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Microcontaminants and microplastics in water from the textile sector: a review and a database of physicochemical properties, use in the textile process, and ecotoxicity data for detected chemicals†

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Microcontaminants (MCs) and microplastics (MPs) originating from the textile sector are today receiving a great deal of attention due to potential environmental concerns. Environmental pressures and impacts related to the textile system include not only the use of resources (*e.g.*, water) but also the release of a wide variety of pollutants. This review's main objective is to highlight the presence of textile MCs and MPs in water, in their full path from textile factories (from raw materials to the final product) to wastewater treatment plants (WWTPs), and finally to the receiving surface waters. Their environmental fate and ecotoxicity were also addressed. Overall, more than 500 compounds were found, many of which are so called "contaminants of environmental concern" such as per- and polyfluoroalkyl substances (PFAS) and alkylphenol compounds. A database of physicochemical properties, ecotoxicity, and place of detection (specific textile process, WWTP, surface water or sediment) (classification by several international agencies) was compiled for the chemical detected. Preliminary risk assessment was conducted for those MCs for which the reported environmental concentrations exceeded the Predicted No Effect Concentration (PNEC). These chemicals were some nonylphenols, nonylphenol ethoxylates and organophosphate esters. Among MPs, polyester and nylon fibres were the most abundant. The highest concentration of MPs was reported in sludge (about 1.4×10^6 MPs per kg) compared to wastewater and surface water which showed MP concentrations at least two orders of magnitude lower. The role of transboundary contamination due to the release of chemicals from imported textile products was also assessed.

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Environmental significance

Microcontaminants and microplastics from the textile sector are important categories of pollutants due to the significant industrial role of the textile industry in the global economy. However, little is known about their emission at the different production stages, and in the receiving wastewater treatment plants, and later, surface waters. This review highlights the path of these substances in water and provides the available concentration data at the production stages, and in wastewater and surface water. This review also includes a database with compiled physical–chemical, regulative, and ecotoxicity data for more than 500 chemicals. Novel aspects include the discussion of the role of transboundary pollution due to the chemicals contained in the imported products and their potential release during further production or use stages.

1. Introduction

The textile industry is responsible for 20% of the global pollution of clean water, due to large quantities of chemicals, such as microcontaminants (MCs) and microplastics (MPs), that can be present in textile wastewater.[1,2] MCs are organic chemicals that are either anthropogenic or of natural origin, found in the ecosystems generally at low concentrations (μg L^{-1} or ng L^{-1}),[3,4] while MPs, according to the ISO definition, are considered "any solid plastic particle insoluble in water between 1 μm and 1000

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μm".[5,6] Both these pollutant classes could enter the environment directly or indirectly through wastewater treatment plants (WWTPs), one of the most important sources of pollution to water bodies.[7,8] WWTP conventional treatments are not designed for the removal of these pollutants and MCs are mostly released to the receiving aquatic basins by means of treated effluents,[9] while MPs are generally transferred to sludge. Moreover, WWTPs might also give rise to metabolites with higher toxicity than the parent compounds, such as azo-dyes.[10–13]

Despite the significant attention given to textile contaminants by the scientific community, there are still some gaps needing attention. It is well known that textile industries produce complex liquid waste.[14] So far, the existing reviews considered either the presence of general classes of textile contaminants,[14,15] such as auxiliary agents, bleaching agents, or only a specific category of chemicals such as dyes and aromatic amines.[16–19] Moreover, textile wastes are also characterized by the presence of MPs.[20] Clothing and textile processes in general contribute to the largest release of MPs into the environment, mostly through WWTPs.[20,21] The existing reviews on textile MPs mainly addressed the release of fibres through the washing of garments and/or only hypothesised the contribution of textile processes.[7,20,22–25] As mentioned by some authors,[25] no data on direct emission of MPs during the individual textile processes (*e.g.*, fibre production, pre-treatment, dyeing, printing *etc.*) are currently available.

This review's main objective is to evaluate measured textile MCs and MPs in their water travel path, from textile factories (starting from raw materials to the final product) to WWTPs, and lastly, to the receiving surface waters. For MCs a database of physicochemical properties, ecotoxicity, and place of detection (specific textile process, WWTP, surface water or sediment) (classification by several international agencies) was compiled. Then, a preliminary risk assessment was also carried out for MCs with the aim of highlighting the potential environmental risks associated with the discharge of chemicals of textile interest.

2. Materials and methods

2.1 Literature search

A focused literature search for textile MCs and MPs was carried out on Scopus and Web of Science. The keywords used were: "textile pollutants", "textile chemicals", "textile wastewater microcontaminants", "textile sludge", "textile surface water", "textile industrial area microplastics and fiber", "textile microplastic discharge" and "water textile microplastics". The research was filtered on articles published in English that were peer reviewed. The first screening was based on titles and abstracts and then the full-length article was analyzed. The reference lists of the identified papers were reviewed and additional publications were manually searched for. The flow chart of article selection, according to the "Preferred reporting items for systematic reviews and meta-analyses" (PRISMA) approach,[26] is reported in Fig. 1.

All measured chemicals present in the collected literature were reported in Table ESI-1 in the ESI material.† For each chemical, its CAS number, registration status to the European Chemical Agency (ECHA) and the Zero Discharge Hazardous Chemical (ZDHC) list,[27] physical–chemical properties, emission point along the textile manufacture process, country of investigation, and investigated matrix were reported. Physical–chemical properties were obtained from Pubchem,[28]

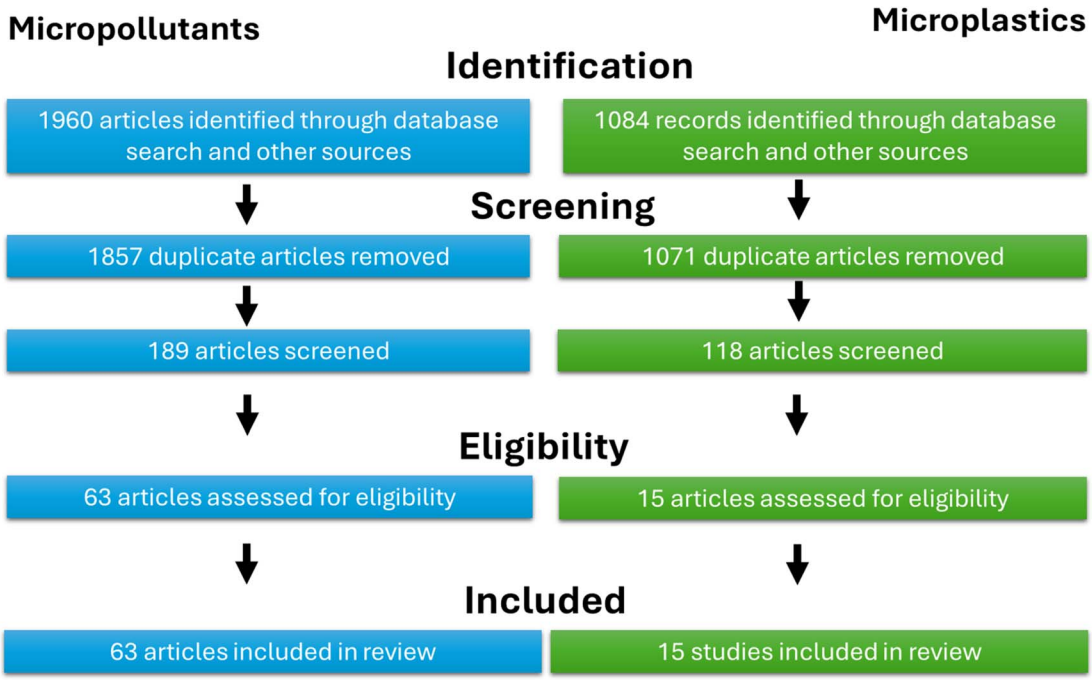

Fig. 1 Flowchart of article selection for the review (see text for details).

ChemSpider[29] or REAXYS[30] databases or other sources.[31–35] We did our best to find the most updated information on the ECHA sites. However, the lack of a final version of the ECHA CHEM database,[36] a unified source for European Union chemical registration information, did not allow a uniform, complete and validated data collection. Ecotoxicity data were also added, when available, and are described in the following section. The full database of 538 chemicals is available as an Excel file in the ESI material.†

2.2 Preliminary risk assessment for the aquatic ecosystem

Due to the lack of chronic data, acute effective or lethal concentration values (EC50/LC50, mg L^{-1}) for three trophic levels (algae, daphnia, and fish) were searched from the USEPA ECOTOX database[37] and the available literature. PNEC (Predicted No Effect Concentration) was calculated considering acute EC50/LC50 data divided by an assessment factor (AF) of 1000.[38] To calculate PNEC, the smallest EC50/LC50 value was chosen from those available among algae, daphnia, or fish.

