



An Overview of Chemical Additives on (Micro)Plastic Fibers: Occurrence, Release, and Health Risks

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Abstract

Plastic fibers are ubiquitous in daily life with additives incorporated to improve their performance. Only a few restrictions exist for a paucity of common additives, while most of the additives used in textile industry have not been clearly regulated with threshold limits. The production of synthetic fibers, which can shed fibrous microplastics easily (<5 mm) through mechanical abrasion and weathering, is increasing annually. These fibrous microplastics have become the main composition of microplastics in the environment. This review focuses on additives on synthetic fibers; we summarized the detection methods of additives, compared concentrations of different additive types (plasticizers, flame retardants, antioxidants, and surfactants) on (micro)plastic fibers, and analyzed their release and exposure pathways to environment and human beings. Our prediction shows that the amounts of predominant additives (phthalates, organophosphate esters, bisphenols, per- and polyfluoroalkyl substances, and nonylphenol ethoxylates) released from clothing microplastic fibers (MFs) are estimated to reach 35, 10, 553, 0.4, and 568 ton/year to water worldwide, respectively; and 119, 35, 1911, 1.4, and 1965 ton/year to air, respectively. Human exposure to MF additives via inhalation is estimated to be up to 4.5–6440 µg/person annually for the above five additives, and via ingestion 0.1–204 µg/person. Notably, the release of additives from face masks is nonnegligible that annual human exposure to phthalates, organophosphate esters, per- and polyfluoroalkyl substances from masks via inhalation is approximately 491–1820 µg/person. This review helps understand the environmental fate and potential risks of released additives from (micro)plastic fibers, with a view to providing a basis for future research and policy designation of textile additives.

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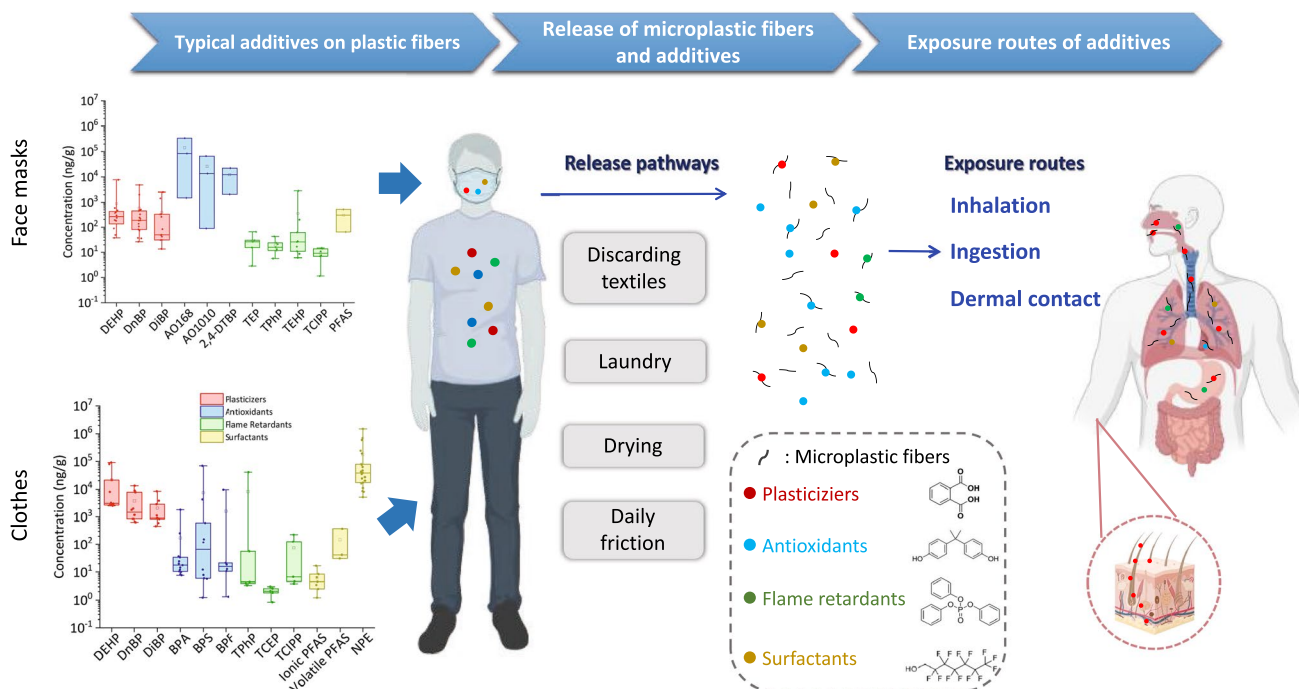
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Graphical Abstract



Abbreviations

2,4-DTBP	2,4-Di-tert-butyl-phenol	MF	Microplastic fiber
AO1010, Irganox 1010	Pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate	NP	Nonylphenol
AO168	Tris(2,4-di-tertbutylphenyl) phosphite	NPE	Nonylphenol ethoxylates
APEO	Alkylphenol polyethoxylates	OPE	Organophosphorus esters
ASE	Accelerated solvent extraction	OPFR	Organophosphorus flame retardants
BBP	Benzyl butyl phthalate	PAE	Phthalate
BFR	Brominated flame retardants	PBB	Polybromobiphenyls
BHA	Butyl hydroxyanisole	PBDE	Polybrominated diphenyl ethers
BHT	2,6-Di-tert-butyl-4-methyl phenol	PFAS	Per- and polyfluoroalkyl substances
BPA	Bisphenol A	PFCA	Perfluoroalkyl carboxylic acids
BPF	Bisphenol F	PFOS	Perfluorooctanesulphonate
BPS	Bisphenol S	PFSA	Perfluoroalkyl sulfonic acids
DCM	Dichloromethane	PP	Polypropylene
DEHP	Bis(2-ethylhexyl) phthalate	TCEP	Tris(2-chloroethyl) phosphate
DIBP	Di-iso-butyl phthalate	TCIPP	Tris(2-chloropropyl) phosphate
DnBP	Dibutyl phthalate	TCPP	Tris(2-chloroisopropyl) phosphate
FTOHs	Fluorotelomer alcohols	TEHP	Tri(2-ethylhexyl) phosphate
HFIP	1,1,1,3,3,3-Hexafluoro-2-propanol	TEP	Triethyl phosphate
Irganox 1076	Octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate	THF	Tetrahydrofuran
MAE	Microwave-assisted extraction	TMPP	Trimethylphenyl phosphate
		TnBP	Tributyl phosphate
		TNPP	Tris(4-nonyl-phenyl) phosphate
		TPhP	Triphenyl phosphate

TRIS	Tris (2,3-dibromopropyl) phosphate
USE	Ultrasonic extraction
XRF	X-ray fluorescence

Introduction

Fibers are ubiquitous polymers in daily life. Common fiber products include clothes, carpets, face masks, etc. There are mainly three types of fibers: natural fibers (cotton, wool), synthetic fibers (polyethylene terephthalate (polyester), polyamide (nylon), acrylic, polyurethane (spandex), polypropylene, polyvinyl chloride, etc.), and artificial fibers (rayon, viscose fiber, cellulose acetate, etc.). Global fiber production was about 109 million tons in 2020, of which synthetic fibers, natural fibers, and artificial fibers account for about 62%, 32%, and 6%, respectively, and the synthetic fiber production is estimated to approach 100 million t/y by 2030 (Pepper 2021). During manufacturing, different additives are incorporated into these textiles to improve their performance for different applications.

The definition of “microplastic” refers to plastic particles < 5 mm in size. The shape of microplastics includes fragments, fibers, and beads (Zhao et al. 2022). Fiber is the predominant shape of microplastics detected in both the atmospheric and aquatic environment (Lin et al. 2018; Liu et al. 2019b; Su et al. 2018). Fibrous microplastics, i.e., microplastic fibers (MFs), refer to synthetic fibers, including polyethylene terephthalate, polyamide, acrylic, polypropylene, etc. MFs are mainly released during use and wear of synthetic textile products and also become the main source of secondary microplastics in the environment. Microfibers have a broader definition than MFs, which contain both natural and synthetic fibers smaller than 5 mm. Microfibers in the air mainly originate from drying of textiles, daily wear and tear, and solid waste incineration (De Falco et al. 2020; Dris et al. 2016; Liu et al. 2019a), while those in aquatic environment mainly originate from activities such as the washing of textiles and use of fishing nets (Napper and Thompson 2016; Xue et al. 2020).

The most common additives are dyes, flame retardants, plasticizers, antibacterial agents, antistatic agents, antioxidants, etc. (Rovira and Domingo 2019). Some chemicals on textiles have been restricted or banned according to the REACH (*Registration, Evaluation, Authorization and Restriction of Chemicals*), including phthalates (bis (2-ethylhexyl) phthalate (DEHP), dibutyl phthalate (DBP), restricted concentration < 0.1%), bisphenol A (BPA, restricted concentration < 0.02% for thermal paper), nonylphenol ethoxylates (NPE, restricted concentration < 0.01%), flame retardants (tris (2,3-dibromopropyl) phosphate (TRIS)), and polybromophenyls (PBB), which should not be used in textiles

contacting with the skin (Schäfer and Herter 2021). However, there is a wide variety of additives up to more than twenty thousand (<https://polymer-additives.specialchem.com/>). With the emergence of more and more novel additives (e.g., synthetic phenolic chemicals) (Tan et al. 2021; Wu et al. 2019), most of the additives have not been reasonably controlled and studied. In most cases, additives are physically rather than chemically bound to the plastic polymer (Hahladakis et al. 2018). Thus, MFs can release additives to the surrounding environment easily during the process of laundry, abrasion, and transport (Akhbarizadeh et al. 2021; Hahladakis et al. 2018). When MFs enter organisms, additives will be released and migrate out. In such cases, the bioaccumulation of pollutants can be altered with the presence of MFs especially in above-fugacity scenario (Li et al. 2022).

