



Assessment of the occurrence and interaction between pesticides and plastic litter from vineyard plots

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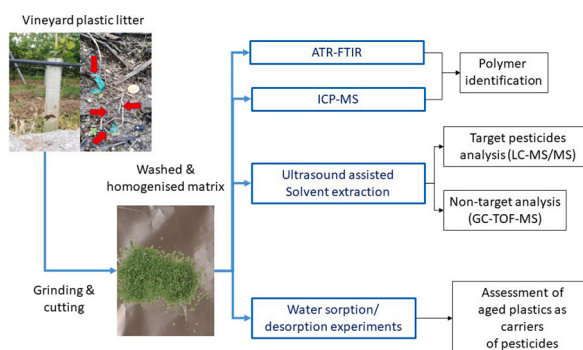
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HIGHLIGHTS

- Aged plastics from vineyards were identified as polypropylene and polyethylene.
- Pesticides were absorbed inside aged debris of vineyard plastics.
- Different profiles of pesticides were noticed in plastic litter and vineyard soils.
- Aged plastics showed a higher interaction with pesticides than new counterparts.

GRAPHICAL ABSTRACT



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ABSTRACT

In this research, aged plastic fragments collected from vineyards were characterized in terms of composition, residues of pesticides, and their potential to exchange these compounds with the aquatic media. To this end, we employed the qualitative and quantitative information provided by complementary analytical techniques, including chromatography, organic and inorganic mass spectrometry, infrared spectroscopy and electronic microscopy. Debris of weathered plastics were identified as polypropylene and polyethylene, containing different types of additives, from organic UV stabilizers to inorganic fillers, such as calcium salts. Regardless of polymer type, plastic litter collected from vineyards contained residues of pesticides, and particularly of fungicides, with total concentrations in the range of values from 114 ng g^{-1} to $76.4 \text{ } \mu\text{g g}^{-1}$. Data obtained under different extraction conditions suggested that a fraction of these compounds was absorbed in aged polymers, penetrating inside the material. The parallel analysis of plastic litter and vineyard soils reflected higher pesticide residues in the former matrix. Furthermore, several fungicides, considered as labile in vineyard soils (i.e. zoxamide and folpet), were those showing the highest levels in plastic litter. Simulated sorption-desorption studies, with plastic debris in contact with surface water, demonstrated the higher affinity of aged materials by moderately polar pesticides than their new counterparts. For the first time, the manuscript highlights the presence of plastic litter in vineyards soils, reflecting the accumulation of several fungicides in this matrix, in some cases, with a different stability pattern to that observed in the soil from same vineyards.

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1. Introduction

Viticulture is a very important economic activity, with 80 % of worldwide wine production concentrated in well-defined areas, from just nine countries (Top wine-producing countries, 2022). The geographic concentration of vineyards makes this crop especially susceptible to pests, particularly to fungi and insect-transmitted infections. To treat and to prevent such diseases, under conventional agronomic managing, winegrowers make intensive use of pesticides, and particularly of fungicides and insecticides. The intensity of treatments applied to vineyards has been evaluated using different indicators, such as the so-called frequency treatment index (Fouillet et al., 2022), and it can be confirmed comparing the pesticide application rates to different crops, available in official websites (Statistics of pesticides consumption per crop in Spain, 2019). Moreover, regional (Pérez-Mayán et al., 2020) and supranational (Silva et al., 2019) survey campaigns, monitoring the presence of pesticides in different kinds of agriculture soils and the surrounding environment (Martin et al., 2022), confirmed the high intensity of treatments applied to vineyards.

The use of plastics in agriculture has become a common practice due to their positive effects in the productivity of crops and in the reduction of production costs (Gao et al., 2019). Degradation of these materials under environmental conditions contributes to the spread of smaller fragments in agriculture fields and, eventually, might lead to the production of micro and nanoplastics (Ramos et al., 2015; Steinmetz and Schröder, 2022). By themselves, plastic debris represent a hazard due to the risks of: (1) entering the terrestrial trophic chains through involuntary intake by soil invertebrates (Song et al., 2023), wild and livestock animals (Beriot et al., 2021; Thrift et al., 2022); and (2), migrating to surface and groundwater (Wanner, 2021). In addition, the fragments of plastics are recognized as a potential vector of concerning pollutants, either employed in the formulation of the original polymer (Hu et al., 2022; Li et al., 2021), or sorbed during their contact with crops (Fajardo et al., 2022), contributing to their spread in the environment.

Main types of plastics used in viticulture are guard tubes (Thomas et al., 2017), and tying items (mainly cord and tape). Plant protection tubes (PPT) are used just once when old vines are replaced by young plants. Usually, farmers do not care about these low cost items, which rest in vineyards for a long time, becoming fragile and leading to smaller size fragments, more difficult to collect and easily transported by run-off water and wind. Tying tape (TT) pieces represent a more concerning residue. These small size plastics (typically 1 cm width x 5–20 cm length) either reach the soil of vineyards at the end of winter, when vine canes are pruned; or they remain attached to wirelines existing in vineyards for years. Every new vegetative period of vines (spring and summer in the North hemisphere), new TT items are used. Due to this continuous use and their small size, they have become ubiquitous, difficult to recover and relatively mobile residues (due to wind and run-off water) on top soil of many vineyards. Obviously, both kinds of plastics are exposed to the range of pesticides applied to vineyards for years. Depending on the features of both, pesticides and plastic residues, certain compounds might present a higher stability in plastic debris than in soil and vine leaves. Moreover, the capability of aged plastic fragments to sorb pesticides sprayed on vineyards (mainly fungicides employed to treat mildium, oidium and botrytis infections) (Pérez-Mayán et al., 2020) might differ to that presented by the new polymers (Lan et al., 2021).

The aim of this research was contributing to understand the interactions between pesticides applied to vineyards and the two types of plastics systematically employed in this permanent crop: TT and PPT. This global aim includes evaluating the efficiency of different extraction conditions, the characterization of the residues of pesticides in plastic debris, and the assessment of the role of plastics as carriers of pesticides in the aquatic environment, identifying those parameters which control the distribution of these substances between vineyard plastics and surface water.

2. Materials and methods

2.1. Solvents and standards

Methanol (MeOH), HPLC grade purity was acquired from Merck (Darmstadt, Germany). Dichloromethane (DCM), hexane (Hex) and formic acid (FA) were purchased from VWR chemicals (Radnor, PA, USA). Acetonitrile (ACN) was provided by Thermo Fischer scientific (Waltham, MA, USA). Ultrapure deionized water ($18.2 \text{ M}\Omega \text{ cm}^{-1}$) was obtained using a Geni-U system (Rephile, Shanghai, China). Hydrophilic and hydrophobic PTFE syringe filters ($0.22 \mu\text{m}$ pore size, 13 mm diameter) were purchased from Phenomenex (Torrance, CA, USA). Glass fiber filters ($0.7 \mu\text{m}$ cut-off limit, 47 mm diameter) were from Merck.

Standards for a group of 30 fungicides and insecticides were acquired from Sigma-Aldrich (Milwaukee, WI, USA) and Dr. Ehrenstorfer GmbH (Augsburg, Germany). Selection of target compounds was made considering information obtained from winegrowers, and data of occurrence in soil (Pérez-Mayán et al., 2020) and wine samples (Pérez-Mayán et al., 2021) obtained, or produced, from the same geographic area where plastic debris were taken. Labelled analogues (either deuterated or ^{13}C species) of some pesticides were provided by Sigma-Aldrich and Toronto Research Chemicals (North York, Canada). They were employed as surrogate standards (SSs) through the analytical procedures employed in this research. Table 1 summarizes the suite of pesticides considered for determination in plastic debris using a target, multiresidue liquid chromatography triple quadrupole mass spectrometry (LC-QqQ-MS) procedure. Data corresponding to retention times and transitions for each compound, including SSs, are also given in Table 1. Residues of the fungicide folpet in the extracts from plastic debris were investigated by gas chromatography mass spectrometry (GC-MS), using a time-of-flight (TOF) instrument, under conditions provided as Supplementary information, Text S1.