3. Results and discussion

Overall, 63 studies were included in the review focusing on MCs, and 15 studies on MP loads. Regarding MCs, 40% of the studies reported pollution scenarios in European countries, followed by China, which accounted for 31% of the studies. Latin America contributed 11% of the studies, while 10% focused on the USA. The most analyzed matrices were WWTPs (54%), followed by clothing (32%) and rivers (27%). In total, 538 chemicals were identified and grouped into 50 classes. Notably, 76% of these chemicals are not listed in any of the ECHA lists, while 3% are included in the ECHA Community rolling action plan (CoRAP) list for further studies and follow-up. Conversely, 20% of the identified chemicals are listed in one or more ECHA Annexes, and 5% are classified as persistent organic pollutants (POPs). In contrast, fewer studies focused on MPs in the textile sector, despite the significant concerns related to microplastics originating from this industry. For MPs, China was the leading country in terms of the number of studies, accounting for 47% of the total, with other studies conducted in countries such as Indonesia, India, and Turkey. Rivers were the most studied matrix (40%), followed by lakes and textile WWTPs (33%).

3.1 Main chemical classes

The research provided a general overview of the status of textile water contaminants with a list of MCs and MPs commonly found in textile production, textile wastewater, sewage sludge,

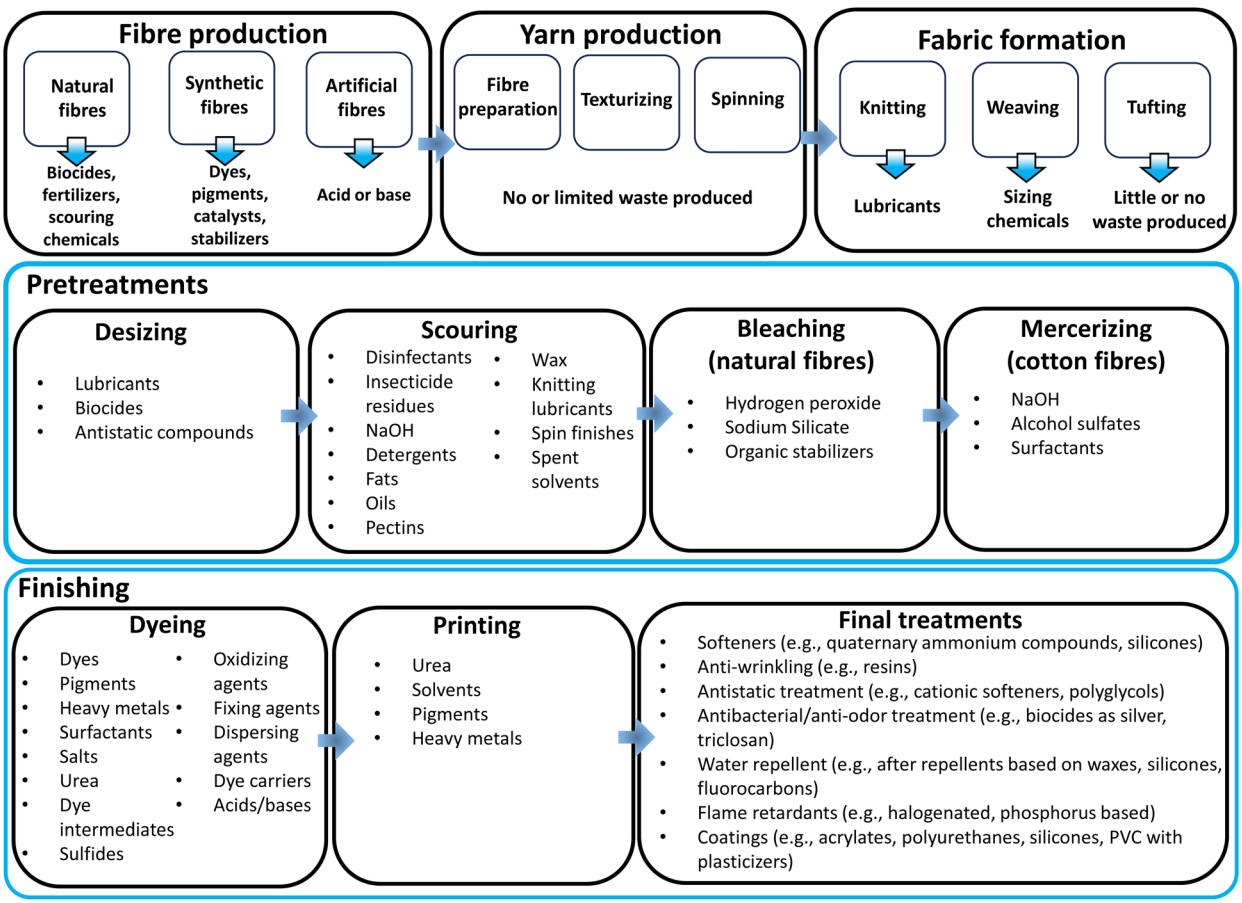

Fig. 2 Main processes involved in the textile supply chain and chemical category that can be released and discharged into wastewaters during each process. (Correia *et al.*,[39] 1994; Holkar *et al.*,[40] 2016; Khan *et al.*,[14] 2023; Lacasse and Baumann,[2] 2004).

Table 1 Main chemical classes used in or related to textile production, their general description, and processes in which they are involved (in alphabetical order by chemical class)

Chemical class	Description/role in textile production	Textile processes	Ref.
Aliphatic carboxylic acids	Aliphatic carboxylic acids include a wide range of chemicals which display different industrial applications. In textiles, they are used as accelerants in dyeing processes	Dyeing and printing processes	13
Alkylphenols (APs) and alkylphenols ethoxylated (APEOs)	APs and APEOs represent a large group of non-ionic surfactants widely used in textile processes as wetting agents, emulsifier/dispersing agents for dyes and prints, impregnating agents, de-gumming for silk production, dyes and pigment preparation, polyester padding and down/feather fillings	Dyeing and printing processes, general finishing processes	41–50
Alkyl sulfonates (benzenesulfonates and naphthalenesulfonates)	Alkyl sulfonates are surfactants, emulsifiers and dispersant agents. They can have different applications in textiles as wetting agents (*i.e.*, carbonising assistant during pretreatment processes), defoaming and felting agents; additives (wool protecting agents in dyeing processes); intermediates involved in the synthesis of dyes	Pre-treatment, dyeing, printing and general finishing processes	51–54
Aromatic amines/dyes/ quinolines	Aromatic compounds represent the basic constituents of azo dyes and pigments. Quinolines are used for the manufacture of dyes	Dyeing and printing processes	13, 41, 52 and 54–61
Benzothiazole and benzotriazole	They represent a class of aromatic compounds which have several applications in the industrial sector. In textiles they can be used as biocides and fungicides, or ultraviolet stabilizers to prevent yellowing and degradation	General finishing processes	62 and 63
Bisphenols (BP)	Bisphenols are characterized by two phenol groups bound together by a carbon or a sulphur bridge. BP are usually used as intermediates in the manufacture of antioxidants and dyes and are therefore employed in dyeing and printing processes and in general finishing processes	Pre-treatment processes, dyeing, printing, general finishing processes	42–44, 46, 55, 60, 64 and 65
Chlorophenols	Chlorophenols are phenolic aromatic compounds characterized by the presence of 1 to 5 chlorine atoms bonded to carbons. They are largely used as biocides in different textile processes	Pre-treatment, dyeing and printing processes, finishing processes	66 and 67
Chlorotoluenes	Chlorotoluenes are a group of chemicals generally used as intermediates in the synthesis of other chemicals. They are used as dye carriers or as auxiliaries and levelling agents	Dyeing and printing	27 and 68
Flame retardants: organophosphate esters (OPEs), polybrominated diphenyl ethers (PBDEs) and polybrominated biphenyls (PBBs)	Flame retardants represent a variety of groups which are added to textile products to impart technical characteristics (fire resistance). They consist of PBBs, PBDE, and OPEs. These are derivates of phosphoric acid and are widely used as flame retardants and plasticizers in textiles	General finishing processes	69–73
N-Nitrosoamine (disinfection by-products)	Nitrosamines, known as disinfection byproducts, are products which may be formed under chlorination (during washing processes) or ozonation in WWTPs	Dyeing and printing	74 and 75
Polycyclic aromatic hydrocarbons (PAHs)	PAHs are ubiquitous pollutants formed mainly by incomplete combustion processes. They can be minor contaminants and transformation intermediates of dyes and can be found in pigments (*i.e.*, carbon black pigments), dyestuff, dye auxiliaries (*i.e.*, dispersant) and printing pastes	Dyeing and printing processes, general finishing processes	76 and 77
PFAS	PFASs are aliphatic substances that contain the perfluoroalkyl moiety. PFAS are often used to impart water-, oil-, and stain-resistance. They have also been used as processing agents to aid in the deposition of dyes and bleaches in textile treatment baths	General finishing processes	78–85
Phosphonates	Phosphonates are a broad class of organic phosphorus compounds which contain one or more phosphonic acid groups. They are sequestering and chelating agents in textiles. They are also used as peroxide bleach stabilizers in textile auxiliaries	Pre-treatment and general finishing processes	86 and 87

Table 1 (*Contd.*)

