Universitat de Girona

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DOCTORAL THESIS

UNDERSTANDING TRANSFORMATION OF ORGANIC MICROPOLLUTANTS DURING PLASMA TREATMENT AND ITS ECOTOXICOLOGICAL IMPLICATIONS

Barbara Topolovec

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Understanding transformation of organic micropollutants during plasma treatment and its ecotoxicological implications

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That the doctoral thesis entitled: **“Understanding transformation of organic micropollutants during plasma treatment and its ecotoxicological implications“** presented by **Barbara Topolovec** to obtain a doctoral degree from the University of Girona and University of Ferrara has been completed under our supervison and fullfils the requirments to opt for an International Doctorate (Double Doctorate), being conducted in the framework of a Marie Sklodowska-Curie Actions (MSCA) European Joint Doctorate (EJD) program.

For all intents and purposes, we herbey sign this document

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Mom tati

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Barbara Topolovec [a,b]. Nikola Škoro [c]. Nevena Puač [c]. Mira Petrovic [a,d *] - Pathways of organic micropollutants degradation in atmospheric pressure plasma processing – A review,

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Barbara Topolovec [a,b], Olivera Jovanovic [c], Nevena Puac [c], Nikola Skoro [c], Elisabeth Cuervo Lumbaque [a], Mira Petrovic [a,d *] - Plasma water treatment for PFAS: study of degradation of perfluorinated substances and their byproducts by using cold atmospheric pressure plasma jet

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List of abbrevations and acronyms

Abbrevation	**Meaning**
OMPs	organic micropollutants
EEA	European Environment Agency
PFAS	per- and polyfluoroalkyl substances
AFFF	aqueous film-forming foams
WWTP	wastewater treatment plant
AOP	advanced oxidation process
UV	ultraviolet
NTP	non-thermal plasma
DBD	dielectric barrier discharge
GAC	granular activated carbon
IX	ion exchange resin
TP	transformation products
LC	liquid chromatography
MS	mass spectrometry
QdQ	triple quadrupole
IT	ion-trap
Q-TOF	quadrupole time-of-flight
Q-LIT	quadruple-linear ion trap
UPLC	Ultra-Performance liquid chromatography
ERA	environmental risk assessment
PEC	predicted environmental concentration
PNEC	predicted no effect concentration
PBT	persistence, bioaccumulative and toxic
REACH	Registration, Evaluation, Authorisation and Restriction
EC	European Commission
EU	European Union
EP	European Parliament
ECHA	European Chemical Agency
WHO	World Health Organization
POPs	Persistent Organic Pollutants
LOD	limit of detection
DW	distilled water
TW	tap water
SE	secondary effluent
HRMS	high resolution mass spectrometry
APPJ	atmospheric pressure plasma jet

SMILES	simplified molecular input line entry system
HQ	hazard quotient
RQ	risk quotient
MEC	measured environmental concentration
PNEC	predicted no effect concentration
QSAR	quantitative structure-activity relationship
P	persistence
O	occurrence
B	bioaccumulation
M	mobility
T	toxicity
OECD	the organization for economic cooperation and development
DT50	biodegradation half-life
r.e.	removal efficiency
NOEC	long-term-no-observed effect concentration
CD	Compound Discoverer
PFAS acronyms	**Meaning**
PFCAs	perfluoroalkyl carboxylic acids/Perfluoroalkyl carboxylates
PFSAs	perfluoroalkane sulfonic acids/Perfluoroalkane sulfonates
PFPEs	perfluoropolyethers
PFPrOPrA/FRD-903	2,3,3,3-tetrafluoro-2-(1,1,2,2,3,3,3-heptafluoropropoxy)propanoic acid
FRD -902	(ammonium, 2,3,3,3- tetrafluoro-2-(heptafluoropropoxy) propanoate
PFOS	Perfluorooctanesulfonic acid
PFOA	Perfluorooctanoic acid
PFHxA	Perfluorohexanoic acid
PFHxS	Perfluorohexanesulfonic acid
PFBA	Perfluorobutanoic acid
PFBS	Perfluorobutanesulfonic acid
ADONA	4,8-dioxa-3H-perfluorononanoic acid (parent acido f ADONA)
HFPO-DA	Perfluoro-2-methyl-3-oxahexanoic acid (parent acid of Gen-X)
PFHpA	Perfluoroheptanoic acid
PFPeA	Perfluoropropanoic acid

