Environmental Research 255 (2024) 119177

Contents lists available at ScienceDirect

Environmental Research

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

Phthalates and other organic chemicals in agricultural soils after use of different types of conventional and biodegradable plastics

Costanza Scopetani [a,*,1], Jukka Pellinen [a], Salla Selonen [b]

[a] Faculty of Biological and Environmental Sciences, Ecosystems and Environment Research Programme, University of Helsinki, Niemenkatu 73, FI-15140, Lahti, Finland
[b] Finnish Environment Institute SYKE, Latokartanonkaari 11, 00790, Helsinki, Finland

ARTICLE INFO

Keywords:
Plastic pollution
Plastic additives
Mulching film
Biodegradable plastic
Phthalates
Agricultural soil

ABSTRACT

Various plastic materials are used in contact with agricultural soil, like mulching films, crop covers, weed controlling fabrics and nets. Polyethylene (PE) mulches have already been recognized as a significant source of plastic in soil and they have been shown to contain additives like phthalates, known as endocrine disruptors.

However, other agricultural plastics are less studied, and little is known on the substances potentially released from them endangering biodiversity and the human health.

This research aims to assess whether different agricultural plastics release additives into soil and to compare the release among various materials.

We collected soil samples from 38 agricultural fields where conventional mulching films (PE), weed controlling fabrics (PP), biodegradable mulches based on polybutylene adipate terephthalate (PBAT), frost covers (PP), and oxo-degradable films (at least OXO-PE) were used. We analyzed the soils for phthalates and acetyl tributyl citrate (ATBC), used as plastic additives, and for polycyclic aromatic hydrocarbons (PAH) and dodecane that have high affinity for plastics. In comparison to the control soils, dibutylphthalate (DBP) and ATBC concentrations were significantly higher in soils mulched with PE and, partly, with biodegradable films. DBP concentration found in soil samples ranged between below the limit of quantification at a control site (1.5 μg kg^{-1}) to 135 μg kg^{-1} at a site mulched with OXO-PE. The highest ATBC concentration, 22 ± 6 μg kg^{-1}, was registered in a site mulched with PE, showing a statistically significant difference not only in comparison to the controls but also when compared to sites mulched with OXO-PE ($p = 0.029$) and PBAT ($p < 0.009$). On the contrary, the use of agricultural plastics did not influence the concentration of PAHs and dodecane. Our results indicate that agricultural plastics are a source of some organic chemicals to agricultural soils, including phthalates that are known for posing threat to soil ecosystem and human health.

1. Introduction

Mulching is an agricultural technique that involves covering the soil surface with a layer of material aiming at improving yield and crop quality by suppressing weed growth, by protecting soil from loss of moisture through evaporation and by modifying the microclimate (Chen et al., 2022; D. Sun et al., 2020; Kader et al., 2017; W. Qin et al., 2015). Zribi et al. (2015) showed that plastic mulching increased water use efficiency by 20–60% by reducing evaporation, and Qui et al. (2015) showed in a meta-analysis of 74 studies that plastic mulching on wheat and maize performed better than straw mulching, and increased yield per units of water and nitrogen by up to 60%. Efficient water usage in food production is paramount, given that agriculture stands as the foremost global water consumer (Qin et al., 2018) and with limited water resources, there is a pressing demand to double food production to accommodate the rapidly expanding global population (Le Mouël and Forslund, 2017).

A wide selection of mulching materials is available nowadays: conventional plastics, biodegradable plastics, straw, grass, starch, paper, sawdust, or gravel from which conventional polyethylene (PE) plastic is the most used (Bläsing and Amelung, 2018; Kader et al., 2017; Kasirajan and Ngouajio, 2012). PE mulching films are cost-effective, but at the same time they are considered one of the major sources of plastic pollution in terrestrial environments (Bläsing and Amelung, 2018; He

* Corresponding author.
E-mail address: costanza.scopetani@helsinki.fi (C. Scopetani).
[1] Present address: Department of Chemistry "Ugo Schiff", University of Florence, 50019 Sesto Fiorentino, Florence, Italy.

https://doi.org/10.1016/j.envres.2024.119177
Received 19 March 2024; Received in revised form 5 May 2024; Accepted 17 May 2024
Available online 23 May 2024

et al., 2018). PE mulches should be removed and disposed after use, but their efficient removal requires specialized equipment and fragments of plastic films are easily left on the fields. Ramos et al. (2015) analyzed fragments of PE film found in horticultural fields and showed that that these film residues comprised 10% of the total surface area sampled in the fields (Ramos et al., 2015).

Over time, the plastic film residues left in the soil, fragment into micro- and nanoplastic that potentially can affect soil physicochemical properties, crops and soil biota (Scopetani et al., 2020; Selonen et al., 2020, 2023; B. Xu et al., 2020). Accordingly, a positive correlation was found between microplastics and the mass of plastic mulch used in agricultural fields, together with higher microplastic concentrations in soil samples collected from fields with a longer history of mulch practices (Billings et al., 2021; B. Huang et al., 2021; Y. Huang et al., 2020; Yu et al., 2021).

Besides the potential to degrade into microplastics, plastic mulching films contain additives, such as plasticizers, stabilizers and pigments, which may be harmful for biota (Anbumani and Kakkar, 2018; Scopetani et al., 2023). As an instance, certain compounds like phthalates are acknowledged as endocrine disruptors, capable of interfering with the hormonal system (Bläsing and Amelung, 2018; Grindler et al., 2018). Exposure to phthalates was found to accelerate bone maturation in humans (S. Huang et al., 2022) and modulate the expression of critical placental genes through epigenetic regulation (Grindler et al., 2018). Other plasticizers such as acetyl tribyl citrate (ATBC) has been used as substitutes for phthalates in plastic applications to overcome these challenges. However, the potential risks of these kind of alternative plasticizers are still poorly known and their use has thus raised concerns (Qadeer et al., 2022).

The concern on the chemicals associated with plastics are not only about the additives that are added in the production process, but also non-intentionally added substances (NIAS) in the plastic material and the chemicals that are present in the environment. Non-intentionally added substances can be e.g. side products formed during the manufacturing of the plastics or plastic additives, breakdown products of the chemicals that are degrading during the manufacturing process of the plastics or contaminants present in recycled plastic material. Plastics can also sorb chemicals from the surrounding environment. For example, polycyclic aromatic hydrocarbons (PAHs), released by incomplete combustion of fossil fuels or other organic compounds and classified as persistent organic pollutants (POPs), are widespread in the environment and tend to sorb to plastics (Scopetani et al., 2022; B. Xu et al., 2020).