Chemical class	Description/role in textile production	Textile processes	Ref.
Phthalic acid esters (PAEs)	PAEs are a class of lipophilic chemicals widely used as plasticizers and additives to provide mechanical extensibility and flexibility to the final product. In the textile industry they can have different applications, for instance as carriers, dispersants and accelerants in dyeing processes; plasticizers and softeners in printing pastes (printing processes); plasticizers in coating (*i.e.*, polyurethane) and laminating auxiliaries (finishing processes); antimicrobial auxiliaries (di-isodecylphthalate) or as wetting agents in finishing processes; constituent of polymers (*i.e.*, polyvinyl chloride)	Dyeing and printing processes, general finishing processes	27, 57, 60, 69, 76 and 88
Volatile organic compounds (VOCs)	VOCs (*e.g.*, styrene, xylene *etc.*) are chemicals which can be used in chemical manufacturing. They may be found also in adhesive and glue, in fabric printing inks, coating formulations, leather finishing formulations, plastic products such as buttons or in solvent	General finishing processes	27 and 58

and receiving surface water (*e.g.*, lakes, rivers). In the following tables (Tables 2–6), studies which described MC and MP concentrations were reported, whereas a full list of 538 chemicals comprehensive of those found using non-target screening is provided in the ESI material (Table ESI-1).† For each chemical a number of parameters were reported whenever available: physicochemical properties (molecular weight (M_W), vapor pressure (V_P), water solubility (W_S), octanol water partition coefficient, (K_{ow}), pKa), potential release/use of the chemicals according to four textile processes (Fig. 2): pre-treatments (P/T), dyeing (D), printing (P) and final treatments (F), country and sampling site, EC50/LC50, and PNEC for "algae", "daphnia" and "fish" (Table ESI-1†). Moreover, each chemical was classified if it was listed as a Substance of Very High Concern (SVHC) or listed in the annexes of Registration, Evaluation, Authorization and Restriction of Chemicals regulation (REACH) XIV or XVII, and whether it was included in the ZDHC Manufacturing Restricted Substances List (MRSL) v. 3.1.[27] The ZDHC MRSL is "a list of chemical substances banned from intentional use in the processing of textile materials, leather, rubber, foam, adhesives and trims used in textiles, apparel, and footwear industry. Intentional use means the substance used deliberately in a chemical product to achieve a desired look or functionality".[27] Some of the chemical classes reported in Table ESI-1† such as bisphenols, alkylphenol and alkylphenol ethoxylated, organophosphate and PFAS were commonly found worldwide in comparison to other chemical classes reported only in some regions, raising concern due to their large use. The main chemical classes which were found in the reviewed literature are reported in Table 1.

Besides MCs, textile effluent could be a source of MPs, especially fibres.[24,89] Different processes in the textile chain, such as yarn manufacturing and fibre processing, can contribute to the release of microfibres into ecosystems throughout wastewater.[90,91]

3.2 Concentrations of MCs and MPs from textile processes to WWTPs, and receiving waters

At the global level, textile processes (including textile and clothing industries) are associated with significant environmental pressure such as high energy and water demand ($\approx$79 billion cubic meters of water), and the discharge of pollutants.[92] More than 3000 chemicals are used in textile production, and most of them were characterized in previous studies as hazardous for humans and ecosystems.[17,40]

The textile supply chain consists of a series of processes involved in the transformation of raw materials into a final garment.[2] A general overview of textile processes is reported in Fig. 2, which lists chemicals potentially released during each phase. Along the textile production chain, five main processes can be distinguished: (i) fibre production; (ii) yarn production; (iii) fabric production; (iv) fabric processing (pre-treatments; finishing, consisting in dyeing/printing and final treatments); (v) textile fabrication.[14] Starting from the production of fibres, whether natural, artificial, or synthetic, various contaminants can be released, such as pesticides used in the cultivation of

natural fibres (of vegetal or animal origin), or in case of man-made or synthetic fibres, catalysts, stabilizers, or process chemicals. Once fibres are produced, they are spun into yarn followed by fabric production (weaving, knitting and tufting). In this phase, to prevent the breaking of the yarn, sizing chemicals (*e.g.*, polyvinyl alcohol, carboxymethyl cellulose, and polycyclic acids) are used, and lubricants and other chemicals are then applied during the desizing processes.[93] The most important processes responsible for the release of chemicals (such as unfixed dyes and auxiliaries) into wastewater are the so called "wet processes".[93] Among them, dyeing/printing and, in general, finishing processes contribute the most to the load of chemicals in wastewater, accounting for 17–20% of global water pollution[1,40] (European Parliament, 2024; Holkar *et al.*, 2016). The following sections will deal with the path of MCs and MPs along these stages (Fig. 2).

3.3 Pretreatment processes

Pretreatment processes are fundamental steps which consist of several chemical applications which increase the affinity of yarn for the following treatment processes: sizing, desizing, scouring, bleaching, mercerization.[2,94,95] Many pollutants derive from the removal of previously applied processing chemicals, such as preparation agents, or agricultural residues (*e.g.*, pesticides). Sizing and desizing are the first treatments applied to fibres. Sizing is the application of a thin layer of adhesives and binders to the yarn surface to increase its tensile strength and smoothness.[39] Desizing is the process which later removes sizing chemicals with the use of surfactants, to facilitate further chemical application. Scouring and bleaching are the following steps. Scouring can be applied on both natural or synthetic fibres, and it consists in the removal of applied or natural substances in fibres such as waxes, spinning oils, and pectin. Bleaching removes the yellowish colour of some natural fibres and is not always a required treatment. It is generally performed with the application of hydrogen peroxide (H_2O_2), peracetic acid, sodium hypochlorite, or sodium chlorite and auxiliary chemicals such as sulphuric acid, hydrochloric acid, caustic soda, sodium bisulphite, surfactants and chelating agents.[39] Most of these processes occur at relatively high temperatures (up to 90 °C) and require other chemicals such as activators and stabilizing agents to prevent pH changes or formation of complex compounds.[96] Lastly, mercerization is a treatment carried out mainly on cotton fabric to give shine and enhance dye uptake.[96]

3.3.1 MCs in pre-treatment processes. Chemicals used in these processes are those involved in the preparation of raw fibres for the following steps. The aim of pre-treatment processes is to eliminate sizing agents, waxes and other impurities. Following these treatments, various MCs can be generated such as oils, waxes and/or pesticides which may be present in raw materials.[39] For example, chemicals belonging to the phosphonates chemicals class such as amino-methylphosphonic acid (AMPA) (also known as a metabolite of the herbicide glyphosate), nitrilotris methylene phosphonic acid (ATMP), 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC), and ethylenediamine tetra(methylene phosphonic acid) (EDTMP) were measured. These compounds are used as stabilizers in bleaching treatments, as measured in wastewater by textile WWTPs and WWTPs which receive wastewater from the textile industry.[87] Another example is that of mirex, an old organochlorine insecticide, currently banned and listed as a POP in the Stockholm Convention on POPs.[97] This insecticide was reported[76] in samples of a WWTP receiving water from textile factories.

3.3.2 MPs in pre-treatment processes. Fibres from textile origin represent the largest MP contributors to freshwater pollution accounting for 90% of MP fibres (MPFs), especially through laundry and washing activities.[7,20,98–100] However, MP release at each stage of textile production was poorly investigated. Textile manufacturing processes involved in synthetic fibre processing such as yarn production, sizing, bleaching, and finishing contribute to the reduction of strength of fibres and can presumably increase the release of fibre fragments in the following processes.[101] However, further studies are needed to confirm and quantify this impact.

3.4 Dyeing and printing processes

Dyeing and printing processes allow the transformation of raw textile materials into finished valuable goods with the application of colours to fabrics.[2,93] Dyeing is the treatment of fabric with dyes, which contain chromophore groups (*e.g.*, azo), responsible for the colour of the fibres, yarn, and textiles. Printing slightly differs from dyeing, since it consists in colouring specific areas of the fabric to obtain a particular pattern.[2]

3.4.1 MCs in dyeing and printing processes. During dyeing and printing processes, non-fixed dyes and auxiliaries can be released.[93] Indeed, numerous chemicals such as dyes or pigments, dye constituents (*e.g.*, heavy metals, aromatic amines, quinoline) or other auxiliary chemicals (*e.g.* formaldehyde, surfactants, chlorophenols, halogenated solvents *etc.*) used in dyeing and printing processes can be found in textile wastewater.[2,41,59,66,93,102] Dyeing and printing represent the main processes which contribute the most to the production of coloured waste, which is generally highly polluted due to the low efficiency of conventional treatments.[41,56,59] Among the main components of dyes, aromatic amines (AAs) represent one of the most alarming chemical classes, followed by quinolines, chlorophenols and halogenated solvents, widely reported in the reviewed literature.[52,55,57,60,103] AAs are the precursor of azo dyes, which are usually more toxic than the original dyes.[104,105] The reviewed literature highlighted a variety of AAs sampled in textile sludge, WWTP textile effluent and rivers, with 4-nitroaniline being the most important compound for its ecotoxicological concern, reported in a river sample.[60] During dyeing and printing processes many auxiliary compounds are used to improve process efficiency.[2] Among these compounds a wide variety of chemicals are employed to support these processes with different functions (*e.g.* carriers, dispersant or accelerant, or other auxiliaries). Some very toxic chemicals such as dioxins and furans (PCDD/Fs) can sometimes be present as trace contaminants in disperse dyes[106] (Zhou *et al.*, 2019); similarly,

