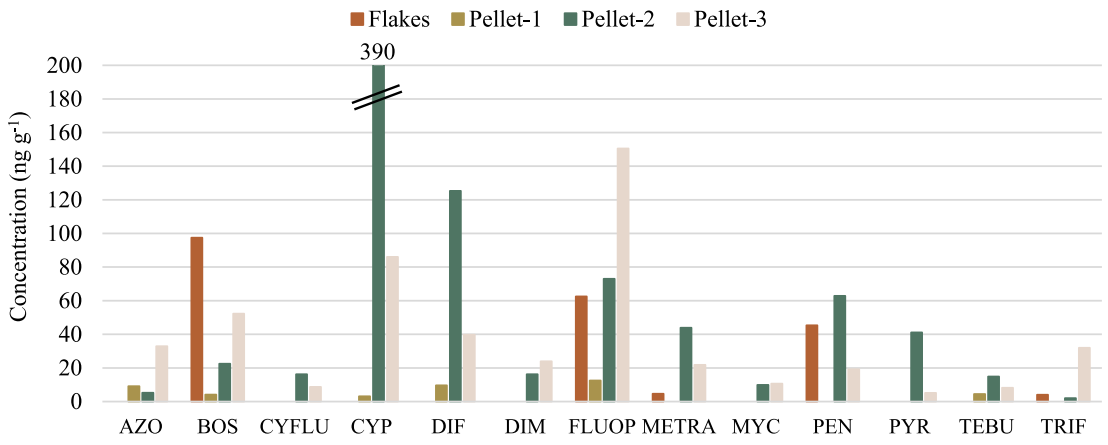

Fig. 5. Residual concentration of pesticides in second-hand raw materials. Average values for duplicate extractions.

addition, thirteen pesticides demonstrate to be resistant to removal during recycling, of which nine of them presented DF higher than 75 %. The measured concentrations in the samples of CYP, DIF and fluopicolide (FLUOP) are particularly concerning, reaching up to 390 ng g^{-1} and 125 ng g^{-1} in the case of CYP and DIF, respectively, in Pellet-2, and 151 ng g^{-1} of FLUOP in Pellet-3. The presence of these 13 residues in the raw materials can be explained by the use of these substances in the fields and their decomposition temperature, being in most cases higher than 220 °C (Table S3), 20 °C above the nominal temperature applied during the recycling process of plastic. Herein, the removal efficiency of these residues was assessed by the application of different temperatures above the melting point of PE plastic, from 120 to 130 °C. Melting tests of the sample presenting the highest concentrations (Pellet-2) were conducted in an oven at two different temperatures 150 and 200 °C for 5 h (*section 2.6.*). According to the obtained results, removal efficiencies of 22 % and 50 % were obtained at 150 °C and 200 °C, respectively, indicating that higher temperatures should be applied during the recycling process at the facilities to ensure the complete removal of these substances (Fig. S3). Nevertheless, processing temperature must be carefully selected due to high operation temperatures leading to thermal and thermo-oxidative polymer degradation, thus compromising the quality of the final product.

To track the transference of these residues from second-hand pellets to new PE items, PE protection tubes made from different percentages of recycled pellets (25 %, 50 % and 100 %, Table 1) were analyzed. Fig. 6 shows the individual concentrations of different compounds depending on the percentage of recycled pellets. Obviously, the higher the percentage of recycled material, the higher the concentration of those substances that survived the recycling process, meaning that total concentrations up to 163 ng g^{-1}, 530 ng g^{-1} and 800 ng g^{-1} can be present in new items proceeding from a 25 %, 50 % and a 100 % of recycled PE, respectively. In addition to compounds compiled in Fig. 6, guard tubes elaborated from 100 % recycled pellets contained also noticeable concentrations of *p,p'*-DDE (9 ng g^{-1}), with this compound below procedural LOQs (5 ng g^{-1}) in guard tubes elaborated with 25 % and 50 % of recycled pellets.