Many studies have focused on the release of MFs from synthetic textile products; however, little attention has been paid to the “trojan horse” effects of MFs for additives. The objectives of this paper are to (1) overview the extraction and quantification methods of additives on textiles and MFs; (2) summarize the types and concentrations of additives on both traditional (i.e., clothes) and emerging MFs contributors (i.e., face masks); (3) analyze the migration and release capability of these additives; (4) and finally, estimate the annual release of additives together with MFs into aquatic and atmospheric environment, and the mass of additives inhaled and ingested into human body through the carrier of MFs.

Analytical Methods for Additives on (Microplastic) Fibers

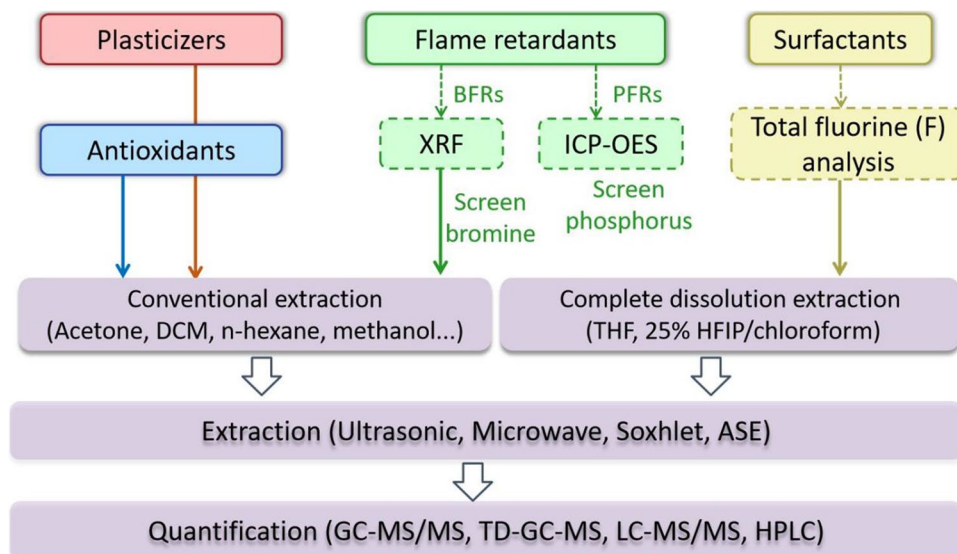
In this section, we mainly introduce the pretreatment methods (especially additive extraction methods) and analytical techniques of the predominant plastic additives, including plasticizers, antioxidants, flame retardants, and surfactants (Fig. 1).

Sample Pretreatment and Extraction

Pretreatment of Fiber Products

For the extraction of plasticizers, antioxidants, and surfactants on synthetic textile products, solvent extraction is the most common method (Kim et al. 2016; Wang et al. 2019a). Ultrasonic extraction (USE) and microwave-assisted extraction (MAE) have the advantages of high extraction efficiency, short time consumption, low solvent amount, and extensive adaptability (Khan and Jahangir 2020; Kim et al. 2016; La Nasa et al. 2021; Llompарт et al. 2019). For instance, USE can be effectively applied in the extraction

Fig. 1 Analytical methods of additives on synthetic textiles. (BFRs: brominated flame retardants; PFRs: phosphorus flame retardants; DCM: dichloromethane; THF: C; HFIP: 1,1,1,3,3,3-hexafluoro-2-propanol. ASE: accelerated solvent extraction; XRF: X-ray fluorescence; ICP-OES: inductively coupled plasma-optical emission spectrometry; GC-MS/MS: Gas chromatography-tandem mass spectrometry; TD-GC-MS: thermal desorption-gas chromatography-mass spectrometry; LC-MS: liquid chromatography-mass spectrometry; HPLC: high-performance liquid chromatography)



of phthalates (PAEs) from polyethylene films and synthetic antioxidants from disposable face masks, with recovery rates of 83.2–116.9% and 51–113%, respectively (Kim et al. 2016; Liu and Mabury 2021). Accelerated solvent extraction (ASE) is another prominent method for organic pollutants extraction from sediment, which has not been widely used for textiles yet (Giergielewicz-Możajska et al. 2001; Hu et al. 2020). Additionally, some conventional solvent extraction methods, such as Soxhlet extraction, can also be used with recovery rates of up to 90% or more; however, it is often time-consuming (more than four hours) (Kim et al. 2016; Li et al. 2015).

In addition to the solvent extraction methods, direct qualitative determination techniques are emerging in recent years, such as X-ray fluorescence (XRF), total fluorine (F) analysis technique, and inductively coupled plasma-optical emission spectrometry (ICP-OES). For instance, bromine (Br) and phosphorus (P) contents can be screened in fiber products with XRF and ICP-OES (Negev et al. 2018; Petreas et al. 2016; Young et al. 2021). The total fluorine (F) analysis technique can be conducted before the extraction of per- and polyfluoroalkyl substances (PFAS) to screen samples containing F quickly (Muensterman et al. 2022; Schellenberger et al. 2022). After the USE step of PFAS, some researches also apply solid phase extraction (SPE) to eliminate matrix compound interference and further concentrate samples (Gremmel et al. 2016; Muensterman et al. 2022).

Pretreatment of Microplastic Fibers

Currently, there are limited methods that specifically target additives extraction from MFs. The bottleneck of additives' extraction from MFs is mainly because of the mass of fiber samples collected from the natural environment is often too

low to meet the detection limits of instruments. Recently, Sorensen et al. (2021) proved that when the collected MFs were heavier than 0.1 g, the additives on MFs can be successfully extracted by the USE and quantified.

The pretreatment methods of microplastic particles can provide referential experiences for MFs. Some pretreatment methods, i.e., Soxhlet extraction and USE methods for microplastics can be applied for MF additives extraction. For instance, Zhang et al. (2018) extracted PAEs and organophosphorus esters (OPEs) from microplastic particles (0.01–0.5 g) by the Soxhlet extraction method with dichloromethane (DCM). Besides, Rani et al. (2017) extracted the antioxidants (Irganox 1010, Irganox 1076, 2,6-di-tert-butyl-4-methylphenol (BHT)) from plastic powders by the USE method with DCM. In addition to conventional extraction methods, direct analysis in real-time high-resolution mass spectrometry (DART-MS) can be used as a rapid fingerprinting method to screen microplastic additives. The complex mixture of polymer degradation products (i.e., “chemical fingerprints” of environmental microplastics) resulted from thermal desorption and pyrolysis can reflect the composition of both the polymers and the additives, which has been successfully used to detect plasticizers and antioxidants in microplastics (Zhang et al. 2020d). Of note, this method can preliminarily identify the presence of some additives, but it cannot be used for accurate quantification. In the future, more studies should be carried out on developing sensitive novel extraction or determination methods for trace contaminants in MFs.

Extraction Solutions Selection

For extraction of plasticizers, antioxidants, and flame retardants on fibers, traditional extractants include DCM, acetone,

ethyl ether, acetonitrile, n-hexane, and methanol. (Abdallah et al. 2017; Freire et al. 2019; Fu et al. 2012; Hajjouni et al. 2022; Negev et al. 2018; Wang et al. 2011). The mixture of hexane and acetone is the most common extraction solution. For example, n-hexane/acetone (1:1) was used to extract 15 PAEs from children's clothes, resulting in high recovery rates ranging from 81.9 to 107%; and this recipe has also been successfully applied to extract 39 BFRs and 16 OPEs from children's sleeping nap mats (made of polyurethane) (Stubblings et al. 2018; Tang et al. 2020). For extraction of surfactants like per- and polyfluoroalkyl substances (PFAS), methanol is commonly used (Muensterman et al. 2022; Schellenberger et al. 2022; Zheng and Salamova 2020). Since PFAS consists of a large number of substances, there are also different extraction solutions and analytical methods for volatile and nonvolatile PFAS, respectively (Table 2). For volatile PFAS (fluorotelomer alcohols (FTOHs)), ethyl acetate and n-hexane can be used as extraction solutions, while methanol and acetone/acetonitrile can be a choice for nonvolatile PFAS, such as perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl sulfonic acids (PFASAs) (Gremmel et al. 2016; Vestergren et al. 2015).

In addition to the traditional extractants mentioned above, some unconventional extraction solutions are also gradually applied. For extraction of phthalate plasticizers, tetrahydrofuran (THF) is recommended by the ISO 14389: 2014 (Wang et al. 2019b) and the Chinese national standard (*Textile—Determination of the phthalate content—Tetrahydrofuran method* (in Chinese), GB/T 20388–2016). Some studies prove that the THF extraction for PAEs usually exhibits better performance than other solvents, with higher recovery rate of 96.7–110.5% than that of methyl tert-butyl ether (MTBE) (38.3–58.0% recovery) or toluene (62.0–83.8%) (Al-Natsheh et al. 2015; Khan and Jahangir 2020).

Moreover, extractants that enable fibers to be “dissolved” exhibit better extraction efficiency than traditional extractants. Miyake et al. (2017) developed a novel complete dissolution extraction method, i.e., using 25% 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP)/chloroform as extractant to extract 18 brominated flame retardants (BFRs) and 15 phosphorus flame retardants (PFRs) in polyester curtains. By applying the complete dissolution method, more flame

retardants were extracted than that via the conventional USE method using toluene or acetone (only 0.5–10% of those measured by the complete dissolution method). Similarly, Li and Kannan (2018) compared two extraction solutions of 25% HFIP/chloroform and acetone/DCM (v/v, 1:4); the former one showed up to 286 times higher extraction efficiency than the latter one. The two examples above confirm that HFIP can well dissolve fibers, such as polyester, nylon, and spandex. Future experiments should focus more on this solvent to gain a better extraction effect.