PAHs can also be found as trace contaminants in dye and printing auxiliaries (dispersant), in pigments (*e.g.*, carbon black pigments) and in dyestuff;[76,77,107] phthalates can also be present[13,60,69,76,108] as plasticizers and softeners in printing pastes and carriers, dispersants and accelerants in dyeing processes, as well as chlorotoluenes,[68] aliphatic carboxylic acids,[51–54] APs and APEOs.[41,42,44–47,108] Bisphenols are detected in many plastic products, while in textiles they may be used as ingredients in dye-fixing agents for polyamide textiles or to increase resistance of fibres such as polyester and elastane, as documented by several studies.[42–44,46,55,60] Chlorophenols (CPs) (*e.g.*, pentachlorophenol), common contaminants of wastewater, are a class of compounds which may be used as preservatives in dyeing and printing pastes or as thickeners in printing paste.[66] Lastly, alkyl sulfonates (benzene and naphthalene sulfonates) are used as auxiliaries in dyeing processes and as wetting agents (*e.g.*, carbonizing assistant in pre-treatment processes).[51–54]

3.4.2 MPs in dyeing and printing processes. The release of MPFs is mostly attributed to the mechanical pressures to which textiles are subjected,[89] especially during dyeing and printing processes. Here textiles are subjected to strong mechanical and chemical treatments, which could lead to a significant release of MPFs, up to about 10^6 microfibres per liter.[89,109–111] Despite printing processes being performed under dry conditions, a lab scale experiment demonstrated that treatments with adhesive chemicals were the main reason for higher microfibre releases in wastewater, with about 10^3 microfibres per cm^2 of fabric.[109] Additionally, during printing, fabric is heated at high temperatures and subsequently washed, and thus printing residues (unfixed dye, thickeners, reaction products) as well as MPs can be eliminated in this subsequent phase.[80,89,112,113]

3.5 Final treatments

Finishing processes include all the treatments (*e.g.*, mechanical, physical and chemical) that are employed to impart specific properties to the final textile products.[2] These properties could be functional ones, such as waterproofing and fire resistance, or visual effects related to fashion trends (*e.g.*, metallic, glossy).[2,114] Some finishing processes are specific of certain types of fibre (*e.g.*, natural fibres), such as biocide treatments during storage of cotton fibres, or mothproofing and anti-felt treatments for wool. Therefore, similarly to dyeing and printing, finishing processes are also responsible for the release of highly polluted wastewater. These wastewaters presented a variegated chemical fingerprint as has emerged from the reviewed literature (Table 1).

3.5.1 MCs in final treatments. The main MCs originating from this process belong to several chemical classes: APs and APEOs as intermediary of resins or biocide treatments,[41–47,49,55,108] flame retardants (FRs) (*e.g.*, PBBs, PBDEs and OPEs),[69–73] PAEs as softeners,[13,52,76,108] CPs as biocides,[66] and PFAS as water repellents, foam stabilizers or coating agents.[79,81–85,115,116] VOCs and halogenated solvents are used as auxiliaries on coatings and carriers in solvent preparations, respectively,[58,103] bisphosphonates and phosphonates as sequestering agents and in detergents,[87] alkyl sulfonates as multipurpose auxiliaries,[51–54] and benzothiazole and benzotriazole as biocides in antimicrobial finishing or as UV stabilizers.[62] Other products (*e.g.*, nitrosamines) may arise from these processes as a consequence of disinfection treatment.[74,75]

3.5.2 MPs in final treatments. Finishing processes give the desired traits to the fabric and improve the look of the final product. They can be responsible for the release of MPs, due to a loosening of surface structure.[98] For example, during finishing processes, several functionalization techniques are applied to textiles to improve the fibre surface.[117] These techniques mainly involve the use of coating binders (*e.g.*, polyvinyl chloride, silicones, acrylates and polyurethane) that can be easily washed out and end up in the environment after finishing or during laundry processes.[117] In the field of textile finishing, more and more advanced techniques are being sought to improve the final garments,[117,118] and thus reducing a possible release of fibres. However, no data dealing with the emission of MPs during these processes is currently available in the literature.

3.6 WWTP and sewage sludge

3.6.1 MCs in WWTPs and sewage sludge. As mentioned before, textile industries represent one of the major sources of pollution into receiving water (*e.g.*, lake, rivers) due to the high load to wastewater treatment plants.[80,94]

MC concentrations in wastewater and sludge, from WWTPs receiving wastes from the textile industry are reported in Tables 2 and 3. Data were reported as the sum of averages for each chemical group provided by the authors or back calculated as an average from raw data available in the ESI materials.†

Several chemicals were reported for wastewater inlet end effluents, such as dyes,[56,59] quinolines, VOCs,[58] nitrosamines,[75] benzenesulfonates,[51] BPA,[42–44,46,52] and PAEs[108] (Berardi *et al.*, 2019).

Some chemicals showed higher concentrations and were deeply investigated by authors. Among these, PFAS represented one of the largest groups commonly found in WWTP waters. The highest concentration reported for PFAS was 6690 ng L^{-1} in WWTP effluents of a textile industry of yarn manufacturing, bleaching and dyeing processes in China.[79] Some studies revealed that polyfluoroalkyl compounds can be transformed into shorter perfluoroalkyl compounds which are not further removed by these processes.[126,127] This was further confirmed by several authors.[80,112,113]

The most encountered compounds were long chain PFASs (PFOS, PFOA, PFDA, PFDoDA) followed by short chain PFASs (PFHpA, PFBA, PFPeA).[79,80,119,120] Also, PAHs were among the most abundant contaminants of wastewater dyeing, printing, and soaping processes. The highest concentration reported was 24.91 μg L^{-1} in WWTP influent, receiving textile and domestic waste. 2-, 3-, and 4 ring PAHs were the main chemicals, among which naphthalene was the most abundant compound reported.[108,121]

Surfactants such as APs and APEOs were a large group of chemicals investigated in WWTPs.[13,76,108] In particular, APs and APEOs were mostly investigated, with NP and NPEOs being among the most abundant compounds found in wastewater, ranging from a few μg L^{-1} up to 10 mg L^{-1}, reflecting the large use in textile wet processing as surfactants.[42–46,49,108,128] Indeed,

Table 2 MC concentrations in wastewater, μg L^{-1} (dissolved phase) or μg L^{-1} (particulate phase)[a]

	Main chemicals	WWTP IN	WWTP OUT	Source investigated	Country	Ref.
PFAS	PFOA, PFOS	0.0159	0.106	Industrial wastewater of a textile factory (synthetic fibre production)	Korea	80
	PFHpA, PFOA, PFPeA, PFDA, 8 : 2 FTUCA in (D); PFDA and PFOA in (P)	—	6.69 (D)–0.372 (P)	Effluent from textile production processes (scouring – dyeing – finishing – drying – heat setting – coating)	China	79
	PFNA, PFDA, PFUnA, PFDoA	—	0.09488	Textile factory (yarn manufacturing, bleaching, and dyeing)	Austria	119
	PFBA and PFOA	0.428	0.268	Textile printing and dyeing factories	China	120
PAH	Nap	24.91	0.13	WWTP receiving textile and domestic wastewater	Italy	108
	Nap, Flo, Phe, Flu, Pyr, BaA, Chr, BbF, BkF, BaP, IcdP, BghiP	3.82	1.12	WWTP receiving domestic water and industrial discharges, including textile wastewater	China	121
PAEs	DEPH	174.71	4.26	WWTP receiving textile and domestic wastewater	Italy	108
BPA	BPA	0.59	0.10	WWTP treating mixed domestic and textile wastewater	Italy	46
	BPA	0.128 (D)–0.047 (P)	0.035 (D)–0.005 (P)	Textile factory (yarn manufacturing, bleaching, and dyeing)	Greece	44
	BPA	0.24		Wastewater from a textile factory	Canada	42
	BPA		0.006	Textile plant effluent	Belgium	43
	BPA		0.005	WWTP effluent (municipal and textile factory)	Italy	43
	BPF		0.01	Textile effluent	Spain	52
APs–APEO	4-NP	0.58 (APs)	0.44 (APs)	WWTP receiving domestic and textile wastewater	Italy	45
	4-NPEO, 4-NPEC	12.66 (APEOs)	4.70 (APEOs)	WWTP receiving domestic and textile wastewater	Italy	45
	NP, NP1EO, OP1EO	78.71	0.85	WWTP receiving textile wastewater	Italy	108
	NP, OP	10.98 (APs)		Wastewater collected from a textile factory	Canada	42
	NP1EO	9112.7 (APEOs)		Wastewater collected from a textile factory	Canada	42
	NP	1.16 (D)–5.2 (P) (APs)	0.54 (D)–4.1 (P) (APs)	Textile factory (yarn manufacturing, bleaching, and dyeing)	Greece	44
	NP1EO	7.9 (D)–15 (P) (APEOs)	0.71 (D)–18 (P) (APEOs)	Textile factory (yarn manufacturing, bleaching and dyeing)	Greece	44
	NP	1.21 (APs)	0.61 (APs)	Textile wastewater	Italy	46
	NP1EO, NP2EO	5.99 (APEOs)	1.92 (APEOs)	Textile wastewater	Italy	46
	NP		0.51 (APs)	Textile plant effluent	Belgium	43
	NP1EO, NP2EO		17.26 (APEOs)	Textile plant effluent	Belgium	43
	NP		1.31 (APs)	WWTP receiving textile effluent	Belgium	43
	NPE1C, NPE2O		9.10 (APEOs)	WWTP receiving textile effluent	Belgium	43
	NP		0.29 (APs)	WWTP receiving textile effluent	Italy	43
	NPE1C, NPE3C, NPE1O		24.55 (APEOs)	WWTP receiving textile effluent	Italy	43
	APEO	27 500	11 600	Textile wastewater	Germany	49