3.6. Pesticide migration from PE items to water samples

Upon demonstrating the presence of pesticide residues in newly manufactured PE irrigation pipes, the subsequent step involved assessing the potential migration of these substances into water during typical usage conditions. To address this, preliminary batch experiments were performed at laboratory scale, using a fraction of a new pipe material (sample code Irrigation-1). Aliquots of 1 mL water were collected and subjected to analysis (*section 2.7.*). The obtained results confirmed the migration of 14 out of 33 monitored pesticides into the water, which displayed total concentrations ($\sum_{14pesticides}$) from 897 ng L^{-1} after 24 h to 1542 ng L^{-1} after 5 days (Table S4). Among the substances, BOS and PEN presented the highest concentrations. In general, the higher the

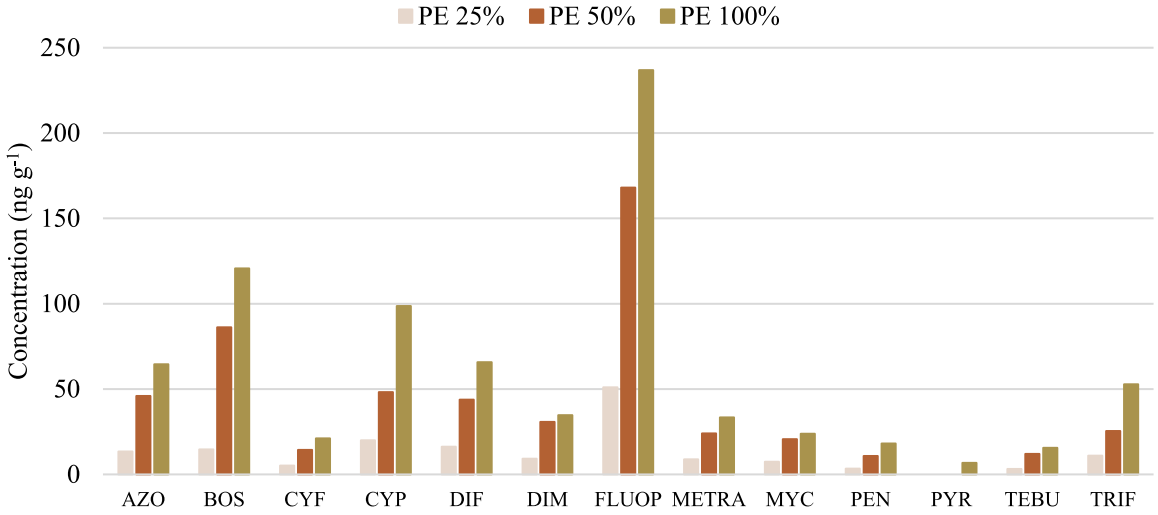

Fig. 6. Pesticide residues in agricultural PE protection tubes containing different percentage of recycling raw materials. Average values for duplicate extraction assays.

polarity of the pesticides, the higher the migration from the material to the water (Cobo-Golpe et al., 2024).

To complement the preliminary laboratory tests, field experiments were also conducted by connecting the sample coded Drip hose-1 to a water outlet. Water aliquots were collected at the end of the pipe at different times (*section 2.7.*). Experiments carried out in winter (average temperature 10 °C, Santiago de Compostela) confirmed the migration of 14 out of 33 substances into water. The number of compounds detected decreased over time, with 15 substances detected after the first hour and only 4 detected after 24 h. As for total concentrations, 1794 ng L^{-1} were measured in the water collected after 30 min, while the concentration measured decreased to 176 ng L^{-1} after 24 h. In contrast, during summer (average temperature 25 °C, Santiago de Compostela), pesticide leaching was more pronounced, with total concentrations in water rising significantly from 1680 ng L^{-1} in winter, to 3755 ng L^{-1} in the summer tests (Table 2).

The obtained results demonstrate that pesticide residues present in PE irrigation pipes can leach into water during use, with the rate and extent of leaching influenced by both exposure time and environmental temperature. Furthermore, these results highlight that recycling of end-of-life agricultural PE items can act as both a carrier and a transport vector for pesticide residues in the agricultural ecosystem.