Biodegradable plastic films have been developed as an alternative to the conventional PE films. Being biodegradable, they are intended to be left in the fields, leading to a reduction of waste and costs of collection, treatment, and disposal. However, degradation of biodegradable plastics can be slower in some environmental conditions, which may lead to accumulation of the plastics in soil by time. It is also not known, if harmful substances could be released from biodegradable mulches and potentially endanger biodiversity and the human health. Because of this lack of information, there is an urgent need to collect data on the chemical additives in agricultural soils, resulting from the application of biodegradable mulching films.

Also oxo-degradable mulching films have been used in agricultural fields. These materials break down into fragments due to oxidation process when exposed e.g. to UV radiation or heat in the presence of oxygen. Typically, oxo-degradable plastics contain pro-oxidant additives, such as transition metal ions or metal complexes, which react with oxygen to promote the breaking of the chemical bonds of the polymer and the disintegration of the plastic material (European Commission, 2016). In European Union, the placing on market of oxo-degradable plastics have been restricted due to their contribution to the microplastic pollution in the environment (EU Directive, 2019/904), but there are still ongoing legal disputes that are hindering the restrictions.

In addition to mulching films, variety of different synthetic materials are used in contact with agricultural soil, like crop covers and weed controlling fabrics. However, these materials as potential sources of microplastics or plastic associated chemicals are even less studied and understood as mulching films.

In our study, we collected soil samples from 38 agricultural fields where different agricultural plastics, used in close contact with soil, were used: PE mulching films, polypropene (PP) weed controlling fabrics, biodegradable mulching films, frost covers (PP), and oxo-degradable plastic (OXO-PE). We analyzed the soil samples for phthalates, ATBC, dodecane and PAHs, in order to be able to determine if there are differences in the concentrations of these chemicals in soils between the sites with different agricultural plastic use. The selection of the chemicals for analysis was based on their presence in selected mulching films, screened by GC-TOF-MS in our laboratory, and on their known impacts on environmental and human health, as highlighted by Cruz et all. (2013). Our research can be seen as a preliminary investigation due to the limited existing data on the concentrations of organic chemicals in agricultural fields where different types of agricultural plastics have been used. It offers valuable insight on the potential release of these chemicals to agricultural soil from many different types of agricultural plastics. This study can thus guide the direction of future research in this area.

2. Material and methods

2.1. Sampling

The samples were taken in May–June 2020 from 38 fields in 16 different farms in Southern Finland Fig. 1). The fields represented six different types of plastic use: i) conventional polyethylene (PE) mulching films used in strawberry farming (n = 5); ii) biodegradable mulching films that are made of polybutylene adipate terephthalate (PBAT) and used in strawberry and vegetable farming (n = 11); iii) weed controlling fabrics made of polypropylene (PP) and used in berry and apple production (n = 4); iv) frost covers made of PP and used in potato and vegetable farming (n = 4); v) transparent oxo-degradable films made at least of PE and used in maize production (n = 9) and vi) control fields, in which these types of agricultural plastics had not been used (n = 5). Information about how many years plastics have been in use in each field were collected and compared with the concentration of chemicals found at the sites to see if there is correlation between these two factors.

At each site, five subsamples of soils were taken and combined into a single composite sample. For each subsample, soil from the area of 20 cm × 20 cm and depth of 5 cm were taken using a sampling grid shown in Fig. 1. From this composite samples, five replicate samples were analyzed. All the sampling equipment and jars were metal or glassware, and no plastic material was in contact with the soil. After the sampling, the soil samples were freeze dried.

2.2. Chemical reagents

Acetone and hexane (VWR International) were used for the sample extraction. For chemical analysis, Phthalate mixture (EPA 506 Phthalate Mix) and PAH mixture (EPA 610 PAH Mix), were purchased from Merck (Darmstadt, Germany), while dodecane, and acetyl tributyl citrate (ATBC) were from TCI Europe (Zwijndrecht, Belgium). As internal standards, acetyl tributyl citrate-d3, DEHP-d4, and chrysene-d12 were purchased from Toronto Research Chemicals, Sigma-Aldrich and Phenova, respectively.

2.3. Sample treatment

Five replicates of each soil sample were analyzed for PAHs, acetyl tributyl citrate (ATBC), dodecane, dimethyl phthalate (DMP), di-n-octyl phthalate (DNOP), diethyl phthalate (DEP), dibutyl phthalate (DBP), benzylbutyl phthalate (BBP), bis(2-ethylhexyl) adipate (DEHA). For the

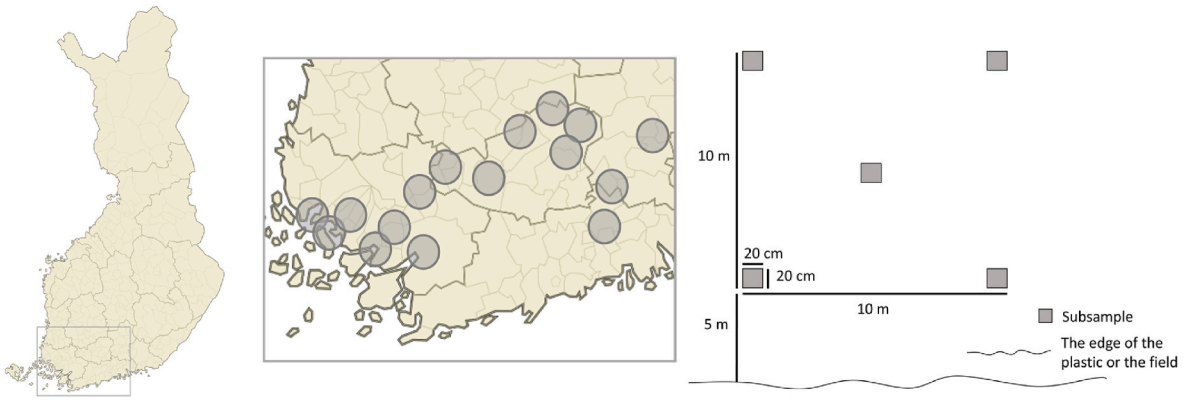

Fig. 1. Sampling sites and sampling scheme for one field. Each circle corresponds to a farm where one or multiple sampling sites were selected. Five subsamples with depth of 5 cm and area of 20 cm × 20 cm were combined into a composite sample.

extraction of the samples, the procedure described by Scopetani et al. (2023) was followed. Briefly, the samples were lyophilized, and 2 g of soil was transferred to 50 ml glass bottles, and 20 ml of hexane was added. The bottles were stirred for 30 min (180 rpm) and then sonicated for 60 min. The whole extraction procedure was repeated three times. Internal standards were added, after which the combined extracts were filtered through glass fiber filters and evaporated with a gentle flow of nitrogen down to 1 mL in a volumetric flask. The recovery range of the target compounds was 94–108%.