PFPrA	Perfluoropropanoic acid
F-53B (6:2 Cl-PFESA)	Potassium 9-chlorohexadecafluoro-3-oxanonane-1-sulfonate
6:2 FTS	6:2 Fluorotelomer sulfonic acid
PFNA	Perfluorononanoic acid
PFDA	Perfluorodecanoic acid
PFUnDA	Perfluoroundecanoic acid
PFDoDA	Perfluorododecanoic acid
PFTrDA	Perfluorotridecanoic acid
PFPS	Perfluoropentanesulfonic acid
PFHpS	Perfluoroheptanesulfonic acid
PFNS	Perfluorononanesulfonic acid
PFDS	Perfluorodecanesulfonic acid
PFUnDS	Perfluoroundecanesulfonic acid
PFDoDS	Perfluorododecanesulfonic acid
PFTrDS	Perfluorotridecanesulfonic acid
11Cl-PF3OUdS	11-Chloroperfluoro-3-oxaundecanesulfonic acid
9Cl-PF3ONS	Perfluoro(2-((6-chlorohexyl)oxy)ethanesulfonic acid)
NFDHA	Perfluoro-3,6-dioxaheptanoic acid
8:2 FTS	8:2 Fluorotelomer sulfonic acid
PFEESA	Perfluoro-2-ethoxyethanesulfonic acid
4:2 FTS	4:2 Fluorotelomer sulfonic acid
PFMPA	Perfluoro-3-methoxypropanoic acid
PFMBA	Perfluoro (4-methoxybutanoic acid)
NEtFOSAA	2-(N-Ethylperfluorooctanesulfonamido) acetic acid
NMeFOSAA	2-(N-Methylperfluorooctanesulfonamido) acetic acid
PFTA(PFTeDA)	Perfluorotetradecanoic acid
TFA	Trifluoroacetic acid

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Summary

This doctoral dissertation investigates the degradation of per-and polyfluoroalkyl substances (PFAS), a prominent class of organic micropollutants (OMPs), using advanced plasma technologies. These chemicals have become an increasing environmental concern due to their persistence, bioaccumulative nature, and potential health risks to both humans and ecosystems. The research aims are to explore how plasma-based water treatment can degrade PFAS, identify the resulting degradation products, and assess the ecotoxicological risks of both the parent compounds and their transformation products, contributing to a more informed regulatory framework for environmental protection.

The dissertation addresses the rising presence of PFAS in aquatic environments, originating from industrial discharges, wastewater, agricultural runoff, and household sources, with the potential to contaminate drinking water supplies. Although typically found in low concentrations, once these pollutants enter water bodies, they can accumulate in aquatic organisms, leading to adverse effects such as endocrine disruption, growth inhibition, and reproductive issues. These, in turn, pose risks to human health through water consumption and bioaccumulation in the food chain. The work also underscores the limitations of conventional water treatment technologies in effectively removing pollutants like PFAS.

PFAS, often referred to as "forever chemicals," are of particular concern due to their resistance to environmental breakdown and their link to adverse health effects, including immune suppression, thyroid diseases, and cancers. Their extreme persistence and mobility in water systems present significant challenges for conventional wastewater treatment plants (WWTPs), which often fail to adequately remove or degrade these compounds.

Advanced oxidation processes (AOPs) have been recognized as promising solutions for removing persistent contaminants from water, with non-thermal plasma (NTP) emerging as a particularly effective technique. Plasma, an ionized gas, generates reactive species such as hydroxyl radicals, atomic oxygen, hydrogen, and nitrogen compounds that can break down complex organic molecules. Unlike other AOPs, plasma can operate at low temperatures and atmospheric pressure, making it a more sustainable and cost-effective approach for wastewater treatment.

Using high-resolution mass spectrometry (HRMS) techniques, including liquid chromatography-mass spectrometry (LC-MS), the study identifies key degradation byproducts, such as short-chain perfluoroalkyl acids (PFAAs), which may still pose ecotoxicological risks despite partial degradation. The research highlights that while NTP can significantly defluorinate PFAS, the formation of potentially harmful byproducts requires careful monitoring. Particular attention is given to the degradation pathways, offering insights into how PFAS molecules break down under plasma treatment and what secondary compounds are produced.

Furthermore, the dissertation incorporates a risk assessment framework to evaluate the environmental risks of PFAS and their transformation products based on their persistence, bioaccumulation potential, and toxicity (PBT). The research also extends beyond traditional PBT criteria to include persistence-mobility-toxicity (PMT) assessments, a relatively new approach especially relevant to PFAS, given their mobility in water systems and the resulting widespread contamination, which can threaten drinking water supplies and remote ecosystems.

