

PFAS and waste water

Current knowledge from the European water sector and the case for control-at-source



PFAS are a group of contaminants that have gained increased attention recently as they can bio-accumulate, and may cause problems to humans and the environment. Studies have identified waste water

treatment plants as a pathway for PFAS to the environment and PFAS in waste water are on the agenda as a growing concern in several EU Member States, especially in relation to drinking water resources.



Summary

PFAS are a group of contaminants that have gained increased attention due to their potential to bio-accumulate, their environmental persistence, potential toxicity and, for many of them, high water solubility. They have been found in all environmental compartments, including wildlife and humans. Studies have identified waste water treatment plants as a pathway for PFAS to the environment. PFAS are a growing concern especially in relation to water resources used for the abstraction of drinking water.

Waste water treatment plants (WWTP) are currently not equipped to completely remove PFAS from waste water. PFAS are very resistant to biological treatment, and as a result, can end up in the WWTP effluent or in sewage sludge. Moreover, the very persistent perfluoroalkyl acids (PFAA, such as PFOS and PFOA) appear to be produced during the biological treatment process in the WWTP following the degradation of polyfluoroalkyl precursor compounds.

The applicability of advanced (industrial) technologies to remove PFAS from urban waste water, based on physical separation or destruction techniques, is currently being investigated in pilot projects in laboratories. The results indicate that the large scale removal of PFAS in urban WWTP will not be economically nor environmentally viable.

Preventing PFAS from entering WWTP through control-at-source measures is the only way to avoid PFAS from being released to the (aquatic) environment through this pathway. A ban of all non-essential uses might be a first step. However, a coherent regulatory framework with clear instruments covering all persistent, mobile, toxic (PMT) and very persistent, very mobile (vPvM) substances needs to be in place to prevent and limit the emission of these substances to the water cycle.





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1. About PFAS

Poly- and perfluoroalkyl substances (PFAS) are a large and diverse group of man-made fluorinated compounds. Due to their unique active surface properties and very high chemical and thermal stability, PFAS have been widely used in many applications of our daily life, such as in consumer goods like textiles, cosmetics and food packaging. They are largely applied in firefighting foams.

According to the OECD (2018) there are about 4,730 PFAS substances known today. The molecules most studied and used in the different industrial sectors are PFOA (perfluorooctanoic acid, CAS no. 335-67-1) and PFOS (perfluorosulfonic acid, CAS no. 1763-23-1).

In the last decades, PFAS have gained increasing attention as a group of environmental contaminants of emerging concern, based on growing evidence of the adverse effects on human health and the environment. PFAS are recognised as highly persistent organic pollutants under natural environmental conditions, due to their extremely strong carbon-fluorine bonds (Vecitis et al., 2009). They have the potential to bioaccumulate, can be toxic and often have high water solubility and mobility.

PFAS have been found in water, soil/sediment, air, sludge, waste and ice caps globally, as well as in wildlife and humans (Houdi et al., 2006; Valsecchi et al., 2013). PFAS have also been detected in drinking water due to the contamination of groundwater or surface water and in the absence of limit values for these substances in water resources. According to the EFSA (European Food Safety Authority) (2018)¹ "Food contributed to 67–84% of the median total intake for PFOA and 88–99% for PFOS using different exposure factors such as the dust ingestion rate. Similarly, the median relative contribution from drinking water varied between 0.57% and 0.68% for PFOS, and 9.1% and 11% for PFOA".

For most PFAS, there is very little knowledge on their real toxicity, so it is difficult to assess the potential risks of exposure for humans and the environment. An EEA briefing note summarises the known main risks associated with PFAS (2019). PFOS was banned in 2006 in the EU and worldwide, following the UN Stockholm Convention on POPs (persistent organic pollutants) (2004). PFOS has been included in the EU POP Regulation since 2010 (recast 2019/2021). This regulation has also covered PFOA and their precursors (Regulation 2020/748) since 2020. This means that the production, import and use of PFOS, PFOA and their precursors are no longer allowed in the EU. A number of other PFAS are on the candidate list of SVHCs (substances of very high concern) under the REACH Regulation. Inclusion on the SVHC list is the first step in the procedure for authorisation (inclusion in annex XIV) or restriction of their use (under annex XVII). This substance approach to specific PFAS, unfortunately, means that banned or nearly banned PFAS are being replaced by other PFAS with largely similar features but a slightly different chemical structure (often with shorter C-chains, making them more mobile). The best examples are the GenX-substances (perfluor-2-propoxypropane acid) and PFBS (perfluorobutane sulfonic acid), as the health and environmental outcomes for these chemicals are also largely unknown, arousing similar

¹ EFSA Journal 2018; 16(12):5194, p.42.



concerns. In 2019 GenX was added to the SVHC list for the first time based on its persistent, mobile and toxic properties.

PFOS and their derivatives were indicated under the Environmental Quality Standards Directive (EQS; 2013/39/EU) as a priority hazardous substance with an environmental quality standard limit value of respectively 0.00065 µg/l (AA-EQS) and 36 µg/l (MAC-EQS) for inland surface waters and 0.00013 µg/l (AA-EQS) in seawater. Member States are due to report on compliance with the PFAS EQS by 2021.

As part of the revision of the priority substances list, discussions are ongoing to include additional EQS for PFAS in surface water.

For the first time, the new EU Drinking Water Directive (2020/2184) introduced a limit value for the 20 most important PFAS in drinking water as follows: sum of PFAS 0,1µg/l (sum of all PFAS listed in annex III of DWD) or PFAS total 0.5µg/l (totality of all PFAS). PFAS have been included in the groundwater voluntary watch list and were proposed for the update of the Groundwater Directive.

Member States pushed the Commission to develop a PFAS Action Plan under the Green Deal, to eliminate all non-essential uses of PFAS (June 2019). The resultant Chemicals Strategy for Sustainability addresses the risks posed by very persistent chemicals under the Green Deal and supports its Zero Pollution ambition for a toxic-free environment.

