frontiers | Frontiers in Environmental Science

TYPE Original Research
PUBLISHED 28 February 2023
DOI 10.3389/fenvs.2023.1129336

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SPECIALTY SECTION
This article was submitted to Toxicology, Pollution and the Environment,
a section of the journal Frontiers in Environmental Science

RECEIVED 21 December 2022
ACCEPTED 13 February 2023
PUBLISHED 28 February 2023

CITATION
Scopetani C, Selonen S, Cincinelli A and Pellinen J (2023), Chemical leaching from polyethylene mulching films to soil in strawberry farming.
Front. Environ. Sci. 11:1129336.
doi: 10.3389/fenvs.2023.1129336

Chemical leaching from polyethylene mulching films to soil in strawberry farming

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Mulching is a widely practiced agricultural technique able to boost crop productivity and to reduce weed growth and water evaporation. One of the most common materials used for mulching is polyethylene. Polyethylene films are known to contain phthalates, plasticizers recognized as endocrine disruptors, thus able to endanger the hormonal system. Only few data exist on the possible transfer of plasticizers from polyethylene mulching films to agricultural soil, especially in Europe, or on the potential implications for the environment and human health. In this study, we analyzed the occurrence of plasticizers such as phthalates and acetyl tributyl citrate from polyethylene mulching films and soil samples collected from strawberry fields where polyethylene films have been used. The samples were analyzed with a gas chromatograph-mass spectrometer and the results indicated that the soil exposed to polyethylene mulches contained a significantly higher concentration, compared to the control soil, of some of the most common plasticizers, including dibuthyl phthalate, benzylbutyl phthalate and acetyl tributyl citrate. These outcomes highlight the need to carry out further research to understand the potential risks that mulching practices can cause for the environment and human health.

KEYWORDS

plastic pollution, contaminant transfer, mulching film, polyethylene, phthalates, acetyl tributyl citrate, agricultural soil

1 Introduction

The rapid growth of the world population and the consequent need to double food production within a planet with limited water resources, are putting increasing pressure on agriculture technologies (Le Mouël and Forslund, 2017). Agriculture accounts up to 70% of global water consumption, and is thus the world's largest water user (El-Beltagi et al., 2022). Due to climate change, shortages in water availability have increased and especially arid and semi-arid regions of the globe are suffering from drought (Kader et al., 2017).

Mulching is one of the most commonly used agriculture techniques to conserve soil moisture, increase water infiltration into the soil and improve crop yields (Kader et al., 2017). Polyethylene (PE) mulching films are among the most widely used, cost-effective and high performance mulching materials (Qin et al., 2015) but still one of the major sources of plastic pollution in agricultural soil (Bläsing and Amelung, 2018). Theoretically, the films should be removed from the fields at the end of their lifetime. In practice, however, small fragments are easily left behind and sometimes the films are just ploughed into the soil (Ramos et al., 2015; Billings et al., 2021). By time, the leftovers from the plastic films start fragmenting and become microplastics, potentially affecting soil physicochemical properties, plant growth, and soil biota (Scopetani et al., 2020; Selonen et al., 2020; 2023; Xu et al., 2020). Furthermore, plastic materials are known to contain, sorb and release chemicals that can be harmful for the environment and humans (Zhong et al., 2023).

Plastic additives are chemicals used to modify the properties of plastics. They are not chemically bound to the polymers and are thus easily released into the environment over time (Hahladakis et al., 2018). Some of the most common plastic additives, such as phthalates, are recognized as endocrine disruptors, thus capable of damaging the reproductive and mobility functions of several living organisms, including humans (Bläsing and Amelung, 2018; Grindler et al., 2018). The use of phthalates has been restricted in the European Union due to health concern, but it has not been completely forbidden (ECHA, 2020).

Plastics do not only release the plasticizers and other chemicals that are added during the production process, but they can also sorb, transfer and later release other harmful substances like persistent organic pollutants (POPs) that are present in the environment (Rios et al., 2007). For example, polycyclic aromatic hydrocarbons (PAHs), ubiquitous environmental pollutants recognized as mutagenic and/or carcinogenic substances (Andersson and Achten, 2015), are often found in association with plastic materials (Rios et al., 2007).

The aim of this study was to gain knowledge on the potential transfer of organic compounds from PE films to agricultural soils. We analyzed PE mulches and soils coming from two different fields at a strawberry cultivation farm, one where PE films have been applied, and one where no mulching materials have been used. The selected chemicals were quantified using gas chromatography-mass spectrometry, to determine if their concentrations differ significantly between the controls and the mulched soils.