A series of calibration solutions, containing increasing concentrations of LC-MS/MS amenable pesticides (from 1 ng mL^{-1} to 200 ng mL^{-1}), and a constant level of isotopically labelled species (25 ng mL^{-1}) were made in MeOH:ACN (1:1). A second series of calibration standards was prepared in ultrapure water, from 50 ng L^{-1} to 5000 ng L^{-1} , with SSs maintained at 500 ng L^{-1} . In case of folpet, calibration standards were prepared in isooctane, within the range of concentrations from 10 ng mL^{-1} to 1000 ng mL^{-1} , with folpet- d_4 maintained at 500 ng mL^{-1} .

In addition to pesticides compiled in Table 1, standards of other organic compounds (either pesticides or plastic additives), tentatively identified in the extracts from aged plastics from their accurate EI-MS spectra, were used for confirmation purposes.

2.2. Sample collection

Plastic debris were collected from 22 different vineyard plots, within the Denomination of Origin Ribeiro, in Galicia (Northwest Spain). In some cultivars, plastics were collected at different dates and positions: from top soil or attached to vine canes. Overall, 34 samples of plastic litter were obtained in the period comprised between July 2022 to February 2023. All, but one, were obtained after grapes harvest. Attending to their uses, vineyard plastics were classified in two groups. The largest one, with 22 different specimens, corresponded to TT, with a width of 1 cm and different lengths from 1 cm to 20 cm. Most of them showed a green colour, although in one of the vineyards, debris of white TT were also noticed and sampled. Depending on their abundance, from 10 g to 50 g of fragments were collected per vineyard, considering a minimum of 10 square parcels (each $2 \text{ m} \times 2 \text{ m}$) distributed randomly in each cultivar. The second group of samples corresponded to PPT. In this case fragments from weathered tubes, dispersed around the protected vines (10 plants per vineyard), were taken. Fig. S1 shows a picture of plastic litter residues commonly noticed at sampling places. Additional to aged materials, their new counterparts were acquired from local distributors. Composite samples of top soil (0–5 cm) were taken from

some of the vineyards, considering same sampling places, and dates, as those selected for collection of soil dispersed plastic debris. Each sample of soil corresponded to a minimum of 10 increments, with individual masses around 250 g.

2.3. Sample preparation

After reception, aged plastics were rinsed using ultrapure water and allowed to dry in a hood. PPT fragments were ground using a cutting mill (Retsch, model SM 100), furnished with a 2 mm mesh. After an additional sieving step, the fraction with particle sizes from 0.2 mm to 2 mm was selected for analysis and plastic-water sorption-desorption experiments. Debris of TT were classified attending to colour (green or white), and cut manually (it was not possible to grind this material following same approach used for PPT) in fragments with a size of 0.5 cm × 0.5 cm.

Sample preparation conditions used in the determination of pesticides associated to aged plastics involved extraction (0.5 g sample), with 10 mL of organic solvents, in an ultrasonic bath for 15 min (Elseblani et al., 2023; León et al., 2019). Under final working conditions, a mixture of Hex:DCM (1:1) was employed for extraction purposes. The primary extract was filtered (using lipophilic PTFE syringe filters), concentrated to a final volume of 2 mL, and divided in two fractions. One of them was exchanged to isooctane and used for the qualitative characterization of semi-volatile compounds (in most cases plastic additives), and quantitative determination of the fungicide folpet by GC-TOF-MS. The second fraction was evaporated to dryness, re-dissolved

with 1 mL of MeOH:ACN (1:1) and analyzed by LC-MS/MS.

Soil samples were sieved immediately after sampling (in some cases a previous air-dry step was necessary). Thereafter, the fraction below 2 mm was freeze-dried, and stored at -20°C until analysis. Soils showed a sandy-loam texture, with organic carbon contents in the range from 1.2 % to 2.8 %. Extraction of pesticides from the soil matrix was carried out by pressurized-liquid extraction (PLE), using a mixture of MeOH:ACN (70:30), under conditions reported elsewhere (Pérez-Mayán et al., 2020). The final extract was concentrated to 2 mL before LC-MS/MS analysis. Considering its limited thermal stability, extraction of folpet was carried out using the same protocol applied to aged plastics, in presence of folpet- d_4 as SS.

2.4. Sorption-desorption experiments

The potential of weathered plastic debris as carriers of pesticides in the aquatic environment was evaluated using surface water, obtained from a pristine stream, as model matrix. Accurately weighed samples of different types of plastics (0.40 g) were placed in contact with 200 mL of surface water (see Table S1 for physicochemical features of the water matrix) in closed glass vessels, under magnetic agitation. Vessels were maintained at room temperature ($20 \pm 2^{\circ}\text{C}$) and protected from light with aluminum foil. Aliquots of water (5 mL) were taken at different times, from 0.5 to 56 h, spiked with SSs (500 ng L^{-1}), filtered and analyzed by LC-MS/MS under conditions reported in Section 2.5, but increasing the injected volume from 0.5 μL to 30 μL . After 56 h, the remaining solution was passed through a 47 mm glass fiber filter (cut-off

Table 1
Summary of retention times, LC-MS/MS determination conditions, and procedural LOQs of pesticides in vineyard soils and agriculture plastic litter.