Extraction Time Selection

The extraction time varies largely among different extraction methods. USE uses small amounts of solvents and allows batch processing of multiple samples. When the additives on fibers are extracted by ultrasonication, the extraction process is usually repeated at least twice, with extraction time ranging from 30 to 60 min (Abdallah et al. 2017; Khan and Jahangir 2020; Wang et al. 2019a). It has been found that for polybrominated diphenyl ethers (PBDEs) extraction from textiles, 30 min is the optimal extraction time, since there is no significant change in the recovery rate beyond 30 min (Abdallah et al. 2017). MAE also has a relatively shorter extraction time of about 15–30 min (Sanchez-Prado et al. 2010). In contrast, Soxhlet extraction method requires longer time, usually at least 4 h for each extraction, making it more costly (Kim et al. 2016; Li et al. 2015; Xu 2021). ASE owns the advantage of high efficiency and automation, with the extraction time of about 15–20 min per sample (Giergielewicz-Możajska et al., 2001). However, ASE cannot be used for batch extraction and may take longer time in case of large number of samples. We summarize the appropriate extraction methods for four additives (Table 1).

Instrumental Analysis

Gas chromatography-mass spectrometry (GC-MS) and liquid chromatography-mass spectrometry (LC-MS) are widely used for quantification of additives extracted from synthetic textiles. GC-MS is especially suitable for additives with low boiling point and good thermal stability. Bernard

Table 1 Recommended extraction methods for four types of additives on plastic (micro)fibers

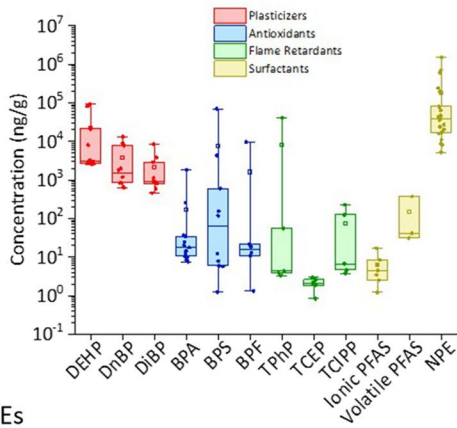
Additives	Pretreatment	Extraction solution		Extraction time
		Conventional	Novel	
Plasticizers	USE	Tetrahydrofuran, n-hexane, acetone	HFIP / chloroform (completed dissolved)	20 min × (2–3 times)
Antioxidants	USE	Acetone, DCM, ethyl acetate		
Flame retardants	USE	Acetone, n-hexane, DCM		
Surfactants	USE	Methanol		

USE ultrasonic extraction

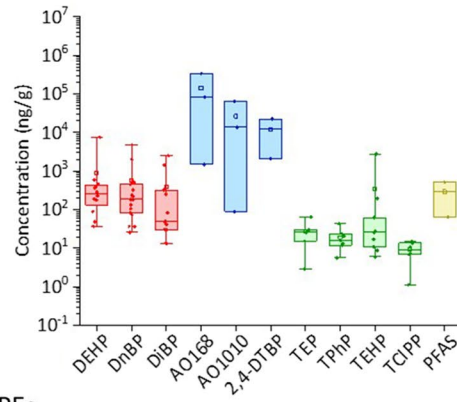
Table 2 Analytical methods for additives on fiber products

Additives	Polymer composition	Fiber products	Extraction	Extractants	Time	Determination equipment	Recovery	Concentration	References
<i>Plasticizers</i>									
PAEs	Polyester, nylon, spandex, cotton	Children clothes	USE	n-hexane/acetone (1:1)	50 min (30+20)	GC-MS	84.0–103%	2.92–223 µg/g	Tang et al. (2020)
PAEs	Polypropylene	Face masks	USE	DCM/ethyl acetate (1:1)	30 min × 2	GC-MS	79.3–113.2%	115–37,700 ng/g	Xie et al. (2022)
PAEs	Polyethylene	Polymer (polyethylene films)	/	/	/	TD-GC-MS	92–103%	/	Kim et al. (2016)
PAEs	/	Childcare items, toys, textiles	USE	Tetrahydrofuran	30 min	GC-MS	83.2–116.9%	/	
PAEs	/	Childcare items, toys, textiles	Soxhlet	n-hexane	6 h	GC-MS	101–104%	/	
PAEs	/	Infant fabrics, printed textiles	USE	Tetrahydrofuran	60 min	GC-MS	100 ± 15%	5.18–1798.14 mg/l	Khan and Jahangir (2020)
PAEs	/	Infant fabrics, printed textiles	Soxhlet	n-hexane	4 h	GC-MS	96.2–100.9%	Infant fabrics: 33.40 ± 2.29 mg/g Printed textiles: 51.60 ± 0.65 mg/g	Li et al. (2015)
Chlorinated Paraffins	/	Hand wipes	USE	n-hexane/acetone (1:1)	20 min × 3	Orbitrap-HRMS	48–103%	43–18,000 ng/participant	Yuan et al. (2020)
<i>Flame Retardants</i>									
BFRs, OPFRs	Polyester, polypropylene, PVC/glass fiber	Carpet, curtain	/	/	/	direct probe-TOF-MS	/	/	Ionas et al. (2015)
BFRs, OPFRs	Polyester, acryl	Curtain	USE	25% HFIP/chloroform	30 min (20+10)	LC-MS/MS	BFRs: 91–121%; OPFRs: 82–122%	n.d.–11,500 µg/g	Miyake et al. (2017)
PAEs, BFRs, OPEs	Polyester, cotton	Fabrics	ASE	n-hexane/DCM/acetone (2:1:1)	/	GC-MS	58–130%	/	Saini et al. (2016b)
OPEs	Polyester, nylon, vinyl, cotton	Infant clothing and raw textiles	Solvent extraction	Methanol	2 h	HPLC-MS/MS	63–136%	4.85–1.18 × 10 ⁶ ng/g	Zhu et al. (2020)
OPEs	Polypropylene	Face masks	USE	n-hexane/acetone (1:1)	15 min × 2	LC-MS/MS	47–115%	9.71–5835 ng/g	Fernandez-Arribas et al. (2021)
OPEs	/	Hand wipes	USE	n-hexane/DCM (1:1)	5 min × 3	HPLC	76.0–89.5%	children's hand wipe: 6.5–304 ng/g adult's hand wipe: 16.1–346 ng/g	Tan et al. (2018)

