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Higher potential leaching of inorganic and organic additives from biodegradable compared to conventional agricultural plastic mulch film

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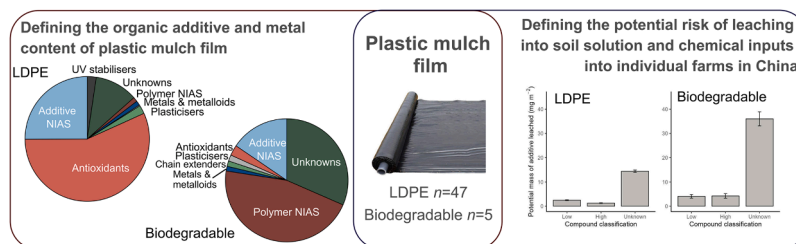[g] *Department of Geography and Environmental Science, University of Reading, Reading, UK*
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HIGHLIGHTS

- Plastic mulch film additive content was highly diverse, and dominated by lubricants and antioxidants.
- Metal and metalloid content and leaching dominated by inert fillers, with minor contribution from heavy metals.
- Majority of compounds in leachate were not present in the parent films.
- Leaching of organic additives was higher in biodegradable films than LDPE films.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

Plastic mulch films support global food security, however, their composition and the potential release rates of organic, metal and metalloid co-contaminants remains relatively unknown. This study evaluates the low molecular weight organic additives, metal and metalloid content and leaching from low density polyethylene (LDPE) and biodegradable plastic mulch films. We identified 59 organic additives, and non-intentionally added substances in the new LDPE films ($39.8\,\mathrm{mg\,m^{-2}}$) and 60 in the new biodegradable films ($129\,\mathrm{mg\,m^{-2}}$). The leaching of organic compounds of high concern for ecosystem and human health (e.g. phthalates, organophosphite antioxidants) was comparable to those of low concern (fatty acids, fatty amides, alkanols). However, the majority of leached compounds have undergone no regulatory scrutiny and their environmental fate and toxicity remain unknown. Leaching of heavy metals (Cu, Zn, Pb) was low relative to inert fillers (Ca, Na). Leaching was higher for both organic and metal/metalloid additives from the biodegradable films ($74.6\,\mathrm{mg\,m^{-2}}$) than the LDPE films ($23.7\,\mathrm{mg\,m^{-2}}$). This untargeted approach allowed assessment of the chemical burden posed

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to individual farms, based on existing use patterns of plastic mulch films, with higher chemical burden coming from biodegradable films, raising the potential for pollution swapping. This research emphasises the need to include the complex mixture of leached additives when assessing the environmental risks presented by plastic mulch films, balancing yield benefits with the protection of our agricultural soils.

1. Introduction

Plastic mulch film covering the soil surface is an essential part of agricultural cultivation to meet increasing global food demands [1]. The adoption of this practice has been due to the numerous benefits of using plastic mulch film, including water conservation [2], improved nutrient use efficiency [3], improved temperature regulation, and increased soil temperature [4]. Furthermore, plastic mulch film can reduce the impact of pests [5] and act as a physical barrier to weed growth [6]. Improved crop yields are subsequently of socioeconomic benefit, supporting the production of cash crops, while increasing food security. Many regions now rely on plastic mulch film for food production, especially China, which is the world's largest user [7], with *ca.* 15 % of the country's arable land under plastic mulch film [2].

However, there are numerous potential environmental impacts associated with the use of plastic mulch film. A key challenge is removing used film, and if removed, the lack of recycling routes for soil-contaminated films [8]. The majority of films are low density polyethylene (LDPE), which are a source of microplastics, formed following mechanical damage, and abiotic (i.e. UV) degradation [9,10], which may alter soil properties and nutrient cycling [11,12] and the soil microbial community [13]. There is growing interest in biodegradable mulch films, which are designed to biodegrade in the soil to minimise microplastic accumulation. However, an emerging concern for both conventional and biodegradable plastic mulch films, and plastics in general, are the additives, or co-contaminants, included within the film to aid processing, and optimise the polymer for its final end purpose. As the additives included are not chemically bound, they are readily leached to the wider environment [14,15]. There are a huge number of potential co-contaminants, acting as lubricants, plasticisers, antioxidants, fillers, pigments and UV absorbers, encompassing a diverse range of organic compound classes including: alkanols, fatty acids, amides and organophosphites, and metal-containing compounds [16]. An evaluation of the potential hazards of additives used in all plastics revealed that while 37 % of known compounds used met no hazard criteria, 24 % were of concern, or potentially of concern, and a further 39 % had insufficient information available to determine their potential hazard [16]. This represents an unknown chemical burden entering our environment, which needs to be included in risk assessments for the continued use of mulch film in agriculture.

The release of co-contaminants from plastic mulch film opens up the potential for xenobiotic chemical uptake by plants, entry into the food chain and leaching to water courses [17]. There is increasing evidence of phthalates, which are known endocrine disruptors [18–20], accumulating in soil [15,21,22] and being taken up into crops [23]. Similarly, organophosphites and UV absorbers (e.g. benzotriazoles and benzophenones) may leach and bioaccumulate in the food chain [20,24]. The metal and metalloid additives can be relatively inert (e.g. $CaCO_3$ as a filler), however, heavy metals added as pigments (e.g. ZnO, Fe_2O_3) [25] are toxic to microorganisms [26] and plants [27,28] at high concentrations (over 500 mg kg^{-1}) [29].

Despite these potential ecotoxicological effects, the environmental burden posed by mulch films is poorly understood, not helped by their unspecified chemical compositions beyond the identity of the parent polymer, as this is manufacturer proprietary information. The metal content of plastic mulch films has not been widely studied, however, for other LDPE film products, Fe and Zn were the most abundant heavy metals [30]. Previous analyses of organic additives have targeted individual compound classes, such as phthalates [21,31] and

organophosphites [24]. In order to identify the wide range of potential additives untargeted approaches need to be applied [32,33], however, these have been limited in terms of the number of films investigated, and comparisons between LDPE and biodegradable films are rarely undertaken. Biodegradable films are suggested as a potential alternative to LDPE films, yet may present a greater source of co-contaminants due to degradation increasing rates of release. Untargeted approaches to assess co-contaminant content and potential release, applied to both types of films and covering inorganic and organic co-contaminants, are urgently needed. Such an approach will permit more accurate risk assessment of co-contaminant compositions in plastic mulch films, balancing potential hazards with the benefits of agricultural plastic mulch film, and identifying areas where risks can be reduced.