Abbreviation	Compound	RT (min)	Precursor ion [M + H] ⁺ (m/z)	Cone (V)	Q1 (CE, eV)	Q2 (CE, eV)	Ratio (Q1/Q2)	SS	LOQ (ng g ⁻¹ , soil/plastic)
AME	Ametoctradin	3.18	276	60	70 (50)	176 (35)	0.16	MYC- d_4	0.1/1
AZO	Azoxystrobin	3.37	404	28	329 (30)	372 (15)	0.24	MYC- d_4	1/2
BEN	Benalaxyl	4.42	326.1	26	91 (34)	148 (20)	0.70	MET- ¹³ C ₆	0.5/1
CAR	Carbendazim	1.69	192	33	132 (28)	160 (18)	0.17	CAR- d_3	0.5/1
CHLOF	Clofentezine	4.84	303	28	102 (35)	138 (22)	0.8	MET- ¹³ C ₆	2/4
CHLOR	Chlorpyrifos	5.74	349.9	36	97 (32)	198 (20)	0.65	MYC- d_4	2/4
CHLORM	Chlorpyrifos Methyl	4.98	321.8	34	125 (20)	289.9 (16)	0.194	MYC- d_4	2/4
CYF	Cyflufenamid	5.23	413.2	36	203 (35)	295.1 (15)	0.55	MET- ¹³ C ₆	1/2
CYP	Cyprodinil	2.9	226	56	93 (33)	108 (25)	0.74	CYP- d_5	1/2
DIF	Difenoconazole	4.55	406	46	111.1 (60)	251.1 (25)	0.37	MYC- d_4	1/2
DIM	Dimethomorph	2.95/ 3.05	388.1	41	165 (30)	300.9 (20)	0.61/0.55	DIM- d_6	1/2
FLUO	Fluopicolide	3.62	383	40	172.9 (20)	365 (15)	0.076	MYC- d_4	1.5/3
IMI	Imidacloprid	2.10	256.1	34	175.1 (20)	209.1 (15)	1	IMI- d_4	5/10
IPROV	Iprovalicarb	3.30	321	28	119 (16)	203.1 (10)	0.32	MET- ¹³ C ₆	1/2
MAN	Mandipropamid	3.5	412	26	125 (35)	328 (16)	0.587	MET- ¹³ C ₆	1.5/3
MET	Metalaxyl	2.71	280.1	26	192.1 (17)	220.1 (13)	0.6	MET- ¹³ C ₆	0.5/1
METR	Metrafenone	5.15	409	28	209.1 (14)	226.9 (16)	0.45	MET- ¹³ C ₆	1/2
MYC	Myclobutanil	3.33	289.1	34	70.2 (18)	125.1 (32)	0.28	MYC- d_4	0.5/1
PEN	Penconazole	3.77	284	34	70.1 (16)	159 (34)	0.31	MYC- d_4	0.5/1
PROP	Propiconazole	4.05	342	46	69 (22)	159 (34)	0.53	MYC- d_4	1.5/3
PYRA	Pyraclostrobin	4.84	388.1	31	163 (25)	193.9 (12)	0.66	MYC- d_4	0.5/1
PYR	Pyrimethanil	2.53	200	51	82 (24)	107 (24)	1.3	PYR- d_5	0.5/1
QUIN	Quinoxifen	5.07	308	61	161.9 (44)	197 (32)	0.70	MYC- d_4	0.5/1
TEBU	Tebuconazole	3.60	308	40	70.1 (22)	125 (40)	0.071	TEBU- d_9	1/2
TETRA	Tetraconazole	3.54	372	41	70.1 (20)	159 (30)	0.88	TEBU- d_9	1/2
TRIAF	Triadimefon	3.42	294.1	31	69.3 (20)	197.2 (15)	0.75	MYC- d_4	1/2
TRIAL	Triadimenol	3.00	296.1	21	70.2 (10)	99.1 (15)	0.11	MYC- d_4	1/2
TRIF	Trifloxystrobin	5.28	409	34	145 (40)	186 (16)	0.46	MYC- d_4	0.5/1
ZOX	Zoxamide	4.70	336	38	159 (38)	187 (16)	0.484	MYC- d_4	1/2
CAR- d_3	Carbendazim- d_3	1.69	195.1	33	132 (28)	160 (18)	0.201		
CYP- d_5	Cyprodinil- d_5	2.88	231	56	93 (33)	108 (25)	0.449		
DIM- d_6	Dimethomorph- d_6	2.94/ 3.03	394.2	40	171.1 (30)	307.1 (20)	0.5/0.5		
IMI- d_4	Imidacloprid- d_4	2.10	260.1	34	179.1 (20)	213.1 (15)	1.18		
MET- ¹³ C ₆	Metalaxyl- ¹³ C ₆	2.70	286.1	26	198.1 (17)	226.1 (13)	0.605		
MYC- d_4	Myclobutanil- d_4	3.31	293	34	70 (18)	129 (32)	0.15		
PYR- d_5	Pyrimethanil- d_5	2.52	205	51	82 (24)	107 (24)	0.82		
TEBU- d_9	Tebuconazole- d_9	3.56	317	40	70.1 (22)	125 (40)	0.076		

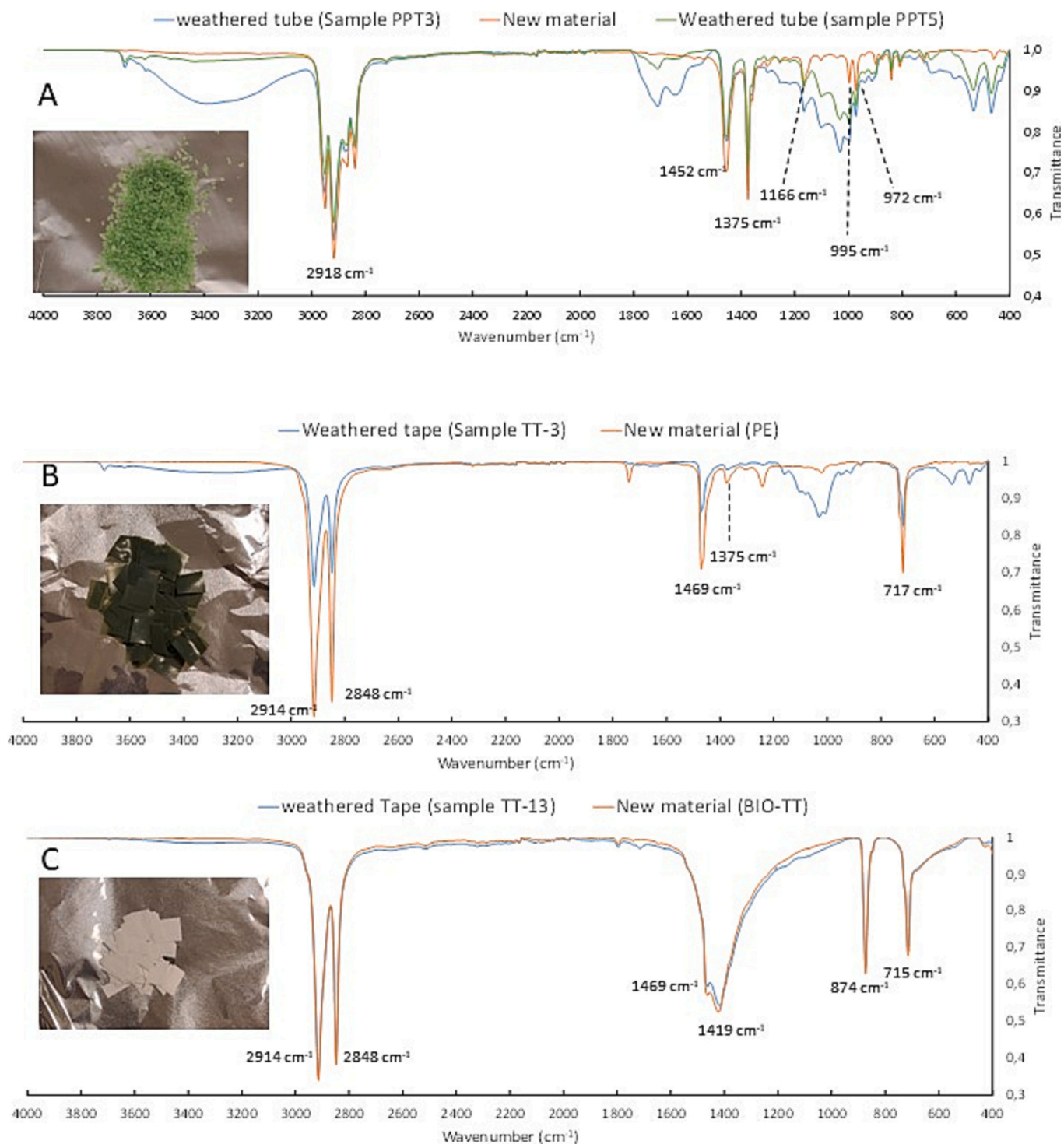


Fig. 1. Pictures of conditioned and ground (or cut) plastic debris collected from vineyards together with the FTIR-ATR spectra for aged materials and their new counterparts. A, Plant protection tube (PPT). B, Conventional tying tape (TT). C, Biodegradable-claimed TT.

threshold $0.7 \mu\text{m}$) to recover plastic debris. The filter, with retained plastics, was rinsed with ultrapure water, spiked with SSS, and extracted with a mixture of Hex:DCM as reported in Section 2.3.

Sorption experiments were performed using new items, and previously cleaned (extracted) samples of aged PPT and TT, identified as polypropylene (PP) and polyethylene (PE), respectively. The volume of water and the mass of plastic were the same as in desorption assays. Surface water aliquots were spiked with target pesticides (2 ng mL^{-1}) and homogenized for 30 min before addition of plastic fragments. After

72 h of magnetic stirring, compounds remaining in the water phase and those sorbed on the plastic material were determined by LC-MS/MS as previously reported. Desorption and sorption experiments were carried out in triplicate. The Statgraphics 19 Centurion (The Plains, VA, USA) software package was used to assess the existence of significant differences among sorbed masses of each compound as function of the tested polymer and its degree of aging. To this end, analysis of variance and the least significant difference test were used.

