PFAS in textile wastewater: An integrated scenario analysis for interventions prioritization to reduce environmental risk

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ABSTRACT

Per- and polyfluoroalkyl substances (PFAS) are used in several industrial applications, such as in textile manufacturing, and are known as "forever chemicals" due to their spread, stability and (eco-)toxicity, gaining increasing concern. To avoid PFAS spread in the environment, reducing the environmental risk on receiving surface water, prevention and removal strategies should be implemented at multiple levels, comprising both textile factories and municipal wastewater treatment plants (WWTP). This study presents an integrated scenario analysis to compare and prioritize prevention and removal strategies based on their potential in risk minimization. Field monitoring campaigns, lab- and pilot-scale experiments on two established removal processes (pressure-driven membrane separation, adsorption on activated carbon) were combined, and environmental risk was assessed due to a mixture of 15 PFAS. About prevention, substitution of long-chain PFAS with short-chain PFAS were considered, as well as the reduction of PFAS used in textile processing. The proposed approach was applied in a textile district in northern Italy without PFAS spikes in the tested wastewaters. This approach has proven to be beneficial in determining the optimal combination of actions to be implemented across different levels of the industrial district (including textile factories and/or municipal WWTP). This methodology provides a clear indication of the environmental advantages, specifically in minimizing risks, resulting from the implementation of diverse PFAS reduction strategies. Compared to the current scenario, resulting in an unacceptable risk (risk quotient, RQ=2.2), the risk can be reduced below the acceptable threshold (RQ=0.9) by the combination of (i) PFAS reduction/replacement in textile processing, (ii) treatment of wastewater discharged by textile factories through membrane separation prior to the discharge in the sewer, and (ii) WWTP upgrade through an activated carbon adsorption downstream the ozonation step.

1. Introduction

Per- and polyfluoroalkyl substances (PFAS) are used in numerous industrial applications, such as in textile manufacturing, for their unique chemical and physical properties, including water and oil repellency, temperature resistance, chemical resistance, and surfactant properties (O'Connor et al., 2022). However, the widespread use of PFAS and their persistence make them ubiquitous compounds of increasing concern due to their (eco-)toxicity (Lewis et al., 2022).

Worldwide PFAS regulations are evolving in different directions. On one side, more and more PFAS are included in regulations banning or restricting their use in semi-finished products (Stockholm Convention on Persistent Organic Pollutants (POPs) in 2001 and REACH 552/2009 list

in 2009). In addition, there are many voluntary initiatives in the textile sector to boost restrictions in the use of fluorinated substances, such as: (i) the certifications GOTS (Global Organic Textile Standard), Oeko-tex Standard 100, Blue Sign, or (ii) the international protocols ZDHC (Zero Discharge of Hazardous Chemicals, https://www.roadmaptozero.com/), and MRSL (Manufacturing Restricted Substances List). In the Impact Report 2021, delivered by ZDHC, collecting wastewater data of a subset of manufacturing factories, 3 hazardous chemical groups are listed that still represent a challenge in the textile sector, one of which is constituted by PFAS (PFOS, PFOA, PFBA, PFBS, PFHxA, PFHxS, PFDA, and PFDS). Besides, PFAS have been included in several national and international regulations related to water protection: (i) the proposed revision of the European Directive on Environmental Quality Standards

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(EQS) limits their concentrations in surface water, marine coastal water and biota, (ii) the European Directive on drinking water sets a limit for the sum of 16 PFAS, (iii) some countries are proposing national PFAS concentration limits in treated wastewater (e.g. Italy), and in sewer sludge used in agricultural applications (e.g. Austria, Denmark, Germany, Norway) (EurEau, 2022). Finally, PFAS are not specifically mentioned in the proposed revision of the Urban Wastewater Treatment Directive (UWWTD), but great importance is given to producers' responsibility for micropollutants discharge into the environment and the implementation of quaternary treatments to remove micropollutants is recommended.

In this context, prevention and removal strategies to reduce micropollutants (including PFAS) spread into the environment should be implemented at multiple levels, comprising textile factories and municipal wastewater treatment plants (WWTP).

Regarding prevention strategies, some studies have explored the substitution of long-chain PFAS with either short-chain PFAS or non-fluorinated compounds in textile processing, comparing water and oil repellency properties of the fabrics. However, it's essential to consider the findings summarized in the "Staff Working Document on PFAS" report of the European Commission in 2020, which accompanies the "Chemicals strategy for sustainability towards a toxic-fee environment". This report stresses the potential drawback of replacing long-chain PFAS with short-chain PFAS, as it can lead to increased production and release, posing higher risks to both the environment and human health. Notably, some studies indicate that from two to three times the amount of short-chain PFAS is needed with respect to the amount of long-chain PFAS, to achieve comparable water and oil repellency of fabrics (Davies, 2014; MIDWOR, 2018). This highlights the complexity of balancing environmental and performance issues when PFAS substitution strategies are assessed in the textile sector.

As for removal strategies, numerous studies investigated the treatment of wastewater from textile factories for the removal of typical pollutants, such as dyes/color (*inter alia*, Samsami et al., 2020) and surfactants (*inter alia*, Collivignarelli et al., 2019). However, very few studies can be found about PFAS removal in these concentrated streams. PFAS are recalcitrant to biodegradation and thus poorly removed in conventional WWTPs, except for the portion removed by sorption on sludge. Several full-scale monitoring campaigns demonstrated that conventional WWTPs are ineffective in reducing PFAS discharge and can even convert PFAS precursors into terminal PFAS, resulting in similar or higher PFAS concentrations in the effluent than in the influent (Coggan et al., 2019; Gallen et al., 2017; Pan et al., 2016; Stasinakis et al., 2013). The upgrade of WWTPs with advanced treatment processes has been suggested as an intervention strategy for the reduction of environmental risk for aquatic environments and water usage (Lenka et al., 2021). The efficiency of advanced processes for PFAS removal from WWTP effluents, including pressure-driven membrane separation, ozonation and activated carbon adsorption, has been evaluated at lab- and pilot-scale, investigating their performance as both stand-alone processes or in combination (*inter alia*, Franke et al., 2019; Mailler et al., 2016; Sousa et al., 2018; Zhang et al., 2016). Innovative technologies have been also investigated in the last years (Ahmed et al., 2020). However, an integrated approach comparing the effectiveness of prevention and removal strategies for PFAS reduction is lacking so far, since there are no studies investigating the application of those strategies at different levels in a textile district, namely at the sources (i.e. textile factories) and at the municipal WWTP.