In September 2020, the EFSA published a new food safety threshold for the main PFAS that accumulate in the body (total of PFOA, PFOS, PFNA, PFHxS)². The threshold – a group tolerable weekly intake (TWI) of 0.0044µg PFAS per kilogram of body weight – is part of a scientific opinion on the risks to human health arising from the presence of PFAS in food. Applying this threshold value in environmental risk assessments can have an impact on limits for PFAS in surface water, drinking water and/or soil.

The EurEau position paper on 'PFAS in the urban water cycle'³ points to the serious threat of PFAS to the environment and human health, and the need to apply the Principles of Control-at-Source and the Polluter Pays as the preferred way to drastically reduce their emissions. A 'Briefing note on PFAS and drinking water'⁴, collecting cases from members, shows that following the recast of the Drinking Water Directive, water consumers will have to pay for the extra treatment needed, unless the above principles are fully applied.

This 'Briefing note on PFAS and waste water' outlines the situation of PFAS for waste water operators. PFAS in waste water are currently not directly regulated but are already a growing concern in some Member States.

Additional information on the use of PFAS and analytical methods is summarised in the annexes of this briefing note.

² PFAS in food: EFSA assesses risks and sets tolerable intake | (europa.eu).

³ EurEau [Position paper on PFAS in the urban water cycle](#).

⁴ EurEau [Briefing note on PFAS and drinking water](#).



2. Key terminology

Poly- and perfluoroalkyl substances (acronym: PFAS) are a group of aliphatic compounds that consist of a carbon (C) chain in which the hydrogen (H) atoms are all (perfluorinated alkyl substances) or partly (polyfluorinated alkyl substances) replaced by fluorine (F) atoms (except those in the functional groups). As such, the C-chain contains at least one perfluoroalkyl moiety $C_nF_{2n+1}^-$.

The **perfluoroalkyl substances** mainly refer to the perfluoroalkyl acids (PFAA). Based on the length of the fluorinated carbon chain, short and long chain PFAS can be distinguished.

'Long chain' refers to:

- ~ perfluorocarboxylic acids (PFCAs) with carbon chain lengths **C8** (according to Buck et al. generally accepted) and higher, including perfluorooctanoic acid (PFOA);
- ~ perfluoroalkane sulfonic acids (PFSAs) with carbon chain lengths **C6** and higher, including perfluorohexane sulfonic acid (PFHxS) and perfluorooctane sulfonate (PFOS); and
- ~ PFAA precursors of these substances that may be produced or present in products (many polyfluoroalkyl substances) and can degrade to PFAA in humans or the environment.

PFAA represent the non-degradable - or often called - 'terminal' PFAS. The long-chain PFAS accumulate in humans, animals, sediment/soil, whereas the short-chain PFAS accumulate in the environment, due to their persistency and high mobility in water and air (German EPA, 2017).

The polyfluoroalkyl substances contain at least one perfluoroalkyl moiety $C_nF_{2n+1}^-$. Thus, whereas the general concept of 'polyfluorination' embraces compounds containing 'scattered' multiple F atoms, as well as 'grouped' ones, only those polyfluorinated substances having at least one perfluoroalkyl moiety $C_nF_{2n+1}^-$ belong to the PFAS family. The non-fluorinated part can be transformed/degraded biologically or chemically into perfluoroalkyl substances.

Many authors also use the acronym 'PFC' (perfluorocarbon), and in many different ways. As a result, the meaning of PFC is unclear and not well defined. However, both PFC and PFAS belong to the overall family of fluorinated chemicals and hence are too closely related to share a common acronym. The scientific community adopted the use of the term PFAS as an acronym for 'perfluoroalkyl and polyfluoroalkyl substances' and the term PFC exclusively for 'perfluorocarbons', hydrocarbons in which all H atoms are replaced by F atoms, so only containing the elements C and F, and in which functional groups are absent. (OECD, 2013; Buck et al., 2011).

PFAS are a growing concern because of their persistence in the natural environment, and tendency to accumulate in water resources. PFAS are frequently added to a variety of industrial and consumer products for their water and oil-repelling abilities (Lau et al., 2007).

Polyfluoroalkyl substances have been manufactured for over 50 years and, because of their unique properties of repelling both water and oil, have been used all over the world. These compounds have emerged as a new class of environmentally persistent pollutants, which



have been widely used in different applications, such as surfactants and surface protectors in carpets, leather, paper, food containers, fabric, upholstery, fire-fighting foams, floor polishes, and shampoos (Kissa 2001). Perfluorooctane sulfonate (PFOS, $C_8F_{17}SO_3^-$) and perfluorooctanoate (PFOA, $C_7F_{15}COO^-$) - the terminal breakdown end-products of polyfluoroalkyl substances - have been detected in a wide array of environmental matrices including biota (Giesy et al. 2001), water (Taniyasu et al. 2003), and sediment and sludge (Higgins et al. 2006; Sinclair and Kannan 2006). In waste water, it was observed that PFOS and PFOA were ubiquitous in waste water treatment plants (WWTPs) effluents (Sinclair and Kannan 2006; Schultz et al. 2006). The substances have extremely poor environmental biodegradability (persistent, P) and many of them accumulate in living organisms (bioaccumulating, B) and are toxic (T). There is a lack of overall knowledge of highly fluorinated substances that would allow to prevent further pre-existing health and environmental problems from building up and persisting for a long time: that it why, it is important to map out the occurrence and use of these substances

3. Role of waste water treatment in the life cycle of PFAS

PFAS are released to the environment through multiple pathways. Direct emissions of PFAS during the manufacturing and industrial processes, as well as the subsequent use and disposal of consumer products containing PFAS (as additives or impurity), play a major part in how they enter waste water. They can also enter the cycle through atmospheric deposition and subsequent street runoff. A Swedish study found that primary emissions (13 PFAAs and perfluorooctane sulfonamide) into the water cycle indicated that PFAS in influent waste water to Bromma WWTP may also originate from indirect recirculation, via tap water, of PFAS that have been present in the environment for several years or decades up to 86% of the total PFAA load for PFBS (Filipovic and Berger, 2015). This portion was less significant for the longer chain PFAAs with more than eight fluorinated carbons and for FOSA. This could be because these compounds are less water soluble and show higher K_d values, making them less susceptible to environmental recirculation in the aqueous phase. The complexity of direct 'new' releases and recirculation of 'historic' PFAS already present in the environment highlights the complexity of the problem and the urgent need to take strict control-at-source measures.