2.5. Analytical techniques

LC-MS/MS was used as main technique to determine the residues of pesticides in aged plastic debris, soils, and to investigate the distribution of these compounds between the aqueous phase and plastic fragments in sorption and desorption experiments. The employed instrument consisted of an ultra-performance liquid chromatograph (UPLC) instrument combined with a triple quadrupole mass analyzer (Waters, Acquity UPLC Xevo TQD), equipped with an electrospray source (ESI). The LC column was a Zorbax Eclipse Plus C₁₈ rapid resolution (50 mm × 2.1 mm, 1.8 μm) acquired from Agilent Technologies (Wilmington, DE, USA). The analytical column was protected with a C₁₈ 2.1 mm i.d. Security Guard™ cartridge, supplied from Phenomenex (Torrance, CA, USA). Chromatographic separation conditions and ESI parameters are provided as Supplementary information, Text S2. Retention times and multiple reaction mode (MRM) detection conditions for native pesticides and isotopically labelled SSs are summarized in Table 1. LOQs achieved for soil and plastic samples are also given in Table 1. In case of water samples analyzed by LC-MS/MS, the concentration of the lowest level standard solution (50 ng L⁻¹) was adopted as the procedural LOQ for all compounds.

Quantification of folpet residues in plastic litter was performed by GC-MS, using an Agilent 7200, TOF instrument, equipped with an electronic ionization (EI) source. Chromatographic separations were carried out using a HP5-MS capillary column (30 m × 0.25 mm, 0.25 μm film thickness), with helium as carrier gas at a flow of 1.2 mL min⁻¹. Additional chromatographic conditions employed during determination of folpet and qualitative characterization of plastic extracts are given as Supplementary information, Text S1. Quantification (Q1) and qualification (Q2) ions for folpet and folpet-d₄ were 259.9334 and 261.9305; 265.9582 and 267.9534, respectively. The Q1 and Q2 ions were extracted using a window of 0.005 Da, and Q2 to Q1 ratios were 0.70 (folpet) and 0.15 (folpet-d₄). Whatever the determination technique (LC-MS/MS or GC-MS), compounds identification was based on retention times match with calibration standards (maximum deviation 0.1 min), and ratios between qualification and quantification product ions (fragments in case of EI-MS) within ±30 % of those obtained for calibration standards.

In addition to chromatography and mass spectrometry techniques,

FTIR spectra, acquired in the total attenuated reflectance mode (ATR), were employed for identification of plastic debris collected from vineyards. This information was completed with images obtained using scanning electron microscopy (SEM), and elemental analysis by ICP-MS. In the latter case, samples (0.5 g) were digested with 25 mL of concentrated nitric acid, at atmospheric pressure, in a hot plate, for 4 h. Thereafter, the liquid phase was adjusted to 50 mL, further diluted with ultrapure water and analyzed by ICP-MS for identification and semi-quantitative determination of metallic elements (Elseblani et al., 2023).

2.6. Quality control procedures

Quality control experiments involved (1) the analysis of procedural blanks (either corresponding to river water employed in sorption, desorption experiments, or to the different solvents employed to recover pesticides from plastic litter and soil samples); (2) the assessment of the stability of pesticides in spiked surface water samples employed in sorption studies; (3) verification of the stability of the calibration curves by injection of a calibration standard every 10 injections; (4) comparison of responses for SSs in calibration standards versus extracts obtained from plastic litter; (5) assessing the repeatability of the extraction process for environmental polluted, aged plastics; and (6) testing the accuracy of the analytical procedure for spiked samples of agricultural soils.

3. Results and discussion

3.1. Characterization of plastic debris

The FTIR spectra for new and aged samples of PPT and two types of TT plastics collected from vineyards are shown in Fig. 1. Spectra of PPT items contain the characteristic bands of PP, with a group of four signals around 2918 cm⁻¹, corresponding to symmetric and asymmetric tension of the carbon hydrogen bond in methylene and methyl groups, and two additional intense absorption bands at 1452 cm⁻¹ and 1375 cm⁻¹, respectively, Fig. 1A. Weathered samples of PPT, labelled as PPT-3 and PPT-5, presented extra bands in the regions above 3000 cm⁻¹, around 1700 cm⁻¹, and between 1200 cm⁻¹ and 1000 cm⁻¹, which point out to oxidation of the hydrocarbon skeleton of PP, Fig. 1A. The experimental

Table 2

Concentrations of fungicides (ng g⁻¹), with standard deviations in parenthesis, measured in sub-samples of different aged plastic debris by LC-MS/MS as function of the extraction solvent, n = 3 replicates.

Sample code	Solvent	CYF	CYP	DIF	IPROV	MAN	MET	MYC	PEN	TEBU	TETRA	ZOX	SUM
PPT-08	MeOH:		64.1			12.3	52.4	116.8	119.3	92.8	28.7	204.2	750.8
	ACN		(19.4)			(4.0)	(14.0)	(22.1)	(35.1)	(11.1)	(3.4)	(26.4)	
	Hex:	17.1	106.3	22.4	186.9		150.0	191.7	179.2	142.1	50.4	208.9	
PPT-09	DCM	(2.5)	(13.9)	(3.7)	(5.8)		(0.9)	(26.3)	(30.4)	(17.0)	(6.2)	(9.9)	1255.0
	MeOH:							191.6		92.2			283.8
	ACN							(17.8)		(54.7)			
Hex:							191.0		80.1				
TT-18	DCM							(11.5)		(4.9)			271.1
	MeOH:		19.8 (2.3)					150.1					169.9
	ACN							(11.5)					
Hex:		106.4					194.0						
TT-20	DCM		(32.4)					(50.2)					300.4
	MeOH:		138.4	12.7			737.5	100.0		20.3	1256.4		2265.3
	ACN		(8.5)	(1.6)			(291.4)	(29.9)		(9.0)	(472.7)		
Hex:		593.8	89.3			2089.8	590.7		62.8	87.0	2622.9		
TT-22	DCM		(110.4)	(22.5)			(304.1)	(126.6)		(74.2)	(10.1)	(500.7)	6136.3
	MeOH:		43.1	13.5	10.4				61.2	89.2	28.9	222.8	540.7
	ACN		(10.4)	(2.2)	(1.1)		5.7 (2.0)	65.9 (7.5)	(8.7)	(12.3)	(5.7)	(20.0)	
Hex:	51.5	305.0	65.5	201.3		12.8 (1.3)	334.9	283.5	376.3	193.7	1987.0		
TT-23	DCM	(10.6)	(40.3)	(8.0)	(20.4)			(45.0)	(7.0)	(35.2)	(6.0)	(197.5)	3811.5
	MeOH:		4.6 (1.3)					17.5 (3.7)		17.1	(4.9)		39.2
	ACN									(4.9)			
Hex:		96.9							74.2				
	DCM		(18.7)					50.7 (3.4)		(13.2)			221.8