In fact, the aim of this study is to propose an integrated scenario analysis to compare and prioritize PFAS prevention and removal strategies based on their potential in risk minimization at district level. It combines (i) field monitoring, (ii) lab- and pilot-scale experiments on two promising removal processes (pressure-driven membrane separation, adsorption on activated carbon both as stand-alone process and in combination with ozonation), and (iii) environmental risk assessment, to evaluate the risk for the receiving surface water due to a mixture of 15

PFAS. No PFAS spikes were performed. This approach has been applied to a textile district in northern Italy, exploring the environmental benefits, in term of mixture risk reduction, which can be obtained by different combinations of actions and processes to be applied at the various levels of the industrial district (textile factories and/or municipal WWTP). This approach encompasses two novel aspects. Firstly, we propose a holistic approach that, unlike the available literature, takes into consideration different PFAS mitigation actions (prevention and remediation) in different points of an anthropized system, from the source to the final discharge into the environment. Secondly, we propose the use of PFAS mixture risk assessment, instead of PFAS concentration or PFAS removal efficiency, as the main tool to evaluate and prioritize the mitigation actions to be put in place.

2. Materials and methods

2.1. The case study

The case study is a textile district in Como province (Italy), where 42 textile factories discharge wastewater in a municipal sewer system, which conveys the mixed wastewater (textile and urban) to the Alto Seveso municipal WWTP (25–40% of the inlet COD load and 34% of inlet flowrate of industrial origin). Alto Seveso WWTP comprises pre-treatments, biological activated sludge treatment (pre-denitrification, nitrification/oxidation), coagulation-flocculation followed by a lamella clarifier, and ozonation. The effluent is then discharged in the Seveso river. A schematic overview of the system is reported in the Supplementary Materials (Fig. S1).

The PFAS to be monitored were selected based on three criteria: (i) reference standards for PFAS in wastewater (ZHDC list) and sludge (from Denmark and Norway regulation); (ii) lists of 30 PFAS analyzed (9 detected) in the surface waters of Lombardy (in particular, in the Seveso river) and in 5 WWTPs spread in the textile districts within the Como province, during several monitoring campaigns carried out from 2017 to 2019 both by ARPA-Lombardia (Regional Agency for Environmental Protection in Lombardy Region) and voluntarily by WWTPs operators; (iii) list of PFAS for which an analytical method had already been developed in laboratories collaborating in this study.

33 PFAS were present in at least one of the above mentioned lists (PFBA, PFHxA, PFBS, GENX, PFPeA, PFHpA, PFHxS, FTOH 4–2, FTOH 6–2, PFOA, PFOS, PFNA, PFDA, PFDS, PFUnA, PFDoA, PFTrA, PFTA, PFOSA, H4PFOS 6–2, FTA 6–2, FTA 8–2, FTA 10–2, FTOH 8–2, FTOH 10–2, N-MeFOSE, N-EtFOSE, N-MeFOSA, 7 H-DoFHpA, 2 H-PFDeA, FTS 8–2, POSF, C6O4): their full names and structures are reported in Table S1. Only 15 PFAS were selected being in at least two of the above-mentioned lists: their main physical-chemical properties and the Relative Potency Factors (RPF) are summarized in Table 1.

2.2. Monitoring campaigns

Three monitoring campaigns have been performed from July 2020 to May 2021 in 4 textile factories that are representative of the textile district: a textile printing, a fabric dyeing and two yarn dyeing factories. For each textile factory, two water streams were sampled: the impregnation bath (one of the steps of the textile finishing where PFAS are mainly employed) and the final discharge of the factories.

Concerning the WWTP, 11 campaigns have been performed between April-July 2020 (3 campaigns) and September 2021-January 2022 (8 campaigns). In detail, the first 3 campaigns have been performed when only urban wastewater was discharged since textile factories were closed due to COVID-19 lockdown. For each campaign, 7 samples were collected (as in Fig. S1): the WWTP inlet, the biological treatment outlet, the ozonation inlet, the WWTP effluent, the biological sludge, the chemical sludge from the lamella clarifier, and the final (biological and chemical) dewatered sludge.

Table 1

List of the 15 selected PFAS, selection criteria and main characteristics: molecular weight (MW), carbon chain length meaning the number of carbon atoms in the molecule, functional group (c: carboxyl group; s: sulfonate group), octanol-water partition coefficient at pH 7.0 (log Dow), acid dissociation constant (pKa), Relative Potency Factor (RPF). As for criteria, the abbreviations stand for: Z = present in the ZDHC list; S = present in the sludge legislation; A = analyzed in previous monitoring campaigns; D = detected in previous monitoring campaigns; L1 = in the list of PFAS measurable by Lab1; L2 = in the list of PFAS measurable by Lab2.

PFAS	CAS Number	Criteria	MW [g/mol]	Carbonchain length	Functional group	Log Dow	pKa	RPF
PFBA	375-22-4	A; S; D; L1; L2	214	4	c	-1.22	1.07	0.05
PFHxA	307-24-4	Z; S; A; D; L1; L2	314	6	c	0.18	-0.78	0.01
PFBS	29420-49-3	Z; S; A; D; L1; L2	300	4	s	0.25	-3.31	0.001
GENX	13252-13-6	L1; L2	347	6	c	0.47	-	0.06
PFPeA	2706-90-3	A; S; D; L1; L2	264	5	c	0.52	0.20	0.03
PFHpA	375-85-9	S; A; D; L1; L2	364	7	c	0.88	-1.36	0.505
PFOA	335-67-1	Z; S; A; D; L1; L2	414	8	c	1.58	-4.20	1
PFHxS	3871-99-6	S; A; L1; L2	400	6	s	1.65	-3.32	0.6
PFOS	2795-39-3	Z; S; A; D; L1; L2	500	8	s	3.05	-3.32	2
PFNA	375-95-1	S; A; D; L1; L2	464	9	c	2.46	-0.17	10
PFDA	335-76-2	S; A; D; L1; L2	514	10	c	2.98	-	7
PFUnA	2058-94-8	A; S; L1; L2	564	11	c	3.37	-	4
PFDoA	307-55-1	S; A; L1; L2	614	12	c	4.39	-	3
C6O4	119093-41-9	L1; L2	357	6	c	-	-	0.06
PFOSA	754-91-6	S; A; L1; L2	499	8	s	4.97	-	-

2.3. Lab- and pilot-scale experiments

As for textile wastewater, pressure-driven membrane separation has been tested, assessing microfiltration (MF), nanofiltration (NF) and their combination. A SEPA CF Cell cross-flow filtration unit was used in "feed and bleed" mode, under pressure and filtration rate conditions comparable to full-scale ones. The tested MF membrane (SEPA PVDF MF - JX Suez, 0.3 μm cut-off) was operated at two pressure and flowrate levels (10 bar/150 L/h, 15 bar/250 L/h). The tested NF membrane (NF90 PA-TFC Sepa Steriltech, 150–200 Da cutoff) was operated at pressure of 10 bar and flowrate of 250 L/h. Three tests were carried out on a mixture of the final discharges collected from the 4 monitored textile factories, with no PFAS spike. Textile wastewater samples were characterized by 23.9 ± 1.1 g/L COD, 13.4 ± 1.5 g/L TSS (Total Suspended Solids), 1589 ± 4.9 μS/cm conductivity, pH of 4.4 ± 0.08, sum of PFAS (only PFBA, PFHxA and PFPeA were detected) equal to 9.5 ± 1.32 μg/L.