The extracts were analyzed with gas chromatography–mass spectrometry (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 same instrument operation conditions were applied as in Scopetani eta al. (2023). The recovery range of the target compounds was 94–108%. The instrumental limits of quantification (LOQ) and detection (LOD) were determined by assessing the signal-to-noise ratio of the lowest concentrations of the standards using Shimadzu software. To avoid contamination, all equipment and glassware underwent a rinsing procedure using ultrapure water (18.2 MΩ), followed by acetone and hexane. Procedural blanks were consistently conducted at each stage of the analysis to identify potential sources of contamination and interferences. Procedural blank correction was then applied.

2.4. Statistical analyses

To allow a proper data analysis and to not bias the results by excluding the data with concentrations below LOQ or using zero concentrations, all values below LOQ were replaced with a value of LOQ/2 before analyzing the data. Statistical analyses were performed using IBM SPSS Statistics version 25 (2017). Shapiro-Wilks and Levene's tests were used to check the data for normality and homogeneity. Since the data were not normally distributed, the differences in the chemical concentrations between the fields with different types of plastic use were compared using Kruskal-Wallis test, followed by Mann Whitney to detect differences amongst the treatments. Pearson's correlation analysis was performed to find out the possible relationships between the concentrations of chemicals and how many years plastics have been in use in the fields. The results were considered significant at the p value of 0.05.

3. Results and discussion

3.1. Polycyclic aromatic hydrocarbons

Naphthalene, acenaphtene, fluorene and dibenzo [ah]anthracene concentrations were below the limit of detection (LOD) in all samples analyzed. Also the other PAH compounds were below LOD for most of the samples except for a few exceptions. Only in one field out of nine where oxo-degradable plastic films were applied, benzo [a]anthracene was detected (7 ± 3 μg kg^{-1} dw). The same applied for benzo [a]pyrene that was detected in only one field out of five where PE mulching films were used (83 ± 25 μg kg^{-1} dw). It seems that the presence of PAHs in some of the selected fields is linked to other sources of pollution rather than mulching practices.

3.2. Dodecane

Dodecane was below LOQ in all samples analyzed (Table 1). Despite not being a plastic additive, dodecane was selected to this study, because preliminary tests done within our laboratory detected dodecane in PE mulching films and it was also found in plastics extracted from compost samples (Scopetani et al., 2022). There are only few studies available on the presence of dodecane in soil samples, and in these studies the occurrence of this alkane was detected but not quantified (Barrutia et al., 2011; Hempfling et al., 1991). Since dodecane was not detected in any of the analyzed soil samples, the release of this specific alkane from the mulching films to the soil seems to be negligible.

3.3. Acetyl tributyl citrate (ATBC)

Acetyl tributyl citrate (ATBC), an alternative plasticizer for phthalates, was detected in all types of plastic use (Table 1; Fig. 2). There was also a weak linear correlation between the concentration of ATBC and the duration of plastic use in the fields, when all sites with different use of plastics were included in the analysis ($r = 0.429$, $p = 0.009$, $n = 36$). However, we acknowledge that comparing different polymers across various fields and soil types in our correlation analysis could be a limiting factor. The desorption rate may vary significantly between different polymers and soil types.

ATBC was below LOQ in controls samples, but it was found in concentrations exceeding LOQ in all other fields. The concentrations were significantly higher than in the controls in all the different mulching materials (determined by replacing control values below LOQ with LOQ/2 value) except for those with just the frost cover (Kruskal-Wallis test $\chi 2$ (5) = 14.89, $p = 0.011$): PE films ($p = 0.008$), oxo-degradable mulching films ($p = 0.042$), PP fabrics ($p = 0.036$), and biodegradable plastic films ($p < 0.001$).

The sites where PE films were used had the highest ATBC concentration (22 ± 6 μg kg^{-1} dw) that was statistically significantly higher not only when compared to the controls, but also in the comparisons to the sites with oxo-degradable plastics ($p = 0.029$) and biodegradable plastics ($p < 0.009$). Our results show that ATBC is mainly released from PE mulching films, but also from PP-fabrics and oxo- and biodegradable plastics, that are left in soil to degrade.

Table 1
Mean organic contaminants concentrations and standard deviations (μg kg-1 dw).

	N° of sites	DMP	DNOP	DEP	DBP	BBP	DEHA	ATBC	Dodecane
LOD		**0.5**	**8**	**0.8**	**0.4**	**1.5**	**0.6**	**2**	**7**
LOQ		**1.5**	**24**	**2.4**	**1.2**	**4.5**	**1.8**	**7**	**23**
Controls	5	<1.5	<24	28 ± 2	30 ± 10	17 ± 19	47 ± 19	<7	<23
PE films	5	<1.5	<24	31 ± 4	54 ± 17[a]	35 ± 20	47 ± 13	22 ± 6[b]	<23
Bio films	11	<1.5	<24	27 ± 1	36 ± 15	17 ± 14	46 ± 15	11 ± 4[b]	<23
Oxo-films	9	<1.5	<24	28 ± 3	73 ± 41[a]	22 ± 15	46 ± 14	11 ± 6[b]	<23
PP fabrics	4	<1.5	<24	27 ± 2	71 ± 40	27 ± 2	48 ± 5	11 ± 5[b]	<23
Frost cover	4	<1.5	<24	26 ± 1	35 ± 19	14 ± 14	43 ± 13	13 ± 10	<23

[a] denotes a significantly higher concentration compared to the controls ($p < 0,05$). All the ATBC controls were ≤ LOQ.
[b] denotes a significantly higher concentration of ATBC compared to the controls ($p < 0,05$) determined by replacing control values below LOQ with LOQ/2 value.

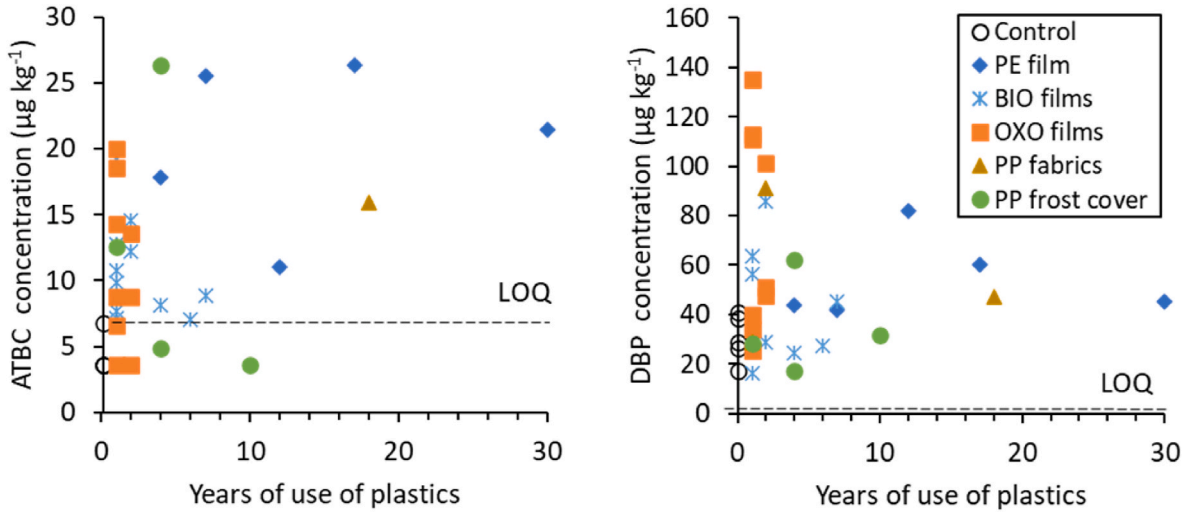

Fig. 2. Concentrations of acetyl tributyl citrate (ATBC) and dibutylphthalate (DBP) in agricultural soil in relation to the duration of the use of plastic at the site.