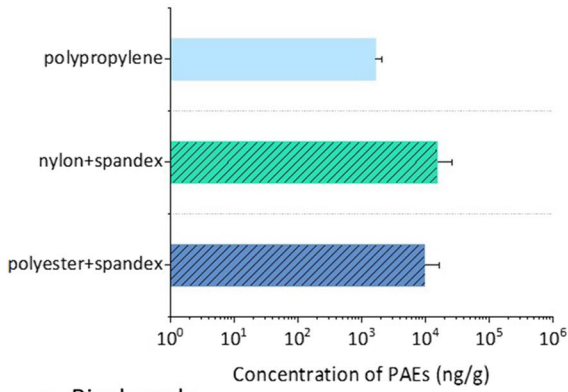
a. Clothes



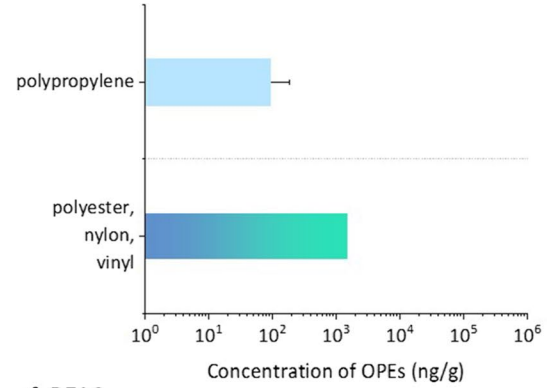
b. Face masks



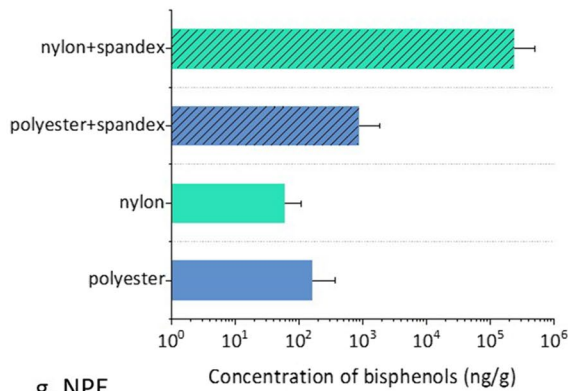
c. PAEs



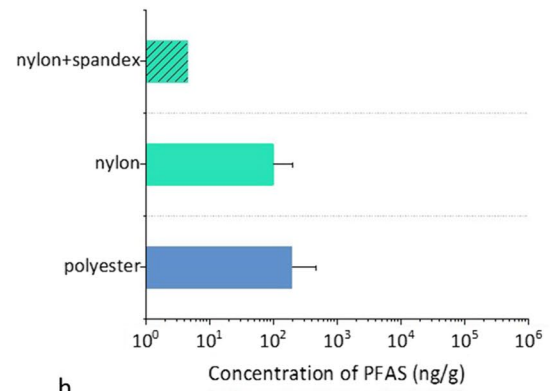
d. OPEs



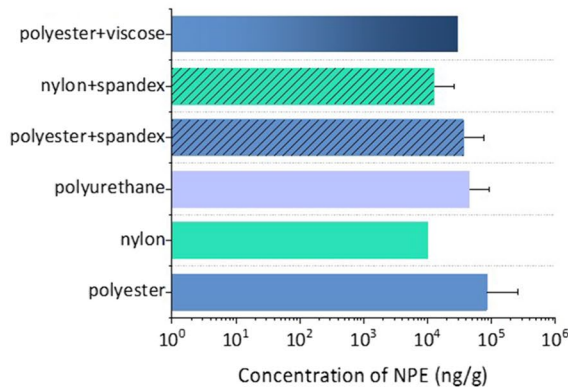
e. Bisphenols



f. PFAS



g. NPE



h

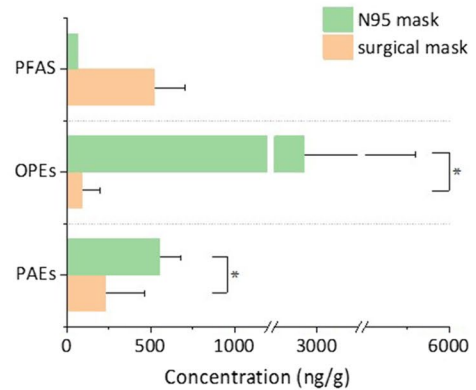


Fig. 2 The concentration of typical additives in **a** clothes and **b** face masks (ng/g). The maximum, minimum, and median values were obtained from the literature. The upper and lower boundaries of each box represent the 75th and 25th percentiles, respectively. The horizontal line represents the median value. The small square represents the mean value. **c–g**: The concentration (ng/g) (mean \pm SD) of additives on different fiber types. Data were collected from the literature and presented as average values (Brigden et al. 2013, 2012; Li and Kannan 2018; Sait et al. 2021; Tang et al. 2020; Wang et al. 2019a, 2022; Xie et al. 2022; Xue et al. 2017; Zheng and Salamova 2020). **h** The concentration (ng/g) (mean \pm SD) of PAEs, OPEs, and PFAS in surgical and N95 face masks. Data were collected from the literature and presented as average values (Fernandez–Arribas et al. 2021; Muensterman et al. 2022; Wang et al. 2022). Of note, the original data of PFAS concentrations are 46 $\mu\text{g}/\text{m}^2$ and 15 $\mu\text{g}/\text{m}^2$. To match the unit of “ng/g,” we cut 10 cm^2 of surgical and N95 masks, respectively, and weighed them to obtain mass average values, followed by a unit conversion to obtain the concentration of ng/g. Statistical analysis was performed using SPSS Statistics 26.0 software. Normality of the data was tested by the Shapiro–Wilk test. Difference between concentrations of additives in surgical and N95 masks was determined through Mann–Whitney U test ($*p < 0.05$). (DEHP: bis(2-ethylhexyl) phthalate; DnBP: dibutyl phthalate; DiBP: di-iso-butyl phthalate; BPA: bisphenol A; BPS: bisphenol S; BPF: bisphenol F; 2,4-DTBP: 2,4-di-tert-butyl-phenol; TPHP: triphenyl phosphate; TCEP: tris(2-chloroethyl) phosphate; TCIPP: tris(2-chloropropyl) phosphate; TEHP: tri(2-ethylhexyl) phosphate; TEP: triethyl phosphate; PFAS: per- and polyfluoroalkyl substances; NPE: nonylphenol ethoxylates)

et al. (2017) compared eight different analytical methods for determination of plasticizers and found that GC–MS possessed higher sensitivity (LOD values ranging from 0.03–0.5 $\mu\text{g}/\text{ml}$) than other methods. LC–MS determination of pollutants is not limited by boiling point. Thus, it can be used to analyze large molecule substances with poor thermal stability and weak-volatilization ability, such as flame retardants like tri(2-ethylhexyl) phosphate (TEHP), triphenyl phosphate (TPHP), trimethylphenyl phosphate (TMPP), nonvolatile PFAS, etc. (Lorenzo et al. 2016; Muensterman et al. 2022). Tandem mass spectrometry (MS/MS) realizes selective reaction monitoring (SRM), which greatly reduces the noise level and improves selectivity in the analysis of complex sample matrices (Wang et al. 2020). Currently, high-performance liquid chromatography-tandem mass spectrometry (HPLC–MS/MS), and ultrahigh-performance liquid chromatography-tandem mass spectrometry (UPLC–MS/MS) have become very important techniques for the analysis of flame retardants, novel synthetic antioxidants, and surfactants, because of their good selectivity and sensitivity, high precision, and low detection limits (Abdallah 2016; Bastiaensen et al. 2018; Gremmel et al. 2016; Guo et al. 2016; Vestergren et al. 2015; Wang et al. 2019a; Wu et al. 2019). The ionization of molecules has an important influence on the final quantification. Electron ionization (EI) is very suitable for polar chemicals (Bourdeaux et al. 2016; Stubbings et al. 2019). However, EI is not suitable for high molecular weight chemicals due to the fragments’ difficulty for volatilization and poor thermal stability after ionization.

Some soft ionization techniques such as electrospray ionization (ESI) and atmospheric pressure chemical ionization (APCI) interfaces can effectively solve this limitation (Wang et al. 2020). For example, Halloum et al. (2017) found that the detection limits of GC–APCI–MS/MS were 2.5–25 and 50–100 times lower than those of GC–EI–MS/MS, respectively, for the quantification of non-brominated OPEs and brominated OPEs.

In recent years, emerging quantification techniques that do not require pretreatment have become increasingly popular (Anuar et al. 2022; Jin et al. 2022; Xu et al. 2022). Thermal desorption-gas chromatography-mass spectrometry (TD–GC–MS) and pyrolysis gas chromatography-mass spectrometry (Py–GC–MS) exhibit the advantages of high sensitivity, automation, and solvent interferences-free (Humbert et al. 2022). TD–GC–MS has been found to be effective for the quantification of brominated flame retardants (especially for BDE-209) in curtains and car interiors (Shin and Baek 2012); meanwhile, Py–GC–MS has been increasingly used for the detection of PAEs, flame retardants, ultraviolet stabilizers, and bisphenols. (Akoueson et al. 2022; Deng et al. 2022).

There are also some new analytical methods, such as time of flight mass spectrometry (TOF–MS), electron probe, and environmental forensic microscopy. The principle of TOF–MS is to measure the time for ions to reach the detector from the ion source. The heavier the ion mass, the longer the time to reach the receiver; and vice versa. As a result, ions of different masses can be separated according to their specific m/z . The advantage of TOF–MS is the fast scan speed and high sensitivity. Ionas et al. (2015) have used the ambient high-resolution mass spectrometry (direct probe–TOF–MS) to qualitatively screen flame retardants in textiles (curtains and carpets). TOF–MS was capable of quickly screening BFRs and PFRs in positive and negative ion APCI modes with $[M + H]$ and $[M - Br + O]^+$, respectively. Moreover, the environmental forensic microscopy is also suitable for investigation of Br distribution (originated from BFRs) on textile surface (Ionas et al. 2015). Nevertheless, environmental forensic microscopy is only recommended for the surface distribution analysis of additives with relatively high concentration. There are also techniques that can quickly screen out samples containing F. Some studies conducted the total F analysis by combustion ion chromatography (CIC) before the extraction of PFAS (Rodgers et al. 2022; Schellenberger et al. 2022). Total F concentration can also be measured by the particle-induced gamma emission (PIGE) technique (Muensterman et al. 2022; Xia et al. 2022). The advantage of CIC or PIGE technique is that total F concentration can be quickly obtained. However, these fast-screening techniques cannot avoid the interference of substances containing fluorine; therefore, they are used as preliminary screening methods. The commonly used extraction methods, solvents, time,

and quantification equipment, as well as chemical recoveries for additives in fiber products are summarized (Table 2).

Occurrence of Additives on Plastic Fibers

The main processes in the textile production include sizing (improving the abrasion resistance of fibers), desizing (removing sizing chemicals from textiles), scouring (removing impurities from fibers), bleaching (removing unwanted colored matters), mercerizing (improving the strength and luster of textiles), dyeing & printing (adding colors or patterns to textiles) (Athira et al. 2018). To improve the softness, flame resistance, and stability of textiles, various additives and aids are incorporated. As a consequence, some of them, such as aromatic amines, plasticizers, flame retardants, phenolic antioxidants, surfactants, antimicrobial agents, ultraviolet stabilizers (benzotriazole), anti-wrinkling resins, heavy metals, etc., may remain in the clothes (Licina et al. 2019). PAEs, bisphenols, and OPEs have been widely detected in synthetic fibers (Fig. 2a) (Tang et al. 2020; Wang et al. 2019a; Xue et al. 2017).

The types of additives are closely related to textile material and functions. Plasticizers are one of the most widely used plastic additives; the addition amount can reach 10–70% (Hahladakis et al. 2018; Hermabessiere et al. 2017). Plasticizers are mainly used in polyurethane (PU) or PVC coating of textiles. In some cases, PVC can even contain 80% of plasticizers (Hahladakis et al. 2018). Clothing having abundant colors with rich prints and coats often exhibits higher concentrations of PAEs (Tang et al. 2020). Nylon ($15,203 \pm 10,382$ ng/g) contains a higher PAEs concentration than polyester (9732 ± 6988 ng/g) (Fig. 2c). Tang et al. (2020) measured that total concentrations of 15 PAEs in children clothing (blends of polyester, nylon, and spandex) were 3.35–33.42 $\mu\text{g/g}$, indicating a moderate level of incorporated phthalates in plastics. REACH regulates that for toys or childcare articles, the individual or combined concentration of DEHP, DBP, BBP equal to or greater than 0.1% (by weight) (1×10^6 ng/g) should not be put on market (Negev et al. 2018). From the collected data (Fig. 2a), it can be seen that the concentration of major PAEs in the clothes does not exceed the standard (1×10^6 ng/g). Meanwhile, PAEs are widely detected in air particulate matter (Li and Wang 2015); in addition to additives remained during manufacturing, fiber fabrics may also adsorb and accumulate airborne plasticizers emitted by indoor furniture (Shi et al. 2018; Zhang et al. 2020b).

Flame retardants are added to reduce the flammability of objects; the addition amount is 3–25% for BFRs and 0.7–3% for PFRs in plastic materials (Hahladakis et al. 2018). Synthetic fibers should be treated with flame retardants, because the molten drops caused by combustion may

burn the skin and lead to the burning of combustible materials around (Bourbigot 2008). Since the ban or restriction of some traditional BFRs according to the Stockholm Convention (Wu et al. 2020), the global consumption of organophosphate flame retardants in textile is increasing yearly (from 186,000 t in 2001 to 680,000 t in 2015) (Pantelaki and Voutsas 2019; Reemtsma et al. 2008). The content of flame retardants in synthetic fibers is often higher than that in cotton fabrics. The average concentration of \sum_{20} OPEs (1.52×10^3 ng/g) in synthetic fibers (polyester, nylon, vinyl) was higher than that in cotton fabrics (442 ng/g), triphenyl phosphate (TPhP), accounting for the highest percentage (40.2% of the total concentration) (Zhu et al. 2020). It is noticed that although the presence of BFRs (e.g., PBDEs) has been detected in textiles, such as carpets, curtains, and seat leather (Abdallah et al. 2017; Portet-Koltalo et al. 2021; Shin and Baek 2012), there are no available reports about BFRs on clothing according to our best knowledge. It may be explained that organophosphorus flame retardants (OPFRs) are more multi-functional, which can act as both flame retardants and plasticizers. On the other hand, some chlorinated OPEs contain both halogens and phosphorus (e.g., tris(2-chloroethyl) phosphate (TCEP), tris(2-chloroiso-propyl) phosphate (TCIPP)), which are versatile in flame retardant action, with less odor and lower toxicity (Pandit et al. 2020). In addition to the elimination of some traditional BFRs, the flame retardants in clothing are therefore dominated by OPFRs. Moreover, fibers may also adsorb semi-volatile flame retardants from the air, since electronic products in offices are sources of flame retardants in air (Fig. 3) (Saini et al. 2016a; Saito et al. 2007).