In the municipal WWTP, several column tests have been performed to assess adsorption on activated carbon (AC) in combination with ozonation as pre-treatment. In detail, the selected AC (AquaSorb MP25, Jacobi Group) was a commercial bituminous, meso/macro-porous AC physically activated and characterized by an Iodine Number of 1000 mg/g. The best PFAS removal efficiencies were obtained when the AC was contacted with the ozonated water collected after the full-scale ozonation. Adsorption was tested at pilot scale with no PFAS spike. The pilot adsorber was sized through the constant-diffusivity downscaling equation (Crittenden et al., 1987): the Empty Bed Contact Time (EBCT) and the AC particle size were set to 3.4 min and 0.5 mm respectively, simulating the performance of full-scale granular AC adsorbers with 20 min EBCT and an AC particle size of 1.7 mm, respectively. The adsorber column (diameter of 10 cm) was filled with 1.6 L of sieved AC, fed downflow with a flowrate of 0.45 L/min, and on-line monitored for pressure drop to stop operation and allow the manual activation of the filter back-washing. Details are reported in Section S2 in Supplementary Material. The test lasted 77 days, corresponding to 33,000 bed volumes (BV), being BV the ratio between the treated water volume up to time instant *t* and the volume of the AC bed in the adsorber column. The influent and effluent to the column were sampled once a day by an automatic sampler: overall, 22 samples of influent and 22 of effluent were analyzed. The ozonated water was characterized by: 30 ± 1.4 mg/L COD, pH of 7.8 ± 0.07, 1401 ± 3.9 μS/cm conductivity, 16.0 ± 0.73 absorbance at 254 nm (UVA$_{254}$), 6850 ± 940 AU total fluorescence, and sum of PFAS (only PFBA, PFBS, PFHxA, PFPeA, PFHpA, PFOA and PFOS were detected) equal to 0.2 ± 0.11 μg/L.

2.4. Analytical methods

Water pH was measured through a Hach-Lange HQ440d pH-meter (MOD), COD and TSS trough APAT CNR IRSA methods. UV spectra and UVA$_{254}$ were measured with a quartz full transparent cuvette of 1 cm optical path using a *Hach Lange* UV–VIS Detector DR6000 spectrophotometer. Fluorescence analyses were performed using the same cuvette in an *Agilent Cary Eclipse* spectrofluorometer, with the following setting parameters: Voltage= 600 V, slit= 5 nm, scanning speed= 120 nm/min (fast).

For PFAS analyses, both for the textile factories and the WWTP samples, the applied method is based on the CEN/TS 15968 methods (widely used in the textile sector) and the ISO 25101 method, both relying on a LC-MS/MS technique in the electrospray ionization (ESI) negative. The sample extraction and concentration process involves the following steps: (i) spike of a certain volume of sample with isotopically labeled standards, Internal Standards (INs) (EPA-5371IS from Wellington, mixture of a mass-labelled: 13 C M2PFOA, 13 C MPFOS and 2 H N-methyl.perfluorooctane-sulfonamidoacetic acid d3-N-MeFOSAA) (10–40 ng); (ii) conditioning of the WAX (Weak Anion Exchange) solid-phase extraction (SPE) cartridge sorbent; (iii) solid-phase extraction of the spiked sample (see step i); (iv) after rinsing with acetate buffer and drying the cartridge, the elution is carried out with methanol and a 1% ammonia/methanol solution; (v) evaporation of the eluate up to a 0.5 mL and addition to solvent in a vial of PP of 700 μL in order to have the same INs concentration as the calibration standards. For each batch of samples the quality control samples are analyzed: procedural blank, spiked matrix samples, laboratory control samples, duplicates. Samples were extracted and concentrated using WAX (Weak Anion Exchange) solid-phase extraction (SPE) cartridges: the mechanism of the WAX cartridges is mixed-made, both ion-exchange and reverse phase. Afterwards, 700 μL of the samples were spiked in a PP vial with 10 μL of a diluted internal standard mixture (EPA-5371IS from Wellington, mixture of a mass-labelled: 13 C M2PFOA, 13 C MPFOS and 2 H N-methyl.perfluorooctane-sulfonamidoacetic acid d3-N-MeFOSAA). PFAS were analyzed using liquid chromatography mass spectrometry (LC-MS/MS, Ultimate 3000 UHPLC from Thermo Fisher with TSQ Quantum Access MAX Triple Quadrupole Mass Detector and with a Hypersil Gold aQ column 100 mm × 2.1 mm, particle size 1.9 mm, PEEK tubing and a delay column with the same phase) and evaluated by a linear calibration built daily and in any case for each batch with 8 calibration points in the range of 0.1 to 20.0 μg/L (PFAS calibration Standard mixture from Agilent and Gen X from Ultrascientific) and correlation coefficients for all the analytes greater than 0.99. The mobile phases were: (A) water with 5 mmol/L ammonium acetate (pH 3.6) and (B) methanol with a

Table 2

Main features of the set scenarios: abbreviation, input data, calculation formulas, assumptions (origin of the data reported in brackets). Abbreviations stand for: $PFAS_L$: Long-chain PFAS; $PFAS_S$: Short-chain PFAS; $PFAS_{IN}$: PFAS in WWTP influent; $PFAS_{EFF}$: PFAS in WWTP effluent; $PFAS_{SLU}$: PFAS in sludge.