Globally, there are no regulations aiming at limiting the presence of ATBC in agricultural soils and the chemical is categorized as non-toxic (Arrieta et al., 2014; Johnson, 2002). This may explain the almost complete absence of studies on the effects and even the occurrence of ATBC in the terrestrial environment. One of our previous studies, investigating the transfer of hazardous contaminants from plastics to compost and soil, detected ATBC in agricultural soils with concentrations ranging from non-detectable to 207 μg kg^{-1} dw (Scopetani et al., 2022). This supports the findings of the present study that agricultural plastics are a source of ATBC in the agricultural soil and this compound can be found in the soils where plastics are used.

Despite being classified as a non-toxic substance, the scientific community is gathering evidence that might prove the opposite (Muhammad et al., 2018; Rasmussen et al., 2017a, 2017b). ATBC was shown to impair zebrafish reproductive system at environmentally relevant concentration of 0.5 μg l^{-1} (Muhammad et al., 2018), to damage mouse ovarian and antral follicle function (Rasmussen et al., 2017a), and to induce symptoms in the brains of the offspring of the exposed parent mice (Liu X D, Zhu S J, 2021). Tang et al. (2022) showed ATBC to cross human placenta by detecting it in 33%–45% of maternal sera.

In thyroid hormone receptor tests, ATBC demonstrated a greater propensity for disrupting thyroid hormone function compared to di (2-ethylhexyl) phthalate (Zughaibi et al., 2022; Qadeer et al., 2024). The findings of Zughaibi et al. (2022) were supported by those of Horie et al. (2022) that studied the effects of ATBC on endocrine hormone activity and its developmental toxicity of ATBC in zebrafish (Danio rerio) and Japanese medaka (Oryzias latipes) embryos. ATBC exposure resulted in increased mortality rates for both zebrafish and Japanese medaka, at concentrations of 443.05 μg L^{-1} and 1937.41 μg L^{-1}, respectively. Furthermore, body curvature, edema, and growth inhibition, were evident in both species post-ATBC exposure. Notably, there was also a significant suppression in thyroid-related gene expression in both species after ATBC exposure.

These findings suggest that ATBC, used as a phthalate substitute plasticizer, might pose similar concerns on health and environment as phthalates (Bläsing and Amelung, 2018; Grindler et al., 2018), and thus, the acquisition of more data is needed for running further ATBC risk assessment.

3.4. Phthalates

Among the phthalates analyzed, DMP and DNOP concentrations were below LOQ in all samples. BBP, DEHA, and DEP were detected in all samples (Table 1), but no difference was found between the control and the mulched fields ($p \geq 0.05$). On the contrary, dibutylphthalate (DBP) was detected in all samples (Table 1) and the concentrations were significantly higher in soils mulched with PE and oxo-degradable plastic films than in the control soils ($p = 0.008$ and $p = 0.042$ respectively). According to Cui et al. (2024), within phthalates, DBP is one of the predominant congeners, comprising, together with di (2- ethylhexyl) phthalate (DEHP), 89–100% of the total concentration of PAEs in plastic mulch films.

The variation in the concentrations of DBP at the sites mulched with oxo-degradable plastics was high even though at all sites the plastics were used for one or two years. On the contrary, at the sites mulched with PE film the variation in the DBP concentration between the sites was much lower although the duration of the use of plastics varied between one to ten years (Fig. 2). Thus, although no linear correlation was found between DBP concentration and how many years plastics have

been in use in the fields ($r = 0.008$, $p = 0.964$, $n = 38$), the type of plastic seems to affect the range of the DBP concentrations found in the soil (Fig. 2). This may indicate different pattern of release of this chemical from conventional PE mulching film that is spread as more or less uniform covering on the soil surface for several years and oxo-degradable plastic that fragmentates to small particles within the same growth season and are mixed in the soil after fragmentation. Overall, this data supports the hypothesis that PE and oxo-degradable plastic films might act as sources of phthalates in agricultural soils.

In accordance with our data, Zeng et al. (2020) and Kong et al. (2012) showed that phthalate concentrations (including DBP) in plastic film covered agricultural fields were up to 208% higher than that found in fields were no plastic films were used. (Billings et al., 2021; S. Kong et al., 2012; Zeng et al., 2020). Another study found a positive correlation between the total phthalate concentrations (from 1.37 to 4.90 mg kg^{-1}-dw) and the use of plastic mulches, with the highest value in the summer (Zhang et al., 2015). It was concluded that most likely the higher occurrence of phthalate in summertime was linked to the higher temperatures that facilitated the transfer of contaminants from the plastic mulches to the soil and the increased use of fertilizers over the summer (Zhang et al., 2015).

DBP concentration found in our soil samples ranged between less than 1.5 μg kg^{-1} (LOQ; a control site) to 135 μg kg^{-1} (a site with oxo-degradable plastic film). Our results were in compliance with the DBP concentration found in agricultural soils from Denmark (between 0.3 and 453 μg kg^{-1} dw) (Vikelsøe et al., 1999), in soils from Serbia (between 30 and 145 μg kg^{-1} dw) (Škrbić et al., 2016) and from the Paris area (between 4 and 92 μg kg^{-1} dw) (Tran et al., 2015). Globally, DBP, together with DEHP, is one of the most abundant phthalates found in soil samples with a wide range of concentration: 0.2–45300 μg kg^{-1} (Škrbić et al., 2016).

Lü et al. (2018) discussed in their review the sources of phthalates contamination into soil, highlighting mulching films as one of the most significant contributors, with conventional mulches typically containing 10–60% of phthalates by weight. As plastic mulching becomes increasingly common, large quantities of plastic residues accumulate in the soil each year, posing a potential pollution threat.

Xu et al. (2024), through laboratory incubation, quantified the release and biodegradation rates of various additives, including phthalates, from mulching films into soil. The study estimated a substantial annual release of around 4000 metric tons of films additives in China alone, underlining the scale of the issue, with phthalates holding a significant share, typically accounting for 25.2% of the total concentrations observed. A preliminary risk assessment suggested moderate hazards to the soil ecosystem, with phthalates posing the greatest risk.