3.7. Environmental and circular economy implications

The presence of pesticide residues in end-of-life and brand-new PE agricultural items poses significant challenges for both environmental sustainability and the implementation of circular economy. According to L. Ramos et al., the presence of PE plastic in horticultural soil of small production units represents around the 10 % of the soil surface, being the small pieces the most abundant (Ramos et al., 2015). As previously documented in literature and in the current study, pesticides can be adsorbed onto the surface of plastics and from there migrate to the surrounded environmental matrices, such as soil, water, and air (Cobo-Golpe et al., 2024; Nerín et al., 1996; Ramos et al., 2015; Wang et al., 2020a). Recycling and reusing agricultural plastic items appear as the main solution to reduce environmental pollution (Picuno et al., 2012). Martínez Urreaga et al. (Martínez Urreaga et al., 2020) proposed to collect the end-of-life PE agricultural plastic and recycling it to produce raw materials that can be used to make new PE agricultural items, such as tube shelters. While this approach exemplifies a circular economy model, the results obtained in the current study indicate that pesticides can survive the mechanical recycling process, at least partially, and remain in pellets and brand-new PE items. Another alternative, proposed by H. Sahai et al., involves the use of biodegradable polybutylene adipate terephthalate (PBAT) films, comparing its characteristics with those displayed by conventional PE. PBAT exhibits greater retention capacity, while simultaneously reducing the migration of pesticides to the environment (Sahai et al., 2024). However, the recyclability of these films has not yet been assessed, in addition to the lack of knowledge of the effectiveness of mechanical recycling in the elimination of pesticide residues in products made from recycled plastic.

Data and trends related to the stability of several pesticides in PE agricultural plastics raise the question whether high concentrations of certain chemicals (e.g., CYP) detected in microplastics collected from the aquatic media are really sorbed in microplastics, or if they correspond to residues existing in the parent polymer, which survived during the fragmentation of the plastic in the environment and, thus, remained in the formed microplastics. What is clear is that the presence of these residues in new PE items might lead to cross-contamination in crops and to contribute to the total concentration of these residues in the environment. Therefore, to improve the circularity of plastic use in agriculture, is essential to implement some changes in the recycling process that maintain the quality of the final product while remaining economically sustainable. Among the current techniques, mechanical and chemical recycling are the main alternatives, with mechanical recycling being the most promising in terms of technical feasibility, costs, and profitability (Filipe et al., 2023). Some improvements in mechanical recycling involve optimized washing protocols based on the use of hot water, advanced detergents, or ultrasound-assisted cleaning. The latter one has been proven effective in removing pesticide residues from vine leaves (Aydar et al., 2023) and fresh vegetables (Azam et al., 2020; Huang et al., 2018). In this line, ultrasonication has been previously tested for reducing organic and inorganic contamination in plastic film waste (Cecon et al., 2024). Cecon et al. concluded that the ultrasound-assisted cleaning does not compromise the properties of the recycled plastic films while reducing ashable materials (Cecon et al., 2024). However, to the best of the authors knowledge, the effectiveness of ultrasonic cleaning has not yet been evaluated for the removal of organic contaminants from aged plastic, but it might help during the removal of pesticide residues. Additionally, improvements in filtration and decontamination during extrusion, such as the use of vacuum degassing and specialized additives (Garcia et al., 2014; Monti et al., 2023), can further reduce contaminants and improve the mechanical properties of the recycled material. On the other hand, attention might be paid to wastewater generated during the recycling of end-of-life agricultural PE.

Table 2
Pesticide concentrations obtained in leaching experiments of sample coded Drip hose-1, which remained connected to a water source for 24 h. Experiments conducted in winter and summer for comparison purposes. Data corresponding to duplicate assays in each season.

	Concentration in water (ng L^{-1})	
Analyte	Winter 2024	Summer 2024
AZO	27.4	62.4
BOS	525	1025
CYP	81.1	68.8
DIF	164	1856
DIM	88.2	311
FLUOP	76.4	235
FLUOPM	162	676
MET	n.d.	58.3
METRA	n.d.	13.2
MYC	30.1	144
PEN	350	453
PROPI	45.3	75.7
SPIRO	23.2	97.6
TEBU	108	350
∑pesticides	**1680**	**3755**