Scenario	PFAS concentration in final textile wastewater: $C_{PFAS,TEX}$ [µg/L]	WWTP effluent load [g/year]	Assumptions and inputs
BAU	0,31	$PFAS_{EFF} = PFAS_{IN} − PFAS_{SLU}$	[concentration and trend derived from monitoring –Section 3.1]
TEX-RED	$0,31 \bullet (1-\eta_{RED})$	$PFAS_{EFF} = PFAS_{IN} − PFAS_{SLU}$	$\eta_{RED} = 35\%$ (percentage reduction of textile PFAS) [from literature]
TEX-REPL	$PFAS_L = 0$; $PFAS_S = (1 − cl,t) \bullet 0,31 + p \cdot cl,t \bullet 0,31$	$PFAS_{EFF} = PFAS_{IN} − PFAS_{SLU}$	$cl,t = 8,3\%$ (long-chain PFAS percentage in textile wastewater) [from monitoring -Section 3.1]; $p = 2$ (short to long-chain PFAS ratio in textile substitution) [from literature]
TEX-MEMB	$0,31 \bullet (1-\eta_{MF+NF})$	$PFAS_{EFF} = PFAS_{IN} − PFAS_{SLU}$	η_{MF+NF} = average removal of each PFAS through MF+NF [from lab-experiments -Section 3.2]
RED-MEMB	$PFAS = PFAS_{(TEX-RED)} \bullet (1-\eta_{MF+NF})$	$PFAS_{EFF} = PFAS_{IN} − PFAS_{SLU}$	
REPL-MEMB	$PFAS_L = 0$; $PFAS_S = PFAS_{S(TEX-REPL)} \bullet (1-\eta_{MF+NF})$	$PFAS_{EFF} = PFAS_{IN} − PFAS_{SLU}$	
WWTP-AC	0,31	$PFAS_{EFF} = (PFAS_{IN} − PFAS_{SLU}) \bullet (1-\eta_{GAC})$	η_{GAC} = average removal of each PFAS operating the MP25 AC after ozonation for 100,000 BV [from lab-experiments -Section 3.2]
RED-AC	$PFAS = PFAS_{(TEX-RED)}$	$PFAS_{EFF} = (PFAS_{IN} − PFAS_{SLU}) \bullet (1-\eta_{GAC})$	
REPL-AC	$PFAS_L = 0$; $PFAS_S = PFAS_{S,(TEX-REPL)}$	$PFAS_{EFF} = (PFAS_{IN} − PFAS_{SLU}) \bullet (1-\eta_{GAC})$	
RED-MEMB-AC	$PFAS = PFAS_{(TEX-RED-MEMB)}$	$PFAS_{EFF} = (PFAS_{IN} − PFAS_{SLU}) \bullet (1-\eta_{GAC})$	
REPL-MEMB-AC	$PFAS_L = 0$; $PFAS_S = PFAS_{S,(TEX-REPL-MEMB)}$	$PFAS_{EFF} = (PFAS_{IN} − PFAS_{SLU}) \bullet (1-\eta_{GAC})$	

flow of 0.3 mL/min at 40 °C. The separation started with 40% (B), changed to 99% (B) in 10 min and was kept constant for another 5 min. Quantification was conducted using precursor-product ion multiple reaction monitoring (MRM) transitions. The limit of quantification (LOQ) of the analytical method is equal to 0.01 µg/L for all the PFAS. For each batch of samples, the quality control samples (procedural blank, calibration check in the batch, spiked matrix sample, duplicate) were analyzed to ensure accuracy of the analytical process.

2.5. Scenario analysis

Eleven scenarios have been simulated over the Como textile district (42 textile factories, urban wastewater, one municipal WWTP) for comparing the effectiveness of the prevention and reduction strategies. The conceptual diagram of each scenario is reported in Fig. S3, while the scenarios description is reported below:

(i) *BAU* (Business As Usual): scenario on PFAS spread in the environment as in the current situation).

(ii) *TEX-RED* (PFAS reduction in textile processes): scenario on voluntary action to reduce the total PFAS amount employed in textile processes by 35%.

(iii) *TEX-REPL* (PFAS replacement in textile processes): scenario on voluntary action to replace all long-chain PFAS with short-chain PFAS in textile production processes, considering that on average twice the amount of short-chain PFAS is needed to produce textiles with performance comparable to those obtaining using long-chain PFAS (Davies et al., 2014; MIDWOR, 2018).

(iv) *TEX-MEMB* (PFAS removal by membrane separation applied to textile wastewater): scenario on treatment of textile wastewater by membrane separation, with micro- and nanofiltration in series (MF+NF).

(v) *RED-MEMB* (PFAS reduction in textile processes and PFAS removal by membrane separation applied to textile wastewater): scenario combining *TEX-RED* and *TEX-MEMB* scenarios.

(vi) *REPL-MEMB* (PFAS replacement in textile processes and PFAS removal by membranes separation applied to textile wastewater): scenario combining *TEX-REPL* and *TEX-MEMB* scenarios.

(vii) *WWTP-AC* (PFAS removal by adsorption on activated carbon applied to the WWTP effluent): scenario on treatment in the municipal WWTP, inserting an AC adsorption after ozonation, operated for 100,000 BV (equal to one year operation).

(viii) *RED-AC* (PFAS reduction in textile processes and PFAS removal by adsorption on activated carbon applied to the WWTP effluent): scenario combining *TEX-RED* and *WWTP-AC* scenarios.

(ix) *REPL-AC* (PFAS replacement in textile processes and PFAS removal by adsorption on activated carbon applied to the WWTP effluent): scenario combining *TEX-REPL* and *WWTP-AC* scenarios.

(x) *RED-MEMB-AC* (PFAS reduction in textile processes and PFAS removal by membrane separation applied to textile wastewater and PFAS removal by adsorption on activated carbon applied to the WWTP effluent): scenario combining *TEX-RED*, *TEX-MEMB* and *WWTP-AC* scenarios.

(xi) *REPL-MEMB-AC* (PFAS replacement in textile processes and PFAS removal by membrane separation applied to textile wastewater and PFAS removal by adsorption on activated carbon applied to the WWTP effluent): scenario combining *TEX-REPL*, *TEX-MEMB* and *WWTP-AC* scenarios.

Each scenario was projected over the whole textile district, extending experimental data collected on the 4 monitored textile factories to the other 38 factories. PFAS occurrence in the various streams and mass balances characterizing each scenario were set up based on monitoring data, experimental data and literature data, in detail:

Table 3

Main characteristics (flowrate, PFAS load and concentration, detected PFAS and mass percentage of long-chain PFAS over the total PFAS mass) for the monitored streams.