The study also discusses regulatory challenges in managing PFAS pollution, calling for more comprehensive risk assessments and enhanced wastewater treatment technologies to mitigate the long-term ecological impact of these substances.

Overall, this dissertation contributes to improve the understanding of how advanced plasma technologies can address the persistent issue of PFAS contamination in water systems. It provides valuable data on PFAS degradation pathways during plasma treatment and offers critical insights into the formation of byproducts and their ecological risks. By integrating plasma technology with environmental risk assessments, the research presents a promising solution for reducing the environmental and public health risks associated with PFAS and other organic micropollutants. The study also emphasizes the need for continued research and policy development to ensure that water treatment technologies can keep up with the evolving challenges of micropollutant contamination.

Resumen

Esta tesis doctoral investiga la degradación de las sustancias per- y polifluoroalquiladas (PFAS), una clase destacada de microcontaminantes orgánicos (OMPs), utilizando tecnologías avanzadas de plasma.Estos químicos han generado una creciente preocupación ambiental debido a su persistencia, naturaleza bioacumulativa y riesgos potenciales para la salud tanto de los humanos como de los ecosistemas. Los objetivos de la investigación son explorar cómo el tratamiento de agua basado en plasma puede degradar los PFAS, identificar los productos resultantes de la degradación y evaluar los riesgos ecotoxicológicos tanto de los compuestos originales como de sus productos de transformación, contribuyendo a un marco regulatorio más informado para la protección ambiental.

La tesis aborda la creciente presencia de PFAS en los entornos acuáticos, procedentes de descargas industriales, aguas residuales, escorrentías agrícolas y fuentes domésticas, con el potencial de contaminar los suministros de agua potable. Aunque generalmente se encuentran en bajas concentraciones, una vez que estos contaminantes ingresan a los cuerpos de agua, pueden acumularse en los organismos acuáticos, provocando efectos adversos como la disrupción endocrina, inhibición del crecimiento y problemas reproductivos. Estos, a su vez, representan riesgos para la salud humana a través del consumo de agua y la bioacumulación en la cadena alimentaria. El trabajo también subraya las limitaciones de las tecnologías convencionales de tratamiento de agua para eliminar de manera efectiva contaminantes como los PFAS.

Los PFAS, a menudo denominados "químicos eternos", son de particular preocupación debido a su resistencia a la degradación ambiental y su vínculo con efectos adversos para la salud, incluidos

la supresión del sistema inmunológico, enfermedades de la tiroides y cánceres. Su persistencia extrema y movilidad en los sistemas acuáticos presentan desafíos significativos para las plantas convencionales de tratamiento de aguas residuales (WWTPs), que a menudo no logran eliminar o degradar adecuadamente estos compuestos.

Los procesos avanzados de oxidación (AOPs) han sido reconocidos como soluciones prometedoras para eliminar contaminantes persistentes del agua, destacando el plasma no térmico (NTP) como una técnica particularmente efectiva. El plasma, un gas ionizado, genera especies reactivas como radicales hidroxilo, oxígeno atómico, hidrógeno y compuestos de nitrógeno que pueden descomponer moléculas orgánicas complejas. A diferencia de otros AOPs, el plasma puede operar a bajas temperaturas y presión atmosférica, lo que lo convierte en un enfoque más sostenible y rentable para el tratamiento de aguas residuales.

Utilizando técnicas de espectrometría de masas de alta resolución (HRMS), incluidas la cromatografía líquida-espectrometría de masas (LC-MS), el estudio identifica los productos clave de la degradación, como los ácidos perfluoroalquilados de cadena corta (PFAAs), que aún pueden representar riesgos ecotoxicológicos a pesar de su degradación parcial. La investigación destaca que, aunque el NTP puede defluorinar significativamente los PFAS, la formación de subproductos potencialmente dañinos requiere un monitoreo cuidadoso. Se presta especial atención a las rutas de degradación, proporcionando información sobre cómo las moléculas de PFAS se descomponen durante el tratamiento con plasma y qué compuestos secundarios se producen.