4. Conclusions

The intensive use of PE plastics in agriculture means that, after use, many of these items that have been exposed to pesticides remain in the soil or in the environment for years, degrading into smaller pieces and producing meso- and microplastics. The results obtained in this research confirm that these plastic products contain pesticides at the end of their useful life, as it has been previously reported by other authors (Ramos et al., 2015). However, this research aimed to assess the footprint of pesticides during their life cycle. To the best of the authors knowledge, the presence of pesticide residues in new items produced from pellets made from recycled agricultural PE is reported for the first time. This paper demonstrates that the higher the percentage of recycled PE in the new product, the higher the concentrations of pesticides detected (total concentrations up to 793 ng g^{-1}). Furthermore, different melting temperatures, commonly used during the plastic extrusion in the recycling process, have been evaluated. According to the obtained results, temperatures of 200 °C are not sufficient to completely remove the total pesticide residues (removal efficiencies of 50 %). Finally, the potential migration derived from the use of these new materials made from recycled PE, such as drip hoses or irrigation pipes, has been evaluated. The selected drip hose contained initial concentrations of 561 ng g^{-1},

which displayed to leach total concentrations of 1680 ng L^{-1} to water in irrigations carried out in the winter season, and 3755 ng L^{-1} in summer irrigations. Therefore, this research underscores the urgent need to improve recycling techniques to mitigate risks from pesticide contamination in recycled agricultural plastics as well as to develop and to evaluate other efficient pesticides with less harmful effects to the environment.

CRediT authorship contribution statement

Gabriela Castro: Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Resources, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Victoria Fernández-Fernández:** Writing – review & editing, Visualization, Validation, Software, Methodology, Investigation, Formal analysis. **Miguel Cobo-Golpe:** Writing – review & editing, Visualization, Software, Methodology, Investigation, Formal analysis. **María Ramil:** Writing – review & editing, Methodology, Investigation, Formal analysis. **Enrique Blázquez-Blázquez:** Writing – review & editing, Methodology, Investigation, Formal analysis. **María L. Cerrada:** Writing – review & editing, Methodology, Investigation, Formal analysis. **I. Bernabé:** Writing – review & editing, Methodology, Investigation, Formal analysis. **J. Martínez Urreaga:** Writing – review & editing, Methodology, Investigation, Formal analysis. **M.U. de la Orden:** Writing – review & editing, Methodology, Investigation, Formal analysis. **Isaac Rodriguez:** Writing – review & editing, Validation, Software, Resources, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization.

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.

Acknowledgments

This work was supported by Xunta de Galicia through contract ref. ED431C2021/06, co-financed with EU-FEDER funds. The contribution of G. Castro was supported by her Maria Zambrano grant through the Spanish Ministry of Science (“UE Next Generation” founds). M. Cobo acknowledges his FPI contract to the Spanish Ministry of Science and Innovation and Xunta de Galicia through grants PGC2018–094613-B-I00, TED2021-129962B-C42, TED2021-130166B-I00 and ED431C 2021/06, respectively. Both projects are co-funded by the EU FEDER program. ATR-IR and Raman-IR analyses were carried out in the General Services Unit of the Universidade de Santiago de Compostela (USC).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.wasman.2025.114767.

Data availability

Data will be made available on request.

References

Antunes, J.C., Frias, J.G.L., Micaelo, A.C., Sobral, P., 2013. Resin pellets from beaches of the Portuguese coast and adsorbed persistent organic pollutants. Estuar. Coast. Shelf Sci. 130, 62–69. https://doi.org/10.1016/j.ecss.2013.06.016.

Atugoda, T., Vithanage, M., Wijesekara, H., Bolan, N., Sarmah, A.K., Bank, M.S., You, S., Ok, Y.S., 2021. Interactions between microplastics, pharmaceuticals and personal care products: Implications for vector transport. In: Environment International. Elsevier Ltd. https://doi.org/10.1016/j.envint.2020.106367

Aydar, A.Y., Aydın, T., Karaiz, A., Alabey, F., Kothakota, A., Raposo, A., Abdullah Albaridi, N., Pandiselvam, R., 2023. Effect of ultrasound assisted cleaning on pesticide removal and quality characteristics of Vitis vinifera leaves. Ultrason. Sonochem. 92. https://doi.org/10.1016/j.ultsonch.2022.106279.

Azam, S.M.R., Ma, H., Xu, B., Devi, S., Siddique, M.A.B., Stanley, S.L., Bhandari, B., Zhu, J., 2020. Efficacy of ultrasound treatment in the and removal of pesticide residues from fresh vegetables: a review. Trends Food Sci. Technol. 97, 417–432. https://doi.org/10.1016/j.tifs.2020.01.028.