| Matrix	Flowrate [m³/d]	Load sum PFAS [mg/d]	Concentration sum PFAS	Detected PFAS	Long-chain PFAS percentage [%]
Urban wastewater	14,240 ± 1169	7213 ± 1563	506 ± 95 ng/L	PFBA, PFBS, PFHxA, PFPeA, PFHpA, PFOA, PFOS	21.6
Textile wastewater	6765 ± 969	1963 ± 1089	309 ± 207 ng/L	PFBA, PFHxA, PFPeA, PFHpA, PFOA	8.3
Urban + Textile wastewater	21,490 ± 1046	9448 ± 1324	439 ± 79 ng/L	PFBA, PFBS, PFHxA, PFPeA, PFHpA, PFOA, PFOS	17.4
Dewatered Sludge	8385 kg$_{SS}$/d	77.6	9255 ng/kg$_{SS}$	PFHxA, PFOA, PFOS, PFDeA, PFUnA,	89.4
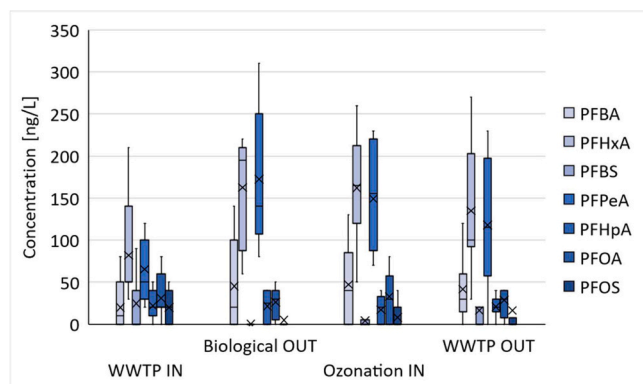
Fig. 1. Boxplot of the concentrations of the 7 detected PFAS at each sampling point within the WWTP water treatment train in the 11 campaigns.

- monitoring data (reported in Section 3.1) were used to build the BAU scenario,
- experimental data (reported in Section 3.2) were used to generate the scenarios comprising the application of removal processes (membrane separation for textile wastewater and activated carbon adsorption for the effluent of the municipal WWTP),
- literature data (reported in Section 1) were used to generate the scenarios related to the prevention actions (reduction and replacement scenarios).

All the formulas and inputs are summarized in Table 2, while average measured values of flowrates and PFAS concentrations in both textile wastewater and urban wastewater are reported in Table 3. The percentage of the total PFAS load leaving the WWTP through the dewatered sludge was 0.8%. In scenarios without additional treatments in the WWTP, PFAS concentrations were assumed stable along the treatment train, as observed during the WWTP monitoring campaigns (see Fig. 1 and Section 3.1). While for scenarios simulating the presence of treatment processes, PFAS removal efficiencies observed at the lab- and pilot-scale were assumed.

2.6. Environmental risk assessment for PFAS mixture

The environmental risk due to the concentration of individual PFAS in the WWTP effluent was calculated according to the methodology reported in the EU Directive proposal for the Environmental Quality Standards (EQS) (EU Parliament, 2022): the concentration of each i-th PFAS was multiplied by its relative potency factor (RPF$_i$, Table 1) to convert it into equivalent PFOA concentration. The total PFAS concentration, as PFOA equivalent, was calculated according to Eq. 1:

$$C_{PFAS,TOT} \left[\mu g \bigg/ L \; PFOA - eq \right] = \sum_{i=1}^{15} C_{PFAS,i} \cdot RPF_i \tag{1}$$

To calculate the environmental risk due to the PFAS discharged into the receiving surface water, total PFAS concentration in the Seveso river was estimated from the concentration in the WWTP effluent (calculated

by Eq. 1), assuming a dilution factor (DF) equal to 0.1, which is the default value for risk assessment. The risk of PFAS mixture was calculated through the risk quotient (RQ), in Eq. 2, that is the ratio between the total PFAS concentration, as PFOA equivalent, expected in the river and the EQS for surface water reported by the proposed EU Directive (0.0044 µg/L of PFOA-eq) (EU Parliament, 2022):

$$RQ_{PFAS,TOT} = \frac{C_{PFAS,TOT} \cdot DF}{EQS} \tag{2}$$

3. Results and discussion

We assessed the effectiveness of various prevention and removal strategies aimed at reducing the environmental risks associated with the dispersion of PFAS in the environment. The comparison of the outputs of several what-if scenarios offers a comprehensive examination of the potential impact of the prevention and removal strategies at the district level, while recommending the optimal strategy to be put in place. The assessment of the prevention and removal strategies relies on a combination of experimental data, field monitoring and available literature about PFAS substitution. These sources serve as inputs for the scenario analyses, which involve comparing the current environmental risk (referred to as the "business as usual" or BAU scenario) with 10 alternative scenarios, each representing different mitigation measures: (i) reduction of the amount of PFAS use; (ii) the replacement of long-chain PFAS with short-chain PFAS; (iii) the introduction of specific removal processes on selected streams, and (iv) combinations of the previous actions. Scenarios were compared in terms of both PFAS mass discharged into receiving surface water on yearly basis (calculated as in Table 2) and associated environmental risk (calculated with Eq. 2).

3.1. Monitoring campaigns for PFAS fate assessment

The performed monitoring campaigns were useful to evaluate which PFAS are present in urban wastewater and in textile wastewater, at which concentration (Table 3) and their fate in the WWTP (Fig. 1). The PFAS load for textile wastewater was estimated as the difference between PFAS load in the 8 campaigns when both urban and textile wastewaters were discharged into the sewer and the average load of the 3 campaigns when only urban wastewater was discharged.

In general, it can be noted a constant presence of PFAS, despite the commitment of textile factories to phase out these compounds. In the WWTP influent a maximum of 7 (PFBA, PFBS, PFHxA, PFPeA, PFHpA, PFOA, PFOS) out of 15 PFAS was detected, with an average sum concentration of 0.44 µg/L. These PFAS are all present in the urban wastewater, while PFBS and PFOS were never detected in textile wastewater. In urban wastewater 21.6% of the total PFAS mass was constituted by long-chain PFAS (PFOA and PFOS), while textile wastewater is mainly characterized by short-chain PFAS (91.7% of the total PFAS). The mixed wastewater entering the WWTP (66% of the total flowrate) has an average percentage of long-chain PFAS of 17.4%.

PFAS load exiting the WWTP through the dewatered sludge (77.6 mg/d) is 0.8% of the average PFAS load in the wastewater (urban and textile) entering the WWTP (9448 mg/d). Some PFAS show good affinity for dry matter, mostly long-chain PFAS (about 90% of the total

PFAS) and the major contribution is given by PFOS (about 60% of the total average concentration of PFAS in the dewatered sludge). This higher contribution long-chain PFAS and particularly of PFOS in dewatered sludge is in agreement with literature (Alder and Van Der Voet, 2014; Coggan et al., 2019; Gómez-Canela et al., 2012; Pan et al., 2016). Short-chain PFAS, except for PFHxA, show little affinity for dry matter, not being detected in the sludge in any monitoring campaign, while they are found at higher concentrations than the long-chain PFAS in water samples. Compared to the limits on PFAS concentration in sludge set in different European countries, the sum of all PFAS (9.25 µg/kg SS on average comprising 4 PFAS) is far below the Danish limit on the sum of 22 PFAS (400 µg/kg SS). However, it is important to highlight that the Danish limit includes 10 PFAS that were not analyzed in this study (PFPS, PFHxS, PFHpS, PFNS, PFDS, PFUnS, PFDoS, PFTrS, PFOSA, 6:2 FTS) while it excludes 2 PFAS that were measured in our study (Gen-X and C6O4). So it would be useful to have additional measurements on the same set of PFAS listed in the regulation, in order to evaluate the situation. However, the sum of the concentrations of the 4 critical PFAS for sludge (PFOA, PFOS, PFNA, PFHxS), equal to 6.94 µg/kg SS is close to the Danish limit of 10 µg/kg SS. Therefore, it is important to monitor these compounds in the sludge, especially when planned to be used in agriculture applications.