Several studies have identified WWTPs as one of the major pathways of PFAS to the aquatic environment, but data on concentrations in urban WWTP influents, effluents and sludge is scarce (Huset et al. 2008; Ahrens et al. 2009; Möller et al. 2010; Sun et al. 2011; Filipovic and Berger, 2015; Lam et al. 2016, Sahlin, 2017). A Europe-wide study of 90 WWTP effluents, in 27 countries, identified PFOA, PFHpA and PFOS in 90% of the waters (Loos et al. 2012). The discharge of waste waters is one of the principal routes of entry of PFOS into surface waters, with waste water being a major contributor to river flows. There is also the potential for the contamination of soil and water resources by the application of contaminated sewage sludge (solid waste of the waste water treatment process) to agricultural land. A study in Bayreuth, Germany, found that all the PFOA was discharged into the river, while about half of the PFOS was retained in the sewage sludge (Becker et al



2010). However, waste water treatment plants were shown to have a negligible contribution to PFOS transport to the Baltic Sea (Filipovic et al., 2013). Treated landfill leachates, on the other hand, showed to be an important source of PFAS to surface waters.

3.1. Biological waste water treatment

The above mentioned studies indicate that PFAS are only partly removed by current urban WWTPs. Conventional urban (and many industrial) WWTPs are mostly so-called 'activated sludge' plants. The removal of pollutants is based on the activity of microbiological organisms, in fact similar to natural self-purification processes. PFAS are very resistant to biological degradation (called 'recalcitrant') and are hence not readily degraded with activated sludge but are rather transferred to the effluent and partly also to the sludge.

Studies indicate that during the conventional waste water treatment process polyfluoroalkyl compounds, acting as precursors, can be degraded into shorter perfluoroalkyl compounds (PFAA) (Hamid 2016), but these PFAA are non-degradable and not efficiently removed during the waste water and sludge processes (Schultz et al., 2006; Guo et al., 2010; Arvaniti et al., 2012; Stasinakis et al., 2013; Ahrens et al. 2011; Sun et al. 2011). In some cases, the concentrations of specific PFAS in treated waste water are higher compared to raw sewage (Loganathan et al., 2007; J. Yu et al., 2009; Arvaniti et al., 2012; Stasinakis et al., 2013), confirming their formation via biodegradation of precursor compounds. So far, very few studies have focused on examining the potential transformation of precursor compounds (e.g., 8:2 FTOH, 6:2 FTOH, 6:2 FTS) to PFAS by activated sludge (Wang et al., 2005, 2011; Zhao et al., 2013).

A study (Guerra et al. 2014) investigating the fate of 21 perfluoroalkyl acids across 20 Canadian WWTPs found that the effects of various treatment processes on the formation of PFAS differed statistically. In terms of high to low formation of PFAS, the ranking was: advanced biological treatment with nutrient removal (median: 160%) > aerated/facultative lagoon (150%) > secondary biological treatment (55%) > chemically assisted primary treatment (-1%) (Guerra et al. 2014). Greater formation of PFAAs (PFBA, PFHpA, PFNA and PFHxA) were observed with higher hydraulic retention times and higher temperatures in the summer, possibly due to increased associated microbial activities (Guerra et al. 2014).

The fate of several PFAS in a typical WWTP was predicted in a study using mass balances and calculated distribution coefficients values (K_d) (Arvaniti et al., 2014). Without taking into account the possible formation of PFAS during treatment, Arvaniti et al. (2014) estimated that PFCAs with fewer than ten carbon atoms are expected to be detected mainly in treated waste water, while the critical K_d values for achieving high (>60%) removal of PFAS via primary and secondary sludge is 2,500 L kg⁻¹. Furthermore, they calculated that a small but not negligible amount of the initial load ($\leq 3\%$) of less hydrophobic PFAS (e.g., PFOA) is expected to end up in leachates of sludge treatment processes and transfer to the inlet of WWTPs.

The reuse of treated sludge (biosolids) on land is considered to be a source of PFAS pollution in soil (Ghisi et al., 2019), surface water and groundwater (Zareitalabad et al. 2013) and the food chain (Lee et al. 2014). Sorption into the sludge through hydrophobic partitioning



could be an important mechanism governing PFAS removal during conventional waste water treatment (Sinclair and Kannan, 2006). Literature data shows that longer PFCA and PFOS exhibit higher sorption capacity compared to short chain compounds (Arvaniti et al., 2012, 2014; Zhang et al., 2013, Filipovic and Berger, 2015). In some studies (Zhou et al., 2010; Zhang et al., 2013; Arvaniti et al., 2014), the role of different parameters such as pH, temperature, ionic strength and cation types on PFAS sorption has been examined. According to the published results, it seems that PFAS sorption decreases with increased pH values (Zhou et al., 2010; Zhang et al., 2013; Arvaniti et al., 2014) and temperature (Zhou et al., 2010).

3.2. Advanced technologies to remove PFAS from waste water

Today, there is no economically or environmentally viable alternative to preventing PFAS from entering the WWTPs other than control-at-source measures.

Several of the available treatment technologies for water (Ross I. et al., 2018), already applied by drinking water suppliers, are currently under investigation at lab/pilot levels on waste water, especially industrial waste water and/or specific types of (waste) water. Only a few of these technologies are in different phases of practical application (Nijhuis, personal communication). These might have to be applied in exceptional and extreme situations for waste water treatment. Selecting appropriate treatment solutions for urban waste water applications will be further complicated by the more complex water composition and higher flows as compared e.g. to drinking water. Selected technologies under investigation are described here.