In this study, we analysed LDPE and biodegradable plastic mulch films with the aim to determine their low molecular weight organic additive and metal content. We undertook an untargeted approach to quantify inorganic and organic co-contaminant content in plastic mulch films and assessed the potential for these to leach into the soil environment. We aimed to then classify co-contaminants in terms of potential hazards to assess the overall co-contaminant risk. To upscale the potential environmental loading of plastic mulch film co-contaminants, we assessed the plastic mulch film use of farmers ($n = 300$) from three Chinese provinces (Gansu, Inner Mongolia, Shanxi). We aimed to provide a farm-level assessment of the chemical burden posed by agricultural mulch films, while considering the vital need for this agricultural practice in many regions globally.

2. Methods

2.1. Solvents and standards

All solvents (dichloromethane (DCM), methanol (MeOH), ethyl acetate, water) were HPLC grade (Rathburn, UK). All standards for in-house libraries were purchased from Merck Life Sciences UK Ltd at 99 % purity. All glassware was washed with Decon, double-distilled water, and acetone, prior to furnacing at 450°C for 2 h. Equipment which could not be furnaced were additionally cleaned with DCM, MeOH and DCM:MeOH (2:1 *v/v*). No plastic equipment was used for extractions, except PTFE caps for GC vials, which were confirmed to not transfer any additive contamination.

2.2. Plastic mulch film

The mulches were collected from 34 manufacturers in 13 provinces in China, the largest user of plastic mulch film (Table S1) and include black ($n = 20$), white/transparent ($n = 26$) and black/silver (reflecting, silver associated with Al content) ($n = 4$) films. The sample set included LDPE ($n = 47$), LDPE oxo-biodegradable (LDPE-ox, n = 1, degradable via oxidative cleavage), and biodegradable (poly(butylene adipate-co-terephthalate) (PBAT) and poly(lactic acid) (PLA) blends and PBAT-only films; $n = 4$). In addition, two films that are available in the UK and also used in China (LDPE $n = 1$, biodegradable PLA-PBAT $n = 1$) were included. The average thickness was 14.1 ± 0.5 μm. All films were produced and obtained between February 2020 and April 2022, and stored in dry, dark conditions until analysis. We focus on LDPE films as these currently dominate the type of films used in China, and confirmed by the use survey (see Section 2.8), with a selection of biodegradable films include due to growing interest in this type of film as an alternative to LDPE.

2.3. Organic co-contaminant extraction and purification

Plastic mulch film (0.1 g) was cut into 0.5×0.5 cm squares and weighed into furnaced glass liners, to which an internal standard (benzyl benzoate; 30 µl of 2.0 µg µl^{-1}) and 15 ml of DCM:MeOH (2:1, *v/v*) was added. This solvent system was found to achieve optimal extraction (i.e. largest number of unique compounds and most representative distribution) of all additives present compared to hexane-acetone (1:1, *v/v*) and MeOH. Additives were extracted using microwave extraction at 70°C (20 min) with a maximum power of 1000 W (Ethos EX). The extract was dried (40°C with a 0.7 ml min^{-1} N$_2$ flow) to yield total additive extracts. Soluble biodegradable polymers were removed via dissolution-precipitation [34], by re-dissolving in 2 ml DCM, then adding MeOH (12 ml) to precipitate the polymer, which was removed by centrifugation (3000 rpm, 15 min) and filtration (0.7 µm furnaced GF/F filters). For all extraction batches, blanks ($n = 3$) were prepared and analyzed in the same manner as the plastic mulches to ensure no additives were introduced during the extraction, work-up or derivatization; no contaminants were observed in these blanks.

2.4. Organic co-contaminant leaching potential

A 10×10 cm square of each plastic mulch film was cut into pieces (0.5 ×0.5 cm) and placed into 10 mM KCl (200 ml). Leaching of organic co-contaminants into a salt solution may be lower than into water [35], however, this solution was selected to mimic the typical ionic strength of the soil solution. The films were passively leached for 14 days at 20°C in the dark, with continuous stirring. It is acknowledged that passive leaching in the same solution over this period may have influenced co-contaminant partitioning, due to the relative solubility of the various compounds. This approach was used to test the potential leaching of new plastic films and reflect chemical contaminant behavior in a soil environment with minimal transport of leached compounds. The films were then removed and leachate solutions concentrated by lyophilization. The dried extracts were redissolved in 2:1 DCM-MeOH (*v/v*) and filtered (0.7 µm furnaced GF/F filters) to desalt. For each leaching batch, blanks ($n = 3$), consisting of 10 mM KCl only was leached, and prepared for analysis in the same manner as the film leachate; no additive contamination was observed in these blanks.

2.5. Organic co-contaminant GC and GC-MS analyses

The extracted and leached additives were derivatized using MSTFA with 1 % TMCS (*N*-methyl-*N*-(trimethylsilyl)trifluoroacetamide with 1 % trimethylchlorosilane, ≥ 98.5 %; 30 µl, 70°C, 1 h). Excess MSTFA was subsequently removed (room temperature, gentle N$_2$ flow) and the derivatized extract redissolved in ethyl acetate for analysis. The extracts were analyzed using gas chromatography (GC, Thermo Fisher Scientific™ Trace™ 1300 Gas Chromatograph) fitted with a HP–1 column (100 % dimethylpolysiloxane 50 m x 0.32 mm ×0.17 µm, Agilent) and an FID. The GC was operated with constant flow of He (2 ml min^{-1}) with a PTV inlet (300°C, split ratio 3:1, spitless time 5 min). The oven temperature programme follows: 50°C (1 min) to 300°C (15 min) at 5°C min^{-1}. Data analysis was performed in Chromeleon® 7 (Version 7.2.1.5833; Thermo Scientific™). The GC-MS (Thermo Fisher Scientific™ ISQ™ LT) was operated under the same conditions as the GC. The MS was operated under electron ionisation (70 eV) scanning the range *m/z* 40–650 at a scan time of 0.2 s. The transfer line to the MS was maintained at 300°C and the ion source temperature was 300°C. Data acquisition and analysis used Xcalibur Version 4.1.31.9 (Thermo Fisher Scientific™ Ltd).

2.6. Identification and quantification of organic co-contaminants

Compound identification was achieved by GC-MS using a combination of external (NIST 14 Main Library, NIST 2019 Additives Library,

NIST 2019 Flame Retardants Library, NIST Stabilisers-Antioxidants Library and the NIST 2019 Plasticisers Library), and in-house libraries constructed following analysis of standards and tentative identification of suspects (Supplementary Methods 1). Additionally, where compounds were not available for purchase, or absent from external libraries, previous identifications and mass spectra in the published literature were used to assign identity. This untargeted approach allowed unbiased determination of readily extractable additives present and avoided targeting specific additive classes. Quantification was achieved with reference to the internal standard (benzyl benzoate) based on peak areas obtained via GC, and relative response to the internal standard determined from external standards, where available, following identification via GC-MS. For unknown compounds, relative quantification was achieved in comparison to the internal standard, assuming a relative response of 1. To classify organic co-contaminants as low, high or unknown cause for concern, we utilized previous assessments of plastic additives by Wiesinger et al. [16], which identified co-contaminants of concern based on hazard criteria under EU REACH, to permit classification of co-contaminants as low or high concern. "High concern" compounds had one or more hazard criteria (persistent, bioaccumulative and toxic, very persistent and very bioaccumulative, carcinogenic, mutagenic, reproductive toxicity, endocrine disruption and chronic aquatic toxicity). Compounds which did not have these hazards associated with them were considered "low concern", while others where insufficient hazard data was available were classified as of "unknown concern". For any compounds identified herein which were not included the previous assessment, the same procedure as previously reported was undertaken. If no hazard information was identified, or compounds could not be identified, then compounds were classified as of "unknown concern", as there is currently insufficient evidence to assess potential hazards.