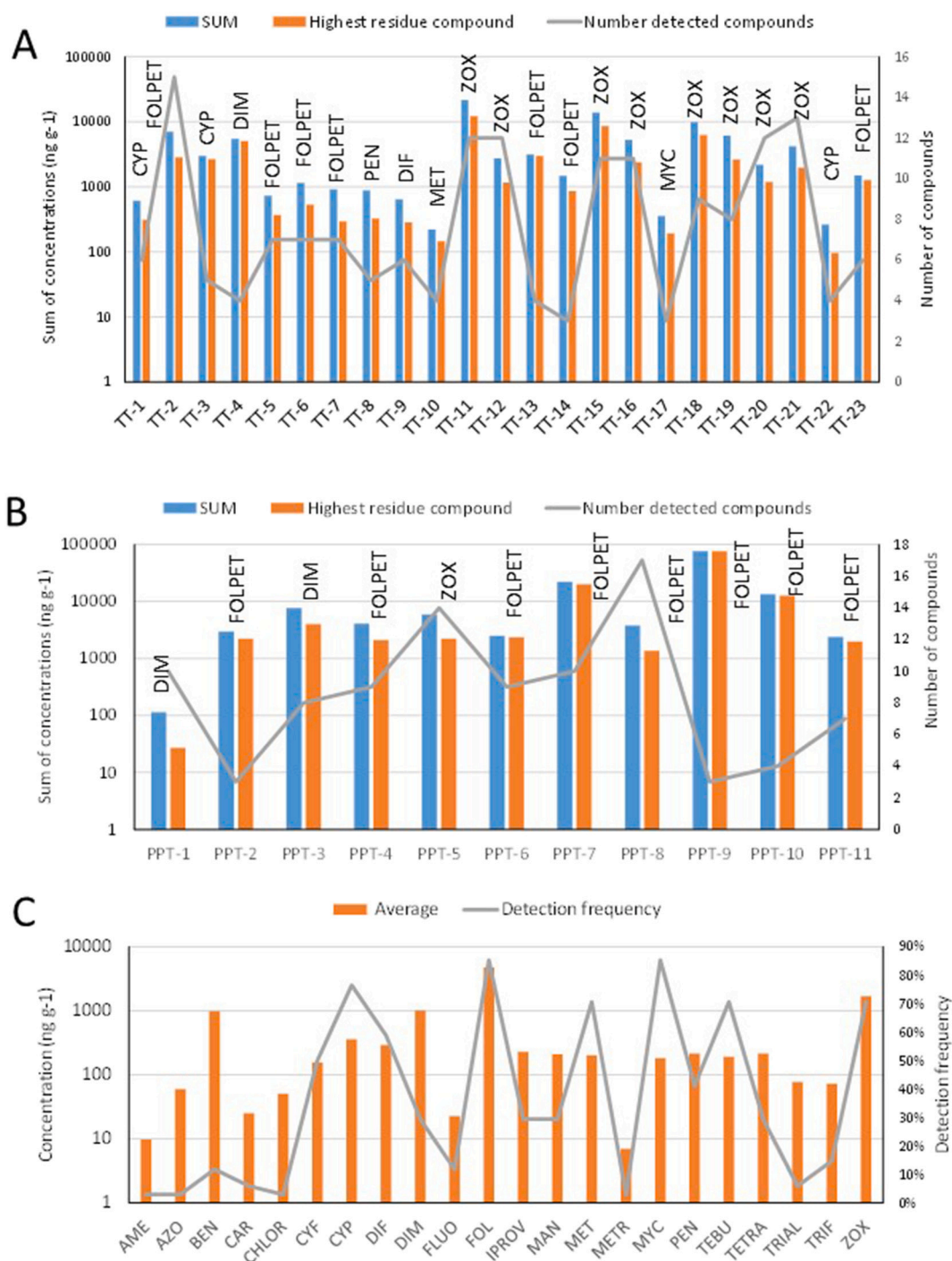


Fig. 2. Summary of total pesticide residues (data in ng g⁻¹) in debris of plastics collected from vineyards. A, Tying tape samples. B, Plant protection tubes. C, Average concentrations of individual pesticides and detection frequencies in all samples.

spectra of a new green-colour TT fitted that of PE, likely low-density PE, considering the low intensity band at 1375 cm⁻¹, Fig. 1B. The record for the aged material keeps most of these bands, showing a moderate degree of oxidation, Fig. 1B. Spectra of TT debris collected from most vineyards matched those shown in Fig. 1B; confirming the prevalent use of PE as material to tie the canes of vines. Fig. 1C presents the spectra for a second type of TT, of white colour, identified just in one of the sampled vineyards. According to the feedback provided by the winegrower, and the available commercial information for new items of the same material, it was sold as biodegradable tying tape. The IR spectra for new and aged pieces of this material retained the four most intense bands noticed

in the spectra of conventional PE, Fig. 1B. Moreover, two extra signals at 1419 cm⁻¹ and 874 cm⁻¹ were present, Fig. 1C.

GC-TOF-MS, ICP-MS and SEM analysis showed also some relevant differences among the three types of plastics. The GC-TOF-MS records for new, green colour, PE tape reflected the presence of TINUVIN-326 as UV absorber. Analysis of weathered samples of TT, with the same colour, confirmed the residues of the UV filter in most samples. In some cases, other UV absorbers belonging to the benzotriazole chemical family (i.e. TINUVIN-328 and TINUVIN-327) were also identified. In the extracts from PPT, a steric hindered amine, termed as TINUVIN-770, was often detected. This compound is also employed as UV filter. The chemical

structures, accurate EI-MS spectra, and linear retention index of these compounds are provided as Supplementary information, Fig. S2. None of these UV absorbers were noticed in samples of the biodegradable-claimed tape.

Images obtained by SEM reflected that this later material showed a rough, irregular surface compared to the smooth one of the conventional PE TT, Fig. S3. ICP-MS analysis of both types of TT reflected higher concentrations of Na, Zn, Mg, and particularly Ca, in the tape commercialized with the biodegradable stamp than in the conventional one, Table S2. Calcium content accounted for 4.3 % of the mass of the former polymer. Calcium carbonate is often used as white dye, and filler in polymeric materials. The database IR spectra of this salt contains a broad, intense absorption band at 1425 cm^{-1} and narrow, medium and low intensity ones at 875 cm^{-1} and 712 cm^{-1} (On-line database of infrared and Raman spectra, 2023), which matched extra bands shown in Fig. 1C versus those existing in the spectrum of conventional PE. Some previous studies suggested that the biotic degradation of PE containing calcium carbonate as filler is advantageous compared to that of conventional PE (Croitoru et al., 2017; Husarova et al., 2010). This fact, combined with the absence of UV absorbers in this kind of TT and its rough surface, which might favour microbiological colonization of the material, contributing to its degradation. However, from an academic perspective, PE is not within the list of biodegradable polymers designed for agriculture uses (Serrano-Ruiz et al., 2021).

3.2. Extraction of pesticides from plastic debris

The extraction of pesticides from weathered agricultural plastics (PPT and TT) was assessed using two different mixtures of solvents: MeOH:ACN (1:1) and Hex:DCM (1:1). The first combination of polar solvents has been employed to recover pesticides from vineyard soils (Pérez-Mayán et al., 2020). Moreover, MeOH has been previously applied to the extraction of organic compounds from marine-origin microplastics (León et al., 2019). Combinations of alkanes and DCM are also proposed to recover organic compounds from plastic debris and microplastics collected from different environmental compartments (Elseblani et al., 2023). Extractions were performed in triplicate, with aged plastics (0.5 g) soaked with 10 mL of solvent for 15 min. Regardless of the employed mixture of solvents, responses obtained in consecutive extractions of the same sample remained below 10 % of those obtained in the 1st cycle. Thus, the volume of solvent and the number of

extraction cycles were limited to 10 mL and 1 cycle, respectively.

Table 2 summarizes average concentrations, with their standard deviations, for a group of 11 fungicides noticed in six different samples, extracted in triplicate using two different mixtures of solvents. Considering 0.5 g of sample and adjusting the obtained extract to a final volume of 2 mL, the limits of quantification of the LC-MS/MS procedure ranged from 1 ng g^{-1} to 10 ng g^{-1} , depending on the compound (Table 1), with a linear response range up to 800 ng g^{-1} . Samples above this value required a further dilution of the primary extract before quantification. The combination of Hex and DCM led to higher concentrations than the mixture of polar solvents, Table 2. The exception was noticed for sample code PPT-9. In this case, both solutions led to similar residues of the fungicides myclobutanil (MYC) and tebuconazole (TEB).