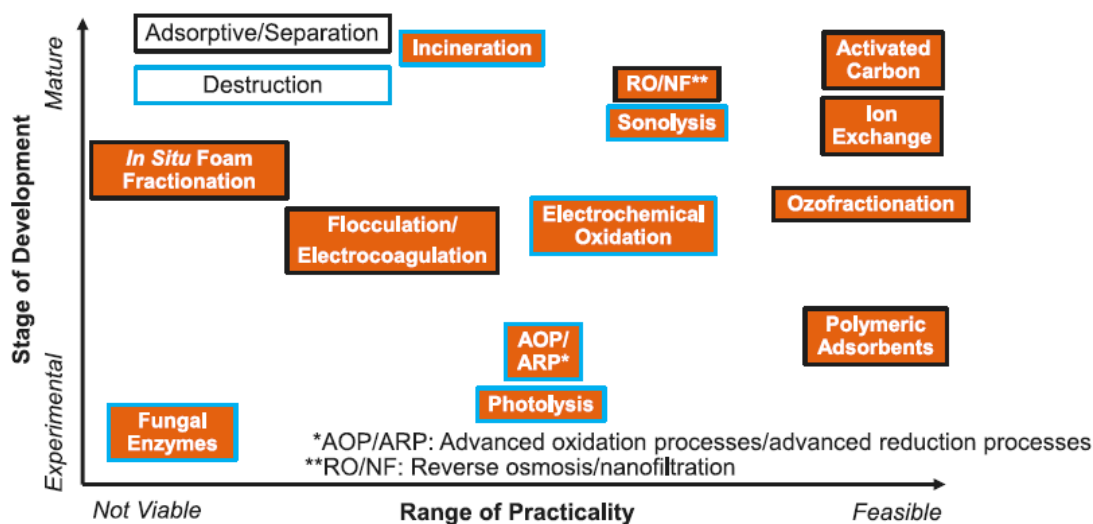


Figure 1: Theoretical PFAS treatment technologies for waste water (Ross I. et al., 2018)

3.2.1. Physical adsorption/separation technologies

Physical separation technologies include adsorption to powdered (PAC) or granular (GAC) activated carbon or to ion-exchange resins (IEX), and separation with high-pressure



membrane filtration, such as nanofiltration (NF) or reverse osmosis (RO). The yield of removal with each of these technologies largely depends on the concentration of the PFAS in the influent as well as on specific operation conditions.

Adsorption

PFAS – mainly in industrial waste water - have been shown to react with powdered activated carbon (PAC) or granular activated carbon (GAC), resulting in the removal of part of the PFAS. Residence time and concentration of other organic ions have an impact on the removal efficiency (yields of >70% have been reported). GAC is currently the best technique for the longer-chain ones like PFOA; it is less effective for the short-chain PFAS. There is, however, a risk that the GAC will be depleted quickly, as they do not degrade biologically after adsorption. Adsorption needs reactivation of the adsorbents and extra post treatment.

Ion-exchange (IEX) is an upcoming alternative especially for the shorter-chain PFAS. The adsorbents (resins) are more expensive, but improved operational conditions may make the process more cost-effective in the long term. Residence time and concentration of inorganic ions have an impact on the removal efficiency.

Active cokes, having a larger pore size than GAC, are being investigated in aerated fixed bed reactors to remove PFAS but also other micropollutants by a combination of adsorption and biological degradation/regeneration. The first applications are promising.

Coagulation was shown to work well to remove PFAS from groundwater. A combination of electrocoagulation with activated carbon for further polishing gave good results.

Separation techniques

Both nanofiltration (NF) and reversed osmosis (RO), two high-pressure membrane filtration techniques, are effective for PFAS removal (up to >70%, depending on transmembrane pressure and membrane fouling by scaling with inorganic compounds), whereas ultrafiltration has no sufficient effect (0-20%).

Foam (oxo)fractionation is a possible alternative.

More than 70% removal through physical separation technologies has been observed in isolated studies. The drawback of these physical separation technologies is, besides being expensive, that they do not destroy PFAS but only remove it from the contaminated water and into PFAS-contaminated waste streams (adsorbents or concentrated brines). The disposal of these streams may pose secondary pollution risks and problems.

Very rough estimates of minimum costs associated with these technologies may be derived from pilot or full scale installations for the removal of other micropollutants (such as pharmaceuticals) from waste water⁵. For GAC these already amount up to €0.3/m³, whereas estimates for the use of membrane technologies may be up to four times higher.

⁵ EurEau Briefing Note on Treating Micropollutants at the WWTP.



3.2.2. Destructive technologies

There are also destructive technologies for permanently degrading PFAS, based on high-energy incineration or advanced oxidations including electrochemical oxidation, microwave thermal treatment, photolytic degradation, pyrolysis, and sonochemistry. These extreme PFAS degradation pathways are very costly, especially when the volume and the flowrate of PFAS waste water are large.

Oxidation - Reduction

Ozone and AOP (advanced oxidation processes) appear not to be suitable for the complete breakdown of PFAS. The PFAS do not react with ozone due to the fluorine and electronegative groups. There is only a partial transformation.

Chemical reduction looks promising, but was thus far only investigated at lab scale.

Incineration

The only currently possible solution for permanently degrading PFAS is destruction by incineration at 1200°C, which is not possible everywhere. Other advanced oxidation solutions are being explored, including electrochemical oxidation, microwave thermal treatment, photolytic degradation, pyrolysis, and sonochemistry. These extreme PFAS degradation pathways are very costly, especially when the volume and the flowrate of PFAS waste water are large.

Estimations of costs for destructive technologies based on lab/pilot experiments are given in Table 1 below. Specific energy demands and costs for the degradation of PFOA and PFOS are given in pictures 2 and 3 (Nzeribe et al., 2019).