2.7. Metal and metalloid content and leaching

Plastic mulch films (each $n = 4$) were cut into 5 cm × 5 cm squares, weighed and placed in a glass vials. The films were then heated in a muffle furnace at 450°C for 16 h, the vials reweighed, and the ash content calculated. The ash was dissolved in 2 ml of 1 M HCl by agitation (200 rev min^{-1}, 2 h). Metal content was subsequently analysed using a S2 PICOFOX TXRF (total reflectance X-rays fluorescence; Bruker, Germany). The dissolved metals and metalloids were mixed with Triton (1 % *w/w*), and a multi-element internal standard, before being added onto a silicone matrix on the carrier disc (10 µl) and dried before analysis. To determine the potential leaching of metals from the plastic mulch film, 5 cm × 5 cm squares of each plastic ($n = 4$) were immersed in 20 ml of ultrapure water. It was not possible to use the same leaching solution as used for organic co-contaminants due the subsequent analysis of metals. Differences in leaching surface area between the two approaches is negligible, given the thickness of the films (Table S1). The vials were agitated (100 rev min^{-1}) for 2 h and leached at 22.5°C for 14 d, at which point the water was recovered for analysis. Subsequently, 50 mM citric acid (20 ml) was added (pH 4.5) and incubated for a further 14 d at room temperature. Citric acid was chosen based on its abundance in the plant root exudates and metal complexation potential. The metal content of the leachate was then analysed by TXRF as above. For both the total and leached metal contents, blanks ($n = 3$) were prepared in the same manner, and metal contents blank corrected for background (<1–3 % of plastic metal content). Na was not included in the citric acid leachate, due to high background content of the citric acid precluding blank correction. The hazards posed by inorganic co-contaminants were based on heavy metals.

2.8. Plastic mulch use survey

Between September 2022 to April 2023, a survey of 300 predominantly maize farmers was conducted in the Provinces of Gansu, Inner

Mongolia and Shanxi in China, and in Quinyang, Chifeng and Shouzhou districts, respectively, to determine the extent of mulch film use. Three locations were chosen from each district through a purposive random sampling procedure. The farming households practising plasticulture were balanced across the locations at district level and organised into categories of land ownership size (marginal <1 ha, small 1–2 ha, semi-medium 2–4 ha, medium 4–10 ha and large >10 ha). Within these sub-classes, households were selected by proportionate random sampling, and then systematic random sampling was adopted for the selection of the exact sample households. Respondents were given individual reference numbers to make data collection anonymous and follow an approved Ethical Protocol. Data entry used KoboToolBox, which is a web-based platform, with the data check able to take place in real time and downloaded into MS Excel for analysis. From this dataset, information about the type of plastic, coverage, and use was extracted and used in the analyses reported in this paper. Using the potential leaching of organic compounds and metals and metalloids, the input of additives and associated degradation products was calculated (see Supplementary Methods 2).

3. Results

3.1. Organic co-contaminant content of parent mulch film

Lubricants ($n = 20$) and antioxidants ($n = 3$) were the most abundant, and frequently occurring co-contaminants in LDPE films (Fig. 1, Table 1). Lubricants included palmitic acid (4.59 ± 3.19 mg m^{-2}) and erucamide (5.24 ± 4.08 mg m^{-2}, Table S2). There were a number of lubricant degradation products, the most frequent of which was docosenenitrile (Table S2). Antioxidants Irganox® 1076 (octadecyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate) and Irgafos® 168 (tris(2,4-di-*tert*-butylphenyl) phosphite) were present in all LDPE mulches alongside associated degradation products (2,4-di-*tert*-butylphenol (24DTP), 2,6-di-*tert*-butylphenol (26DTP), and Irgafos® 168ox (tris(2,4-di-*tert*-butyl-phenyl) phosphate)). Phthalate acid esters (di(2-ethylhexyl phthalate (DEHP) and dibutyl phthalate (DBP)), which have been identified as priority pollutants [36], were present at 0.22 ± 0.09 mg m^{-2} (detection frequency (df)= 47 %), and 0.026 ± 0.024 mg m^{-2} (df=20 %), respectively (Table S2). Non-phthalate alternatives (di-2-ethylhexyl adipate, tri-2-ethylhexyl trimellitate) were present at lower frequencies (Table 1, Table S2), only contributing 0.8 % (Fig. 1). UV stabilising additives were less frequent; two benzotriazole type UV stabilisers, Tinuvin 326 (df=11 %; 2-(2′-hydroxy-3′-*tert*-butyl-5′-methylphenyl)-5-chloroben zortriazole) and Tinuvin 329 (df=2.3 %; 2-(2′-hydroxy-5′-(1,1,3,3-tet-ramethylbutyl)phenyl)benzotriazole). Other common compounds tentatively identified were ethoxylated amines and amides (Table S2 and Table S3), which are used as antistatic agents in LDPE (e.g. Armostat® antistatic agents). There were also three related compounds (4a-4c; Table S2) likely originating from oligomeric hindered amine

Table 1

Summary of organic additives classes extracted from LDPE ($n = 47$) and biodegradable ($n = 5$) plastic mulch films. All values are mean $\pm$ SE. *n.d.* indicates no compounds of this type were detected.

Additive type	LDPE concentration (mg m^{-2})	Biodegradable concentration (mg m^{-2})
Lubricants	12.8 ± 9.8	40.6 ± 14.7
Plasticisers	0.32 ± 0.045	2.0 ± 0.3
Antioxidant	15.9 ± 7.9	4.7 ± 3.3
UV stabilisers	0.65 ± 0.53	*n.d.*
Additive NIAS	7.0 ± 4.2	26.1 ± 3.5
Chain extender	*n.d.*	2.7 ± 0.3
Other	0.069 ± 0.037	*n.d.*
Unknowns	3.1 ± 2.3	53.0 ± 3.8
Polymer NIAS	0.33 ± 0.03	77.2 ± 12.0

light stabliser (HALS)-type additives, for which the parent compounds (e.g. Chimasorb 944) were beyond the analytical window used herein [37]. Other non-intentionally added substances (NIAS) included polymer-derived alkanes, likely originating from the production process (C$_{16}$ to C$_{34}$; average chain length 22), contributing 0.8 % of the total organic compounds determined (Fig. 1).