Boughattas, I., Hattab, S., Zitouni, N., Mkhinini, M., Missawi, O., Bousserrhine, N., Banni, M., 2021. Assessing the presence of microplastic particles in Tunisian agriculture soils and their potential toxicity effects using Eisenia andrei as bioindicator. Sci. Total Environ. 796, 148959. https://doi.org/10.1016/j.scitotenv.2021.148959.

Cascone, S., Gagliano, A., 2022. Recycled agricultural plastic waste as green roof drainage layer within the perspective of ecological transition for the built environment. J. Clean. Prod. 380, 135032. https://doi.org/10.1016/j.jclepro.2022.135032.

Castillo-Díaz, F.J., Belmonte-Ureña, L.J., Camacho-Ferre, F., Tello-Marquina, J.C., 2021. The management of agriculture plastic waste in the framework of circular economy. Case of the almeria greenhouse (Spain). Int. J. Environ. Res. Public Health 18 (22), 12042. https://doi.org/10.3390/ijerph182212042.

Castro, G., Cobo, M., Rodríguez, I., 2024. Identification of hazardous organic compounds in e-waste plastic using non-target and suspect screening approaches. Chemosphere 356, 141946. https://doi.org/10.1016/j.chemosphere.2024.141946.

Cecon, V.S., Munshi, M., Mukta, S., Vorst, K.L., Curtzwiler, G.W., 2024. Utilization of ultrasonication as a method of reducing organic and inorganic contamination in post-consumer plastic film waste. Macromol. Mater. Eng. https://doi.org/10.1002/mame.202400310.

Cobo-Golpe, M., Blanco, P., Fernández-Fernández, V., Ramil, M., Rodríguez, I., 2024. Assessment of the occurrence and interaction between pesticides and plastic litter from vineyard plots. Sci. Total Environ. 912, 169273. https://doi.org/10.1016/j.scitotenv.2023.169273.

da Silva, D.J., Wiebeck, H., 2022. ATR-FTIR spectroscopy combined with chemometric methods for the classification of polyethylene residues containing different contaminants. J. Polym. Environ. 30 (7), 3031–3044. https://doi.org/10.1007/s10924-022-02396-3.

De La Orden, M.U., Montes, J.M., Martínez Urreaga, J., Bento, A., Ribeiro, M.R., Pérez, E., Cerrada, M.L., 2015. Thermo and photo-oxidation of functionalized metallocene high density polyethylene: effect of hydrophilic groups. Polym. Degrad. Stab. 111, 78–88. https://doi.org/10.1016/j.polymdegradstab.2014.10.023.

Elseblani, R., Cobo-Golpe, M., Godin, S., Jimenez-Lamana, J., Fakhri, M., Rodríguez, I., Szpunar, J., 2023. Study of metal and organic contaminants transported by microplastics in the Lebanese coastal environment using ICP MS, GC-MS, and LC-MS. Sci. Total Environ. 887, 164111. https://doi.org/10.1016/j.scitotenv.2023.164111.

FAO. (2021). Assessment of agricultural plastics and their sustainability: A call for action. In *Assessment of agricultural plastics and their sustainability: A call for action*. FAO. Doi: 10.4060/cb7856en.

Fernández-Fernández, V., Ramil, M., Cela, R., Rodríguez, I., 2023. Occurrence and risk assessment of pesticides and pharmaceuticals in viticulture impacted watersheds from Northwest Spain. Chemosphere 341, 140098. https://doi.org/10.1016/j.chemosphere.2023.140098.

Filipe, S., Mourão, P.M., Couto, N., Tranchida, D., 2023. Towards a sustainable future: advancing an integrated approach for the recycling and valorization of agricultural plastics. Polymers 15 (15), 4529. https://doi.org/10.3390/polym15234529.

Garcia, P.S., Cruz, S.A., Nerín, C., 2014. Comparison of different extrusion processes for cleaning the recycled polypropylene removing volatile and non-volatile contaminants. Prog. Rubber Plast. Recycl. Technol. 30 (1), 37. https://doi.org/10.1177/147776061403000103.