Phthalates in agricultural soil can find their route also to cultivated crops. Study by Sun et al. (2015) showed that lettuce, strawberry and carrot can uptake and accumulate phthalates from the soil, further transforming them into their monoesters (J. Sun et al., 2015). DBP has been shown to bioaccumulate also in peanuts (*Arachis hypogaea* L.; (Kairong Wang et al., 2017), rapeseeds (*Brassica napus*; (Kong et al., 2018), cucumbers (Wang et al., 2016), wheat (Gao et al., 2017) and rice (Cai et al., 2017).The environmental behavior of phthalates, including distribution, decomposition, transformation, and uptake by crop plants, is significantly influenced by soil profiles with varying levels of soil organic matter and microorganism compositions (Cui et al., 2024). Detailed investigations into the behavior and toxicity of phthalates across diverse soil conditions are crucial for systematically assessing phthalates contamination and its potential impact on the environment and human health.

Dibutylphthalate is commonly used as a plasticizer in the synthesis of polymers, and it is recognized as an endocrine disruptor able to cause adverse reproductive effects in living organisms (Czubacka et al., 2021; ECHA – EU Member State Committee, 2014). The European Commission has restricted DBP use in children toys since 1999 (European Commission, 1999) and banned its presence in cosmetics such as nail polishes (European Commission, 1976). The European Chemicals Agency (ECHA) has identified this phthalate as a substance of very high concern under the REACH Regulation (ECHA – EU Member State Committee, n. d.).

The scientific studies assessing the high hazard level of DBP on mammals are numerous (Czubacka et al., 2021, Mitsuhashi et al., 2004; Moody et al., 2013). Also in soils, adverse effects on microbes (Gao et al., 2019a,b; Kong et al., 2018, 2012; Xu et al., 2018), invertebrates (Du et al., 2015; Ma et al., 2015; G. Wang et al., 2018) and plants (Wang et al., 2016; Yao et al., 2022) have been found.

DBP has been found to affect microbial community structure and diversity (Kong et al., 2018, 2019; Gao et al., 2019a,b; Xu et al., 2018) and to increase the gene abundances of the carbon, sulfur and nitrogen metabolism (Xu et al., 2018). In earthworms (*Eisenia fetida*), DBP has been found to induce various molecular or biochemical responses indicating oxidative stress, DNA damage or detoxification of xenobiotics (Du et al., 2015; Ma et al., 2015; G. Wang et al., 2018). DBP has also been shown to pose negative effects on cultivated plants. It was found to decrease the growth of roots, stems and leaves, hamper photosynthesis, induce oxidative stress in wheat (*Triticum aestivum* L; Gao et al., 2017; Gao et al., 2019a) and in pachoi (*Brassica campestris*; Yao et al., 2022) and to affect the nutritional quality of crop species (Kong et al., 2018; Yao et al., 2022; Wang et al., 2016). However, most of these adverse effects detected in plants or soil organisms were present already at the lowest test concentration, varying between 1 mg kg^{-1} and 50 mg kg^{-1}. Thus, the impacts of DBP at the concentration levels found at the present study cannot be estimated based on these existing data.

Among phthalates, DBP is one of the most abundant compounds found in food items. Da Costa et al. (2023), in their systematic review examined the presence of various phthalates in different food categories and outlined their sources, migration from food contact materials, and associated risks. DBP, along with DEHP, showed high incidence levels and the risk of surpassing tolerable daily intake levels was notable for both DBP and DEHP in fish, fats/oils, cereals, and dairy products. Particularly, fats/oils were highlighted as critical for several phthalates, including DBP.

Similar findings were shown by the study of Zhang et al. (2023) where various grain, vegetable, and fruit samples were thoroughly analyzed to assess the presence of 22 phthalates. DBP was detected across all samples in notably amount. Estimated daily intake of phthalates from human diets generally remained below reference doses, except for DBP in grains and vegetables, which approached or exceeded tolerable daily intake levels, warranting attention, especially concerning the health of children and adolescents. Considering that mulching films are commonly utilized in the cultivation of vegetables, grains, cereals, and fruits, they emerge as a potential source of phthalates for these food items.

All this evidence points out that the accumulation of DBP in agricultural soil can be a serious environmental and health hazard. In addition, the lack of data on the possible impacts of DBP at lower soil concentrations hamper the risk assessment of these compounds. Our results indicate that PE and oxo-degradable plastic films are able to transfer DBP to the soil, highlighting the necessity for further studies on this research topic and the potential need for updating the current regulation on mulching practices, considering the risk of the potential transfer of phthalates from the soil to the edible crops.

4. Conclusions

Our research contributes to the growing amount of evidence indicating the contamination of agricultural soils with plastics and associated organic chemicals.

. Specifically, we focused on assessing the potential release of organic chemicals from different types of agricultural plastics by measuring chemical concentrations of agricultural soils at sites with different types of plastic uses. Our results indicate that mulching practices can affect the

presence of some organic chemicals in soil, as noted by Lü et al. (2018), who identify mulching films as significant contributors to the presence of phthalates in soil. Dibutylphthalate (DBP) and acetyl tributyl citrate (ATBC) were found in higher concentrations in soils where certain agricultural plastic types were used. The soil samples collected from the fields where PE and oxo-degradable mulching films were used had significantly higher concentrations of DBP than the samples from the other sites. ATBC concentration was higher in comparison to the controls at all the sites with conventional or biodegradable plastic use except the sites, where the frost cover mulch was applied, and a positive correlation was detected between the ATBC concentration in soil and the number of years the plastics were used. Our data support the hypothesis of a contaminant transfer pathway from mulching materials to the soil.

Notably, the presence of plastic additives at sites mulched with biodegradable films raises concerns regarding their potential environmental impact, especially considering that biodegradable mulches can be left in the soil after use, allowing for continued chemical release. Moreover, fragments of PE plastic mulches, which should ideally be removed at the end of their life, are often left behind in fields, further exacerbating soil contamination (Billings et al., 2021).

Our results highlight the risks associated with mulching practices and suggest that biodegradable materials may not offer a significantly safer alternative to non-biodegradable ones. Different agricultural plastics can contain and transfer variety of chemicals. The diverse composition of agricultural plastics underscores the need for further research to comprehensively assess their impacts on soil health and to develop regulatory guidelines for their use. Thus, further studies are needed to assess the composition of mulches and the impacts of plastic additives in soil with wide range of concentrations to understand the potential risks associated with both conventional and biodegradable agricultural plastics.

Moreover, a thorough understanding of how plastic additives migrate within soil is crucial for assessing their bioavailability and bioaccessibility. As highlighted by Ramanayaka et al. (2023), both the type of the plastic additive and the soil's physicochemical characteristics determine the environmental fate of these additives. Such efforts are essential for understanding and mitigating the environmental impacts of plastic use in agriculture.