TABLE 1 LOD (signal to noise ratio = 3:1) and LOQ (signal to noise ratio = 10:1) of the selected contaminants.

Compound	LOD (ng/g)	LOQ (ng/g)
Acetyl tributyl citrate (ATBC)	2	7
Dodecane	7	23
Dimethyl phthalate (DMP)	0,5	1,5
Di-n-octyl phthalate (DNOP)	7	24
Diethyl phthalate (DEP)	0,8	2,5
Dibutyl phthalate (DBP)	0,4	1,5
Benzylbutyl phthalate (BBP)	1,5	5
Bis(2-ethylhexyl) adipate (DEHA)	0,6	2
Naphthalene (NAP)	0,1	0,5
Acenaphthylene (ACY)	0,4	1
Acenaphthene (ACE)	0,3	1
Phenanthrene (PHE)	0,4	1,5
Fluorene (FLE)	0,5	1,5
Anthracene (ANT)	0,7	2,5
Fluoranthene (FLA)	0,3	0,9
Pyrene (PYR)	5	17
Benzo [a]anthracene [B (a)A]	0,2	0,8
Chrysene (CHR)	0,3	0,8
Benzo [b]fluoranthene ((B [b]F)	0,5	1,5
Benzo [k]fluoranthene [B (k)F]	0,5	1,5
Benzo [a]pyrene [B (a)P]	3	10
Indeno [1,2,3-cd]pyrene [I (1,2,3-cd)P]	1	4
Dibenzo [ah]anthracene [D (ah)A]	2	6
Benzo [ghi]perylene [B (ghi)P]	8	26

2 Methods

2.1 Sampling

Soil samples and PE mulching films were collected from a strawberry farm located in Southern Finland. The name of the farm and information about the locations cannot be given because of anonymity reasons. Two fields located close together were selected for sampling, one in which PE mulching films were currently in use and from which PE fragment films were also collected, and the other one where no mulching films were ever applied. At each field, a metal shovel was used to collect five subsamples from an area of 30 cm × 30 cm and separated 5 m from each other. The subsamples were placed in metal buckets previously rinsed with ultrapure water and combined to a single composite sample. The samples were collected to 5 cm depth, because literature studies (Cousins et al., 1999) have shown that the concentrations of organic contaminants such as PAHs and PCBs usually have a peak at or just below the soil surface and decline with soil depth. From each composite sample, ten replicate samples were extracted and analyzed. The samples were freeze dried and stored in a cold room at 5°C prior to analysis.

2.2 Chemical reagents

The chemicals to be analyzed were selected based on their occurrence in polyethylene and on their potential toxicity for the environment and human health (Cruz, 2013) and comprised PAHs (EPA 610 PAH Mix), phthalates (EPA 506 Phthalate Mix), acetyl tributyl citrate (ATBC) and dodecane (TCI Europe, Zwijndrecht, Belgium) (which should not be in plastics but was found in plastic mulches during preliminary screening). Deuterated solutions of DEHP-d4 (Sigma-Aldrich), dodecane-d26 (Toronto Research Chemicals), acetyl tributyl citrate-d3 (Toronto Research Chemicals), chrysene-d12 (Phenova) were used as internal standards. Hexane and acetone were purchased from VWR International. Glass microfiber filters (GF/A, 45 mm diameter, Whatman) were used for sample clean-up.

2.3 Extraction and analysis of soil samples and polyethylene films

Ten replicates of each soil sample and five replicates of PE mulching films collected from the strawberry fields were analyzed for the selected chemicals. The extraction of the samples was performed following the procedure described by Scopetani et al. (2022). Briefly, after lyophilization, 2 g of sample was transferred to glass bottles with 20 mL of hexane. The samples were stirred for 30 min (180 rpm) and then sonicated for 60 min. The same procedure was repeated three times. Deuterated internal standards were added and the samples were filtered through glass fiber filters and evaporated with a gentle flow of nitrogen down to 1 mL in a vial. Gas chromatography–mass spectrometry analysis was performed with a Shimadzu GC–MS-QP2010 Ultra system equipped with an AOC-20i autoinjector and a 30-m ZB-5MS column (0.25 mm i.d., 0.25 µm film thickness). The instrument operation conditions were as follows: 250°C injection temperature, split-less injection mode, 1 µL injection volume, He carrier gas. The temperature program was initially 60°C hold for 1 min, ramped at 10°C min^{-1} to 280°C and maintained for 6 min.