Table 2 (*Contd.*)

	Main chemicals	WWTP IN	WWTP OUT	Source investigated	Country	Ref.
	NP	4.83	14.29	Wastewater from textile WWTPs	China	122
	NPEO	7.61	5.37	Wastewater from textile WWTPs	China	122
	∑10NPEOs	425	66	Wastewater from textile WWTPs	China	122
Quinolines	Benzyl-quinoline		0.01	Textile effluent	Spain	52
Dyes	DB 373, DR 1		0.22	WWTP effluent	Brazil	59
	DB373, DR1, DV 93	6.26	2.60	Wastewaters from textile WWTPs	Brazil	123
	DO 37, DB 373	385.9	199.03	Textile dyeing wastewater	Brazil	56
N-Nitrosamine	NDMA, NDEA, NPYR, NMOR, NDBA	3.40	4.35	Textile printing and dyeing wastewater	China	75
Phosphonates	HEDP, NTMP	5467.1	22.45	Textile dyeing treatment plant	China	87
	IDMP, AMPA	855.91	10.80	Textile dyeing treatment plant	China	87
	DTMP	842.11	44.82	WWTPs receiving wastewater from textile factories	Switzerland	86
Sulfonic acid	Sodium 2-naphthalenesulfonate	0.8–2377	—	Untreated textile wastewater	Spain and Portugal	51
VOCs	Toluene and xylenes	6.74	0.65	Textile dyeing wastewaters	China	58

[a] D: dissolved phase; P: particulate phase; PFAS: Per- and polyfluorinated substances; PAH: polycyclic aromatic hydrocarbons; PAEs: phthalic acid esters; BPA: bisphenol A; BPF: bisphenol F; APs–APEO: alkylphenols and alkylphenol ethoxylate; PFOS: perfluorooctanesulfonic acid; PFHpA: perfluoroheptanoic acid; PFPeA: perfluoropentanoic acid; 8 : 2 FTUCA: fluorotelomer unsaturated carboxylic acid; PFDA: perfluorodecanoate; PFOA: perfluorooctanoic acid; PFNA: perfluorononanoic acid; PFUnA: perfluoro-*n*-undecanoic acid; PFDoA: perfluoro-*n*-dodecanoic acid; PFBA: perfluorobutanoic acid; Nap: naphthalene; Flo: florene; Flu: fluoranthrene; Phe: phenanthrene; Pyr: pyrene; BaA: benzo[*a*]anthracene; Chr: chrysene; BbF: benzo[*e*]fluoranthene; BkF: benzo[*k*]fluoranthene; BaP: benzo[*a*]pyrene; IcdP: indeno [1,2,3-*cd*] pyrene; BghiP: Benzo[ghi]perylene; DEHP: di(2-ethylhexyl) phthalate; NP: nonylphenol; NPEO: 4-nonylphenol monoethoxylate; NPEC: nonylphenol mono ethoxy carboxylate; OP1EO: 4-*tert*-octylphenol monoethoxylate; OP: octylphenol; NP2EO: 4-nonylphenol diethoxylate; NPE3C: nonylphenol triethoxy carboxylate; DB: disperse blue; DO: disperse orange; DR: disperse red; DV: disperse violet; NDMA: *N*-nitrosodimethylamine; NDEA: *N*-nitrosodiethylamine; NPYR: *N*-nitrosopyrrolidine; NMOR: *N*-nitrosomorpholine; NDBA: *N*-nitrosodibutylamine; HEDP: 1-hydroxyethane 1,1-diphosphonic acid; NTMP: aminotris (methylenephosphonic acid); IDMP: iminodi (methylenephosphonic acid); AMPA: aminomethylphosphonic acid; DTPMP: diethylenetriamine penta (methylene phosphonic acid).

Table 3 MC concentration in sludge (ng per g dw)[a]

Sludge					
	Main chemicals	Concentration	Source investigated	Country	Ref.
Dyes	DO37	7410	Textile dyeing factory	Brazil	56
CPs	TeCPS, TCPs, PCP	1682.45	Textile dyeing WWTP	China	124
PAH	Nap, Acy, Ace, Fl, Phe, Ant, Flu, Pyr, BaA, Chr, BbF, BkF, BaP, DBA, InP, BP	6386	Textile dyeing plant	China	125
	Nap, Flo, Phe, Ant, Flu, Pyr, BaA, Chr, BbF, BkF, BaP, IcdP, BP, Acy	4450	WWTP treating textile dyeing wastewater	China	77
PFAS	PFOS, PFOA	9.53	Textile WWTP	Korea	80
	PFOS, PFOA, PFDA	222.28	Textile WWTP	Switzerland	115
	PFOS, PFDA, PFOA	700–1500	Finishing textile WWTPs	Germany	82
BP	BPA, BPF, BPS, BPZ	3270 (industrial WWTP); 1820 (mixed WWTP)	Textile WWTP and mixed industrial WWTP	Korea	64
	BPA	29.9	Textile factory (yarn manufacturing, bleaching, and dyeing)	Greece	44
AA	2-Methoxy-5-methylaniline and 5-nitro-*o*-toluidine	25 000	Textile-dyeing plants	China	58
APs–APEOs	NP	1268 (APs)	Textile factory (yarn manufacturing, bleaching, and dyeing)	Greece	44
	NP1EO	1104.2 (APEOs)	Textile factory (yarn manufacturing, bleaching, and dyeing)	Greece	44
Phosphonates	HEDP, IDMP	5 300 000 (PC)–380 000 (DP-PCs)	Textile dyeing treatment plant	China	87

[a] CPs: chlorophenols; TeCPS: tetra chlorophenols; TCPs: trichlorophenols; PCP: pentachlorophenol; PAH: polycyclic aromatic hydrocarbons; Nap: naphthalene, Acy: acenaphthylene, Ace: acenaphthene, Fl: fluorene, Phe: phenanthrene, Ant: anthracene, Flu: fluoranthene, Pyr: pyrene, BaA: benz[*a*]anthracene, Chr: chrysene, BbF: benzo[*b*]fluoranthene, BkF: benzo[*k*]fluoranthene, BaP: benzo[*a*]pyrene, DBA: dibenz[*a*,*h*]anthracene, InP: indeno[1,2,3 *cd*]pyrene, BP: benzo[ghi]perylene. PFAS: Per- and polyfluorinated substances; PFOS: perfluorooctane sulfonate; PFOA: perfluorooctanoic acid; PFDA: perfluorodecanoic acid; BP: bisphenol; BPA: bisphenol A; BPF: bisphenol F; BPS: bisphenol S; BPZ: bisphenol Z; AP: alkylphenols; APEOs: alkylphenols ethoxylated; NP: nonylphenol; NP1EO: nonylphenol mono-ethoxylate; HEDP: 1-hydroxyethane 1,1-diphosphonic acid; IDMP: iminodi(methylenephosphonic acid); PC: phosphonate chelators; DP-PCs: degradation products of phosphonate chelators.

long chain NPEOs are generally degraded into short chain NPEOs including, NP, NP1EO, and NP2EO.[129] Eventually, bisphosphonates and phosphonates were found in wastewater on average up to 5470 μg L^{-1} at the inlet and 22 μg L^{-1} in the outlet.[87,129]

Studies analyzing sludge reported the presence of several compounds related to dyeing and printing processes such as pentachlorophenol (92 ng g^{-1} of sludge)[124] and AAs with a mean concentration of 25 μg per g dw ($\sum$14 AAs)[58] and PAHs, between 1463 ng per g dw to 17 ng g^{-1}, with a high abundance of 3–4 ring PAHs followed by 5 ring PAHs.[58]