The total additive content (excluding unknowns and polymer NIAS) was higher for biodegradable films (76.1 ± 2.1 mg m^{-2}) than the LDPE films (36.7 ± 22.1 mg m^{-2}). The differing additive compositions of the two type of film are illustrated in Fig. 1, with UV absorbers only present in the LDPE film, while chain extenders were only observed in the biodegradable films. Different additive classes present in both films also had different relative abundances between the two polymer types. For example, relative abundance of antioxidants were much lower in the biodegradable films (2.3 % vs. 39.6 % in the biodegradable and LDPE, respectively), while plasticisers account for 1.0 % of additives in the biodegradable films, compared to only 0.8 % in the LDPE films. Principal component analysis also confirmed the distinct additive content of biodegradable films compared to LDPE films (Figure S2). The compositions of extractable co-contaminants of the biodegradable mulch were more variable (Table 1, Table S3). Lubricants were the most abundant additive class, similar to the LDPE mulches, alongside the antioxidant Irgafos® 168 (df=60 %; Table S3). Diisooctyl phthalate (DiOP) and DBP have been identified as priority pollutants [36] and were only detected in one mulch at 0.60 mg m^{-2} and 0.16 mg m^{-2}, respectively, while ethyl hydrogen sebacate, a phthalate alternative, was the most abundant plasticiser for the biodegradable films (9.7 mg m^{-2}). The chain extender 2,6-diisopropylphenyl isocyanate was detected in 60 % of the biodegradable mulches. Additive NIASs in biodegradable films included antioxidant degradation products (24DTP, Irgafos® 168ox, 26DTP), and tributyl aconitate, from the plasticiser tributyl citrate. The most abundant additive NIAS were tentatively identified as pentaerythritol and
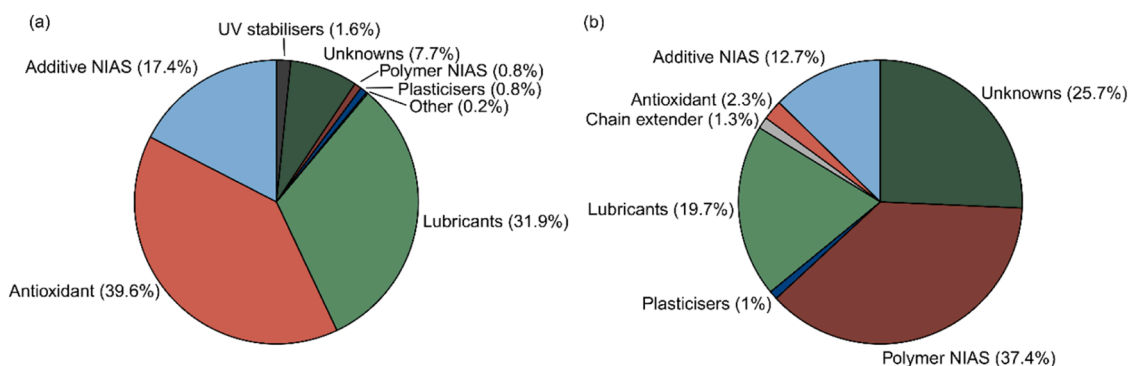

Fig. 1. Average relative contribution of organic additives and polymer and additive NIAS to total organics extracted from new (a) LDPE and (b) biodegradable plastic,mulch films. Values are averages (LDPE $n = 47$, biodegradable $n = 5$).

pentaerythritol esters in one mulch film (Table S3), likely degradation products of high molecular weight additives with a pentaerythritol center (e.g. Irganox® 1010 (pentaerythritol-tetrakis(3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propionate)), pentaerythritol fatty acid esters [38] or secondary phosphite antioxidants (e.g. Ultranox® 626 (bis(2,4-di-*tert*-butylphenyl) pentaerythritol diphosphate)), which can support PLA degradation [39]. Unknown compounds (Table S3) are proposed to be degradation products of higher molecular weight additives beyond the scope of this study. Parent plastic monomers (adipic acid, lactic acid, butanediol), short-chain oligomers derived from polybutylene-adipate (PBA) and polybutylene-terephthalate (PBT) and cyclic oligomers (e.g. lactide, cyclic PBA, PBT and PBA-PBT dimers; [40]), deriving from the polymerization of the parent polymer were also present in all biodegradable films.

3.2. Metal and metalloid additive content of plastic mulch films

Metals and metalloids are included in plastic mulch films as various salts (e.g. $CaCO_3$, Na_2SO_4) and oxides (e.g. ZnO, Fe_2O_3), although quantified as free ions herein and are referred to as metal additives. The overall metal content was higher in the biodegradable films (139 $\pm$ 13.2 mg m^{-2}, 3.49 $\pm$ 0.28 % w/w of plastic) than LDPE (74.0 $\pm$ 22.8 mg m^{-2}, 0.47 $\pm$ 0.09 % w/w of plastic). The most abundant metal additives in the films included Na and Ca (Table 2) for both types of plastic. These likely originated from widely used inert fillers, such as calcium carbonate ($CaCO_3$) and sodium sulphate (Na_2SO_4). The most abundant heavy metals were Fe, Zn and Ti, derived from pigments. Other heavy metal additives (Mn, Cd, Pb, Cu, Cr, Co, As) were only detected at low concentrations (< 0.05 mg m^{-2}; Figure S3 and Figure S4). These include metals and metalloids which are included in regulations around food contact materials (e.g. Pb, As, Cd and Cr; EU 2020/1245), although this does not apply to plastic mulch film, despite their obvious role in food production [25].

3.3. Leaching of organic and metals co-contaminants from mulch films

A total of 612 compounds were identified following passive leaching of the plastic mulch films, with the leachate composition highly variable between films, although the leachate compositions of the biodegradable films were distinct from those of the LDPE films (Figure S1). The average concentration leachate from LDPE into 10 mM KCl (chosen to mimic soil pore water) over 14 d was 1.05 $\pm$ 0.15 mg m^{-2}, which was equivalent to 2.3 % of the extractable additives from the new plastic. The degree of leaching was higher from the biodegradable mulch (53.6 $\pm$ 2.6 mg m^{-2}), equivalent to 28 % of the additive content extracted using DCM-MeOH.