GC-MS chromatograms corresponding to extracts obtained from the same sample in both mixtures of solvents are provided as Supplementary information, Fig. S4. Whatever the type of polymer (PE or PP), the total ion current (TIC) chromatograms corresponding to the Hex:DCM solution were more complex than those recorded for extracts in MeOH:ACN. The extracted chromatograms (EICs) for characteristic ions of alkanes (m/z values of 57.0698, 71.0855 and 85.1012) in Hex:DCM extracts showed peaks at increasing retention times. Thus, both polyolefins not only swell, but they are partially solubilized in contact with the mixture of Hex:DCM.

Considering data summarized in Table 2, and GC-MS profiles in Fig. S4, it seems feasible that pesticides sprayed in vineyards are not only retained on the surface of plastic debris, but they penetrate inside the polymer. That is, at least one fraction of fungicides identified in the aged debris of PPT and TT is absorbed by the polymeric materials. This assumption agrees also with data reported for non-polar insecticides in laboratory experiments carried out with films of undisturbed PE (Ramos et al., 2015).

If we assume that the interaction between pesticides and aged plastics is different to that observed for new materials, and that the strength of the interaction increases with contact time, assessing the accuracy of data obtained for polluted plastic debris becomes a very difficult task. Considering responses obtained for isotopically labelled compounds, added to samples before extraction, absolute recoveries measured for TT and PPT ranged from 79 % to 114 %, Table S3. The average relative standard deviations of the sample preparation procedure ($n = 6$ replicates of 0.5 g fractions from two different aged plastics) for compounds noticed above their LOQs were 17 % and 20 %, Table S4.

Table 3

Comparison of average concentrations (ng g^{-1}) measured for pesticides in top-soil samples and soil-dispersed plastic fragments obtained from different vineyards by LC-MS/MS. Average values for duplicate extractions.

Sampling site	1		2		3		4		5			6		7	
Sample type	TT	Soil	TT	Soil	TT	Soil	TT	Soil	TT	PPT	Soil	PPT	Soil	TT	Soil
AZO		6.5		3.8		2.5		92.9			17.0				
BEN										858.0					
CAR						30.0		95.5	41.3	8.6	37.0				
CYF	95.0	15.9	63.0				115.0		51.5	17.1					
CYP	150.8		134.7		593.8	30.3	62.0	6.0	305.0	106.3	11.8			106.4	90.5
DIF	201.6	42.8	222.5	21.3	89.3		1407.8		65.5	22.4	2.8				
DIM		16.7		14.0		32.8		115.0		100.2	36.7		10.0		
FLUO									44.1	16.9	46.3				
IPROV	22.6		14.3				42.6		201.3	186.9					
MAN	32.2	45.3	29.6	21.0			34.4				49.5	563.1	6.9		
MET	13.2	64.5	8.7		2089.8	34.8	56.2	20.6	12.8	150.0	8.8	130.9	6.5		
MYC	36.6	54.5	4.6	30.8	590.7	79.8	48.6	105.3	334.9	191.7	57.0		92.8	194.0	205.8
PEN	75.8	8.4	85.9	4.23					283.5	179.2	21.8				
TEBU	157.0	146.6	189.2	88.5	62.8	14.3	313.4	166.0	376.3	142.1	59.0				
TETRA	26.6		19.9		87.0	2.5	663.2		193.7	50.4	3.8				
TRIAL										151.8					
TRIF					10.6					35.5					
ZOX	1157.4	51.6	1190.7		2622.9		2370.0		1987.0	208.9	5.2	112.2	2.5		
SUM	1968.8	452.8	1963.1	183.5	6146.9	226.8	5113.2	610.4	3896.9	2426	415.5	806.2	128.7	300.4	296.3

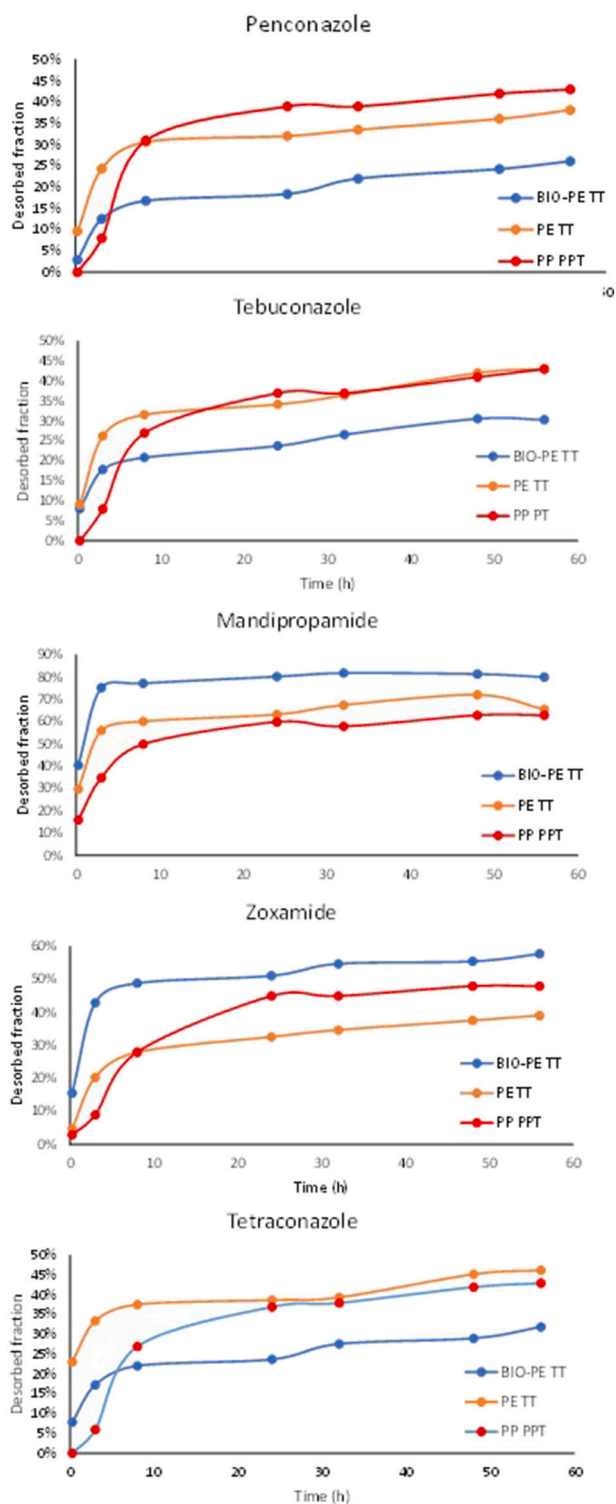


Fig. 3. Time-course of desorbed pesticides fractions from weathered agriculture plastics (0.4000 g) in contact with river water (200 mL). Average values (fraction desorbed to the water phase) for triplicate experiments with each material.