Table 1: Summary of cost estimation of physico-chemical processes for PFAS degradation

Process	PFAS	C _{initial} (mg/L)	k (min ⁻¹)	t ₅₀ (min)	EE/O (kWh/m ³)	Energy cost (US\$/m ³)	Chemical requirement (Kg/m ³)	Chemical cost (US\$/m ³)	Total cost (US\$)	References		
Activated Persulfate	Microwave and Iron Activated Persulfate	PFOA	100	0.0147	157	9595	864	0.10	0.09	864	Lee et al. (2010)	
	Microwave-hydrothermal Induced Persulfate		105.17	0.0112	206	8178	736	0.60	0.9	737	Lee et al. (2009)	
	Microwave- Activated Persulfate		105.17	0.0137	168	4653	419	0.60	0.9	420	Lee et al. (2012)	
Electrochemical Oxidation	Ti/RuO ₂ /stainless steel	PFOA	0.01	0.0062	371.4	860	77	0	0	77	Schaefer et al. (2015)	
		PFOS	0.02	0.0057	404.0	935	84	0	0	84		
	Nanocrystalline BDD	PFOA	15	0.0200	115	180	16	0	0	16	Schaefer et al. (2017)	
		PFOS	10	0.0062	373	500	45	0	0	45		
Ultrasound	Ti/SnO ₂ -Sb	PFOA	100	0.0270	27.7	132	12	0	0	12	Lin et al. (2012)	
	Ultrasound	PFOA	10.00	0.0320	72	4852	437	0	0	437	Moriwaki et al. (2005)	
		PFOS	10.00	0.0160	144	20091	1808	0	0	1808		
	Ultrasound and Sulfate	PFOA	49.69	0.0313	74	568	51	16.62	0.83	52	Lin et al. (2015)	
Photochemical	Ultrasound and Periodate	PFOA	70.39	0.0222	104	475	43	10.35	26	69	Lee et al. (2016)	
	Ultrasound	PFOA	0.10	0.0410	56	179	16	0	0	16	Vecitis et al. (2008)	
		PFOS	0.10	0.0270	85	273	25	0	0	25		
	UV- Fe ³⁺	PFOS	24	0.0067	344	377	34	0.03	0.0004	34	Wang et al. (2008)	
ARPs	UV-Pb-TiO ₂	PFOA	50	0.0012	1985.0	4411	397	0.5	2	399	Chen et al. (2016)	
	UV/Cu-TiO ₂	PFOA	50	0.0031	742.8	4735	426	0.5	2	428	Chen et al. (2015)	
	UV/Fe-TiO ₂	PFOA	50	0.0015	1535	20120	1811	0.5	2	1813		
	UV-Pt-TiO ₂	PFOA	60	0.0121	190	1188	107	0.5	100	207	Li et al. (2016)	
	UV-Pd-TiO ₂	PFOA	60	0.0073	316	4441	400	0.5	50	450		
	UV-Fe ³⁺	PFOS	10	0.0012	1985	576	52	0.03	0.07	52	Jin et al. (2014)	
	UV-KI	PFOA	10.35	0.0295	78.1	24	2	0.04	0.8	3	Qu et al. (2014)	
		PFOA	10.35	0.0073	315	87	8	0.05	1	9	Qu et al. (2010)	
	Plasma	Laminar jet with bubbling (LJB) [†]	High-efficiency	PFOA	8.28	0.0740	31	28	3	0	3	Stratton et al. (2017)
			High rate	PFOA	8.28	0.0120	192	75	7	0	7	
DC plasma within oxygen bubbles			PFOA	41.40	0.0300	77	1073	97	0	0	97	Hayashi et al. (2015)
			PFOA	64.60	0.0318	72	15	1.36	0	0	1.36	Takeuchi et al. (2014)

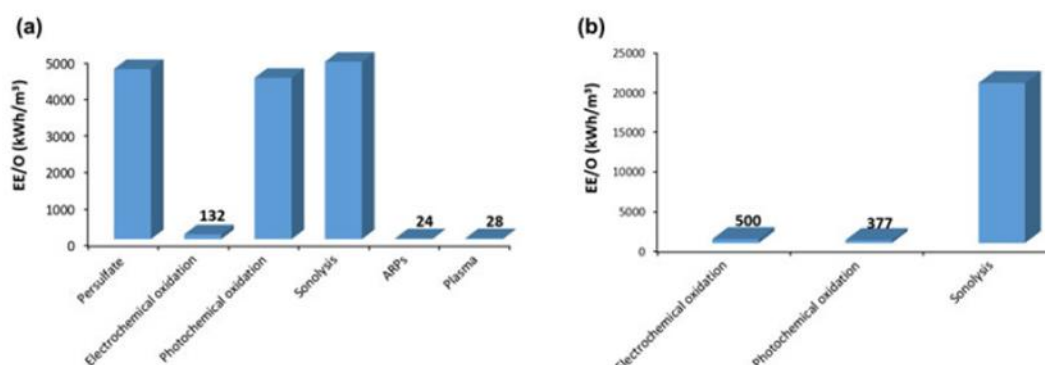


Figure 2 Energy demand of physico-chemical treatment processes for (a) PFOA and (b) PFOS degradation (Nzeribe et al., 2019)

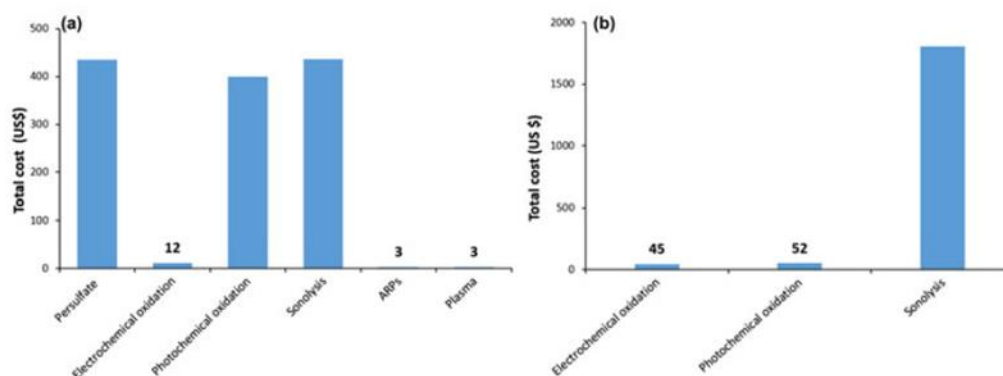


Figure 3: Cost of physico-chemical treatment for (a) PFOA and (b) PFOS degradation (Nzeribe et al., 2019)

4. The way forward for urban waste water treatment

Applying available (industrial) technologies to remove PFAS in urban WWTPs must not be considered as an option to abate the global problem of PFAS.