Funding

This work was funded by KordelinFoundation, Finnish Cultural Foundation, and Maaperän Tutkimus-ja Kunnostusyhdistys ry (MUTKU) within the MiCoMul project and Makera funding from the Ministry of Agriculture and Forestry of Finland within the MicrAgri project.

CRediT authorship contribution statement

Costanza Scopetani: Writing – original draft, Resources, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation. **Jukka Pellinen:** Writing – review & editing, Supervision, Resources, Investigation, Funding acquisition, Data curation, Conceptualization. **Salla Selonen:** Writing – review & editing, Supervision, Resources, Investigation, Funding acquisition, Data curation, Conceptualization.

Declaration of competing interest

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

Data availability

Data will be made available on request.

Acknowledgment

We thank AlmaLab staff for assisting in the laboratory work, Essi Roininen for the help in the sampling, Liisa Maunuksela, Ansa Palojärvi and the members of the steering group of MicrAgri project for the help in finding study sites and all farmers that provided the possibility to take samples from their fields.

References

Anbumani, S., Kakkar, P., 2018. Ecotoxicological effects of microplastics on biota: a review. In: Environmental Science and Pollution Research, vol. 25. Springer Verlag, pp. 14373–14396. https://doi.org/10.1007/s11356-018-1999-x, 15.

Arrieta, M.P., López, J., Rayón, E., Jiménez, A., 2014. Disintegrability under composting conditions of plasticized PLA–PHB blends. Polym. Degrad. Stabil. 108, 307–318. https://doi.org/10.1016/j.polymdegradstab.2014.01.034.

Barrutia, O., Garbisu, C., Epelde, L., Sampedro, M.C., Goicolea, M.A., Becerril, J.M., 2011. Plant tolerance to diesel minimizes its impact on soil microbial characteristics during rhizoremediation of diesel-contaminated soils. Sci. Total Environ. 409 (19), 4087–4093. https://doi.org/10.1016/j.scitotenv.2011.06.025.

Billings, A., Jones, K.C., Pereira, M.G., Spurgeon, D.J., 2021. Plasticisers in the terrestrial environment: sources, occurrence and fate. Environ. Chem. 18 (3), 111–130. https://doi.org/10.1071/EN21033.

Bläsing, M., Amelung, W., 2018. Plastics in soil: Analytical methods and possible sources. Sci. Total Environ. 612, 422–435. https://doi.org/10.1016/j.scitotenv.2017.08.086.

Cai, Q.Y., Xiao, P.Y., Zhao, H.M., Lü, H., Zeng, Q.Y., Li, Y.W., Li, H., Xiang, L., Mo, C.H., 2017. Variation in accumulation and translocation of di-n-butyl phthalate (DBP) among rice (Oryza sativa L.) genotypes and selection of cultivars for low DBP exposure. Environ. Sci. Pollut. Control Ser. 24 (8), 7298–7309. https://doi.org/10.1007/s11356-017-8365-2.

Chen, B., Cui, J., Man, X., Dong, W., Yan, C., Mei, X., 2022. The climate cost of saving water by different plastic mulching patterns. J. Clean. Prod. 359 (November 2021), 132011 https://doi.org/10.1016/j.jclepro.2022.132011.

Cui, J., Bai, R., Ding, W., Liu, Q., Liu, Q., He, W., Yan, C., Li, Z., 2024. Potential agricultural contamination and environmental risk of phthalate acid esters arrived from plastic film mulching. J. Environ. Chem. Eng. 12 (1), 111785 https://doi.org/10.1016/j.jece.2023.111785.

Czubacka, E., Czerczak, S., Kupczewska-Dobecka, M.M., 2021. The overview of current evidence on the reproductive toxicity of dibutyl phthalate. Int. J. Occup. Med. Environ. Health 34 (1), 15–37. https://doi.org/10.13075/ijomeh.1896.01658.

da Costa, J.M., Kato, L.S., Galvan, D., Lelis, C.A., Saraiva, T., Conte-Junior, C.A., 2023. Occurrence of phthalates in different food matrices: a systematic review of the main sources of contamination and potential risks. Compr. Rev. Food Sci. Food Saf. 22 (3), 2043–2080. https://doi.org/10.1111/1541-4337.13140.

Du, L., Li, G., Liu, M., Li, Y., Yin, S., Zhao, J., Zhang, X., 2015. Evaluation of DNA damage and antioxidant system induced by di-n-butyl phthalates exposure in earthworms (Eisenia fetida). Ecotoxicol. Environ. Saf. 115, 75–82. https://doi.org/10.1016/j.ecoenv.2015.01.031.

ECHA – EU Member State Committee, 2014. Opinion of the Member State Committee on the Identification of Dibutyl Phthalate (DBP) as a Substance of Very High Concern.

European Commission, 1976. Council Directive 76/768/EEC of 27 July 1976 on the approximation of the laws of the Member States relating to cosmetic products. https://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:31976L0768:EN:HTML.

European Commission, 1999. Ban of Phthalates in Childcare Articles and Toys (Issue November).

Gao, M., Dong, Y., Zhang, Z., Song, W., Qi, Y., 2017. Growth and antioxidant defense responses of wheat seedlings to di-n-butyl phthalate and di (2-ethylhexyl) phthalate stress. Chemosphere 172, 418–428. https://doi.org/10.1016/j.chemosphere.2017.01.034.

Gao, M., Guo, Z., Dong, Y., Song, Z., 2019a. Effects of di-n-butyl phthalate on photosynthetic performance and oxidative damage in different growth stages of wheat in cinnamon soils. Environ. Pollut. 250, 357–365. https://doi.org/10.1016/j.envpol.2019.04.022.

Gao, M., Liu, Y., Dong, Y., Song, Z., 2019b. Physiological responses of wheat planted in fluvo-aquic soils to di (2-ethylhexyl) and di-n-butyl phthalates. Environ. Pollut. 244, 774–782. https://doi.org/10.1016/j.envpol.2018.10.095.

Grindler, N.M., Vanderlinden, L., Karthikraj, R., Kannan, K., Teal, S., Polotsky, A.J., Powell, T.L., Yang, I.V., Jansson, T., 2018. Exposure to phthalate, an endocrine disrupting chemical, alters the First Trimester placental methylome and transcriptome in women. Sci. Rep. 8 (1), 1–9. https://doi.org/10.1038/s41598-018-24505-w.

He, D., Luo, Y., Lu, S., Liu, M., Song, Y., Lei, L., 2018. Microplastics in soils: analytical methods, pollution characteristics and ecological risks. TrAC, Trends Anal. Chem. 109, 163–172. https://doi.org/10.1016/j.trac.2018.10.006.

Hempfling, R., Schulten, H., Fresenius, F., Analysis, T., Wiesbaden, W.-., 1991. Pyrolysis-(gas Chromatography/) Mass Spectrometry of Agricultural Soils and Their Humic Fractions, vol. 1990, pp. 425–430.