3.3. Occurrence of pesticides in agriculture plastics

Fig. 2 summarizes data of pesticides found in the set of 34 samples of aged plastic debris obtained from different vineyards, processed in duplicate. Values corresponding to TT fragments are shown in Fig. 2A

and those measured in PPT in Fig. 2B. The set of compounds investigated in the processed samples were those included in the multiresidue LC-MS/MS procedure (Table 1) plus folpet, determined by GC-TOF-MS. LOQs of the LC-MS/MS method for plastic debris varied between 1 ng g^{-1} and 10 ng g^{-1} . Regarding folpet, a LOQ of 40 ng g^{-1} and a linear range up to 4000 ng g^{-1} was obtained using GC-TOF-MS detection. Every sample of plastic debris contained residues of at least one of the considered pesticides, with a maximum of 17 compounds above their LOQs in sample code PPT-8. Total pesticide residues ranged from 114 ng g^{-1} to above $76,000 \text{ ng g}^{-1}$, case of samples PPT-1 and PPT-9, respectively. Concentrations measured for each individual compound are given as Supplementary information, Table S5. All residues found in aged plastics, except chlorpyrifos, corresponded to fungicides. Species showing detection frequencies equal or above 50 % were cyflufenamid (CYF), cyprodinil (CYP), difenoconazole (DIF), folpet, metalaxyl (MET), myclobutanil (MYC), tebuconazole (TEB) and zoxamide (ZOX), Fig. 2C. Among them, the highest average concentrations corresponded to ZOX and folpet. Folpet is a non-systemic fungicide, included in the formulation of commercial mixtures applied to vineyards at concentrations up to 40 %. It is hardly transferred to wine (Cabras et al., 1997), and shows a limited stability in soil (Bermudez-Couso et al., 2007). On the other hand, folpet has been pinpointed as one of the most often detected compounds in air samples obtained close to arable fields (Zaller et al., 2022), and particularly in the vicinity of vineyards (Martin et al., 2022). ZOX is also regarded as non-persistent in soil (Liu et al., 2023). To the best of our knowledge, none of both fungicides were previously reported in samples of aged agriculture plastics.

In addition to pesticide residues quantified in aged plastics, traces of two fungicides (propiconazole, PROP; and MET) were noticed in new samples of TT and PPT at concentrations between the LOQs of the method and 10 ng g^{-1} . The origin of these compounds remains unclear, and it is not straightforward to determine if agriculture plastics were contaminated with these compounds during production or later, in the distribution process. Both possibilities seem feasible due to recycling of end-of-life agriculture plastics (Martínez Urreaga et al., 2020) and commercialization of new materials in locals which stock and sell commercial fungicide formulations. Conversely to the low residue levels of both fungicides, metrafenone (METR) was quantified in different items of new TT, at levels in the range of 3700 ng g^{-1} to 4000 ng g^{-1} . Such values were considered too high to be regarded as an accidental contamination. Thus, we assume that the fungicide was intentionally included in the formulation of this material. Levels of METR in new items decreased in more than 90 %, when the PE material was exposed to outdoors conditions for 48 h. This behavior agrees with the fast dissipation of the pesticide under simulated solar light (López-Fernández et al., 2018); moreover, it explains why METR was hardly identified in aged samples of agriculture plastics, Table S5.

Deconvolution of GC-TOF-MS records for extracts of aged plastics reflected the existence of some additional pesticides. In brief, 50 % of the analyzed PPT contained residues of the fungicide dichlofluanid; moreover, the herbicide oxyfluorfen was often noticed in this type of plastics and the insecticide deltamethrin in fragments of TT. Although their concentrations were not determined, the identity of these species was confirmed using authentic standards. Dichlofluanid lost the authorization of use by 2009; thus, its presence in weathered debris of PP confirms the stability of both, the fungicide and the debris of PP in the environment of vineyards. Another example of a non-currently authorized fungicide, quantified in aged fragments of PPT was triadimenol, Table S5. Regarding oxyfluorfen, according to the Spanish Ministry of Agriculture (Statistics of pesticides consumption per crop in Spain, 2019), this is one of the most often used herbicides to control vegetation in vineyards. Considering that PPT are in direct contact with soil, it is not strange that this material retains residues of herbicides sprayed on vineyards.

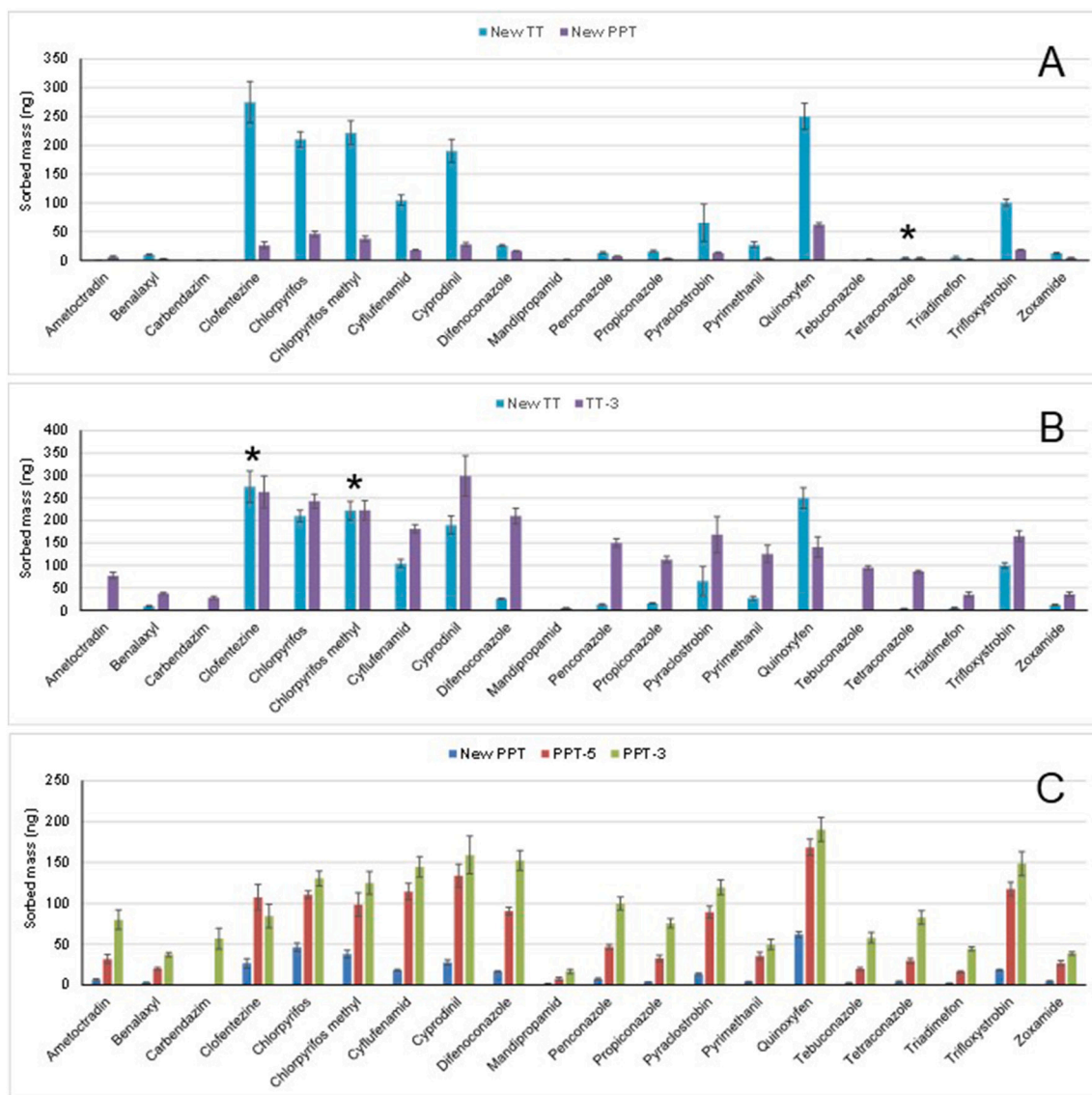


Fig. 4. Comparison of sorbed amounts (mass in ng) of pesticides in PE-made tying tape (TT) and PP plants protection tubes (PPT) in contact with pesticide spiked river water (200 mL, addition level 2 ng mL^{-1}). Average data with standard deviations ($n = 3$ replicates). A, Comparison of new polymers. B, Effect of aging in the masses sorbed by TT made of low-density PE. C, Effect of aging in masses sorbed by PPT made of PP. Asterisk marked bars correspond to non-significant differences (95 % confidence level) of sorbed masses between investigated conditions.