For both LDPE and biodegradable films, a sub-set of compounds identified in the mulch ($n = 45$ and $n = 33$, respectively) were also present in the leachate. There was a significant linear relationship between leachate concentration and the concentration in the new plastic for the biodegradable films ($p < 0.001$). However, the relationship was not significant for the LDPE films ($p = 0.38$), likely due to the hydrophobicity of the co-contaminants and crosslinking and/or polymer film pore size, which influenced extractability. The most abundant compounds leached from the LDPE films (Table S4), which are also substances of potential or unknown concern, were Irgafos® 168ox (0.088 $\pm$ 0.011 mg m^{-2}) and DBP (0.032 $\pm$ 0.003 mg m^{-2}). However, compounds of low concern, such as erucamide (0.038 $\pm$ 0.005 mg m^{-2}) and octadecanoic acid (0.050 $\pm$ 0.012 mg m^{-2}), were also leached. Some compounds present in high concentration in the solvent extract (e.g. Irganox® 1076, 6.51 $\pm$ 0.52 mg m^{-2}) only appeared at low concentration in the leachate (0.023 $\pm$ 0.002 mg m^{-2}), due to low water solubility. Surprisingly, despite their lack of solubility in water, alkanes were detected in the leachate. This may be due to micro/nanoplastic (<0.7 µm) particles produced during the leaching experiment not being removed by filtration. Alongside the parent additives, leached compounds included additive degradation products, notably DTBODD (7,9-di-*tert*-butyl-1-oxaspiro[4.5]deca6,9-diene-2,8-dione $n = 28$, 0.019 $\pm$ 0.003 mg m^{-2}), a degradation product of Irganox® 1010, and 24DTP ($n = 12$, 0.0075 $\pm$ 0.0004 mg m^{-2}), a degradation product of Irgafos® 168 [41]. Similar to the LDPE film, the antioxidant Irgafos® 168 (1.06 $\pm$ 0.06 mg m^{-2}) alongside the priority pollutant DBP (0.031 $\pm$ 0.008 mg m^{-2}) were leached from the biodegradable films. The concentration of these leached compounds, relative to the film solvent extract concentrations, was higher in the biodegradable film than in the LDPE (all $p < 0.02$). Degradation products of additives leached from the biodegradable film (Table S6) included tributyl aconitate (2.54 mg m^{-2}), Irgafos® 168ox (0.40 $\pm$ 0.19 mg m^{-2}), 24DTP (0.284 $\pm$ 0.071 mg m^{-2}), and pentaerythritol esters (0.73 $\pm$ 0.28 mg m^{-2}). In addition, polymer-derived compounds observed in the film solvent extracts were also leached, alongside linear oligoesters (e.g. PBA trimer).

Leached compounds were classified according to their potential ecotoxicological concerns, to indicate the potential risk associated with the leached chemical burden from mulches to the environment (Fig. 2). The potential leaching of compounds of "high concern" was lower in the LDPE (1.29 $\pm$ 0.13 mg m^{-2}) than those of "low concern" (2.50 $\pm$ 0.16 mg m^{-2}), although comparable for the biodegradable films (4.25 $\pm$ 0.95 mg m^{-2} and 4.07 $\pm$ 0.74 mg m^{-2}, respectively). The majority of compounds classed as "unknown", comprising a combination of unidentified compounds, and identified compounds with insufficient data to determine their potential ecotoxicity, accounted for 14.4 $\pm$ 0.47 mg m^{-2} and 36.0 $\pm$ 2.9 mg m^{-2} for LDPE and biodegradable mulch films, respectively.

The leaching of metal additives from the plastic mulch films was compared using water and citric acid (Fig. 3). This showed that the leaching medium had a significant effect ($p < 0.05$) for individual

Table 2

Elemental content of LDPE ($n = 47$) and biodegradable ($n = 5$) mulches following acid digestion and TXRF analysis. All values are mean $\pm$ SE. Other includes Mn, Cd, Pb, Cu, Cr, Co and As, which were detected at low levels (<0.05 mg m^{-2}; Figure S3).

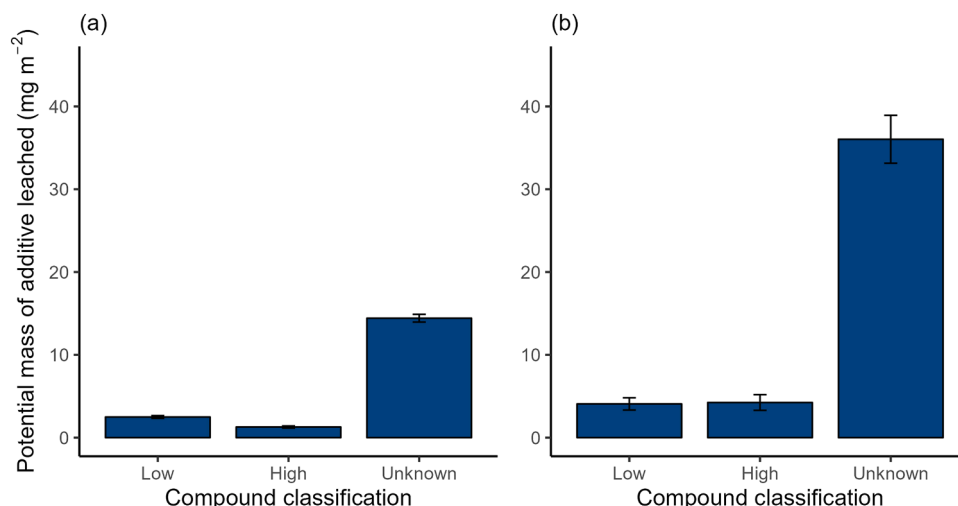| Element	LDPE		Biodegradable	
	Concentration (mg m^{-2})	Percentage of total metals (%)	Concentration (mg m^{-2})	Percentage of total metals (%)
Na	15.8 $\pm$ 4.3	38.0	27.2 $\pm$ 3.0	44.1
Ba	12.3 $\pm$ 5.6	29.7	29.1 $\pm$ 27.7	0.47
Al	6.36 $\pm$ 3.66	15.3	45.4 $\pm$ 0.06	0.73
Ca	5.43 $\pm$ 2.56	13.1	31.4 $\pm$ 2.5	50.9
Ti	0.73 $\pm$ 0.32	1.7	0.068 $\pm$ 0.02	0.11
Zn	0.49 $\pm$ 0.09	1.2	0.23 $\pm$ 0.14	0.38
K	0.13 $\pm$ 0.03	0.32	0.013 $\pm$ 0.006	0.02
Mg	0.12 $\pm$ 0.04	0.28	1.51 $\pm$ 0.18	2.4
Fe	0.11 $\pm$ 0.019	0.26	0.39 $\pm$ 0.24	0.62
Sr	0.042 $\pm$ 0.016	0.10	0.073 $\pm$ 0.038	0.12
Other	0.038 $\pm$ 0.016	0.09	0.064 $\pm$ 0.023	0.10
Percentage of plastic (w/w)	0.47 $\pm$ 0.09		3.49 $\pm$ 0.28	