Horie, Y., Yap, C.K., Okamura, H., 2022. Developmental toxicity and thyroid hormone-disrupting effects of acetyl tributyl citrate in zebrafish and Japanese medaka. Journal of Hazardous Materials Advances 8, 100199. https://doi.org/10.1016/j.hazadv.2022.100199.

Huang, B., Sun, L., Liu, M., Huang, H., He, H., Han, F., Wang, X., Xu, Z., Li, B., Pan, X., 2021. Abundance and distribution characteristics of microplastic in plateau cultivated land of Yunnan Province, China. Environ. Sci. Pollut. Control Ser. 28 (2), 1675–1688. https://doi.org/10.1007/s11356-020-10527-3.

Huang, S., Su, Z., Su, H., Jiao, Y., Su, Q., Yao, Y., Zhou, L., Zheng, X., Zhang, X., 2022. Association between phthalate exposure and accelerated bone maturation in Chinese girls with early puberty onset: a propensity score-matched case-control analysis. Sci. Rep. 12 (1), 15166 https://doi.org/10.1038/s41598-022-19470-4.

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

Johnson, W., 2002. Final report on the safety assessment of acetyl triethyl citrate, acetyl tributyl citrate, acetyl trihexyl citrate, and acetyl trioctyl citrate. Int. J. Toxicol. 21 (Suppl. 2), 1–17. https://doi.org/10.1080/10915810290096504.

Kader, M.A., Senge, M., Mojid, M.A., Ito, K., 2017. Recent advances in mulching materials and methods for modifying soil environment. Soil Tillage Res. 168, 155–166. https://doi.org/10.1016/j.still.2017.01.001.

Kairong Wang, K., Song, N., Cui, M., Shi, Y., 2017. Phthalate esters migration from two kinds of plastic films and the enrichment in peanut plant. Fresenius Environ. Bull. 26 (7), 4409–4415.

Kasirajan, S., Ngouajio, M., 2012. Polyethylene and biodegradable mulches for agricultural applications: a review. Agron. Sustain. Dev. 32 (2), 501–529. https://doi.org/10.1007/s13593-011-0068-3.

Kong, S., Ji, Y., Liu, L., Chen, L., Zhao, X., Wang, J., Bai, Z., Sun, Z., 2012. Diversities of phthalate esters in suburban agricultural soils and wasteland soil appeared with urbanization in China. Environ. Pollut. 170, 161–168. https://doi.org/10.1016/j.envpol.2012.06.017.

Kong, X., Jin, D., Jin, S., Wang, Z., Yin, H., Xu, M., Deng, Y., 2018. Responses of bacterial community to dibutyl phthalate pollution in a soil-vegetable ecosystem. J. Hazard Mater. 353, 142–150. https://doi.org/10.1016/j.jhazmat.2018.04.015.

Le Mouël, C., Forslund, A., 2017. How can we feed the world in 2050? A review of the responses from global scenario studies. Eur. Rev. Agric. Econ. 44 (4), 541–591. https://doi.org/10.1093/erae/jbx006.

Lü, H.X., Mo, C.H., Zhao, H.M., Xiang, L., Katsoyiannis, A., Li, Y.W., Cai, Q.Y., Wong, M. H., 2018. Soil contamination and sources of phthalates and its health risk in China: a review. Environ. Res. 164, 417–429. https://doi.org/10.1016/j.envres.2018.03.013.

Ma, T., Teng, Y., Christie, P., Luo, Y., 2015. Phytotoxicity in seven higher plant species exposed to di-n-butyl phthalate or bis (2-ethylhexyl) phthalate. Front. Environ. Sci. Eng. 9 (2), 259–268. https://doi.org/10.1007/s11783-014-0652-2.

Muhammad, S., Zhang, Z., Pavase, T.R., Guo, H., 2018. Long-term exposure of two plasticizers di (2-ethylhexyl) phthalate (DEHP) and acetyl tributyl citrate (ATBC): Toxic effects on gonadal development and reproduction of zebrafish ("Danio rerio"). Indian Journal of Geo-Marine Sciences 47 (4), 789–797.

Qadeer, A., Kirsten, K.L., Ajmal, Z., Jiang, X., Zhao, X., 2022. Alternative plasticizers as emerging global environmental and health threat: another regrettable substitution? Environ. Sci. Technol. 56 (3), 1482–1488. https://doi.org/10.1021/acs.est.1c08365.

Qadeer, A., Anis, M., Warner, G.R., Potts, C., Giovanoulis, G., Nasr, S., Archundia, D., Zhang, Q., Ajmal, Z., Tweedale, A.C., Kun, W., 2024. Global environmental and toxicological data of emerging plasticizers: current knowledge, regrettable substitution dilemma, green solution and future perspectives. Green Chem. https://doi.org/10.1039/D3GC03428C.

Qin, S., Li, S., Yang, K., Hu, K., 2018. Can plastic mulch save water at night in irrigated croplands? J. Hydrol. 564 (July), 667–681. https://doi.org/10.1016/j.jhydrol.2018.07.050.

Qin, W., Hu, C., Oenema, O., 2015. Soil mulching significantly enhances yields and water and nitrogen use efficiencies of maize and wheat: a meta-analysis. Sci. Rep. 5 (November), 1–13. https://doi.org/10.1038/srep16210.

Ramanayaka, S., Vithanage, M., Zhang, H., Semple, K.T., 2023. Role of soil organic matter on the retention and mobility of common plastic additives, Di(2-ethylhexyl) phthalate, Bisphenol A and Benzophenone, in soil. Environ. Res. https://doi.org/10.1016/j.envres.2023.116725.

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

Rasmussen, L.M., Sen, N., Liu, X., Craig, Z.R., 2017a. Effects of oral exposure to the phthalate substitute acetyl tributyl citrate on female reproduction in mice. J. Appl. Toxicol. 37 (6), 668–675. https://doi.org/10.1002/jat.3413.

Rasmussen, L.M., Sen, N., Vera, J.C., Liu, X., Craig, Z.R., 2017b. Effects of in vitro exposure to dibutyl phthalate, mono-butyl phthalate, and acetyl tributyl citrate on ovarian antral follicle growth and viability. Biol. Reprod. 96 (5), 1105–1117. https://doi.org/10.1095/biolreprod.116.144691.

Scopetani, C., Chelazzi, D., Cincinelli, A., Martellini, T., Leiniö, V., Pellinen, J., 2022. Hazardous contaminants in plastics contained in compost and agricultural soil. Chemosphere 293. https://doi.org/10.1016/j.chemosphere.2022.133645. October 2021.

Scopetani, C., Esterhuizen, M., Cincinelli, A., Pflugmacher, S., 2020. Microplastics exposure causes negligible effects on the oxidative response enzymes glutathione reductase and peroxidase in the oligochaete *Tubifex tubifex*. Toxics 8 (14), 1–8. https://doi.org/10.3390/toxics8010014.