Gardette, M., Perthue, A., Gardette, J.L., Janecska, T., Földes, E., Pukánszky, B., Therias, S., 2013. Photo- and thermal-oxidation of polyethylene: comparison of mechanisms and influence of unsaturation content. Polym. Degrad. Stab. 98 (11), 2383–2390. https://doi.org/10.1016/j.polymdegradstab.2013.07.017.

Gu, F., Guo, J., Zhang, W., Summers, P.A., Hall, P., 2017. From waste plastics to industrial raw materials: a life cycle assessment of mechanical plastic recycling practice based on a real-world case study. Sci. Total Environ. 601–602, 1192–1207. https://doi.org/10.1016/j.scitotenv.2017.05.278.

Guo, B., Meng, J., Wang, X., Yin, C., Hao, W., Ma, B., Tao, Z., 2020. Quantification of pesticide residues on plastic mulching films in typical farmlands of the North China. Front. Environ. Sci. Eng. 14 (1), 2. https://doi.org/10.1007/s11783-019-1181-9.

Huang, D., Xu, Y., Lei, F., Yu, X., Ouyang, Z., Chen, Y., Jia, H., Guo, X., 2021. Degradation of polyethylene plastic in soil and effects on microbial community composition. J. Hazard. Mater. 416, 126173. https://doi.org/10.1016/j.jhazmat.2021.126173.

Huang, K., Wrenn, S., Tikekar, R., Nitin, N., 2018. Efficacy of decontamination and a reduced risk of cross-contamination during ultrasound-assisted washing of fresh produce. J. Food Eng. 224, 95–104. https://doi.org/10.1016/j.jfoodeng.2017.11.043.

Huang, Y., Liu, Q., Jia, W., Yan, C., Wang, J., 2020. Agricultural plastic mulching as a source of microplastics in the terrestrial environment. Environ. Pollut. 260, 114096. https://doi.org/10.1016/j.envpol.2020.114096.

Lan, T., Wang, T., Cao, F., Yu, C., Chu, Q., Wang, F., 2021. A comparative study on the adsorption behavior of pesticides by pristine and aged microplastics from agricultural polyethylene soil films. Ecotoxicol. Environ. Saf. 209, 111781. https://doi.org/10.1016/j.ecoenv.2020.111781.

Li, K., Ma, D., Wu, J., Chai, C., Shi, Y., 2016. Distribution of phthalate esters in agricultural soil with plastic film mulching in Shandong Peninsula, East China. Chemosphere 164, 314–321. https://doi.org/10.1016/j.chemosphere.2016.08.068.

Liu, P., Qian, L., Wang, H., Zhan, X., Lu, K., Gu, C., Gao, S., 2019. New insights into the aging behavior of microplastics accelerated by advanced oxidation processes. Environ. Sci. Tech. 53 (7), 3579–3588. https://doi.org/10.1021/acs.est.9b00493.

Lwanga, E.H., van Roshum, I., Munhoz, D.R., Meng, K., Rezaei, M., Goossens, D., Bijsterbosch, J., Alexandre, N., Oosterwijk, J., Krol, M., Peters, P., Geissen, V., Ritsema, C., 2023. Microplastic appraisal of soil, water, ditch sediment and airborne dust: the case of agricultural systems. Environ. Pollut. 316, 120513. https://doi.org/10.1016/j.envpol.2022.120513.

Madrid, B., Wortman, S., Hayes, D. G., DeBruyn, J. M., Miles, C., Flury, M., Marsh, T. L., Galinato, S. P., Englund, K., Agehara, S., & DeVetter, L. W. (2022). End-of-Life Management Options for Agricultural Mulch Films in the United States-A Review. In: *Frontiers in Sustainable Food Systems* (Vol. 6). Frontiers Media S.A. Doi: 10.3389/fsufs.2022.921496.

Martínez Urreaga, J., Beltrán, F.R., Acosta, J., Aguinaco, T., Fonseca, C., Ochoa, A., Oliet Palá, J.A., González-Sánchez, C., de la Orden, M.U., 2020. Tube shelters from agricultural plastic waste: an example of circular economy. J. Clean. Prod. 268, 122401. https://doi.org/10.1016/j.jclepro.2020.122401.