Además, la tesis incorpora un marco de evaluación de riesgos para evaluar los riesgos ambientales de los PFAS y sus productos de transformación en función de su persistencia, potencial de bioacumulación y toxicidad (PBT). La investigación también va más allá de los criterios tradicionales de PBT para incluir evaluaciones de persistencia-movilidad-toxicidad (PMT), un enfoque relativamente nuevo especialmente relevante para los PFAS, dada su movilidad en los sistemas acuáticos y la consecuente contaminación generalizada, que puede amenazar los suministros de agua potable y los ecosistemas remotos.

El estudio también discute los desafíos regulatorios en la gestión de la contaminación por PFAS, abogando por evaluaciones de riesgo más completas y tecnologías avanzadas de tratamiento de aguas residuales para mitigar el impacto ecológico a largo plazo de estas sustancias.

En general, esta tesis contribuye a mejorar la comprensión de cómo las tecnologías avanzadas de plasma pueden abordar el problema persistente de la contaminación por PFAS en los sistemas acuáticos. Proporciona datos valiosos sobre las vías de degradación de los PFAS durante el tratamiento con plasma y ofrece información crítica sobre la formación de subproductos y sus riesgos ecológicos. Al integrar la tecnología de plasma con evaluaciones de riesgo ambiental, la investigación presenta una solución prometedora para reducir los riesgos ambientales y de salud pública asociados con los PFAS y otros micropoluentes orgánicos. El estudio también enfatiza la necesidad de continuar la investigación y el desarrollo de políticas para garantizar que las tecnologías de tratamiento de agua puedan hacer frente a los desafíos en evolución de la contaminación por micropoluentes.

Resum

Aquesta tesi doctoral investiga la degradació de les substàncies per- i polifluoroalquilades (PFAS), una classe destacada de microcontaminants orgànics (OMPs), mitjançant tecnologies avançades de plasma. Aquests productes químics han esdevingut una creixent preocupació ambiental a causa de la seva persistència, naturalesa bioacumulativa i els possibles riscos per a la salut humana i dels ecosistemes. Els objectius de la recerca són explorar com el tractament d'aigua basat en plasma pot degradar els PFAS, identificar els productes resultants de la degradació i avaluar els riscos ecotoxicològics tant dels compostos originals com dels seus productes de transformació, contribuint a un marc regulador més informat per a la protecció ambiental.

La tesi tracta la creixent presència d'PFAS en entorns aquàtics, que provenen de descàrregues industrials, aigües residuals, escorrenties agrícoles i fonts domèstiques, amb el potencial de contaminar els subministraments d'aigua potable. Encara que generalment es troben en baixes concentracions, un cop aquests contaminants entren als cossos d'aigua, poden acumular-se en organismes aquàtics, causant efectes adversos com disrupcions endocrines, inhibició del creixement i problemes reproductius. Aquests efectes, al seu torn, representen riscos per a la salut humana mitjançant el consum d'aigua i la bioacumulació a la cadena alimentària. El treball també subratlla les limitacions de les tecnologies convencionals de tractament d'aigua per eliminar eficaçment contaminants com els PFAS.

Els PFAS, sovint anomenats "químics eterns", són de particular preocupació per la seva resistència a la degradació ambiental i el seu vincle amb efectes adversos per a la salut, incloent-hi la supressió del sistema immunològic, malalties de la tiroide i càncers. La seva extrema persistència i mobilitat

en els sistemes aquàtics presenten reptes significatius per a les plantes convencionals de tractament d'aigües residuals (WWTPs), que sovint no aconsegueixen eliminar o degradar adequadament aquests compostos.

Els processos avançats d'oxidació (AOPs) han estat reconeguts com solucions prometedores per eliminar contaminants persistents de l'aigua, destacant el plasma no tèrmic (NTP) com una tècnica particularment efectiva. El plasma, un gas ionitzat, genera espècies reactives com radicals hidroxil, oxigen atòmic, hidrogen i compostos de nitrogen que poden descompondre molècules orgàniques complexes. A diferència d'altres AOPs, el plasma pot operar a baixes temperatures i a pressió atmosfèrica, cosa que el converteix en un enfocament més sostenible i rendible per al tractament d'aigües residuals.

Mitjançant tècniques d'espectrometria de masses d'alta resolució (HRMS), incloent la cromatografia líquida-espectrometria de masses (LC-MS), l'estudi identifica els productes clau de la degradació, com els àcids perfluoroalquilats de cadena curta (PFAAs), que encara poden representar riscos ecotoxicològics malgrat la seva degradació parcial. La investigació destaca que, tot i que l'NTP pot defluorinar significativament els PFAS, la formació de subproductes potencialment nocius requereix una supervisió acurada. Es presta especial atenció a les vies de degradació, proporcionant informació sobre com les molècules de PFAS es descomponen durant el tractament amb plasma i quins compostos secundaris es produeixen.