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

Selonen, S., Dolar, A., Jemec Kokalj, A., Skalar, T., Parramon Dolcet, L., Hurley, R., van Gestel, C.A.M., 2020. Exploring the impacts of plastics in soil – the effects of polyester textile fibers on soil invertebrates. Sci. Total Environ. 700 https://doi.org/10.1016/j.scitotenv.2019.134451.

Selonen, S., Jemec Kokalj, A., Benguedouar, H., Alavian Petroody, S.S., Dolar, A., Drobne, D., van Gestel, C.A.M., 2023. Modulation of chlorpyrifos toxicity to soil arthropods by simultaneous exposure to polyester microfibers or tire particle microplastics. Appl. Soil Ecol. 181 https://doi.org/10.1016/j.apsoil.2022.104657.

Škrbić, B.D., Ji, Y., Đurišić-Mladenović, N., Zhao, J., 2016. Occurrence of the phthalate esters in soil and street dust samples from the Novi Sad city area, Serbia, and the influence on the children's and adults' exposure. J. Hazard Mater. 312, 272–279. https://doi.org/10.1016/j.jhazmat.2016.03.045.

Sun, D., Li, H., Wang, E., He, W., Hao, W., Yan, C., Li, Y., Mei, X., Zhang, Y., Sun, Z., Jia, Z., Zhou, H., Fan, T., Zhang, X., Liu, Q., Wang, F., Zhang, C., Shen, J., Wang, Q., Zhang, F., 2020. An overview of the use of plastic-film mulching in China to increase crop yield and water-use efficiency. Natl. Sci. Rev. 7 (10), 1523–1526. https://doi.org/10.1093/NSR/NWAA146.

Sun, J., Wu, X., Gan, J., 2015. Uptake and metabolism of phthalate esters by edible plants. Environ. Sci. Technol. 49 (14), 8471–8478. https://doi.org/10.1021/acs.est.5b01233.

Tang, S., Sun, X., Qiao, X., Cui, W., Yu, F., Zeng, X., Covaci, A., Chen, D., 2022. Prenatal exposure to emerging plasticizers and synthetic antioxidants and their potency to cross human placenta. Environ. Sci. Technol. 56 (12), 8507–8517. https://doi.org/10.1021/acs.est.2c01141.

Tran, B.C., Teil, M.J., Blanchard, M., Alliot, F., Chevreuil, M., 2015. Fate of phthalates and BPA in agricultural and non-agricultural soils of the Paris area (France). Environ. Sci. Pollut. Control Ser. 22 (14), 11118–11126. https://doi.org/10.1007/s11356-015-4178-3.

Vikelsøe, J., Thomsen, M., Johansen, E., Carlsen, L., 1999, 1999. Phthalates and Nonylphenols in Soil: A Field Study of Different Soil Profiles, vol. 268. National Environmental Research Institute, p. 128. NERI Technical Report.

Wang, G., Wang, J., Zhu, L., Wang, J., Li, H., Zhang, Y., Liu, W., Gao, J., 2018. Oxidative damage and genetic toxicity induced by DBP in earthworms (Eisenia fetida). Arch. Environ. Contam. Toxicol. 74 (4), 527–538. https://doi.org/10.1007/s00244-017-0451-4.

Wang, L., Sun, X., Chang, Q., Tao, Y., Wang, L., Dong, J., Lin, Y., Zhang, Y., 2016. Effect of di-n-butyl phthalate (DBP) on the fruit quality of cucumber and the health risk. Environ. Sci. Pollut. Control Ser. 23 (23), 24298–24304. https://doi.org/10.1007/s11356-016-7658-1.

Xu, B., Liu, F., Cryder, Z., Huang, D., Lu, Z., He, Y., Wang, H., Lu, Z., Brookes, P.C., Tang, C., Gan, J., Xu, J., 2020. Microplastics in the soil environment: occurrence, risks, interactions and fate–A review. Crit. Rev. Environ. Sci. Technol. 50 (21), 2175–2222. https://doi.org/10.1080/10643389.2019.1694822.

Xu, W., You, Y., Wang, Z., Chen, W., Zeng, J., Zhao, X., Su, Y., 2018. Dibutyl phthalate alters the metabolic pathways of microbes in black soils. Sci. Rep. 8 (1), 1–13. https://doi.org/10.1038/s41598-018-21030-8.

Xu, Y., Xiong, B., Yu-ming, M.H., Xu, J., He, Y., Lu, Z., 2024. Exploring additives beyond phthalates: release from plastic mulching films, biodegradation and occurrence in agricultural soils. Sci. Total Environ., 170763 https://doi.org/10.1016/j.scitotenv.2024.170763.

Yao, X., Zhang, J., Wang, C., Wang, Q., Li, X., Zhang, D., Wang, J., Zhu, L., Wang, J., 2022. Toxicity of dibutyl phthalate to pakchoi (Brassica campestris L.): evaluation through different levels of biological organization. Sci. Total Environ. 849 https://doi.org/10.1016/j.scitotenv.2022.157943.

Yu, L., Zhang, J. Di, Liu, Y., Chen, L.Y., Tao, S., Liu, W.X., 2021. Distribution characteristics of microplastics in agricultural soils from the largest vegetable production base in China. Sci. Total Environ. 756, 1–9. https://doi.org/10.1016/j.scitotenv.2020.143860.

Zeng, L.J., Huang, Y.H., Chen, X.T., Chen, X.H., Mo, C.H., Feng, Y.X., Lü, H., Xiang, L., Li, Y.W., Li, H., Cai, Q.Y., Wong, M.H., 2020. Prevalent phthalates in air-soil-vegetable systems of plastic greenhouses in a subtropical city and health risk assessments. Sci. Total Environ. 743, 140755 https://doi.org/10.1016/j.scitotenv.2020.140755.

Zhang, Y., Wang, P., Wang, L., Sun, G., Zhao, J., Zhang, H., Du, N., 2015. The influence of facility agriculture production on phthalate esters distribution in black soils of northeast China. Sci. Total Environ. 506–507, 118–125. https://doi.org/10.1016/j.scitotenv.2014.10.075.

Zhang, T., Ma, B., Wang, L., 2023. Phthalic acid esters in grains, vegetables, and fruits: concentration, distribution, composition, bio-accessibility, and dietary exposure. Environ. Sci. Pollut. Control Ser. 30 (2), 2787–2799. https://doi.org/10.1007/s11356-022-22415-z.

Zughaibi, T.A., Sheikh, I.A., Beg, M.A., 2022. Insights into the endocrine disrupting activity of emerging non-phthalate alternate plasticizers against thyroid hormone receptor: a structural perspective. Toxics 10 (5), 263. https://doi.org/10.3390/toxics10050263.