Antioxidants are used to delay the overall oxidative degradation of plastics, the addition amount of which is 0.05–3% in plastic materials (Hahladakis et al. 2018). Antioxidants include phenolic antioxidants (e.g., BPA, BPS, BHT, Irganox 1010, Irganox 1076) and organophosphite antioxidants (tris(4-nonyl-phenyl) phosphate (TNPP), tris(2,4-ditertbutylphenyl) phosphite (AO168), etc.) (Hahladakis et al. 2018). The concentration of bisphenols is closely related to the type of the fibers; spandex exhibits higher levels of bisphenols, especially for fibers blended of nylon and spandex (Fig. 2e). Socks (blends of spandex, nylon, polyester, and cotton) are found to contain higher levels of PAEs and BPA than other clothing (Tang et al. 2020; Xue et al. 2017). Spandex is a typical elastic fiber widely used in stretchable clothing; the addition of bisphenols improves its flexibility (Bodaghi 2020). A study found that the mean concentration of \sum_7 bisphenols in pantyhose made of 21–50% spandex (535,000 ng/g) was significantly higher than that in pantyhose made of 0–20% spandex (170,000 ng/g) (Li and Kannan 2018). Studies have also shown that polyester products contain more additives than cotton ones (Xue et al. 2017). Clothes made of polyester and spandex had

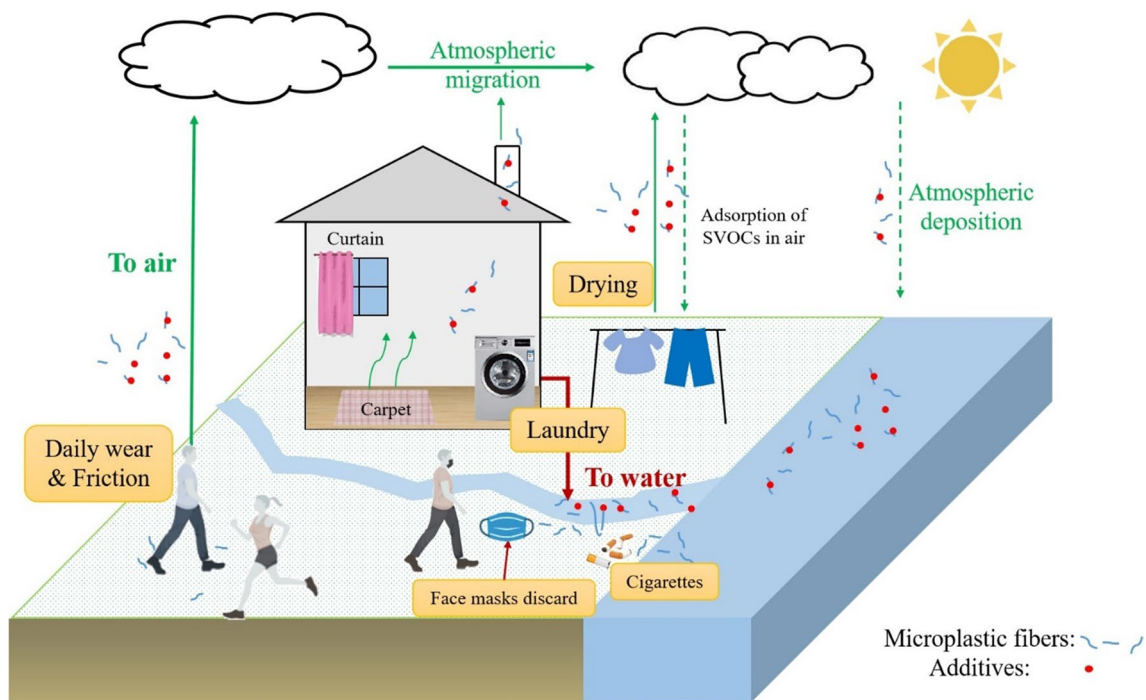


Fig. 3 Migration and release pathways of additives from microplastic fibers. Icons are created with BioRender.com. (SVOCs: semi-volatile organic chemicals with boiling points range between 240 °C and 400 °C (Lucattini et al. 2018))

high concentrations of bisphenols (1823 ng/g for BPA and 536 ng/g for BPS), while mean concentration of bisphenols (BPA + BPS) was only 21 ng/g in cotton clothes (Wang et al. 2019a). The use of synthetic phenolic antioxidants has gradually increased in recent years; synthetic antioxidants have been detected in disposable face masks (Liu and Mabury 2021). However, there are only few reports on synthetic antioxidants on clothing. Thus, more attention should be paid to the content of synthetic antioxidants in clothing fibers in the future.

To improve softness, smoothness, and water resistance of clothes, especially for functional garments, surfactants (e.g., per- and polyfluoroalkyl substances (PFAS), alkylphenol polyethoxylates (APEO), NPE) are often added during production process (Gremmel et al. 2016; Heydebreck et al. 2016; Holmquist et al. 2016; Licina et al. 2019; Zhang et al. 2015). The environmental hazards of PFAS have been gradually recognized due to their environmental persistence and low degradability. Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) have been listed in *Stockholm Convention* (Groffen et al. 2021). Exposure to PFAS poses various health risks, including effects on fertility, endocrine function, obesity of children, etc. (Espartero et al., 2022). The concentration of PFAS did not show significant difference among fiber types; the mean concentration in polyester (193 ± 268 ng/g) is higher than in nylon (98 ± 100 ng/g) (Fig. 2f). PFAS has also been detected in furniture textile

products (e.g., curtain, carpet, table cloth) (Vestergren et al. 2015). A study indicated that the concentrations of PFOS in two carpet samples ($0.74 \mu\text{g}/\text{m}^2$ and $1.04 \mu\text{g}/\text{m}^2$) approached or even exceeded the EU regulation ($1 \mu\text{g}/\text{m}^2$) (Herzke et al. 2012). PFAS function as surfactants, fabrics with fluorinated coatings may release fewer fibers after washing; however, fluorinated wastewater has a negative impact on the environment (Schellenberger et al. 2019). NPE compounds are another cheap and common surfactants. NPE and their degradation products, nonylphenol, are typical endocrine disruptors, which can affect sperm quality and lead to cancer development (Noorimotlagh et al. 2017, 2020). A survey conducted by *Greenpeace International* in 2012 revealed that NPE compounds were the most frequently detected substances in 20 branded textile products, with a detection rate of 63% and median concentration of 5.2–1500 mg/kg (Brigden et al. 2012). For 8 luxury brands, the detection rate of NPE was 44%, with concentrations ranging from 1.7 to 760 mg/kg (Brigden et al. 2013). It can be seen that the concentrations of NPE in some clothes exceed the *REACH* standard (1×10^6 ng/g) (Fig. 2a). The concentrations of NPE in polyester ($84,789 \pm 179,215$ ng/g) are higher than that in nylon (10,000 ng/g); the presence of spandex has no effect on NPE concentration (Fig. 2g). In addition, it has been found that the mean concentration of $\sum_{20}\text{OPEs}$ in water-repellent fabrics made of nylon or polyester (1940 ng/g) was significantly higher than that in conventional fabrics made of

cotton or polyester (313 ng/g) (Zhu et al. 2020), suggesting that functional garments may contain more additives.

With the Covid-19 pandemic, face masks made of non-woven polypropylene (PP) or polyethylene terephthalate have become emerging MFs contributors to the environment (Fadare and Okoffo 2020; Wang et al. 2022). Chemicals such as antioxidants, plasticizers, and surfactants may be added during the manufacturing of face masks (Liu and Mabury 2021; Muensterman et al. 2022; Sungur and Gulmez 2015; Xie et al. 2022). Total concentrations of PAEs and synthetic antioxidants in face masks ranged from 115 to 37,700 ng/g and from 20.0 to 575 µg/g, respectively (Liu and Mabury 2021; Xie et al. 2022). DEHP, DnBP, DiBP, 2,4-di-tert-butyl-phenol (2,4-DTBP), pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate) (AO1010), and AO168 have been frequently detected in face masks (Liu and Mabury 2021; Xie et al. 2022). The antioxidant contents in face masks are quite high (Fig. 2b), while the types of antioxidants on face masks are different from those of clothes. Bisphenols are widely detected in clothes, while lower or undetectable levels of bisphenols are found in face masks. Only one study reported the presence of BPA in surgical masks leachates (0.8–3.2 µg/L) (Liu et al. 2022). This phenomenon may be attributed to high toxicity of bisphenols. Some other phenolic antioxidants such as BHT and butyl hydroxyanisole (BHA) may be relatively “safer,” which can even be used as food additives to extend the shelf life of fried foods (Liu and Mabury 2020; Wang et al. 2021). On the other hand, some novel antioxidants (e.g., AO168, AO1010) receive less attention and lack of effective regulatory measures.