In sludge, the main chemicals reported were CPs, up to 1683 ng per g dw,[66] PAHs up to 6386 ng per g dw,[125] PFASs, up to 1500 ng per g dw,[80,82,115] BPs, up to 3270 ng per g dw,[44,64] APs up to 1268 ng per g (ref. 44) and PCs, up to 5.3 mg g^{-1}.[87]

3.6.2 MPs in WWTPs and sewage sludge. To date, only MP emissions from domestic and laundry processes have been deeply studied.[130,131] However, recent findings,[89] investigating a textile production park in China, reported that textile factories could be larger contributors of microfibres to WWTPs, in terms of concentration, than domestic discharges.[132] It was argued[89] that textile processes use much higher forces and stronger conditions (oxidants, alkalis, acids, *etc.*) than domestic washing, suggesting that textile printing and dyeing would be more important in generating microfibres. The microfibre concentrations of dyeing and printing wastewaters could be 10–10 000 times higher than those of municipal and domestic effluents,[89] making the textile factory districts and related WWTPs relevant point sources. Table 4 reports the number of MPs found in wastewater and sludge. MP abundance appears to be highly variable, with generally the highest values found in textile slurry (1.4×10^6 MPs per L).[109] The most common polymers were polystyrene (PS), polypropylene (PP), polyethylene terephthalate (PET), and polyether sulfone (PES). The size range of the investigated MPs was also variable and depended mainly on the analytical technique employed for particle characterization and mesh size selected.[134] The most abundant particle size was between 100 and 500 μm.[89,109,133]

3.7 Surface water contamination

3.7.1 MCs in surface water. MC concentrations in surface water bodies receiving treated effluent of textile origin are reported in Table 5. Concentrations were reported as the sum of the averages for each chemical class whenever possible or as a range (min–max).

Non-target analyses highlighted the presence of a wide variety of chemicals such as VOCs, phosphonates, alkyl sulphonates, aliphatic carboxylic acid, halogenated solvents and AAs,

Table 4 MP presence in wastewater (MP per L) and sludge (MP per kg dw)[a]

WWTPs and sludge						
Source investigated	Number of MPs	Shape	Size (mm)	Colour	Polymer	Ref.
Slurry wastewater printing effluent	$1.39 \times 10^6 \pm 4.26 \times 10^5$	Fibres	0.1–0.5	—	—	109
WWTP effluent	1.79 ± 1.03	Fibres, fragment, pellets	<0.1–1 mm		PET, PP, PE, HDPE, PDAP and others	133
Textile dyeing and printing wastewater	$9.76 \times 10^3 \pm 1.70 \times 10^4$	Fibres	<0.05–3	Colourless, black, blue, brown, red, green, grey, purple	—	89
Textile wastewater	$3.34 \times 10^2 \pm 2.43 \times 10^1$ (inlet), $1.63 \times 10^1 \pm 1.2$ (outlet)	Fibres	0.01–0.18	Blue, light blue, pink, brown, light purple, black, dark blue, red, grey, purple, yellow, transparent	Cotton, linen or wool, PES, PP, PAN, RA	111

[a] HDPE: high density polyethylene; PET: polyethylene terephthalate; PP: polypropylene; PE: polyethylene; PDAP: poly (L-diaminopropionic acid); PES: polyether sulfone; PAN: polyacrylonitrile; RA: rayon.

that may be released during textile processes.[13,51,53,55,58,60,74,75,87,103]

Many chemicals were investigated in river and river sediment. The reviewed studies highlighted the presence of several chemicals, widely used in textile production, in rivers at sampling points located both upstream and downstream of treated effluents of textile origin. Some authors[80] estimated an effluent load of 0.055 ton per year of PFAS into receiving water in Korea. Some chemicals were present at concentrations up to μg L^{-1} and sometimes mg L^{-1}, such as dyes (up to 6.3 μg L^{-1}),[123] APEOs (up to 4.16 μg L^{-1}),[43] OPEs (9.66 μg L^{-1}) (ref. 72) and chlorotoluenes (up to 2.6 μg L^{-1}).[68]

3.7.2 MPs in surface water. MPs are ubiquitous pollutants in the aquatic ecosystem reported in many global rivers and lakes.[137] Most of the sources of MPs are land-based, such as WWTP effluents, although secondary and tertiary wastewater treatments can remove up to 90% of MPs from water.[138–140] However, due to the low concentration in surface water, large water volumes were sampled in these studies. An overview of the typical concentrations of MP in the aquatic environment, which received domestic and/or textile WWTP treated water, is reported in Table 6.

MP numbers are usually not particularly high in aquatic environments; the highest amount reported was 600 MPs per L (ref. 89) in surface waters receiving textile dyeing and printing effluents. More generally, MPs showed higher concentration in sediment. The highest concentration of MPs in sediment reported was 8100 MP per kg dw.[145] Fibres represent the most common shape found, followed by fragments, while polyamide (PA), cotton, PET, PS, PP, polyethylene (PE) and cellulose were the most abundant polymers.[20,147] MP size varied from 40 μm up to 2000 μm, with larger particles mostly found in sediments.[90,146]

3.8 Chemicals of environmental concern by chemical classes

Textile processes are known to produce complex matrices in wastewaters.[76,108] In the absence of tertiary and quaternary treatment in WWTPs, chemicals are scarcely removed and can be discharged through effluents into receiving water bodies with possible environmental implication on aquatic ecosystems.[76,108] In addition, some contaminants can be transformed into more toxic intermediates (*e.g.* aromatic amine intermediates of azo-dyes, nitrosamine – degradation byproducts) than their precursors, resulting in negative effects on aquatic organisms.[75,102,148] Among the main families of compounds reported in surface waters, APs, APEOs, and flame retardants are certainly the most abundant, and are known for their possible adverse effects on aquatic organisms.[72,73,149] APs and APEOs are known as being endocrine disruptors with several effects reported in the literature, especially when found in mixtures.[14,150–152] Also, several PFAS were reported to have negative effects on aquatic life at concentrations up to 13.5 μg L^{-1} for secondary consumers.[153] Out of the 538 compounds that emerged from the reviewed literature, acute toxicity (EC50/LC50) data were available (Table ESI-1†) for only about one third of them (157 chemicals); therefore, a risk evaluation was possible only for these compounds. Within these chemicals, 46 were found through the direct analysis of clothes (listed as "clothes" in Table ESI-1†). These chemicals were included in the list since they can be released during washing processes.[57,62,65,154]

A preliminary risk assessment was performed calculating risk quotients (RQs) obtained by dividing the measured environmental concentrations (MECs) in surface waters (Table 5) by the PNECs, at the single chemical level. RQs were therefore obtained for chemicals measured in surface water for which concentrations in water and acute toxicity data were available (Fig. 3).

PNECs were calculated according to the Technical Guidance Document guidelines.[38] Risk is present when RQ ≥ 1, although often a fraction close to that value (*e.g.*, 0.01 to 1) is often considered as a non-acceptable risk. All reported MECs were well below the calculated PNEC (RQ $\ll 1$), except for NP, NP2EO,[43] TEHP and TPHP,[72] confirming, at least for single chemicals, that for most classes no appreciable risk seems to be

Table 5 MC concentrations in surface waters reported as μg L^{-1} (river) and ng per g dw (sediment)[a]

Surface water					
	Main chemicals	Concentration in surface water	Source investigated	Country	Ref.
Dyes	DR1, DB373	0.28–1.50	River	Brazil	59
	DB373, DO37	3.38–41	River sediment	Brazil	56
	DO37, DB373	0.01–0.40	River	Brazil	56
	Disperse violet 93, DB373	0.3588 (downstream)	River	Brazil	123
APs APEOs	NP	1.74 (upstream)–1.09 (downstream)	River	Belgium	43
	NP	0.49 (upstream)–0.59 (downstream)	River	Italy	43
	NP	0.016 (downstream)	River	Canada	47
	NPE1C	4.16 (upstream)–2.30 (downstream)	River	Belgium	43
	NPE2O, NPE3O	2.11 (upstream)−7.80 (downstream)	River	Italy	43
	NPE1O	0.008 (downstream)	River	Canada	47
BP	BPA	0.51 (upstream)–0.84 (downstream)	River	Belgium	43
	BPA	0.04 (upstream)–0.10 (downstream)	River	Italy	43
OPEs	TCIPP, TNBP, DNBP, TECP, TPHP, TEHP	1550	River sediment	China	71
	TPHP-TBOEP-TCIPP-TDCIPP-TEHP	9.66	River	Brazil	72
	γ HBCD	0.63	River	Japan	70
	γ HBCD	1619.95	River sediment	Japan	70
PAEs	DEHTBP	0.002 (river)–0.001 (estuary)	River	Spain	69
PFASs	PFOA	0.18	River	China	83
	PFOA, PFOS, PFNA	0.06	River	Korea	81
	PFOA, PFOS PFUnDA (dissolved phase); PFTeDA, PFDoDA (suspended particle phase)	0.09 (dissolved phase)–540.30 (particulate phase)	River	China	85
	PFOA, PFBS	0.20	River	China	135
	PFOA, PFUnDA	0.10 (dissolved phase)–0.01 (particulate phase)	River	China	79
	PFOA, PFOS	0.1926 (upper sediment)–0.1765 (bottom sediment)	River sediment	China	136
Nitrosamines	NDMA, NDBA	0.02	River	China	75
Chlorotoluenes	2.3 DCT, 3.4 DCT, 2.5 DCT, 2.4 + 2.6 DCT	2.65–5.53	River	Spain	68