Focusing on PFAS trend along the WWTP (Fig. 1), it can be noted the relevant variability in PFAS concentration over the various monitoring campaigns. This variability is mainly due to the weekly and seasonal variable contribution of the textile factories discharges to the wastewater entering the WWTP. Besides, some of the PFAS, especially those with shorter chains, were measured in higher concentrations in the final effluent than in the untreated wastewater entering the WWTP, with a median increase from 5% to 200% depending on the compound. The average PFAS concentration and its variability increase mainly in the biological treatment, in agreement with what has been reported in the literature (Coggan et al., 2019; Gallen et al., 2017; Pan et al., 2016; Schultz et al., 2006; Stasinakis et al., 2013). At the outlet of the ozonation, a decrease of the average concentration by 5% was observed for PFPeA, PFHxA and PFOS, while no variations were observed for PFBA, PFHpA and PFOA. Overall, it is possible to state that PFAS sum does not change in a conventional WWTP. The outcomes coming from the field monitoring were used to build the BAU scenario and are the basis for some assumptions adopted in the scenario analysis, as reported in Table 2.

3.2. Experimental studies for setting the removal strategies

Fig. 2 shows the experimental results on removal efficiencies achieved by membrane separation on textile wastewater, and adsorption on the ozonated effluent of the WWTP.

As for tests on MF and NF on textile wastewater, the volumes and macro-characteristics (COD, conductivity) obtained in the three tests are shown in Table S2, together with the overall filtration times. The removal of COD reached 60%. Looking at the combination of the MF+NF compared to MF alone, MF+NF rejection increased to > 90% for COD.

As for PFAS removal (Fig. 2a), the rejection performance in the test with the MF1 operating at 10 bar/150 L/h (removals between 60% and 92% depending on the PFAS) was better than in the test with MF2 operating at 15 bar/250 L/h (removals between 40% and 70% depending on the PFAS), with higher rejections for compounds with higher molecular weight. Previous research studies have highlighted the limitations of low-pressure membranes, like microfiltration membranes, in effectively retaining PFAS dissolved in the liquid phase. These membranes, with an average cut-off size of about 100 nm, have been reported to struggle with PFAS retention due to the smaller effective diameter of these molecules. However, Thompson et al. (2011) found a marginal decrease in PFAS concentration following ultrafiltration, that is characterized by a bigger pore-size compared to microfiltration. This has been associated with the removal of suspended and colloidal particles rather than direct molecular retention. Therefore, the high removal efficiencies observed in microfiltration tests within this study are likely a result of the nature of textile wastewater, characterized by substantial contents of colloidal and suspended particles (see average data in Section 2.3 and Table S2), on which PFAS are partly sorbed. Moreover, the obtained rejection values could be influenced by the closure errors that occur in the mass balances (Fig. S2), ranging from 15% to 40% in MF1 test at 10 bar/150 L/h, 10–34% in MF2 test at 15 bar/250 L/h; while the closure error is < 20% in the NF test. A reason for positive closure errors, meaning that the mass at the outlet is less than the mass at the inlet, might be PFAS adsorption onto piping and membranes. Hence, the amount of PFAS adsorbed in the membranes after filtration was also measured, but the detected quantity, although not negligible, was not enough to compensate for the closing errors.

The removals obtained by NF, fed with the microfiltration permeate from the MF1 test at 10 bar/150 L/h, are of the order of 80%, independently of the analyzed PFAS. Overall, the rejection obtained with the MF+NF is 88% for PFBA and 90% for the other compounds and for the sum of the PFAS.

As for the tests on activated carbon adsorption on the municipal WWTP effluent, the removal efficiency for each PFAS at a specific bed volume was calculated as the ratio between the mass removed and the total mass that entered the adsorber up to that specific bed volume. Adsorption efficiency values for the single PFAS are shown in Fig. 2b: they improve with PFAS chain length. This can be explained by the
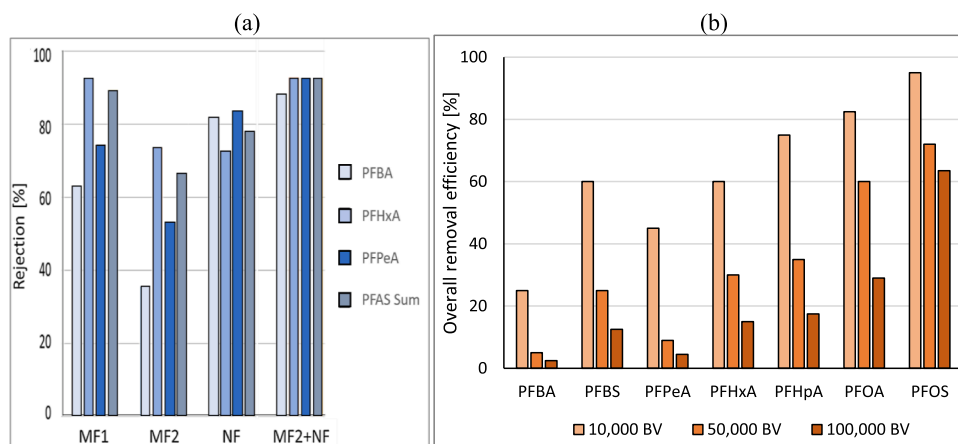

Fig. 2. Results of the lab- and pilot-scale tests: (a) PFAS rejections by MF and NF membranes applied to the textile wastewater; (b) PFAS removal efficiency by adsorption on activated carbon at three different bed volumes (BVs) applied to ozonated WWTP effluent.

higher hydrophobicity (higher Log Dow, Table 1) for longer chain-PFAS, in accordance with previous literature studies (Cantoni et al., 2021; Park et al., 2020). In particular, PFBA removal efficiency varies from 25% to 2.5% as a function of the adsorber operation time from 10,000 BV to 100,000 BV, while PFOS removal efficiency at these bed volumes is, respectively, equal to 95% and 63.5%. The 100,000 BV was assumed as operation time for the scenario analysis, since it corresponds to a one-year full-scale operation for the analyzed WWTP. After 100,000 BV operation time, the average removal efficiency varies from 2.5% to 17.5% for short-chain PFAS and from 29% to 63.5% for long-chain PFAS.