2.4 Quality assurance/quality control (QA/QC)

To avoid contamination with phthalates or other analyzed compounds, all equipment and glassware were rinsed first with ultrapure (18.2 MΩ) water, then with acetone and hexane. Potential sources of contamination and interferences were identified performing procedural blanks throughout all steps of the analysis. Procedural blank correction was applied when necessary. Bis(2-ethylhexyl) phthalate (DEHP) was removed from this study because of background contamination.

The recovery range of the target compounds was 95%–105%. The instrumental limit of quantification (LOQ) and limit of detection (LOD) were calculated based on the signal to noise ratio of the lowest standard concentrations (calculated by Shimadzu software, with LOD equal to signal to noise ratio = 3:1 and LOQ equal to signal to noise ratio 10:1) and are reported in Table 1.

2.5 Data analysis

The amount of leached chemicals per hectare was calculated by multiplying the mean organic compound concentrations in soil with the mass of soil per hectare, using the bulk density ($bd = \frac{mass}{volume}$) of 1.1 g/cm^3 of the sampled soil and 5 cm sampling depth:

$$Mass\,of\ soil\ per\ hectare = bd \times 1000m^2 \times soil\ depth$$

$$= 1.3\frac{g}{cm^3} \times 10^7 cm^2 \times 5cm = 5.5 \times 10^7 g$$

TABLE 2 Mean PAHs concentrations and standard deviations (n = 5) (ng/g dw). Fluorene (FLE), phenantrene (PHE), anthracene (ANT), fluoranthene (FLA), and pyrene (PYR).

	FLE	PHE	ANT	FLA	PYR
LOD	0.5	0.4	0.7	0.3	5
LOQ	1.5	1.5	2.5	0.9	17
Mulched soil	<LOD	<LOD	<LOD	<LOD	<LOD
Controls	<LOD	<LOD	<LOD	<LOD	<LOD
Mulching films	58 ± 8	271 ± 64	131 ± 102	58 ± 30	40 ± 20

IBM SPSS Statistics version 25 (2017) was used to perform statistical analysis. The data were checked for normality and homogeneity with Shapiro-Wilks and Levene's test. *t*-test was applied for normally distributed data in order to identify statistically significant differences in the concentrations of analyzed chemicals between the PE mulches, mulched soils and the control soils. Mann-Whitney test was applied when the data were not normally distributed. The differences were considered significant at a *p*-value of 0.05.

3 Results

Acenaphthylene, benzo [a]anthracene, chrysene, benzo [b] fluoranthene, benzo [k]fluoranthene, benzo [a]pyrene, indeno [1,2,3-cd]pyrene, dibenzo [ah]anthracene, and benzo [ghi] perylene were not detected in any of the analyzed samples, while all the others (fluorene, phenantrene, anthracene, fluoranthene, and pyrene) were found only in PE mulching films (Table 2).

Dodecane was not detected in any of the samples except in PE mulching films with an average concentration of 268 ± 19 ng/g (Table 3).

Amid the phthalates selected in this study, dimethyl phthalate (DMP) and di-n-octyl phthalate (DnOP) concentrations were below LOD in all samples analyzed (Table 3). Bis(2-ethylhexyl) adipate (DEHA), and diethyl phthalate (DEP) were detected in all samples, but the *t*-test did not show any statistically significant difference in the concentrations between the mulched soil and the controls (the soil where no mulching materials have been applied). On the contrary, the Mann-Whitney test highlighted a statistical difference between the controls and the mulched soil in terms of dibutyl phthalate (DBP) concentration (p = 0.046). Benzylbutyl phthalate (BBP) was detected in the mulching films and in the mulched soils, but not in the control soil. BBP, DBP and DEP were found in higher concentrations in the mulching materials in comparison to the soils.

Acetyl tributyl citrate (ATBC) was detected in PE mulching films and in the mulched soil (Table 3), but not in the soil where no mulching materials had been applied.

The amount of leached chemicals per hectare was calculated by multiplying the mean organic compound concentrations in soil with the mass of soil per hectare (see Methods) and the results are reported in Table 4.