[a] DR1: disperse red 1; DB373: disperse blue 373; DO37: disperse orange 37; NP: nonylphenol; NP1EC: nonylphenol mono ethoxy carboxylate; NP2EO: 4-nonylphenol diethoxylate; NP3EO: nonylphenoltriethoxylate; NP1EO: nonylphenol monoethoxylate; BPA: bisphenol A; TCIPP: tris(2-chloroisopropyl) phosphate; TNBP: tris(butyl) phosphate; DNBP: di-*n*-butyl phosphate; TCEP: tris(2-chloroethyl) phosphate; TPHP: tris(phenyl) phosphate; TEHP: tris(2-ethylhexyl) phosphate; TBOEP: tris(2-butoxyethyl) phosphate; TDCIPP: tris(1,3-dichloroisopropyl) phosphate; γ HBCD: hexabromocyclododecane; DEHTBP: bis (2-ethylhexyl)-3,4,5,6 tetrabromo-phthalate; PFOA: perfluorooctanoic acid; PFOS: perfluorooctanesulfonic acid; PFNA: perfluorononanoic acid; PFUnDA: perfluoroundecanoic acid (dissolved phase); PFTeDA: perfluorotetradecanoic acid; PFDoDA: perfluorododecanoic acid (suspended particle phase); PFBS: perfluorobutane sulfonic acid; NDMA: *N*-nitrosodimethylamine; NDBA: *N*-nitrosodibutylamine; 2.3 DCT: 2,3-dichlorotoluene; 3.4 DCT: 3,4-dichlorotoluene; 2.5 DCT: 2,5-dichlorotoluene; 2.4 + 2.6 DCT: 2,4-dichlorotoluene + 2,6-dichlorotoluene.

evident, with MECs being generally two orders of magnitude (or more) lower than corresponding PNECs.

3.9 The transboundary pollutants issue in Europe for textile products

Several strategies were introduced at the European level to limit textile pollution for the protection of receiving water bodies, also according to the Water Framework Directive (WFD).[155] The European parliament recently approved the proposed directive with a new road map to improve urban wastewater treatments (*e.g.*, secondary, tertiary, quaternary) implemented at different times and WWTP size.[156] The quaternary treatment (to remove a broad spectrum of micro-pollutants) will be mandatory for all plants over 150 000 population equivalents (p.e.) (and over 10 000 p.e. based on a risk assessment) by 2045.

Chemical sale and use in Europe are regulated by REACH,[157] which aims to improve the protection of human health and ecosystems. Under REACH, chemicals are classified according to their presence in several lists under two regulations: reg. 2019/1021 POPs[158] and reg. 2006/1907 REACH with the candidate List SVHC,[159] Annex XIV[160] and XVII.[161] The SVHC list (substances of very high concern) includes substances that may pose serious risks to human health or to the environment due to their hazardous properties. These substances are candidates for further regulation under the Authorisation List (Annex XIV) of the REACH regulation. The Authorisation List (Annex XIV) includes substances that require special authorization before they can be used within the European Union (EU). These substances are considered particularly hazardous and are only granted authorisation if there are no suitable alternatives available. Then, the restriction process in Annex XVII involves

Table 6 Overview of the typical concentrations of MPs in the aquatic environment, which received domestic and/or textile WWTP treated water

Surface water						
Source investigated	Number of MPs	Shape	Size (μm)	Colour	Polymer	Ref.
River	5.83	Fibres	50–100	—	Polyester polymer type, followed by nylon and cotton	90
River sediment	3.67 MPs per 100 g (dw)	Fibres	1000–2000	—	Polyester polymer type	
Lake sediment	919 MPs per 25 g (dw)	Fibres	49–4951 μ	Transparent, black, blue, red, pink-yellow-green	PP, PET, PS, acrylic polymers	141
Delta sediment	1297 MPs per 25 g (dw)	Fibres, fragment, film	180–4900	Black, blue, yellow, transparent, white, red, green	PE, PP, PET, PS, polyacrilates and PVC	
River	4.65 ± 2.06 (2019)–6.90 ± 5.16 (2020)	Fibres, fragments, pellets, foams, rubbers and other	45–5000	Black, blue	PET, PA, PS	142
River sediment	97.90 ± 71.72 (2019)–277.76 ± 207.2 (2020)					
Freshwater organisms	29 MPs in chironomids, 15 MPs in copepods, 5 MPs ephemeropterans, MPs 1 nematodes	Fibres, fragment	5–400	Blue, transparent	PA, EVA, PE, PET, PE-PP, textile cellulose	143
Lake	5.257 and 0.00157[a]	Fibres, fragment	0.6–1380	Blue, red, black, other	Cotton fibre (stained with indigo blue, phthalocyanine and naphthol), AC, PET	144
Lake sediment	8100 (NTH)–5300 (SWTH)	Fibre, film, fragments, pellets	250–5000	White, black, blue and red	PA, AA, PET, CA, HDPE, PP	145
River	4.87 ± 1.08 (surface)–2.51 ± 1.45 (bottom)	Fibres	<50–5000	Transparent, followed by blue, red, and grey	PET, PA, PS, PE	91
River	2.1 to 71.0	Fibres, fragments	100–1000	Blue, red, black	PES, RA, PP, cotton, cellulose	100
River sediment	16.7 to 1323.3					
River	22 to 251	Fibres	40–300	Blue, red, grey, black, green	—	146
River	600	Fibres	<50–3000	Colorless, black, blue, grey	—	89

[a] Samples were collected with a 50 μm net. AA: acrylic acid; CA: cellulose acetate; EVA: ethylene-vinyl acetate; HDPE: high density polyethylene; PA: polyamide; PE: polyethylene; PET: polyethylene terephthalate; PES: polyether sulphone; PP: polypropylene; PS: polystyrene; PVC: polyvinyl chloride; RA: rayon.

the identification and inclusion of hazardous substances, mixtures, or articles that pose risks to human health and the environment, or have other negative impacts. The restrictions in Annex XVII can include concentration limits, total content limits, or bans on the use of certain substances. These restrictions may be updated or amended periodically, and businesses must ensure compliance. Finally, at ECHA is present another list, the Community Rolling Action Plan,[162] which includes some chemical substances, proposed by the member states, which have been evaluated or will be evaluated in the coming years.

A large part of textile products is imported from non-EU countries, which might not fall within the same restriction policies of European countries.[92] Considering the global trade transport, many of these contaminants can enter Europe from abroad (*e.g.*, piggybacking in raw materials contaminated by pesticides or other unknown compounds banned in EU countries). Fabrics and clothes may contain a large range of chemicals and other toxic substances which could eventually be released during production or consumer use.[154] This has been observed for some textile fabrics present on the European market, coming from different parts of the world, through direct analysis of the garments.[57,62,65,163–168] Several cases of "transboundary contaminants", restricted within European boundaries, were present in the literature. Carlsson *et al.*[154] detected several organic contaminants, by the direct analysis of clothes coming from abroad (Vietnam, China, Bangladesh, Pakistan, Turkey). Benzothiazole and quinolines were the most common. Quinoline is considered a carcinogen and suspected mutagen,[157] and therefore is regulated under REACH.

Moreover, 12 dioxin-like polychlorinated biphenyls (PCBs) (*e.g.*, PCB-77, PCB-118) and 8 non-dioxin-like ones were found[168] in infant clothes purchased in large stores and online stores in Spain, as well as bisphenols.[65,164,166]

Another transboundary chemical case was that of the detection[169] in recycled plastics and textiles of chemicals such as pesticides, dyes and other auxiliaries mainly attributed to previous use and the recycling process itself.