3.3. Scenario analysis and risk assessment for intervention prioritization

The *BAU* scenario describes the Como textile district in its current situation, based on the monitoring campaigns performed at the textile factories level and in the municipal WWTP, as described in Section 3.1. The *BAU* scenario supports the evaluation of the main sources and fate of PFAS and the estimation of the overall environmental risk currently posed by the WWTP final effluent discharged in the Seveso river. Then, the other investigated scenarios describe possible intervention strategies to limit the spread of PFAS in both treated wastewater and sludge, comparing them in terms of expected risk reduction. For each scenario, the outputs of the mass balance are summarized in Table 4 and Fig. S3, where the PFAS masses (as PFAS sum) present in each stream on yearly basis are reported. In addition, the overall environmental risk posed by the PFAS mixture present in the WWTP final effluent discharged in the Seveso river is reported for each scenario in Table 4. The contribution of each PFAS to the estimated risk is shown in Fig. 3, highlighting the compliance with the proposed EQS for surface water (EU Parliament, 2022), being the risk quotient (RQ) threshold equal to 1. In fact, the mass load is a common output for the scenario analysis, but here the novel aspect lies on the conversion of PFAS concentrations in risk generated to the environment by the PFAS mixture.

Both in the current scenario (*BAU*) and in the simulated intervention scenarios, the contribution of textile wastewater to the total mass load of PFAS entering the WWTP is significantly lower than the contribution given by urban wastewater. Currently, in the *BAU* scenario textile wastewater contributes 23% of the total PFAS input load. Looking at the overall environmental risk in the receiving body, in the *BAU* scenario the risk is equal to 2.1, indicating that the overall concentration of PFAS, expressed as PFOA-equivalents, estimated in the receiving water is 2.1
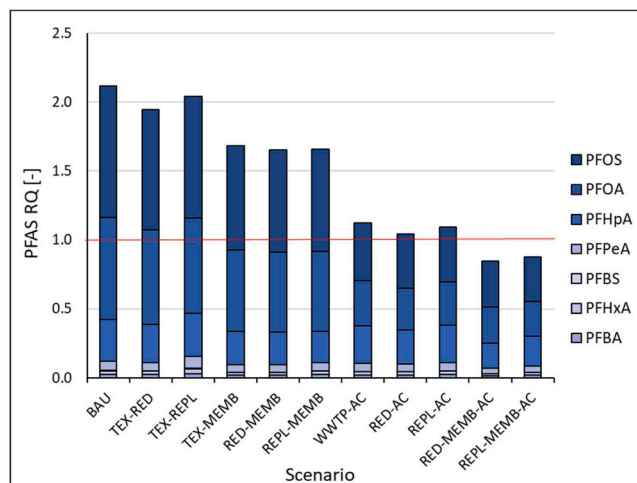

Fig. 3. Overall environmental risk due to PFAS mixture for different intervention scenarios. The red line represents the risk threshold RQ= 1, which corresponds to the proposed EQS for PFAS in surface water.

times higher than the EQS envisaged by the proposed European Directive. Notably, the largest contributions to the risk are attributed to PFOS and PFOA ($RQ_{PFOS}=0.95$, $RQ_{PFOA}=0.74$), followed by PFHpA ($RQ_{PFHpA}=0.3$). It must be stressed that PFOS and PFOA are mainly present in urban wastewater with respect to textile wastewater, as emerged in the monitoring campaign. The power of the proposed approach is clear when we compare the outputs in terms of mass load and risk: even though the concentrations of long-chain PFAS are lower than those of short-chain ones (Table 3 and Fig. 1), their greater ecotoxicity (higher RPF values, Table 1) plays a crucial role in the overall risk. This result emphasizes the importance to evaluate current and future scenarios focusing on the risk and not on the single PFAS concentrations and discharged load, because indications about the most effective strategies, which should then be prioritized, can be markedly different, as stressed in other studies related to emerging contaminants mixture risk assessment both in drinking water and wastewater discharge and reuse practices (Ianes et al., 2023; Penserini et al., 2023, 2022).

Concerning the evaluation of the effectiveness of mitigation actions, described in the 10 investigated scenarios, both at the source (textile

Table 4

Annual total PFAS load [g/year] for each stream in the textile district for each simulated scenario. A color scale is used to highlight critical values: PFAS load from green (minimum) to dark red (maximum).

		Scenario										
		BAU	*TEX-RED*	*TEX-REPL*	*TEX-MEMB*	*RED-MEMB*	*REPL-MEMB*	*WWTP-AC*	*RED-AC*	*REPL-AC*	*RED-MEMB-AC*	*REPL-MEMB-AC*
Load PFAS [g/year]	Urban wastewater	2,599	2,599	2,599	2,599	2,599	2,599	2,599	2,599	2,599	2,599	2,599
	Textile wastewater	765	498	829	77	50	83	765	498	829	50	83
	IN WWTP	3,364	3,096	3,428	2,675	2,649	2,682	3,364	3,096	3,428	2,649	2,682
	OUT BIO	3,364	3,096	3,428	2,675	2,649	2,682	3,364	3,096	3,428	2,675	2,649
	OUT CHEM-PHYS	3,337	3,072	3,400	2,654	2,627	2,660	3,337	3,072	3,400	2,654	2,627
	OUT O₃	3,337	3,072	3,400	2,654	2,627	2,660	3,337	3,072	3,400	2,654	2,627
	OUT GAC	-	-	-	-	-	-	2,652	2,441	2,787	2,088	2,122
	WWTP Effluent	3,337	3,072	3,400	2,654	2,627	2,660	2,652	2,441	2,787	2,088	2,122
	Dewatered Sludge	27	25	27	21	21	21	27	25	27	21	21

factories) and at the municipal WWTP, it refers to their potential in reducing the environmental risk below the threshold value of 1. It should be mentioned that the complete exclusion of PFOA and PFOS would reduce the overall risk RQ to 0.41, below the threshold, but this will be a gradual process due to the out of stock of the already-manufactured textiles which will be used for futures years, or of textiles manufactured in countries in which there are no regulations or ban for PFAS.