Fig. 2. Potential leaching of organic additives of low, high and unknown concern from (a) LDPE and (b) biodegradable mulch films. Values are mean $\pm$ SE ($n = 47$ for LDPE and $n = 5$ for biodegradable).
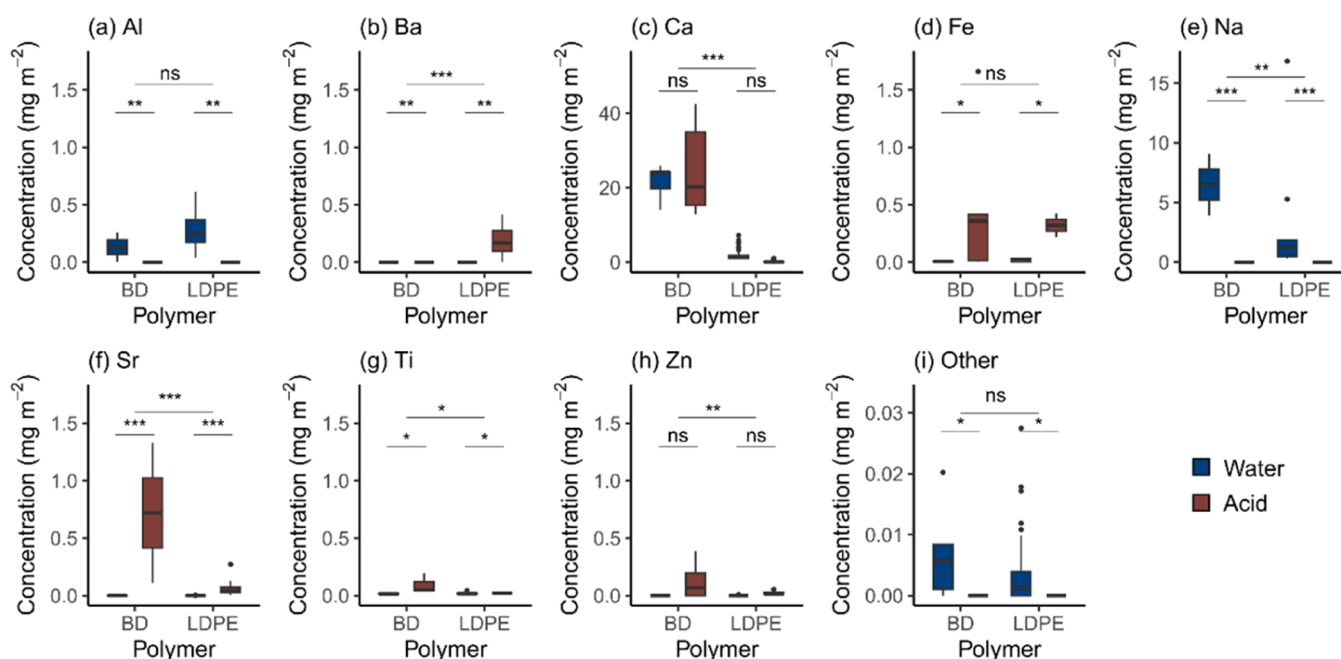

Fig. 3. Leached metal and metalloid additives and non-metals from biodegradable (BD, $n = 5$) and LDPE ($n = 47$) mulch films into successive water and then acid matrices. The significant effects of polymer type and matrix following ANOVA analysis are indicated (***$p < 0.001$; **$p < 0.01$, *$p < 0.05$; ns $p > 0.05$). Na leaching was not determined for acid extracts due to the Na present in the citric acid matrix. Note different axis scales for parts (c), (e) and (i).

metals, with the majority of metal additives showing higher leaching in citric acid than in water (e.g. Ca, Fe, Sr and Zn; all $p < 0.01$ for matrix effect). Metal additives were only detected at low concentrations (Other in Table 2) in the water leachates (Cr, Cu, Pb). A number of metal-containing additives present in the parent plastic are not presented in Fig. 3 as they were not detected via TXRF following leaching into either citric acid or water. The leaching of metals additives from biodegradable films was significantly higher (all $p < 0.03$) than from LDPE films for all metal additives except for Ba in citric acid, Cr, Cu and Pb in water, and Fe and Al in both citric acid and water, due to the higher concentrations in the parent film. The relative extent of leaching from both LDPE and biodegradable mulches largely reflected the concentrations of the metal additives in the parent film, which was higher for biodegradable films (Fig. 4). The correlation between total metal and leached concentrations was significant ($p < 0.05$) for LDPE for Ca ($p < 0.001$) and Ti

($p = 0.003$) in water, and LDPE for Ba ($p < 0.001$) and Fe ($p < 0.001$), and biodegradable for Ba ($p < 0.001$), Fe ($p = 0.005$), Sr ($p = 0.004$) and Zn ($p = 0.003$) for citric acid. The lack of relationship for other metal additives may be due to partitioning into the water or citric acid media, reabsorption of the metal additive onto the plastic mulch film or precipitation as metal hydroxides during leaching.

3.4. Potential chemical burden in Chinese farms using plastic mulch film

In the three provinces of China, farms using plastic mulch film had coverage on 87.9 ± 1.4 % of the farm land area, and the relative area covered did not vary by farm size ($p = 0.80$), although it did vary by province ($p < 0.001$), due to varying topography. There were significant differences in the number of years of plastic mulch film use between farm sizes, with small, semi-medium and medium farms (15–17 years)
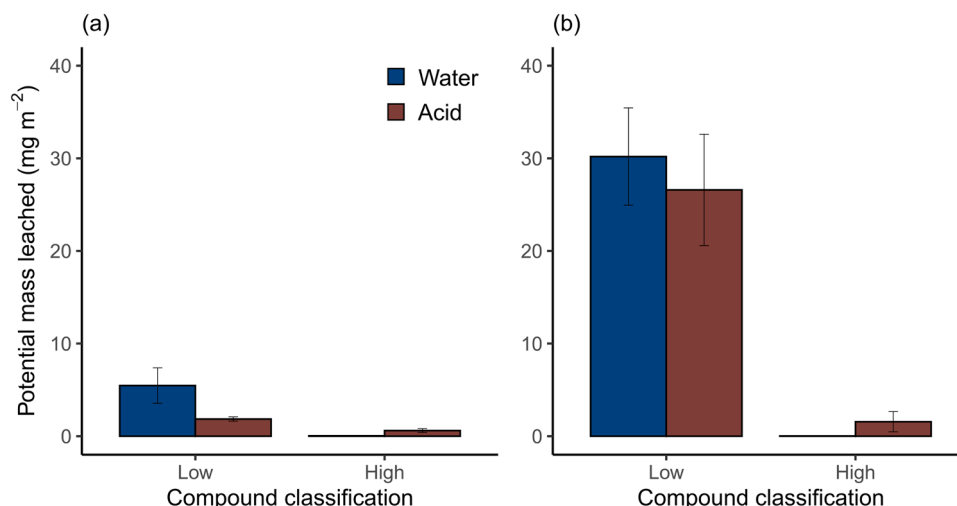
Fig. 4. Potential leaching of metals of low (Al, Ca, Na) and high (i.e. heavy metals Ba, Fe, Sr, Ti, Zn, Cr, Cu, Pb) concern in water and then citric acid from (a) LDPE and (b) biodegradable mulch films. Values are mean $\pm$ SE ($n = 47$ for LDPE and $n = 5$ for biodegradable films).