Technologies to remove/destroy PFAS at WWTPs are not ready. The few available lab/pilot studies indicate that additional treatment steps would require very high investments and operational costs. It is therefore not realistic to put the burden of preventing the release of PFAS to the environment on waste water operators. The affordability of water services would be seriously affected.

Furthermore, applying these technologies would lead to a significant increase in the environmental footprint of WWTPs (energy use, resource use, GHG emissions, toxic waste etc.).

Tackling PFAS should be part of a broader coherent regulatory framework, with clear instruments, covering all persistent, mobile, toxic (PMT) and very persistent, very mobile (vPvM) substances including PFAS.



In the short-term, it is necessary to implement strict source control actions on PFAS emissions through the waste water pathway:

- ~ Restricted use of PFAS under REACH (banning all non-essential uses);
- ~ Application of very stringent industrial discharge standards and/or disconnection of industrial discharges into urban sewer systems.

PFAS are one group of suspected PMT/vPvM substances and tackling PFAS. Therefore actions should be part of a more general solution within the European chemicals legislation. This would provide clear instruments to prevent, monitor and take measures towards third parties against pollution of water and water resources in a more coherent way⁶.

If, in exceptional cases, WWTPs must implement additional treatment steps to degrade/remove PFAS, extended producer responsibility⁷ must apply.

5. Case Studies

5.1. The Netherlands

The Netherlands have been confronted with PFAS in surface water, air, soil and dredging for several years. This is partly due to the presence of the Chemours factory in Dordrecht.

For some time now, a lot of efforts are aimed at gaining control and direction over PFAS and (potentially) very harmful substances. The focus is source control, with the aim of completely eliminating PFAS and (potentially) very harmful substances in the long term. A national cooperation programme is being set up for PFAS in water, which includes research into the sources. The Netherlands has set up a policy on how to deal with PFAS in soil and dredging and is working on an integrated policy approach for very harmful substances and substances of emerging concern in water, soil and air.

The Dutch Water Authorities (DWA) continue to advocate for source control measures and promoting substitutes that are less harmful to the environment. An additional purification step at the WWTP is not considered as the preferred way forward if substances such as PFAS are tackled at source.

Research is being conducted into PFAS in influent, effluent and sludge at the WWTPs to gain insight into the amount of PFAS that ends up in the WWTP as a result of industrial discharges and household discharges. The results are expected at the beginning of 2021.

5.2. Italy

In 2013, it became known that approximately 127,000 people in the Veneto Region of Italy were exposed to PFAS through their drinking water. The contamination resulted primarily from the industrial emissions of a chemical plant in the area that produces these substances. It had affected the groundwater, surface water and drinking water in 21 municipalities in an area covering more than 150 square kilometres in the south-western part of the province of

⁶ EurEau [Briefing note on Moving Forward on PMT and vPvM Substances](#).

⁷ [Deloitte – Study on the Feasibility of Applying EPR to Micropollutants and Microplastics Emitted to the Aquatic Environment from Products during their Life Cycle](#) (2020).



Vicenza (Veneto region, Italy). Acque del Chiampe Spa, the publicly-owned company for the integrated water management in the region, dealt with this PFAS contamination.

In April 2016, the Italian national health authority (Istituto Superiore di Sanità) defined limits specifically in the Veneto Region for the PFAS substances in waste water effluents discharges into surface waters, being equal to the Italian limits of PFAS in drinking water:

- ~ PFOS: 0.03 µg/L
- ~ PFOA: 0.5 µg/L
- ~ PFBA: 0.5 µg/L
- ~ PFBS: 0.5 µg/L
- ~ Other PFAAs: 0.5 µg/L.

In March 2017, the Veneto Region adopted a new authorisation decree for the integrated water service operators, establishing a technical/administrative path for the progressive reduction of the limits on the discharge of PFAS to be achieved by 2020. This decree defined year by year the value of the discharge limits to be respected: the average value is calculated from the controls made by regional environment authorities with reference to the previous solar year values.

Following this, Acque del Chiampe adopted and implemented an action plan to comply with the PFAS limits in waste water.

1. Every industrial user connected to the WWTP received a procedure for the revision of the discharge authorisation. This introduced limits for the PFAA substances. It was requested, in relation to the use of products containing PFAA substances, to provide:
 - ~ The list and type of used products in which PFAS are present (attaching the safety data sheet and the technical data sheet with explicit indication of the type of PFAS and relative% contained);
 - ~ Production phase in which the declared above products are used;
 - ~ Frequency of use of PFAS in the production cycle.
2. Development of analytical method to identify the presence of 'potential' PFAS in the waste water discharge from industries.
3. Request to every industrial user to replace products that contain long chain PFAS (C8) with other with short chain (C4) in every phase where the substitution allows equal qualitative performance to the finished products.
4. Start of laboratory tests to study the best technology to remove the PFAS from waste water.
5. Every industrial user, who abstracted PFAS-affected groundwater from a private well, was requested to install an activated carbon plant to avoid the transfer of these substances to the discharge.
6. Tests on an activated carbon pilot plant to test for verification of yields and technical and economic feasibility of the use of activated carbon at the discharge of waste water treatment plants.
7. Study and evaluation of the possibility of segregation and treatment of waste water with PFASs that cannot be eliminated.