Among the intervention scenarios specifically related to mitigation actions at textile factories level, the 35% voluntary reduction of the total PFAS used in textile processes (*TEX-RED* scenario) leads only to an 8% reduction of PFAS load in the WWTP final effluent, and the environmental risk does not decrease below 1. This is due to the lower PFAS load and lower long-chain PFAS percentage in the textile factories wastewater compared to the urban wastewater that is the main source for PFAS in the studied district. The replacement of all long-chain PFAS used in textile processes with short-chain PFAS (*TEX-REPL* scenario) entails a deterioration in the quality of the WWTP final effluent in terms of PFAS concentration compared to the *BAU* scenario. This is a confirmation of the potential effects of PFAS substitution described in the "Staff Working Document on PFAS" report of the European Commission in 2020. In fact, although short-chain PFAS are characterized by lower eco-toxicities than long-chain PFAS (RPF values<1, Table 1), the use of a greater amount of these compounds causes the overall risk to be higher (RQ=2) than the one in *TEX-RED* scenario. This output stresses the importance of case-specific evaluation of the replacement of long-chain PFAS with short-chain PFAS in textile processes. Textile wastewater treatment through membrane separation (*TEX-MEMB* scenario) involves a 20% reduction of the PFAS load in the WWTP final effluent, but the environmental risk does not decrease below 1. This is due to the fact that PFAS in textile wastewater are mainly short-chain PFAS having a lower eco-toxicity with respect to long-chain PFAS, that still remain unremoved in this scenario. The scenarios combining the reduction or replacement of PFAS in textile processes and the simultaneous application of a membrane separation (MF+NF) treatment (*RED-MEMB* and *REPL-MEMB* scenario) do not lead to a significant benefit compared to *TEX-MEMB* scenario.

About the scenario comprising an upgrade of the WWTP through an adsorption process downstream the ozonation step (*WWTP-AC* scenario), it reduces the overall PFAS load in the WWTP final effluent by 20% compared to the *BAU* scenario (2652 g/year from 3337 g/year). This percentage is comparable to the one obtained in *TEX-MEMB* scenario, however, in the *TEX-MEMB* scenario the RQ was equal to 1.7, while in *WWTP-AC* scenario the environmental risk (RQ=1.1) is halved compared to the *BAU* scenario. From the experimental outcomes it is possible to state that a more frequent activated carbon regeneration (every 95,000 BV, corresponding in this case to an operating time of 11.5 months) is required to guarantee a risk value below the RQ threshold of 1. It is interesting to note that, although adsorption removal efficiencies (2.5%−63.5%) are lower than the ones of MF+NF (90%), the overall PFAS risk reduction is higher in *WWTP-AC* scenario than in *TEX-MEMB* scenario. As stressed previously, this is because membrane separation is applied only on textile wastewater, which contributes only for the 23% of the total PFAS input load and contains mainly short-chain PFAS, while adsorption in the WWTP treats both textile and urban wastewater, the latter containing greater amount of long-chain PFAS which display higher affinity towards activated carbon and whose eco-toxicity is more critical (higher RPFs compared to short chain PFAS, Table 1). Once again, these results stress the importance of the application of risk assessment, which considers the eco-toxicological effect of each PFAS, with respect to the sole evaluation of the mass balances and the expected concentrations in the wastewater, for the meaningful comparison and prioritization of different interventions.

Scenarios combining the reduction or replacement of PFAS in textile processes and the simultaneous application of adsorption downstream the ozonation in the municipal WWTP (*RED-AC* and *REPL-AC* scenario)

do not lead to a significant benefit compared to *WWTP-AC* scenario.

The most comprehensive scenarios, combining the reduction or replacement of PFAS in textile processes, the treatment of the textile wastewater through membrane separation in textile factories, and the upgrade of the WWTP with an activated carbon adsorption downstream the ozonation (*RED-MEMB-AC* and *REPL-MEMB-AC* scenario), reduce the PFAS load in the WWTP final effluent by 37% compared to the *BAU* scenario. In these scenarios, risks below 1 are reached. However, RQ values between 0.1 and 1 are still to be carefully managed as they imply a potential risk (Baken et al., 2018), especially because the performed risk estimation does not take into consideration possible variability and uncertainties of the input variables.

4. Conclusions

In this study we present an integrated scenario analysis to evaluate mitigation actions regarding PFAS spread in the environment. In detail, a textile district was the case study, where PFAS monitoring campaigns were combined with lab- and pilot-scale tests of the most credited removal processes (adsorption on activated carbon and pressure-driven membrane separation), and data used for environmental risk assessment. Such integrated analysis has proved to be helpful in supporting the identification of the optimal combinations of prevention and treatment interventions to be applied at different level in the textile district, to effectively reduce the environmental risk. Results highlight that risk assessment provides more valuable information about the effectiveness of the investigated mitigation actions, compared to the sole estimation of the expected concentrations through mass balances, as conventionally happens in scenario analyses. In fact, this study showed that taking into account the toxicity of each PFAS is crucial to have a proper estimation of the current risk, its apportionment among the various sources and a sound indication about where to act to reduce such risk. Actually, to fulfill the final goal of reducing PFAS spread into the environment, multiple stakeholders have to take actions. In fact, a risk below the acceptable threshold can be obtained only by combining: (i) PFAS reduction/replacement in the textile processes, (ii) treatment of wastewater at textile factories through membrane separation prior to the discharge in the municipal sewer, and (ii) WWTP upgrade through an activated carbon adsorption downstream the ozonation step.

Summarizing, the approach developed in this study can serve as a valuable template for tackling complex environmental issues and can be adapted and customized to address a wide range of environmental challenges and case studies. The methodology's adaptability lies in its versatility, making it transferable to other geographical locations, industrial sectors, and environmental challenges. By tailoring the analysis to specific scenarios and assessing the efficacy of mitigation strategies in terms of risk, this approach can effectively inform decision-making and policy development. Whether addressing pollutants beyond PFAS or dealing with different environmental issues, this approach offers a valuable framework for stakeholders to identify optimal combinations of prevention and treatment measures.

Finally, to have a more comprehensive assessment and prioritization of the proposed interventions, the integrated scenario analysis here proposed could be combined to a cost analysis (capital and operating), and an overall environmental impact assessment through Life Cycle Assessment (LCA) methodologies.

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CRediT authorship contribution statement

BC: Conceptualization, Methodology, Formal analysis, Writing – original draft, Writing – review & editing. **GB**: Conceptualization, Writing – review & editing, Funding acquisition. **EB**: Resources, Validation, Writing – review & editing. **FM**: Methodology, Validation, Writing – review & editing. **MA**: Conceptualization; Methodology, Validation, Writing – review & editing.

Declaration of Competing Interest

All authors confirm the absence of any financial and personal relationships with other people or organizations that could inappropriately influence (bias) their work.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.psep.2024.01.005.

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