having used plastic for longer than marginal and large farms (12 and 10 years, respectively; $p < 0.001$, Table S7). The potential input of all organic and metals co-contaminants from the plastic mulch film for individual farms, and the potential cumulative input across all years of plastic mulch use is shown in Table S7. The water leaching for metals most closely reflected the soil environment, and thus was used to upscale the potential metal burden arising from plastic mulch films. The total chemical loading arising from large (>10 ha) farms constituted the largest chemical burden (9.26 and 114 kg for LDPE and biodegradable, respectively), due to their size and extent of plastic mulch film use. However, despite the size of small (1–2 ha), semi-medium (2–4 ha) and medium (4–10 ha) sized farms, the higher numbers of such farms cumulatively increases their overall environmental loadings due to longer use of plastic mulch films. When the long-term use patterns are normalised to the farm area, the relative input of additives from small, semi-medium and medium farms is significantly higher ($p < 0.001$) than large farms, which were comparable to marginal farms (Figure S5). Table S7 accounts for cumulative potential chemical burden, however, this may overestimate actual concentrations in soil, due to unknown degradation rates of organic contaminants [20,42], or transport off-site (e.g. losses to groundwater and rivers). All farms surveyed had previously only used LDPE plastic mulch film, although biodegradable films are being proposed as a potential alternative to reduce microplastic accumulation [43]. Therefore, the estimated potential chemical burden arising from biodegradable films is given in Table S7, and 11 times higher than for LDPE films for all farm sizes.

4. Discussion

4.1. Additives and NIAS in plastic mulch films

Plastic mulching using polymer films is an increasing popular agricultural practice used to ensure food security, which reduces inputs of agrochemicals. However, the associated co-contaminants represent a relatively ill-defined and poorly quantified chemical input into agricultural soils. This study is the first to bring together inorganic and organic co-contaminants, and combine potential leaching with use data to assess the chemical burden constituted by both LDPE and biodegradable films. The co-contaminant content of the film largely reflected the mechanical and functional properties demanded by mulch production and use, and the variability observed reflected the redundancy within available additives. Lubricants (e.g. fatty acids, amides, alkanols) aid film production, and field application, while antioxidants (e.g. Irgafos® 168 and Irganox® 1076) and UV stabilisers (e.g. Tinuvin 326,

Tinuvin 329) are included to extend the lifespan of the product [44,45]. UV stabilisers were only observed in LDPE films, however, antioxidants were present in biodegradable films. Given biodegradable films are designed to breakdown in the soil, the inclusion of antioxidants may be unnecessary. For inorganic co-contaminant metals and metalloids, were dominated by Na, Ca and, in the case of the black/silver films, Al, which are derived from inert inorganic fillers ($CaCO_3$, Na_2SO_4), with only minor contributions from heavy metals. However, the inclusion of plasticisers was variable, and relatively low compared to lubricants and antioxidants. The findings herein confirm that phthalate content is low within LDPE films, and phthalates detected in soils may be derived from other agricultural practices, such as polytunnels [36,46]. Given phthalates are not required for LDPE plastic mulch films, they may have been added unintentionally, making this a key compound class where tighter control is required.

The known organic additives present in the plastic mulch films have largely been assessed for their hazard to human and environmental health [16,47]. However, degradation products of additives and the polymer itself were also shown to be present in both new biodegradable and LDPE mulch films, likely formed during production of the films. Some (e.g. 24DTP) have been assessed for their hazard potential, yet Irgafos® 168ox, also produced from Irgafos® 168, including during film production [48], has not yet been included in EU REACH separately from Irgafos® 168 [47]. Furthermore, polymer-derived NIASs, such as cyclic oligomers of biodegradable polymer monomers, formed during processing [49], have only recently been identified in PBAT mulch films [40] and are yet to be assessed for potential hazards. Monomers of PBAT have been shown to hinder plant development [50,51], and such polymer derivatives may alter the soil pH, affecting microbial community structure and function [52]. Therefore, while there have been extensive efforts to assess the potential hazards of plastic additives, monomers and processing agents [16], there is accumulating evidence that a number other compounds are present, in appreciable concentrations, that need to be assessed.

4.2. Leaching increases the complexity of compounds associated with plastic mulch films

The already complex mixture of plastic mulch film co-contaminants became more complex during passive leaching, with the majority of leached compounds (80 % and 90 % for biodegradable and LDPE, respectively) not present in the original plastic mulch. The majority of the leached compounds were not identifiable through available in-house libraries or literature (61 % for biodegradable and 64 % for LDPE films).

As a result, the proportion of compounds of unknown concern within the leachates is much higher than previously detailed in assessments of known plastic additives, monomers and processing aids. These compounds likely originate from the abiotic degradation of additives, or the polymer itself in the case of biodegradable films, both identified in the analytical window used herein, and beyond [44,53]. As degradation products of additives and polymers, the majority of the compounds have not, as of yet, undergone sufficient assessment to determine if they are substances of potential concern (Fig. 2), such that have not been subject to any regulatory scrutiny (e.g. under EU REACH; [47]).

The complexity of the mixture of degradation products of additives and polymers will likely increase further through microbial processing in agricultural settings [54]. Leaching dynamics may also vary for weathered plastics, and climatic influences (e.g. precipitation). Hence, the leaching data presented herein represents potential leaching in the short-term immediately following mulch application, when the highest chemical loading exists in the film. To date, in the soil environment, the ecotoxicological effect of leached additives has been limited to single additives (e.g. DEHP [18]), or more complex mixtures of unknown chemical composition (e.g. microplastic leachate [55]). Our work highlights the need not just to consider the compounds intentionally added to mulch film, but also the additional compounds produced during the lifetime of the film, akin to work conducted in aquatic settings [53,56,57]. Many of the compounds may pose little hazard, and/or be leached at sufficiently low concentrations to minimise the risk. However, the potential for (bio)accumulation increasing the overall chemical burden should not be underestimated (Table S7) when considering the risks to soil health posed by agricultural mulch films.