3.4. Pesticide residues in plastics versus soil

To confirm the different levels of pesticides in aged plastics, in direct contact with the soil of vineyards, and soils, samples of both matrices were simultaneously taken in seven cultivars and analyzed using LC-MS/MS as determination technique. Accuracy of results obtained from soil samples were evaluated with samples spiked at two different concentration levels (10 ng g^{-1} and 100 ng g^{-1}), processed in triplicate. Recoveries varied between 75 % and 111 %, with average standard deviation values of 16 % and 7 % for low and high addition levels, respectively, Table S6. In case of folpet, using GC-MS analysis, the recovery for soil spiked at 800 ng g^{-1} was 118 %, with a standard deviation of 6 %. Table 3 summarizes the concentrations of LC-MS/MS amenable pesticides in these pairs of samples. Folpet was not included in this Table 3, since this compound was found only in aged plastic debris but not in soil samples at concentrations above its LOQ (25 ng g^{-1}). Even without considering the contribution of this compound, the sum of concentrations for the rest of pesticides found in plastic were

higher than those existing in soils, except for samples obtained at site number 7. As expected, concentrations of ZOX were significantly higher in plastic debris than in soil. Apart from the parent compound, potential degradation products of ZOX (sharing the most intense fragment ion in the spectra of the parent fungicide for the methyl-dichloro-benzamide moiety) were tentatively identified in GC-TOF-MS chromatograms corresponding to aged plastics. Their experimental accurate EI-MS spectra are given as Supplementary information, Fig. S5. On the other hand, azoxystrobin and carbendazim were quantified in soil from several fields; however, they remained undetected in plastics collected from same sites, Table 3. It is worth to note that, the range of values for total pesticide residues in vineyard soils (from 129 ng g^{-1} to 610 ng g^{-1}) was similar to that reported in our former study from year 2020, for top soil samples collected between 2017 and 2019 (Pérez-Mayán et al., 2020). On the other hand, literature references to compare residues measured in plastic debris could not be found. Overall, data in Table 3 suggest that the relative stabilities, and the degradation routes of fungicides in vineyard soil and plastic debris show significant differences.

3.5. Desorption and sorption experiments

Fragmented plastics noticed in the soil of vineyards are susceptible of migration to surface water due to run-off; thus, we investigated the potential transference of pesticides from weathered, partially oxidized, plastics to the water phase. The study was limited to LC-MS/MS amenable compounds, so migration of folpet was not assessed. Fig. 3 shows the average water migration fraction ($n = 3$ replicates) for a selection of fungicides noticed in the three different types of weathered plastics identified in this research. Time-course fractions for compounds whose desorption could be followed in one of the investigated materials are provided as Supplementary information, Fig. S6. As a general statement, the equilibrium between desorbed concentrations and pesticide residues associated to plastic litter was achieved after 24 h, with little (case of penconazole and TEB), or null increase in dissolved concentrations (mandipropamide, ZOX and tetraconazole) at longer times. In some cases, significant desorbed percentages were noticed just after 0.5 h. This behavior points out to a readily available adsorbed fraction of pesticides in some plastics, whilst further desorption processes require the migration of the compounds from inside the materials to the bond with the water sample. For pesticides in Fig. 3, equilibrium desorbed fractions ranged from 20 % to 80 %, depending on the considered compound and the type of plastic. Likely, the lower the polarity and the water solubility of a pesticide, the smaller the fraction released to the water phase. On the other hand, the type of polymer, and its oxidation degree might also affect the desorption equilibria. In this vein, polar compounds might be more strongly retained by highly oxidized polymers than by their new, lipophilic polyolefin (PE or PP) counterparts.

To verify the latter hypothesis a 2nd series of experiments was carried out. In this case, the sorption capabilities of new and aged materials were compared. The employed samples corresponded to PP PPT and conventional PE TT, whose IR spectra are shown in Fig. 1A and B, respectively. Fig. 4 summarizes the masses of 20 compounds found in the plastic residue above their LOQs after 72 h. Eight pesticides (azoxystrobin, dimethomorph, fluopicolide, imidacloprid, iprovalicarb, MET, MYC and triadimenol) remained under their LOQs in plastic material. Thus, taking into account their initial amount in the water solution (400 ng) and their LOQs for plastics (Table 1), it can be concluded that the sorption efficiencies of these eight compounds remained below 2.5 %. METR was also excluded from Fig. 4 since it could not be completely removed from the new TT material. The influence of the type of polymer on pesticides sorption capabilities is shown in Fig. 4A. In general, pieces (0.5 cm \times 0.5 cm) of new PE tape showed a higher sorption capability (95 % confidence level) than ground new PP guard tubes. The only exception corresponded to tetraconazole. In this case, no significant differences were noticed between amounts sorbed by the two polymers. The effect of environmental oxidation in the sorption capability of each material are shown in Fig. 4B and C. For PE-made TT, the sorbed amounts of less polar compounds (clofentezine, and methyl chlorpyrifos; log D values from 3.8 to 5.0, at pH 7) were equivalent (95 % confidence level) for new and aged PE, for quinoxyfen (log D 5.2 at pH 7) the sorbed amount decreased for the aged polymer, and the rest of compounds showed a higher, statistically significant affinity to pieces of aged PE tape than to the new items, Fig. 4B. In case of PP, the sorbed masses of every compound (except clofentezine) increased significantly with the oxidation degree of the polymer, Fig. 4C. That is, in general, changes in the composition of both kinds of agricultural plastics (PE and PP) under environmental conditions increase significantly (95 % confidence level) their capability to sorb medium polarity fungicides used to protect vines against mildium, oidium and botrytis infections.

4. Conclusions

Most of the residues of tying tape and plant protection tubes collected from vineyards corresponded to low-density PE and PP

polymers. The analysis of these materials reflected the presence of significant levels of several pesticides, particularly fungicides, including compounds considered as non-persistent in soils, as it is the case of folpet and ZOX. Assessment of extraction conditions applied to aged plastics reflected that fungicides are not only adsorbed on the surface, but also absorbed inside the polymeric materials. The strength of the interaction plastic-pesticide is function of the type of plastic and the features of the pesticides. Moreover, aging of tying tape and plant protection tubes polymers significantly increased their capability to sorb medium polarity compounds from model surface water solutions. On the opposite direction, migration of same compounds from aged, polluted plastic litter to surface water is expected to be also affected by the previous weathering of the host materials. Despite sorption studies reflecting a low affinity of new and aged plastic residues by medium polarity fungicides (i.e. MET, MYC, ZOX), most of these compounds were found in aged plastic debris collected from vineyards, suggesting a good environmental stability when sprayed directly on these materials.

Findings obtained in this manuscript reveal the need to adopt an unambiguous definition of biodegradable plastics developed for agricultural uses, including information of the employed polymer. It is also advised to be aware of the existence of pesticide residues in vineyard plastics before considering the possibility of being recycled to produce new goods. Further research on other kinds of agricultural plastics, employed in higher amounts (i.e. greenhouse and mulching films), must be performed to assess the extent of pesticide residues in these materials.

CRedit authorship contribution statement

M. Cobo-Golpe: Investigation, Methodology, Writing – review & editing. **P. Blanco:** Investigation, Methodology, Writing – review & editing. **V. Fernández-Fernández:** Investigation, Methodology, Writing – review & editing. **M. Ramil:** Funding acquisition, Investigation, Supervision, Writing – review & editing. **I. Rodríguez:** Conceptualization, Funding acquisition, Project administration, Supervision, Writing – original draft.

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

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.scitotenv.2023.169273>.

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