Although REACH and the Regulation on Classification, Labelling and Packaging (CLP) represent a key part of the chemical legislation within the EU, limitations are imposed only on chemicals which exceed 1 ton per year of chemical amount manufactured or imported.[157] Therefore, all chemicals which are below this threshold are not registered and escape control. Concerning MPs, the EU issued to regulate MPs under Annex XVII of REACH with Regulation of the European Commission no. 2023/2055 (ref. 170) amending the Annex XVII of Regulation (EC) no. 1907/2006 in which substances

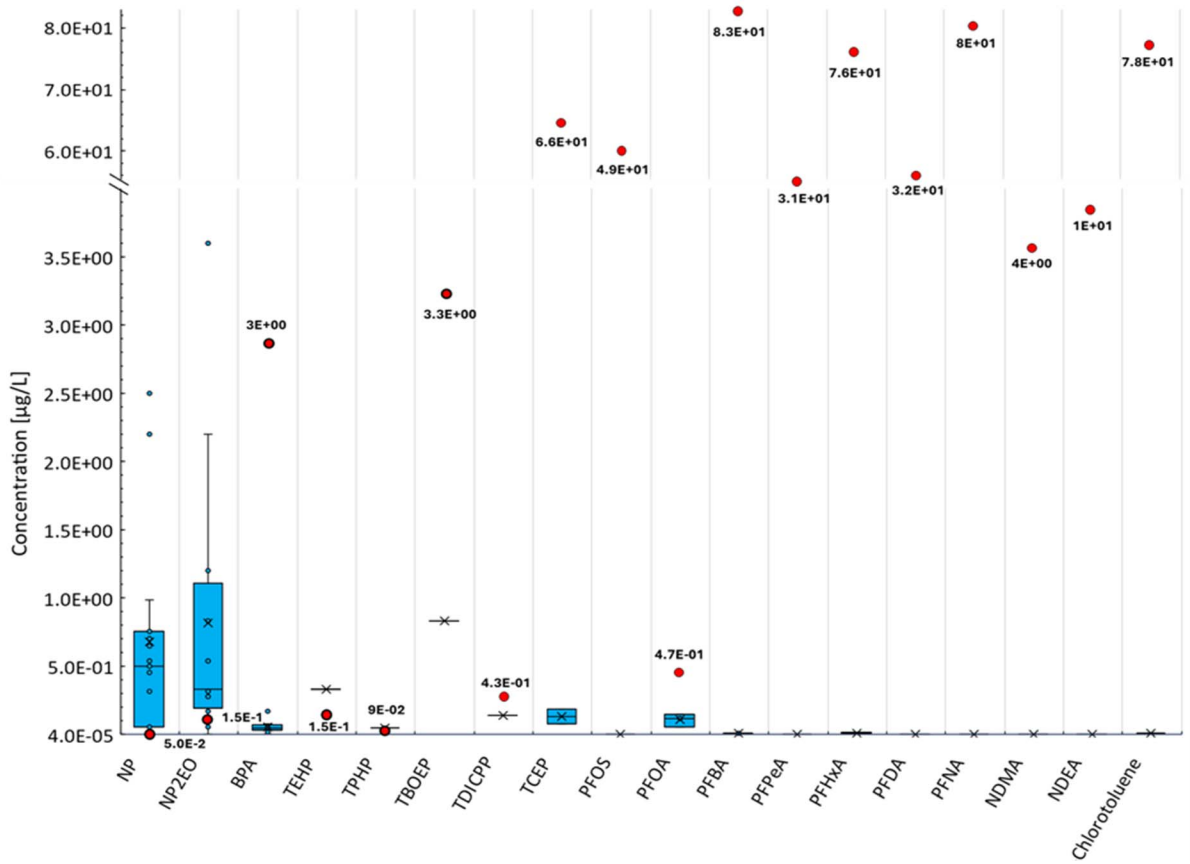

Fig. 3 Preliminary risk assessment (MEC *vs.* PNEC) for textile chemicals reported in rivers and for which ecotoxicity data were available. Red spots represent PNEC values, while blue box plots represent available MEC ranges. Bottom and top whiskers represent the 10th and 90th percentiles; in the box the first, second and third horizontal lines represent the 25th, 50th, and 75th percentiles while the "*X*" mark represents the average.

containing microparticles of synthetic polymers in mixtures with concentrations equal to and/or greater than 0.01% by weight may not be placed on the market.

3.10 General discussion

Table 1 and Fig. 2 report the main classes of chemicals used in the textile sector. Tables 2–6 show instead the measured MCs and MPs among those measured in the different phases and processes, collected from the reviewed literature. Wastewater and sludge were surely the most studied matrices worldwide. An exhaustive list of chemical classes and individual chemicals, measured in textile treatment wastewater, WWTPs receiving textile wastewaters, and surface water, is reported in Table ESI 1†. Dyes and their constituents (*e.g.*, aromatic amines, quinolines *etc.*), PFAS, PAH, PAE, AP-APEOs and CPs were among the most common pollutants encountered. Their presence was also observed in surface water, as would result given the WWTP emission into the aquatic environment. However, most of the chemicals from the list were found in wastewaters and sludge, probably because of the highest concentrations found in these phases. This can also be due to the few measurements of surface water for the same substances. This underlines the general lack of data and the need to carry out research on chemicals of environmental relevance worldwide. This issue was raised by Di Guardo and Hermens,[171] who underlined the requirement of more temporally and spatially resolved monitoring data to perform a better exposure assessment in ecological risk assessment. However, the preliminary risk assessment showed values generally well below the PNECs, with a limited number of chemicals which exceeded the PNECs, as previously reported.[43,72] Nevertheless, as mentioned by Di Guardo and Hermens,[171] mixtures of chemicals are rarely considered when performing ecological risk assessment. These mixtures should include not only textile chemicals but also the other compounds found in water, such as pharmaceuticals, pesticides, and metabolites.[172–175] Risk assessment for MPs was not possible due to the lack of established regulatory guidelines.

Despite a very high number of microfibre and microplastic-related publications in the literature, most of them considered just MPs released during domestic washing. Studies on the specific textile processes are urgently needed to understand the impact of each of them to the mass balance as already stated.[25] Due to the prevailing fast fashion trend, the textile production significantly increased lately, resulting in higher emissions from textile plants.[1] Looking at the data, most MPs were of fibre shape (80–100%) and most of them were found in sludge. The results showed a moderate MP pollution level in water, while MPs were mainly reported in sediment, a long-term sink of MPs.[48,176] In addition, there is a general lack of consistency in terms of quality assurance procedures, sample collection, sample processing, characterization and identification techniques, and reported results of MPs. MPs are often reported in terms of number per liter and not in terms of concentration (mass per unit volume). While numbers and sizes of fragments/fibres could be useful for characterizing sources, weathering, and possibly ecological effects, the knowledge of true concentrations for each polymer would allow mass balances to be performed and the fate of MPs to be reconstructed in their journey from production to use and environmental occurrence. Additionally, the adoption of standardized procedures for MP measurement steps would increase the accuracy and precision of results, reduce the time and effort required, and help to make meaningful interpretations and comparisons between studies.[177]

4. Conclusions and recommendations

This review highlights the presence of MCs and MPs derived from the textile industry. Overall, 538 chemicals were found, many of which belong to contaminants of environmental concern such as PFAS or alkylphenol compounds. However, it would be relevant to increase the number of chemicals monitored in the environment, through suspect and non-target screening (SNTS) techniques, useful to direct and improve the evaluation of the environmental occurrence of chemicals.

MPs were reported to be mostly present in sludge, with polyester and nylon fibres being the most abundant polymers. The lack of standardized procedures in the assessment of MPs is critical since the knowledge of the number of fragments or fibres alone is not sufficient to perform a mass balance. The use of chromatographic techniques (such as pyrolysis-GC-MS) to measure mass and therefore concentration (such as $\mu g\ L^{-1}$) of the different polymers could allow the evaluation of the environmental path of MPs from sources to the environment in a more meaningful way.

Preliminary risk assessment was possible only for MCs for which environmental concentrations reported in surface water exceeded PNEC: NP, NP2EO, TEHP and TPHP. This was not achievable for metabolites/transformation products, since they are often not known or not measured. Risk assessment was not possible for MPs, since their effects on the organisms are still being questioned and no official regulatory procedures exist. Despite the improvement of WWTP treatments in reducing the impact of textile pollution on the environment, many chemicals (*e.g.* dyes, PFAS, alkylphenols) are still scarcely removed, raising concern for their ecotoxicity. MPs instead are removed from water around 90% and more, although they are mostly transferred to sludge. This leads to subsequent sludge disposal or reuse issues. Regarding WWTPs, even when quaternary treatments are implemented, the activation of the bypass flow in case of abundant precipitations would imply the transfer of untreated wastewater to surface waters. This means, for MPs, a direct load to surface waters, since sequestration by sludge during secondary and later treatments will not occur.

The problem of *trans*-boundary contaminants is still overlooked, allowing many chemicals to reach ecosystems of territories where these chemicals would be restricted or banned. This is also true when recycled polymers are used for textile production, possibly carrying restricted use chemicals.

Finally, there are still no limits in the European Union on MCs entering and leaving WWTPs. Additional treatments should be implemented in WWTPs to reduce the amount of MCs and MPs reaching surface water and sludge. The effect of such treatments should be monitored and refined to evaluate and possibly mitigate the production of metabolites/transformation products or reactive species which could be more toxic to the aquatic ecosystem than the parent compounds.

Data availability

The data supporting this article have been included as part of the ESI† in the form of an excel file (*.xlsx) containing physical–chemical, regulative, and ecotoxicity data for 538 chemicals.

Author contributions

Isabella Gambino: investigation, writing –original draft preparation, writing – reviewing and editing; Elisa Terzaghi: investigation, writing – reviewing and editing; Enrica Baldini: reviewing and editing; Giovanni Bergna: reviewing and editing; Giovanni Palmisano: writing – reviewing and editing; Antonio Di Guardo: funding, resources, data curation, writing – reviewing and editing, supervision.

Conflicts of interest

There are no conflicts to declare.

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