Different types of face masks exhibit different additive concentrations (Fig. 2h). N95 masks contained more flame retardant OPEs and PAEs (OPEs: 11.6 ± 10.3 µg/mask (2924.4 ± 2873.2 ng/g), PAEs: 2300 ± 150 to 5200 ± 800 ng/mask (556.0 ± 124.5 ng/g)) than surgical masks (OPEs: 0.24 ± 0.27 µg/mask (93.6 ± 107.1 ng/g),

PAEs: 55 ± 35 – 1700 ± 140 ng/mask (230.9 ± 236.6 ng/g)) (Fernandez–Arribas et al. 2021; Wang et al. 2022). However, this phenomenon has not been clearly interpreted. We speculate that this may be due to the higher filtering capacity of N95 masks for bacteria or particulate matter. The density of polypropylene in N95 masks is higher than in normal masks. Therefore, the manufacturing process is more complex, resulting in higher OPEs or PAEs levels. However, there are exceptions that not all N95 masks have higher additive levels. For instance, Muensterman et al. (2022) found that the total PFAS concentrations in surgical masks (46 µg/m², converted to be 521.7 ng/g) were higher than that in N95 masks (15 µg/m², converted to be 64.8 ng/g).

Compared with non-fiber plastics or microplastics, the contents of additives in plastic fibers are generally equivalent to the same order of magnitude or even higher. For example, the concentrations of 16 PAEs in PP take-out food containers were 1.62–8.62 µg/g, while the concentrations of 15 PAEs in clothing fibers were 3.35–33.42 µg/g (Han et al. 2021; Tang et al. 2020). Compared with PP fragments (Table 3), face mask fibers (made of PP) exhibit lower levels of phenolic antioxidants and higher levels of plasticizers such as PAEs.

Release of Additives from (Micro)Plastic Fibers

Release to Water

Washing of synthetic textiles is one of the most important routes for the release of additives from plastic fibers (Luongo et al. 2016; Wang et al. 2019a; Zheng and Salamova 2020). Abrasion of synthetic textiles during laundry is also an important source of microplastics released to aquatic environment (Siegfried et al. 2017). About 2.1×10^5 MFs could

Table 3 Comparison of typical additive concentrations in plastic fibers and other shapes of plastics

Additives	Concentration of additives in fibers	Reference	Concentration of additives in plastics	Reference
AO1010	PP fibers (face masks) 0.0898–65.4 µg/g	Liu and Mabury (2021)	PP plastic fragments 17–155 µg/g	Rani et al. (2017)
AO1076	0–49.9 µg/g		0–169 µg/g	
BHT	0–2.38 µg/g		0.02–1.0 µg/g	
2,4-DTBP	0–22.5 µg/g		0.64–11 µg/g	
∑ phenolic antioxidants	4.44–91.5 µg/g		53.2–200.3 µg/g	
PAEs	PP fibers (face masks) 115–37,700 ng/g	Xie et al. (2022)	PP flakes and fragments 0.29–27.2 ng/g	Zhang et al. (2018)
OPEs	9.71–5835 ng/g	Fernandez–Arribas et al. (2021)	6.38–2377.5 ng/g	

be released from polyester clothes during a single machine wash (Sillanpaa and Sainio 2017).

The release of MFs and additives is affected by the following factors summarized in Table 4: water volume, temperature, duration, washing program, use of detergent/softener/textile finishes, fabric types, numbers of washing, fabric weave construction, and chemical properties of additives (De Falco et al. 2018; Hernandez et al. 2017; Kelly et al. 2019; Napper and Thompson 2016; Saini et al. 2016b;

Wang et al. 2019a) (Table 4). The factors affecting cotton fiber release were also included, since cotton fibers and plastic fibers may have the same release pattern (such as the use of textile finishes released more fibers, regardless of the fiber type). On the other hand, different fiber types may have different release patterns during washing.

The release of MFs to water depends on the washing conditions, while the release of additives is related to their chemical properties. Additives with higher polarity

Table 4 Factors affecting the release of plastic fibers, natural fibers, and fiber additives to water

Target	Factors		References	
MFs release	Water volume	High water volume wash caused more MFs release than lower water volume	Kelly et al. (2019)	
	Temperature/time	Higher temperature and longer time caused more MFs release	Cotton et al. (2020); Dalla Fontana et al. (2020)	
	Detergent/softener	The use of detergent caused more MFs release, while the use of softener reduces the MFs release	De Falco et al. (2018); Hernandez et al. (2017)	
	Fiber type*	Polyester or acrylic fabrics shed more fibers than cotton blended fabric	Napper and Thompson (2016)	
		Polyester fabrics released fewer fibers than cotton ones	Sillanpaa and Sainio (2017)	
		Polypropylene and polyurethane face masks released fewer microfibers than cotton ones	De Felice et al. (2022)	
	Fabric weave construction	Textile with short spun-staple yarn construction shed more MFs than those with woven construction and filamentous yarns	Vassilenko et al. (2021)	
		Fabrics sewed with double heat-sealing released less MFs than those sewed with normal thread	Dalla Fontana et al. (2021)	
	Mechanical treatment (brushed, sanded or sheared)	Mechanically treated fabrics shed more MFs than untreated ones	Vassilenko et al. (2021)	
	Textile finishes*	Fabrics treated with finishes (dyes, durable press, and water repellent) shed more microfibers during laundering than untreated ones	Zambrano et al. (2021)	
Additives release	Chemical properties of additives	Polarity ($\log K_{OW}$)	Polar chemicals ($\log K_{OW} < 4$, e.g., aliphatic OPEs: TnBP, TCEP, TCIPP) are more likely to be released to water; non-polar chemicals ($\log K_{OW} > 6$, e.g., DEHP, BFRs) hardly release to water	Saini et al. (2016b)
		Hydrophilicity	Migration rate of PFAS from infant clothes reached 100% at 20 °C and 50 °C	Zheng and Salamova (2020)
	Salinity	For polyamide MFs, 2 chemicals were identified in the 14-day seawater leachates, but not in freshwater leachates	Sait et al. (2021)	

or hydrophilicity are more prone to be released to aquatic environment (Table 4). Besides, additives can be released to the surrounding environment since most of them are not chemically bound to the polymer matrix (exception: TBBPA is chemically bounded) (Hermabessiere et al. 2017).

In addition to the washing of synthetic fiber products, discarding cigarette butts or face masks can also cause MFs or chemicals released to aquatic environment (Fig. 3). Discarded cigarette butts result in about 300,000 tons of cellulose acetate MFs entering the aquatic environment annually. What accompanied is the release of toxic chemicals such as nicotine, carcinogenic tar, polycyclic aromatic hydrocarbons, and heavy metals (cadmium, lead), which have been proven to pose toxic risk to marine organisms (Shen et al. 2021; Torkashvand et al. 2020; Wright et al. 2015). Micro and nano scale polymeric fibers and heavy metals such as cadmium, lead, and antimony have also been detected in face mask leachate. The presence of heavy metals may be attributed to the dyes used in production of colored masks (Sullivan et al. 2021; Sungur and Gulmez 2015). MFs released from face masks can also become carriers of additives and contaminants. It is estimated that approximately 3.4 billion disposable face masks are discarded globally every day, which cause complex environmental problems (Aragaw 2020; Benson et al. 2021). Moreover, there is also growing interest in novel environmental friendly face masks, such as polylactic acid (PLA) biodegradable masks (Soo et al. 2022). With the advantage of faster degradation rate, biodegradable fibers are also more likely to release additives.

Once MFs enter the aquatic environment, ultraviolet irradiation will accelerate fiber degradation and additives release. Ultraviolet exposure of two months resulted in surface degradation (holes appearance) of polyamide fibers and fragmentation (length reduction) of polyester fibers. In seawater leachates, the concentration of additives (TPhP, TCEP, etc.) released by MFs increased with increasing time (Sorensen et al. 2021). The leaching of additives caused by fragmentation or degradation of plastic fibers deserves further attention.

Release to Air

The release of MFs and additives to the air is also an important pathway. Via daily wear of polyester clothes and human activity, one person can release about 1.03×10^9 MFs to the air per year (De Falco et al. 2020). The drying process is another important source of MFs release (Kapp and Miller 2020). A household tumble dryer could release 433,128 (cotton) and 561,810 (polyester) microfibers in 15 min; the annual release of microfibers by a dryer may be even greater than the number of microfibers released through washing (Tao et al. 2022). Although many literatures reported the release of MFs to the air, little attention has been paid to the

additives on MFs. Future study should focus more on additives release to the air together with MFs.

There are two main pathways for additives to be released to the air from MFs: (1) direct release by evaporation effect; (2) indirect release by the MFs generated by abrasion. The latter pathway is less studied. Schellenberger et al. (2022) explored the emission mechanism of PFAS from functional textiles (polyamide) under outdoor weathering conditions, revealing that in addition to the direct evaporation release, PFAS could also be released from abrasion and degradation of fibers. Moreover, some flame retardants (e.g., decabromodiphenylethane (DBDPE), PBDEs) released from electronic dryer may become indirect source of additives released to the air together with MFs (Saini et al. 2016b; Schecter et al. 2009).

MFs can account for up to 33% of the total microplastics in urban dust (Dehghani et al. 2017). These MFs can become carriers of additives during suspension, deposition, and migration in the air. PAEs, bisphenols, and flame retardants have widely been detected in airborne dust (Mitro et al. 2016). Zhang et al. (2020a) reported that the concentration of BPA in indoor dust samples was proportional to the concentration of polycarbonate (PC)-based microplastics, which also further confirmed that microplastic (fibers) is an important source of contaminants in dust.

After the outbreak of Covid-19 pandemic, face masks have become a contributor of polypropylene MFs. Additives like PAEs, OPEs, or synthetic antioxidants in them may be released to the air together with the use and abrasion of face masks. The exposure to MFs or additives through inhalation deserves attention. In regard to the humidity during breathing and higher temperature in summer, the release of some additives (e.g., OPEs) from face masks may increase (Fernandez-Arribas et al. 2021).