TABLE 3 Mean organic compound concentrations and standard deviations (n = 10) (ng/g dw). * denotes a significant higher concentration compared to the controls ($p < 0,05$). All compounds were found in higher concentrations in the mulching materials in comparison to the soils. No statistics have been performed to compare the PE mulching films and the soil samples. Abbreviations: dimethyl phthalate (DMP), di-n-octyl phthalate (DnOP), bis(2-ethylhexyl) adipate (DEHA), diethyl phthalate (DEP), dibuthyl phthalate (DBP), benzylbutyl phthalate (BBP), acetyl tributyl citrate (ATBC).

	DMP	DNOP	DEP	DBP	BBP	ATBC	DEHA	Dodecane
LOD	0.5	7	0.8	0.4	1.5	2	0.6	7
LOQ	1.5	24	2.5	1.5	5	7	2	23
Mulched soil	<LOD	<LOD	45 ± 10	90 ± 32*	40 ± 26	14 ± 3	56 ± 10	<LOD
Controls	<LOD	<LOD	39 ± 5	62 ± 19	<LOD	<LOD	59 ± 14	<LOD
Mulching film	<LOD	<LOD	127 ± 9	559 ± 112	135 ± 1	61 ± 9	111 ± 4	268 ± 19

TABLE 4 Mean amount of leached organic compounds per hectare up to 5 cm depth (g). Abbreviations: dimethyl phthalate (DMP), di-n-octyl phthalate (DnOP), bis(2-ethylhexyl) adipate (DEHA), diethyl phthalate (DEP), dibuthyl phthalate (DBP), benzylbutyl phthalate (BBP), acetyl tributyl citrate (ATBC).

	DMP	DNOP	DEP	DBP	BBP	ATBC	DEHA	Dodecane
Mulched soil	<LOD	<LOD	2,47	4,95	2,20	0,77	3,08	<LOD
Controls	<LOD	<LOD	2,14	3,41	<LOD	<LOD	3,24	<LOD

4 Discussion

Strawberry represents about 80% of the total yield of cultivated berries in Finland (Luke, 2021) and strawberry cultivation is an important part of the Finnish local economy (Hietaranta and Karhu, 2014). The northernmost commercial strawberry farms locate near the Arctic Circle, and winter injury is the major factor limiting strawberry cultivation in the whole Finland (Hietaranta and Karhu, 2014). The harsh weathering conditions and the likelihood of spring frosts reduce significantly the growing season and the harvesting period is usually no more than 1 month (Hietaranta and Karhu, 2014). One way to prevent winter injury is to use polyethylene mulching films, that can extend the fruiting season up to 4 months. This is one of the reasons why the use of plastic mulches has become very common among strawberry farmers (Hietaranta and Karhu, 2014). On the downside, polyethene mulching films are potential source of variety of organic compounds in agricultural soil. Being so globally widespread (Qin et al., 2015), the practice of polyethylene mulching could represent a significant source of plasticizers and other potentially harmful compounds into the soil.

This study identified PE mulching films as a source of phthalates in agricultural soils. DBP and BBP concentration in our soil samples ranged between 32 ng/g d.w. (controls) to 143 ng/g d.w. (mulched soil) and from <1.5 ng/g d.w. (controls) to 57 ng/g d.w (mulched soil), respectively. Our data are in compliance with the ones from Zeng et al. (2020) and Kong et al. (2012) that showed how agricultural fields mulched with plastic materials presented significantly higher concentrations of phthalates.

Mulching films are potential sources of phthalates not only to agricultural soil, but also to crops cultivated using plastic mulching, as reported in several studies in China. In the study of Sun et al. (2015), strawberries and other edible plants were cultivated to evaluate the potential of crop uptake, translocation, and metabolism of phthalates. All the phthalates were detected in the plant tissues and they were soon transformed into their monoesters (Sun et al., 2015). Phthalates contamination in food plants as a result of widespread plasticulture were studied also by Wang et al. (2021), who found that maize roots could absorb and accumulate phthalates from soil with a bio-concentration factor ranging between 1.6 and 2.3. The average phthalate concentrations found in stems, leaves, and grains were 79%–80% of those in roots (Wang et al., 2021). In the study of Sun et al. (2021), phthalate concentrations in soil and wheat grains were significantly higher in the treatments with plastic mulches compared with the control, especially in terms of di-(2-ethylhexyl)-phthalate, dibutyl phthalate, and diisobutyl phthalate. In a exposure assessment of pesticides, phthalates, and heavy metals in strawberries from Shanghai by Shao et al. (2021), bis-2-ethylhexyl phthalate, diisobutyl phthalate, and dibutyl phthalate were detected in the strawberry samples, with a frequency of detection of 100, 100, and 89.9%, respectively.