The chemical complexity of leached metal and metalloid additives is lower than that of the organic additives, however, the release of heavy metals into the environment in large quantities is potentially hazardous [25–27]. Leached metals and metalloids were dominated by those derived from inert fillers (e.g. Ca, Na, Fig. 3), thus the level of concern was low. Although heavy metal leaching (e.g. Fe, Ti, Zn, Cr, Cu, Pb) was low in water, metals still associated with macro and microplastics may be transported to the wider environment where leaching dynamics may change [45]. Soils with low pH may increase the leaching of heavy metals, although this is unlikely in agricultural soils, which tend to be maintained close to neutral pH through liming. The potential leaching of heavy metals from plastic mulch films should be set into the context of other anthropogenic sources. While heavy metal contamination affects 13.3 % of Chinese soils [58], this has largely arisen from heavy industry, atmospheric deposition, fertilisation and sludge application [59,60]. This work indicates plastic mulch films represent relatively low input of heavy metals into soils, even with continued use (Table S7).

4.3. Biodegradable films raise risk of pollution swapping

A key concern for LDPE plastic mulch film use is the formation of microplastics through mechanical damage and UV degradation [10]. Biodegradable films are currently suggested as an alternative to traditional LDPE plastic mulches, with the degradation of the polymer seen as a favourable way of reducing microplastic loading, and obviating the need to remove plastic from the soil and subsequent recycling. However, the relatively higher leaching of organic additives, polymer degradation products (Fig. 2) and metal and metalloid additives (Fig. 4) from biodegradable films, compared to LDPE films, raises concerns in relation to pollution swapping (i.e. substituting one environmental pollutant for another). Increased input of organic additives of unknown and potentially high concern and heavy metals from biodegradable mulch films may offer greater risks to soil health than the accumulation of microplastic polymers derived from mulch films [61], e.g. as suggested for organic UV absorbers [62].

4.4. Implications and future outlook

The complex chemical composition of leachates from plastic mulch films have not been fully included in life cycle assessments of biodegradable mulches [63]. The risk associated with the release of such compounds must be more thoroughly assessed before the current formulations of biodegradable mulch films are confirmed as truly sustainable alternatives to LDPE mulches. Ideally, additives of potentially high concern should be replaced with more benign alternatives in both biodegradable and non-biodegradable films. Furthermore, improving the lifespan of LDPE mulches, and the removal and recycling of aged films would help to reduce the risks arising from microplastic production.

Critically, when assessing the potential environmental risks associated with plastic mulch film use, their vital importance in agriculture must not be neglected. Smallholders rely on their soil for food production and income, providing huge social and economic benefits. We have revealed the potential for leaching of organic and metal additives from a range of LDPE and biodegradable mulches, and subsequent cumulative environmental loadings in farms utilising plastic mulch films in China (Table S7). The potential farm-level loadings of metals and organic compounds leached from plastic mulch films in a single growing season suggests in the short term, the chemical burden posed by agricultural mulch films is low, relative to other sources, including fertiliser [64] and irrigation water [65]. However, their continued use, with multiple cropping seasons per year, will increase the cumulative chemical burden posed by plastic mulch film, however, non-persistent compounds will degrade and not accumulate. When the potential total additive input is normalised to farm area, small, semi-medium and medium farms show the largest relative input over this history of plastic use, indicating these may be the soil most vulnerable to additive accumulation (Figure S5). The work herein represents a farm-specific assessment for the release of metal and plastic additives, beneficial to indicating soils which may be most at risk for accumulation of additives, and therefore the development of monitoring and tailored mitigation strategies. Further work should consider the removal of the plastic mulch film, and potential hazards posed by film-derived microplastics, and absorption of the full range of agricultural chemicals (e.g. pesticides, herbicides) or heavy metals. Current additive levels across different farm sizes should be evaluated to establish variations between different farm sizes, with particular interest on farms which have been shown in this study to have higher relative loadings due to historic plastic mulch use (i.e. small-medium).

5. Conclusions

Herein, we demonstrate the total additive composition of plastic mulch films, with a focus on low molecular weight additives susceptible to leaching. LDPE films are dominated by antioxidants and lubricants, while antioxidants are a minor component of biodegradable films. The chemical complexity of leachates was much higher than solvent extracts. Furthermore, the majority of leached compounds have not undergone any regulatory scrutiny, and while they may pose little risk, chemically complex leachates of plastic mulch films should be assessed for potential ecotoxicological effects. This is particularly important for biodegradable plastics, which exhibited higher overall leaching of inorganic and organic co-contaminants, and higher leaching relative to the content in the original film. While biodegradable films are purported to reduce agricultural macro-, micro- and nano-plastic pollution, the observed higher leaching of additives and co-contaminants highlights the potential for pollutant swapping. There has been extensive ecotoxicological research on single classes of chemical co-contaminants in plastic mulch films. Importantly, the results reported herein reveal a previously unappreciated level of chemical complexity of extractable components of agricultural plastics, raising a new level awareness of the chemical burden at the farm-scale. This new information is a vital first step in

assessing the potential ecological risks of plastic mulch films. This approach will ultimately inform policy and education around the use and disposal of plastic mulch film, through improved regulation and balancing the potential risks with the undoubtable benefits of plastic mulch film for food security.

Environmental implication

Plastic mulch film is important for food security, however, the chemical burden of organic and inorganic additives which may leach into soil remains highly uncertain. This study evaluates organic additives, alongside metal and metalloid additives in both new mulch and leachate. Our results indicate that while the additive content of films is dominated by additives of low concern, the complexity of plastic mulch film leachate means the majority of compounds potentially leached into agricultural soils have not been assessed for ecotoxicological or human health effects. Finally, higher leaching loads from biodegradable films raises concerns of switching pollution from LDPE microplastics to additives with unknown ecotoxicological effects.

CRediT authorship contribution statement

Michaela Reay: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Martine Graf:** Writing – review & editing, Validation, Methodology, Investigation, Formal analysis, Conceptualization. **Madelyn Murphy:** Writing – review & editing, Validation, Investigation, Formal analysis. **Gupeng Li:** Writing – review & editing, Validation, Investigation, Formal analysis. **Changrong Yan:** Writing – review & editing. **Mondira Bhattacharya:** Writing – review & editing, Investigation, Formal analysis. **Henny Osbahr:** Writing – review & editing, Funding acquisition. **Ji Ma:** Investigation. **Wen Chengtao:** Investigation. **Xiner Shi:** Investigation. **Siyang Ren:** Investigation. **Jixiao Cui:** Writing – review & editing. **Christopher Collins:** Writing – review & editing. **Dave Chadwick:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization. **Davey Jones:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization. **Richard Evershed:** Writing – review & editing, Funding acquisition. **Charlotte Lloyd:** Writing – review & editing, Funding acquisition.

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

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2025.137147.

Data Availability

Data will be made available on request.

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