Release in Organisms

Plastics can act as a carrier of additives and transport over long distances. The disposal of face masks has become an emerging environmental problem in the last two years. For the first time, a PP face mask has even been found in the feces of a green sea turtle (*Chelonia mydas*) near the coast of Japan; the risk of exposure to additives through plastics ingestion is of concern (Chowdhury et al. 2021; Fukuoka et al. 2022). MFs are ubiquitous in the marine environment, which are easily ingested by organisms of all trophic levels due to their small sizes. Ingestion of MFs by aquatic organisms can lead to growth inhibition, impairment of the immune system, and disruption of the gut microbiota; MFs have higher acute toxicity for lower taxa aquatic organisms (Rebelein et al. 2021). However, many exposure studies of MFs fail to distinguish between the toxicity effects of MFs and their additives (Alnajjar et al. 2021). Although some

indoor exposure experiments point out that MFs can be excreted gradually by organisms from their bodies through digestion (Grigorakis et al. 2017; Song et al. 2019), the additives loaded on MFs may be desorbed under intestinal conditions.

Most current experiments only focus on the biological effects of MFs, ignoring the exposure risks caused by additives in MFs. Additives have been proven to be released in organism from plastics or microplastics. In addition to chemical property of additives ($\log K_{OW}$), unique gastric environment of certain organisms such as higher temperature (body temperature of seabirds $\approx 40^\circ\text{C}$), low pH value, and the occurrence of stomach oil may accelerate the leaching of additives (Andrade et al. 2021; Kühn et al. 2020; Sun et al. 2021; Tanaka et al. 2013). At present, indoor exposure experiments on biological effects of microplastics and chemicals mostly focus on granular microplastics, due to the ease of purchase or preparation of granular microplastics. However, fibrous microplastics rather than granular ones are the most common type of microplastics in actual aquatic environment. In view of this, there exists a vacancy in research on the release of additives to organisms from fibers or MFs.

Estimation of Additive Amounts Released by Microplastic Fibers

As estimated by De Falco et al. (2020), one person could release about 2.98×10^8 polyester MFs to water via laundry and 1.03×10^9 to air via wearing polyester clothes per year. We converted the MF number concentration to mass concentration referring to the formula of Leusch and Ziajahromi (2021), i.e., 129.2 g to water and 446.5 g to air.

Here, we took the most common plastic additives PAEs as an example. According to the collected data, the concentration of PAEs in clothes ranges about 3.35–33.42 $\mu\text{g/g}$ (Chai et al. 2017; Li et al. 2019; Liu et al. 2020; Tang et al. 2020). Assuming that the concentration of PAEs on the MFs is the same as clothes, i.e., the additives in clothes can all be released with the fiber without loss. The mass of PAEs released per person per year:

$$\text{To water} : (3.35 \sim 33.42) \times 129.2 = 0.43\text{--}4.32 \text{ mg}$$

$$\text{To air} : (3.35 \sim 33.42) \times 446.5 = 1.50\text{--}14.92 \text{ mg}$$

Based on a global population of 8 billion, the global mass of PAEs released to water is 3.46–34.55 t per year via washing, and to air is 11.97–119.39 t per year via wearing polyester clothes. Similarly, the global mass of OPEs, bisphenols, PFAS, and NPE released from MFs per year is 0.0050–10.09 t, 0.0060–552.98 t, 0.0046–0.39 t, and 1.24–568.48 t to water, respectively; and 0.017–34.88 t,

0.021–1911.02 t, 0.016–1.36 t, and 4.29–1964.6 t to air, respectively (Table 5).

Exposure and Health Risks

Dermal Exposure

Clothes cover approximately 85% of human skin and act as a barrier to block environmental pollutants. However, clothes can also be a potential exposure source of certain chemicals (Fig. 4). For textiles (especially clothes), dermal exposure is an important exposure pathway. Dermal exposure doses of PAEs and bisphenols were 11.83–950 ng/kg BW/d (302.3–24,272.5 $\mu\text{g/year}$) and 0.21–0.26 ng/kg BW/d (5.4–6.6 $\mu\text{g/year}$), respectively (Liu et al. 2020; Tang et al. 2020; Xue et al. 2017). Socks containing BPA had great effect on infant, with a maximum BPA exposure dose of 7.28 ng/kg BW/d (Xue et al. 2017). As mentioned above, PVC prints are mostly found in children's clothing, which contain high levels of PAEs. Children and infants are the most vulnerable groups to endocrine disruptors. Sweating can increase the risk of dermal exposure to additives such as PAEs or BPA (Liu et al. 2020; Xue et al. 2017). Bad habits such as biting and sucking fingers of infants and children may also pose exposure risk of oral ingestion. According to a survey, the mean levels of PAEs (DEHP 6.74%, DINP 1.32%) in childcare products (toys, baby mattresses and textiles, baby diaper pads) exceed the 0.1% standard of the European Union, which are likely to pose high oral or dermal exposure risks (Negev et al. 2018).

Inhalation and Ingestion (of Microplastic Fibers)

Human beings and other organisms are exposed to MFs mainly via three routes, including inhalation, ingestion, and dermal exposure. Only the former two exposure routes can cause actual MF intake. Inhalation of MFs can adversely affect the respiratory tracts (Lim et al. 2021; Moolgavkar et al. 2001), which has also been suggested to be associated with the formation of ground glass nodules in human lungs (Chen et al. 2022). Ingestion of MFs has been confirmed in various organisms, including aquatic organisms (fish, decapods, bivalves, zooplankton, etc.), terrestrial organisms (earthworm, snails), and even human beings (Lahive et al. 2022; Rebelein et al. 2021; Song et al. 2019; Zhang et al. 2022). MFs ingestion can cause oxidative stress and inflammation in fish (Zhao et al. 2021), MFs ingestion may be associated with inflammatory bowel disease in human beings (Yan et al. 2022), and even immune disorders and increased risk of neoplasia in the long run (Prata et al. 2020).

As a necessity under the Covid-19 pandemic, the additive inhalation risks caused by wearing face masks deserve

Table 5 Estimation of the mass of additives released and exposure concentrations

Additives	Concentrations of additives on fibers or MFs ($\mu\text{g/g}$)	Mass of additives released from polyester MFs by a person per year (mg/person) ^a		The global mass of additives released per year (t) (based on a population of 8 billion)		Exposure of additives through MFs released by clothing per year ($\mu\text{g/person}$) ^b		Estimated daily intakes ($\text{ED}_{\text{inhalation}}$) of additives from face masks	Exposure of additives through direct inhalation associated with face masks per year ($\mu\text{g/person}$) ^c	Tolerable daily intakes (TDIs) ($\mu\text{g/kg BW/d}$) ^d
		To water	To air	To water	To air	Inhalation	Ingestion			
PAEs	3.35–33.42	0.43–4.32	1.50–14.92	3.46–34.55	11.97–119.39	0–391.40	0.34–12.37	surgical masks: 0.3–4.9 ng/kg BW/d (adults) 1.9–30 ng/kg BW/d (toddler)	Surgical masks: 5.46–89.18 (adults) N95 masks: 6.42–101.4 (toddler)	254.8–491.4 (adults) 287.3–540.8 (toddler)
OPEs	0.00485–9.764	0.0006–152.46	0.0021–526.87	0.0050–10.09	0.017–34.88	0–114.34	0.00049–3.61	Wang et al. (2022) surgical masks: 0.04–1.02 ng/kg BW/d (adults) N95 masks: 0.46–29.2 ng/kg BW/d (adults)	0.73–18.56 (adults)	8.37–531.44 (adults)
Bisphenols	0.00585–535	0.0008–69.12	0.0026–238.88	0.0060–552.98	0.021–1911.02	0–6264.85	0.00059–197.95/	Fernandez–Arribas et al. (2021)	/	/

Table 5 (continued)

Additives	Concentrations of additives on fibers or MFs ($\mu\text{g/g}$)	Mass of additives released from polyester MFs by a person per year (mg/person) ^a		The global mass of additives released per year (t) (based on a population of 8 billion)		Exposure of additives through MFs released by clothing per year ($\mu\text{g/person}$) ^b		Estimated daily intakes ($\text{ED}_{\text{inhalation}}$) of additives from face masks	Exposure of additives through direct inhalation associated with face masks per year ($\mu\text{g/person}$) ^c	Tolerable daily intakes (TDIs) ($\mu\text{g/kg BW/d}$) ^d
		To water	To air	To water	To air	Inhalation	Ingestion			
PFAS	0.0045–0.382	0.0005–0.05	0.002–0.17	0.0046–0.39	0.016–1.36	0–4.48	0.00045–0.14	0.04–0.10 $\mu\text{g/kg BW/d}$ (adults) 0.1–0.13 $\mu\text{g/kg BW/d}$ (toddler)	728–1820 (adults) 338–439.4 (toddler)	/
NPE	1.2–550	0.15–71.06	0.54–245.58	1.24–568.48	4.29–1964.6	0–6440.5	0.12–203.5	/	/	/
DEHP	2.68–3.22	0.34–0.42	1.20–1.44	2.77–3.33	9.57–11.50	0–37.71	0.27–1.19	surgical masks: 0.87–1.2 ng/kg BW/d (adults) 5.3–7.5 ng/kg BW/d (toddler)	/	50
TCIPP	0.0038–0.23	0.0005–0.03	0.0017–0.10	0.0039–0.24	0.013–0.82	0–2.69	0.00038–0.085	N95 masks: 4.2–14 ng/kg BW/d (adults) 25–85 ng/kg BW/d (toddler)	/	10
BPA	0.0076–1.81	0.001–0.23	0.0034–0.81	0.0078–1.87	0.027–6.46	0–21.20	0.00076–0.67	Wang et al. (2022) Not mentioned	/	50

^aone person could release 129.2 g MFs to water via laundry and 446.5 g MFs to air via wearing polyester clothes per year, according to the estimation by De Falco et al. (2020)

^bone person could inhale and ingest about 0–11.71 g and 0.10–0.37 g MFs per year, according to the estimation by Zhang et al. (2022, 2020c)

^cAverage body weight was assumed to be 70 kg for adults and 13 kg for toddlers (Fernandez-Arribas et al. 2021; Wang et al. 2022), assuming that the mask is worn 260 days per year (the approximate number of working days per year)

^dTolerable daily intake (TDI) values were obtained from the literature (Fernandez-Arribas et al. 2021; Wang et al. 2022)