Phthalates are considered as endocrine disrupting compounds (EDCs) and there are several studies pointing out the toxicity and carcinogenic of DBP and BBP (Min et al., 2014; Herrero et al., 2015; Wang et al., 2016; Czubacka et al., 2021; Wang et al., 2022). Wang et al. (2016) showed that concentration of phthalates ranging from 0.05 to 5.72 mg/kg, and thus lower than the ones we found in the present study, can decrease soil microbial activity. Further studies should be done to investigate the overall risks associated with the phthalates related to the use of polyethylene in mulching purposes.

Our data also indicate a transfer of acetyl tributyl citrate (ATBC) from PE films to the soil where the strawberries were cultivated using plastic mulching. Acetyl tributyl citrate is used as a phthalate substitute in plastic materials. It is not considered a toxic substance (Johnson, 2002; Arrieta et al., 2014), and European Chemicals Agency (ECHA) has stated that it should not be classified as dangerous/hazardous to the environment (ECHA, 2008). On the contrary, literature studies have pointed out that ATBC could have some toxic effects like impairing the reproductive system of zebrafish and mice and inducing cognitive decline in the mice offspring (Rasmussen et al., 2017a; Rasmussen et al., 2017b; Muhammad et al., 2018). A recent research conducted by Tang et al. (2022) showed that ATBC is able to cross human placenta. These evidences raise concerns about the extensive use of ATBC as plasticizer and highlight the need of further investigation.

The polycyclic aromatic hydrocarbons (PAHs) and dodecane detected in PE mulches suggest a potential transfer of these compounds from the mulching films to the soil, but their absence in the soil indicate that the transfer rate is negligible. However, it cannot be excluded that transfer of PAHs and dodecane from the mulching films to the soil could occur under different climatic condition or when the soil is exposed to PE for a longer time.

Dodecane is not a plastic additive, but it has a strong affinity for polyethylene (Castleman et al., 2021), and in preliminary studies it was found in PE mulching films and plastic fragments recovered from compost (Scopetani et al., 2022). Dodecane is a plant derived alkane mainly used as a solvent and as a component of kerosene (Herbinet et al., 2007). It is considered not toxic by the International Fragrance Association (IFRA) Environmental Standards (Api et al., 2020) and no limits have been set for its use by the EU regulation on fertilizing products (EU 2019/1009) (Regulation EU, 2019). Even though dodecane is considered a safe substance, literature studies have shown that it can cause cell death, skin irritation in rats, developmental impairment in aquatic organisms and papillomas in mice (Baxter and Miller, 1987; Babu et al., 2004; Burýšková et al., 2006; Kleinegris et al., 2011). These evidences highlight the need to collect further data on the exposure assessment of dodecane.

5 Conclusion

The focus of this case study was to evaluate the role of PE mulching films in transferring organic chemicals to agricultural soil. The selected chemicals comprised PAHs, phthalates, ATBC and dodecane. The transfer of PAHs and dodecane from the mulching materials to soil seemed to be negligible, but it cannot be excluded that the transfer rate could be higher under different conditions, such as climate and the contact time of soil with PE mulching films. In the contrary, our study shows significant leaching of dibutyl phthalate, benzylbutyl phthalate, and acetyl tributyl citrate from the mulching films to soil. Overall, our data point to PE mulching films being a source of phthalates and ATBC in agricultural soils. Considering the potential of the leachates to be taken up by crop plants, and the potential harm for the biota and humans associated with the exposure to phthalates, there is an urgent need to assess the ecological and health risks linked to the use of plastic mulches in agriculture.

Data availability statement

The raw data supporting the conclusions of this article will be made available by the authors, without undue reservation.

Author contributions

CS—Experimental design, Sampling, Samples treatment, Measurements, Data analysis and interpretation, Tables, Writing of the article SS—Revising Text and tables AC—Revising Text and tables JP—Experimental design, Data discussion and Revising Text and tables.

Funding

This work was funded by Kordelin Foundation, Finnish Cultural Foundation, and Maaperän Tutkimus-ja Kunnostusyhdistys ry within the MiCoMul project.

Acknowledgments

We thank the staff of the faculty's environmental laboratory, AlmaLab, for assisting in the laboratory work.

Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Publisher's note

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