The replacement of products containing 8C long chain PFAS with other compounds containing short chain 4C PFAS, as provided in point n°3 of the Action Plan, resulted on one side, in the decrease of the content of PFOA and in part of the PFOS, but, on the other side, in a temporary increase of the short chain PFAS (PFBA and in particular PFBS).

Although setting discharge limit values identical to the ones indicated by the Istituto Superiore di Sanità (Italian National Health Authority) for water intended for human consumption, and the fact that these limits are applied only in the Veneto Region raised some questions. The Acque del Chiampo management committed to comply with the schedule of reductions of the presence of PFAS in the WWTP effluents.

The action plan has shown its effect. The sum of the quantities of the various PFAA substances discharged by the WWTP, calculated on the basis of self-analysis data, are as follows:

Year	PFBA kg/y	PFBS kg/y	PFOA kg/y	PFOS kg/y	Other PFAS kg/y
2014	1.11	14.50	1.71	0.17	6.69
2015	0,80	18,44	1,14	0,07	8,91
2016	0,72	25,81	0,87	0,07	5,34
2017	0,49	14,86	0,64	0,08	2,01
2018	0,58	14,38	0,70	0,04	1,64
2019	0,42	11,83	0,46	0,08	1,07

The reductions obtained are attributable exclusively to the actions implemented by industrial companies.



Annex 1 - Use of PFAS

PFAS, both polymeric and non-polymeric, have been extensively used in various industries world-wide, due to their properties such as dielectrical properties, resistance to heat and chemical agents, low surface energy and low friction properties, etc. The highly stable carbon-fluorine bond and the unique physicochemical properties of PFAS make these substances valuable ingredients for products with high versatility, strength, resilience and durability, which provide benefits to manufacturers and consumers.

As described by the OECD (OECD / UNEP, 2013), the most common areas of use of PFAS are:

- ~ Aviation, aerospace and defence;
- ~ Automotive;
- ~ Biocides;
- ~ Cable and wiring;
- ~ Construction products;
- ~ Electronics;
- ~ Energy;
- ~ Fire-fighting;
- ~ Household products;
- ~ Medical articles;
- ~ Metal plating (hard metal plating and decorative plating);
- ~ Oil and mining production;
- ~ Paper and packaging;
- ~ Polymers manufacturing;
- ~ Semiconductors;
- ~ Textiles, leather, carpets, apparel and upholstery.

PFAS on the international market are found in a large number of fluoroorganic groups (Table 1). One large group comprises different types of PFAS-containing polymers. The most common polymer type is (meth)acrylate-based. A second major group comprises fluorosurfactants, principally various sulfonamide derivatives. Other major PFAS groups include phosphates, alkanes, esters, sulfonic acids (surfactants), carboxylic acids, silicones/siloxanes, (meth)acryl monomers, iodides, sulfonamides, thiols, etc. (KEMI, 2015).

Table 2: Chemical grouping of PFAS found on the global market and the number of different substances in each group (KEMI, 2015).

Fluoro group	Number of substances
fluorinated (meth)acrylate polymers	234
N-alkyl perfluoroalkyl sulfonamides	226
poly/perfluorinated polymers	173
poly/perfluorinated phosphoorganics	143
polytetrafluoroethylene (PTFE)	137
poly/perfluorinated alkanes/alkenes	120



poly/perfluorinated sulfonic/sulfinic acids	93
poly/perfluorinated carboxylic acids	93
other poly/perfluorinated organics	90
poly/perfluorinated ethers	80
poly/perfluorinated esters	69
poly/perfluorinated alkanoyl/sulfonyl chloride or fluorides	68
poly/perfluorinated iodides	64
poly/perfluorinated (meth)acrylates	58
poly/perfluorinated alcohols	56
poly/perfluorinated sulfonamides	52
poly/perfluorinated siloxanes/silicones/silanes/silicates	50
poly/perfluorinated thiols	45
poly/perfluorinated copolymers	35
fluorinated urethanes polymers	33
poly/perfluorinated amines	34
polyfluoro siloxane and silicone polymers	29
poly/perfluorinated ammonium organics	21
poly/perfluorinated naphthalenes	16
poly/perfluorinated oxiranes	14
poly/perfluorinated ethoxylates	8
fluorinated oxetane polymers	8
poly/perfluorinated iodides	4
poly/perfluorinated urethanes	3
perfluoroalkyl sulfonamides	2
polyvinylidene fluoride (PVDF)	2
Total number	2060



Annex 2 - Alternative substances

Since 2002, there has been a trend amongst global manufacturers and downstream users to replace long-chain PFAS, in particular PFOS and PFOA, with alternative chemicals or non-chemical techniques.

Three types of alternatives are available:

- ~ **substances with shorter per- or polyfluorinated carbon chains:** various substances have been developed that may be used for replacement of many uses of long-chain PFAS (eg. GenX);
- ~ **non-fluorine containing substances:** are available for some applications, but may not work as well as long-chain PFAS, particularly in situations where extremely low surface tension and/or durable oil- and water-repellence is needed;
- ~ **non-chemical techniques:** in some cases, it is possible to use non-chemical techniques to replace long-chain PFAS (OECD, 2013).



Annex 3 - Analytical methods

In scientific literature, there are many articles about methods to analyse PFAS. The choice of analysis technique depends on the type of matrix that needs to be analysed.

PFAS in aqueous matrices

ASTM D7979 – 20 is the standard Test Method for the determination of PFAS in water, sludge, influent, effluent, and waste water by Liquid Chromatography Tandem Mass Spectrometry (LC-MS/MS).

Water samples and sewage treatment plant influent and effluents may be filtered (e.g. on glass fibre filters) to separate solids from the liquid phase. However, filtration can result in adsorption losses of PFAS on the filters. On the other hand, levels can increase by PFAS contamination originating from the filters, as was found in one study for four types of filters (namely glass fibre, nylon, cellulose acetate, and polyethersulfone filters). They applied centrifugation as an alternative for separation the liquid from the solids (S.P.J. van Leeuwen et al., 2007).