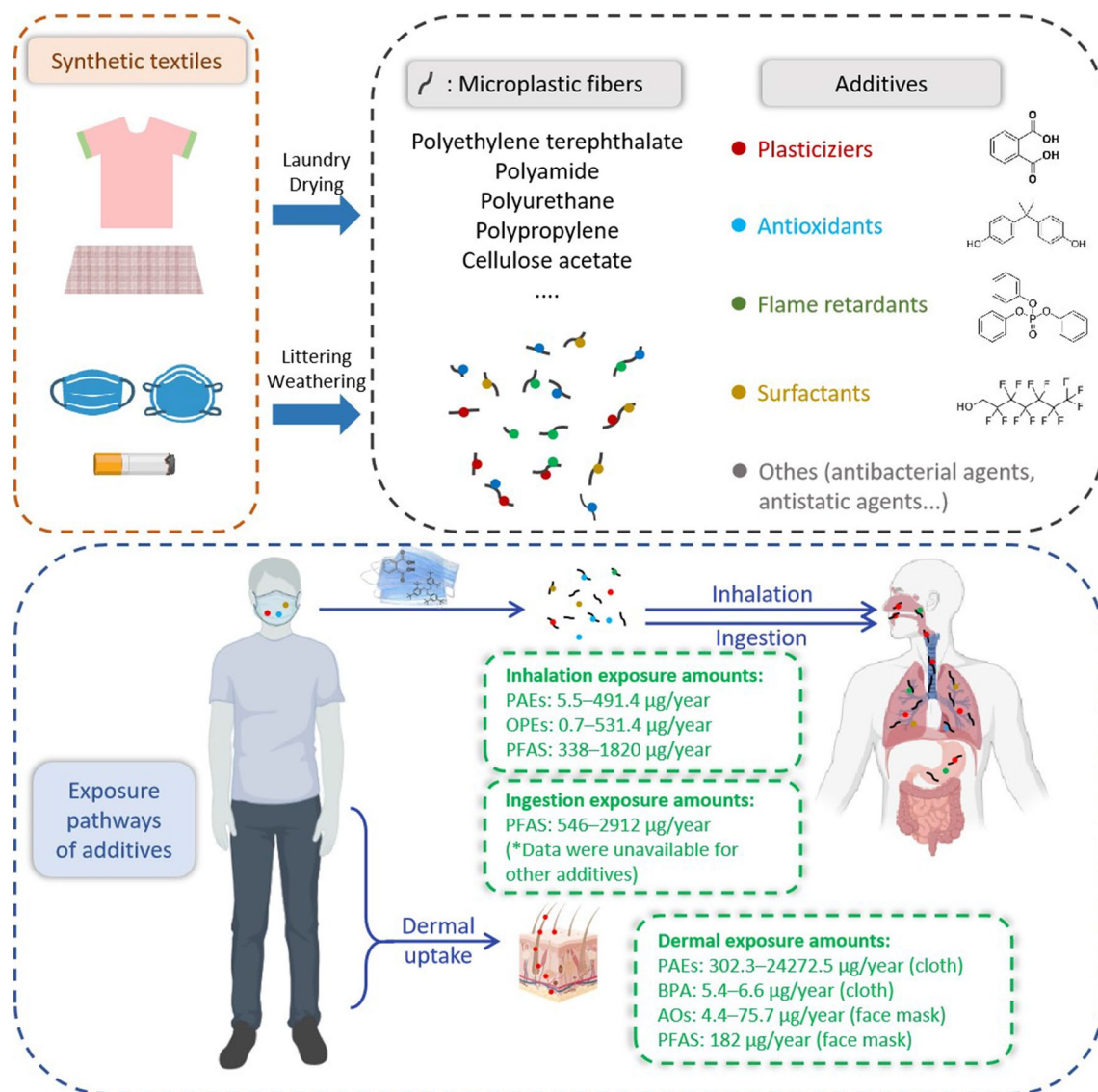


Fig. 4 The additives in MFs and human exposure pathways of additives in textiles. The exposure amounts (i.e., estimated daily intake (EDI) values, expressed in the unit of $\text{ng}/\text{kg BW}/\text{d}$ or $\mu\text{g}/\text{kg BW}/\text{d}$), were obtained from the literature (Fernandez-Arribas et al. 2021; Liu and Mabury 2021; Liu et al. 2020; Muensterman et al. 2022; Tang et al. 2020; Wang et al. 2022; Xue et al. 2017). Average body weight was assumed to be 70 kg for adult. We assumed that the mask is worn

260 days per year and clothes are worn 365 days per year. The unit of exposure amounts is expressed as $\mu\text{g}/\text{year}$ in Fig. 4. Icons are created with BioRender.com. (MFs: microplastic fibers; PAEs: phthalates; BPA: bisphenol A; OPEs: organophosphorus esters; AOs: synthetic antioxidants, including synthetic phenolic antioxidants and organophosphite antioxidants; PFAS: per- and polyfluoroalkyl substances)

attention. N95 masks may cause higher inhalation risk than general surgical masks (Table 5). According to the collected estimated daily intake (EDI) values, the exposure amounts of additives from face masks are 0.7–1820 $\mu\text{g}/\text{person}/\text{year}$ through inhalation and 546–2912 $\mu\text{g}/\text{person}/\text{year}$ through ingestion (Fig. 4, Table 5). Attentionally, although the EDI value of DEHP is at a safe level (not exceed the TDI value of 50,000 $\text{ng}/\text{kg BW}/\text{d}$, Table 5), wearing N95 masks for long time (occupational groups, such as doctors), taking high physical activity, and under higher temperature

or humidity in summer may pose higher inhalation risk (Fernandez-Arribas et al., 2021; Muensterman et al. 2022). The chemicals in face masks may be inhaled or ingested orally under long time of wearing; thus, it is necessary to regulate the type and content of additives in face masks in the context that Covid-19 will possibly coexist with humans for a long time.

In addition to the risk caused by direct release of additives on fiber products, there are also effects posed by additive release from MFs, posing higher risks than plastic

monomers (Rodrigues et al. 2019). MFs can enter organisms directly via inhalation through the respiratory tract or ingestion through the digestive tract. We calculated the exposure amounts of additives through microplastic fibers inhalation and ingestion and are listed in Table 5. Based on the data provided by Zhang et al. (Zhang et al. 2022, 2020c), i.e., one person could ingest approximately $(2.3\text{--}8.5) \times 10^4$ microfibers via dining and inhale $(0\text{--}3.0) \times 10^7$ microplastics per year. Since airborne microplastics are mainly fibrous, we assumed that 90% of the inhaled MPs are fibers. After conversion, the mass of microfibers inhaled and ingested per person per year is 0–11.71 g and 0.10–0.37 g, respectively (the conversion of MF mass and quantity refer to the formula of Leusch and Ziajahromi (2021)). We selected the three most common chemicals (DEHP, BPA, TCIPP) as an example. For instance, one person may inhale about 0–37.71 μg DEHP (the most typical PAE with high detection frequency and concentration) and ingest about 0.27–1.19 μg DEHP with MFs per year (Table 5). The tolerable daily intake (TDI) value of DEHP is 50 $\mu\text{g}/\text{kg}$ BW/d. Assuming that average body weight to be 70 kg for adult, the TDI value for DEHP is 1.28 g/person per year (50 $\mu\text{g}/\text{kg}$ BW/d * 70 kg * 365 d = 1.28 g), the mass of DEHP that one person may inhale or ingest per year does not exceed the TDI value. Similarly, the mass of BPA or TCIPP that one person may inhale or ingest per year does not exceed the TDI value. According to our estimation (Table 5), the maximum exposure amounts of additives through inhalation and ingestion of MFs released from clothing are 4.48–6440.5 $\mu\text{g}/\text{person}/\text{year}$ and 0.14–203.5 $\mu\text{g}/\text{person}/\text{year}$, respectively. Such situation still cannot be ignored and deserves further attention.

Conclusions and Outlook

MFs are ubiquitous in our daily lives, since actions such as the washing, drying, and abrasion of clothes, human contact friction, and the use and discard of face masks all cause MFs release into the environment. However, there is insufficient understanding about additives on MFs. When MFs are abraded and released, the additives can also be released into the environment accordingly, posing potential ecological and health risks to organisms.

In this review, we first summarized analytical methods of additives in synthetic textiles, and recommended sample extraction and compounds quantification methods for typical additives. Second, we comprehensively analyzed the types and concentrations of additives in textile fibers and MFs. Typical additives in traditional fiber products (clothes) and emerging fiber product (face masks) include plasticizers (DEHP, DBP), flame retardants (TCEP, TPhP, TEHP), antioxidants (bisphenols, AO168, AO1010, DBP), and surfactants (PFAS, NPEs), at concentrations of $10^0\text{--}10^6$ ng/g.

Finally, we discussed the main release pathways of additives in MFs to the environment, i.e., release to water through washing and release to the air through abrasion or drying. Additives in fiber products pose health risks through inhalation (0.7–1820 $\mu\text{g}/\text{person}/\text{year}$), ingestion (546–2912 $\mu\text{g}/\text{person}/\text{year}$), and dermal exposure to MFs (4.4–24,272.5 $\mu\text{g}/\text{person}/\text{year}$).

Collectively, we reviewed the occurrence and abundance of additives in synthetic textiles, which can release MFs via various daily life processes, including laundry, drying, abrasion, etc. The wide occurrence and exposure amounts of additives from MFs/fibers were confirmed, indicating that MFs pollution in daily life and the potential health risks should not be underestimated.

Finally, several perspectives on the research of chemical additives in MFs were proposed: (1) There exists a vacancy in extraction or analysis methods targeting additives on MFs. Since the mass of environmental MFs collected is too low to meet the detection limits of instruments, future research could focus more on the development of equipment with high sensitivity, automation, and approaches without extraction pretreatment. (2) Current studies mainly focus on the release of additives from large plastic fibers, whereas little attention has been paid to the carrier role of MFs. Much more future work needs to be performed to understand the potential leaching of additives from MFs. (3) The chemical additives exposure risk is mainly obtained by estimating EDI values from large plastic fibers. However, humans are more easily to be exposed to additives released from MFs, which only received little attention yet and warrant further in-depth research.

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Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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