Monti, M., Perin, E., Conterosito, E., Romagnolli, U., Muscato, B., Girotto, M., Scrivani, M.T., Gianotti, V., 2023. Development of an advanced extrusion process for the reduction of volatile and semi-volatile organic compounds of recycled HDPE from fuel tanks. Resour. Conserv. Recycl. 188. https://doi.org/10.1016/j.resconrec.2022.106691.

Nerín, C., Tornés, A.R., Domeño, C., Cacho, J., 1996. Absorption of pesticides on plastic films used as agricultural soil covers. J. Agric. Food Chem. 44, 4009–4014. https://doi.org/10.1021/jf960326k.

Picuno, P., Godosi, Z., Picuno, C., 2022. Agrochemical contamination and ageing effects on greenhouse plastic film for recycling. Appl. Sci. (Switzerland) 12 (19), 10149. https://doi.org/10.3390/app121910149.

Picuno, P., Sica, C., Laviano, R., Dimitrijević, A., Scarascia-Mugnozza, G., 2012. Experimental tests and technical characteristics of regenerated films from agricultural plastics. Polym. Degrad. Stab. 97 (9), 1654–1661. https://doi.org/10.1016/j.polymdegradstab.2012.06.024.

Ramos, L., Berenstein, G., Hughes, E.A., Zalts, A., Montserrat, J.M., 2015. Polyethylene film incorporation into the horticultural soil of small periurban production units in Argentina. Sci. Total Environ. 523, 74–81. https://doi.org/10.1016/j.scitotenv.2015.03.142.

Sahai, H., Hernando, M.D., Martínez Bueno, M.J., Aguilera del Real, A.M., Fernández-Alba, A.R., 2024. Evaluation of the sorption/desorption processes of pesticides in biodegradable mulch films used in agriculture. Chemosphere 351, 141183. https://doi.org/10.1016/j.chemosphere.2024.141183.

Santana-Viera, S., Montesdeoca-Esponda, S., Sosa-Ferrera, Z., Santana-Rodríguez, J.J., 2021. UV filters and UV stabilisers adsorbed in microplastic debris from beach sand. Mar. Pollut. Bull. 168, 112434. https://doi.org/10.1016/j.marpolbul.2021.112434.

Schade, A., Melzer, M., Zimmermann, S., Schwarz, T., Stoewe, K., Kuhn, H., 2024. Plastic waste recycling—a chemical recycling perspective. ACS Sustain. Chem. Eng. 12 (33), 12270–12288. https://doi.org/10.1021/acssuschemeng.4c02551.

Seah, C.C., Tan, C.H., Arifin, N.A., Hafriz, R.S.R.M., Salmiaton, A., Nomanbhay, S., Shamsuddin, A.H., 2023. Co-pyrolysis of biomass and plastic: circularity of wastes and comprehensive review of synergistic mechanism. Results Eng. 17, 100989. https://doi.org/10.1016/j.rineng.2023.100989.

Vahur, S., Teearu, A., Leito, I., 2010. ATR-FT-IR spectroscopy in the region of 550-230 cm-1 for identification of inorganic pigments. Spectrochimica Acta - Part A: Mol. Biomol. Spectroscopy 75 (3), 1061–1072. https://doi.org/10.1016/j.saa.2009.12.056.

Wang, F., Gao, J., Zhai, W., Liu, D., Zhou, Z., Wang, P., 2020a. The influence of polyethylene microplastics on pesticide residue and degradation in the aquatic environment. J. Hazard. Mater. 394, 122517. https://doi.org/10.1016/j.jhazmat.2020.122517.

Wang, T., Yu, C., Chu, Q., Wang, F., Lan, T., Wang, J., 2020b. Adsorption behavior and mechanism of five pesticides on microplastics from agricultural polyethylene films. Chemosphere 244, 125491. https://doi.org/10.1016/j.chemosphere.2019.125491.

Wu, C., Pan, S., Shan, Y., Ma, Y., Wang, D., Song, X., Hu, H., Ren, X., Ma, X., Cui, J., Ma, Y., 2022. Microplastics mulch film affects the environmental behavior of adsorption and degradation of pesticide residues in soil. Environ. Res. 214, 114133. https://doi.org/10.1016/j.envres.2022.114133.