In one study, each sample was filtered through 0.7 µm microfibre filters using a micro-filtration assembly under vacuum to remove suspended particulates (Vanisree Mulabagal et al., 2018).

Water samples, and liquid samples in general, are usually pre-concentrated using SPE (solid phase extraction). SPE is the method of choice for liquid samples (e.g. water, blood, serum, plasma), and may be automated in an on-line set-up for (large volume) sample enrichment and sample clean-up. Prior to SPE, sample pre-treatment (filtration or centrifugation for water or protein precipitation for blood) may be required. Liquid-liquid extraction can also be used for liquid samples (and does not require above-mentioned sample pretreatment) (S.P.J. van Leeuwen et al., 2007).

Due to their different polarities, PFAS require different extraction strategies. The ionic PFCAs and PFSAs require moderately polar media (OasisWAX SPE or methanol and acetonitrile) for efficiently trapping of water soluble short-chain (C4–C6) compounds. For longer chains, less polar or non-polar SPE phases (C18 and Oasis HLB) may be applied. When an ion-pairing agent is used that decreases the polarity of the ion pair complex, a non-polar solvent (MTBE) may be used. Non-ionic PFAS may be extracted from the matrix by non-polar media (C18 SPE or hexane). Moderate polar media (Oasis HLB and OasisWAX SPE, a hexane–acetone mixture or acetonitrile) have also been applied for extraction of non-ionic PFAS. Clean-up of water samples is generally performed by a washing step after sample enrichment on the SPE cartridge (S.P.J. van Leeuwen et al., 2007).

As a final clean-up step, extracts may be filtrated over e.g. nylon filters to remove solids from the final extract, but care should be taken to avoid PFAS losses or contamination of the sample extract. Several nylon filter types were tested for removal of solids from the final extract and it was found that some filters contained trace amounts of PFOS and PFOA. A simple methanol washing step reduced the filter originating PFOS and PFOA to below the



LOQ . A nylon syringe filter is commonly applied for water filtration (S.P.J. van Leeuwen et al., 2007).

For the analysis of the sample, usually a mass spectrometry (MS) is carried out. Most laboratories use LC/MS/MS (Liquid chromatography–mass spectrometry). For the newly-identified PFAS, since they are ionic semi-volatile PFAS, LC coupled with triple quadrupole (QqQ) tandem mass spectrometry using electrospray ionization (ESI) is the preferred method to quantify emerging PFAS (Yitao Pan et al., 2020). In one study, an ultra-high performance liquid chromatography-triple quadrupole mass spectrometry (UHPLCMS/ MS) was used for the analysis (Vanisree Mulabagal et al., 2018).

After obtaining the suspected MS spectra, the next step is to propose a reasonable formula based on the exact mass within given mass errors. Generally, mass error is controlled below 5 ppm for modern HRMS (high resolution mass spectrometry). The predicted formula is further checked based on isotopic patterns. Comparing the formula between molecular ions and fragments can further reduce the number of potential molecular formulae. The exact mass, MS/MS fragments, and isotopic patterns of adducts and dimers further support the predicted molecular formula. Finally, the structure is elucidated by the MS/MS spectra. The structure is confirmed with authentic standards (if possible) or information from chemical databases (Yitao Pan et al., 2020).

A study has also proposed a method to measure PFAA precursors, by using hydroxyl radical to oxidize precursors to PFCA products. By comparing PFCA concentrations before and after oxidation, the concentrations of chain length-specific PFAA precursors are inferred. It's an alternative to combustion ion chromatography method (Erika F. Houtz et al., 2012).

PFAS in solid matrices

ASTM D7968 - 17a is the standard Test Method for the determination of polyfluorinated compounds in soil by Liquid Chromatography Tandem Mass Spectrometry (LC-MS/MS).

Solid matrices require a pre-treatment, consisting in filtration, or centrifugation or drying. When designing extraction techniques for these matrices, electrostatic and hydrophobic interactions should be taken into account. Medium polar to polar solvents are most successful (S.P.J. van Leeuwen et al., 2007).

The extraction of emerging PFAS in abiotic solid matrices (e.g., soil and sediment) is often based on solid-liquid extraction (SLE). Extractions are usually conducted with the aid of ultrasonication in multiple cycles to better disperse the sample matrix and improve extraction efficiency. Polar organic solvents such as methanol and acetonitrile under mild acidic or basic conditions are sufficient to extract most emerging PFAS. Particular attention should be paid to the extraction of cationic and zwitterionic PFAS in soil and sediment due to their diverse characteristics and organic matter content, which may affect the extraction efficiencies of the compounds (Yitao Pan et al., 2020).

Ruan et al. analyzed n:2 Cl-PFAES, PFSA, and fluorotelomer sulfonates in sewage sludge samples using a single analytical procedure involving extraction with 50 mM sodium hydroxide in acetonitrile followed by dispersive clean-up (Envi-Carb powder added to the



extracts). Similar extraction methods were used for soils and sediments (Gabriel Munoz et al., 2019).

Abiotic matrices (soil, sediment, sewage sludge) can be cleaned-up by addition of Envi-carb (graphitized carbon) and glacial acetic acid. Higgins et al. cleaned their sediment extracts by C18-SPE. After loading the crude sample extract, the cartridge was washed with Milli-Q water and the target compounds were eluted with 4mL methanol (S.P.J. van Leeuwen et al., 2007).

TOPA - Total Oxidisable Precursor Assay

Polyfluoroalkyl substances, more specifically PFAA precursors are difficult to quantify due to lack of analytical standards for measuring them.

Current conventional methods for PFAS analysis allow to analyse a list of around 30 different compounds. There are, however, much more PFAS left undetermined, which might be of (high) risk and can be converted into the persistent perfluorinated alkyl substances (e.g. PFOA) under certain conditions e.g. in the environment. The TOP assay is a hydroxyl radical based oxidation reaction. Precursors are transformed to dead end perfluoroalkylic acids (PFAAs) in such reactions. The evaluation of pre- and post-TOP assay data may therefore offer a clearer view of PFAS being present in specific samples.



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