A més, la tesi incorpora un marc d'avaluació de riscos per avaluar els riscos ambientals dels PFAS i els seus productes de transformació en funció de la seva persistència, potencial de bioacumulació i toxicitat (PBT). La investigació també va més enllà dels criteris tradicionals de PBT per incloure avaluacions de persistència-mobilitat-toxicitat (PMT), un enfocament relativament nou especialment rellevant per als PFAS, donada la seva mobilitat en els sistemes aquàtics i la conseqüent contaminació generalitzada, que pot amenaçar els subministraments d'aigua potable i els ecosistemes remots.

L'estudi també discuteix els reptes reguladors en la gestió de la contaminació per PFAS, advocant per avaluacions de risc més completes i tecnologies avançades de tractament d'aigües residuals per mitigar l'impacte ecològic a llarg termini d'aquestes substàncies.

En general, aquesta tesi contribueix a millorar la comprensió de com les tecnologies avançades de plasma poden abordar el problema persistent de la contaminació per PFAS en els sistemes aquàtics. Proporciona dades valuoses sobre les vies de degradació dels PFAS durant el tractament amb plasma i ofereix informació crítica sobre la formació de subproductes i els seus riscos ecològics. Integrant la tecnologia de plasma amb avaluacions de risc ambiental, la investigació presenta una solució prometedora per reduir els riscos ambientals i per a la salut pública associats amb els PFAS i altres microcontaminants orgànics. L'estudi també subratlla la necessitat de continuar investigant i desenvolupant polítiques per assegurar que les tecnologies de tractament d'aigua puguin fer front als reptes en evolució de la contaminació per microcontaminants.

Riassunto

Questa tesi di dottorato indaga la degradazione delle sostanze per- e polifluoroalchiliche (PFAS), una classe importante di microinquinanti organici (OMPs), utilizzando tecnologie avanzate al plasma. Questi composti chimici sono diventati una crescente preoccupazione ambientale a causa della loro persistenza, natura bioaccumulativa e dei potenziali rischi per la salute umana e degli ecosistemi. Gli obiettivi della ricerca sono esplorare come il trattamento delle acque basato sul plasma possa degradare i PFAS, identificare i prodotti di degradazione risultanti e valutare i rischi ecotossicologici sia dei composti originali che dei loro prodotti di trasformazione, contribuendo a un quadro normativo più informato per la protezione ambientale.

La tesi affronta la crescente presenza di PFAS negli ambienti acquatici, provenienti da scarichi industriali, acque reflue, deflussi agricoli e fonti domestiche, con il potenziale di contaminare le riserve di acqua potabile. Sebbene di solito presenti a basse concentrazioni, una volta che questi inquinanti entrano nei corpi idrici, possono accumularsi negli organismi acquatici, provocando effetti avversi come la disfunzione endocrina, l'inibizione della crescita e problemi riproduttivi. Questi, a loro volta, rappresentano rischi per la salute umana attraverso il consumo di acqua e la bioaccumulazione nella catena alimentare. Il lavoro evidenzia anche i limiti delle tecnologie convenzionali di trattamento delle acque nell'eliminare efficacemente inquinanti come i PFAS.

I PFAS, spesso definiti "prodotti chimici eterni", destano particolare preoccupazione per la loro resistenza alla degradazione ambientale e il loro legame con effetti negativi sulla salute, inclusi soppressione immunitaria, malattie della tiroide e tumori. La loro estrema persistenza e mobilità nei sistemi idrici presentano sfide significative per gli impianti di trattamento delle acque reflue

convenzionali (WWTPs), che spesso non riescono a rimuovere o degradare adeguatamente questi composti.

I processi avanzati di ossidazione (AOPs) sono stati riconosciuti come soluzioni promettenti per la rimozione di contaminanti persistenti dall'acqua, con il plasma non termico (NTP) che emerge come una tecnica particolarmente efficace. Il plasma, un gas ionizzato, genera specie reattive come radicali idrossilici, ossigeno atomico, idrogeno e composti di azoto che possono scomporre molecole organiche complesse. A differenza di altri AOPs, il plasma può operare a basse temperature e pressione atmosferica, rendendolo un approccio più sostenibile ed economico per il trattamento delle acque reflue.

Utilizzando tecniche di spettrometria di massa ad alta risoluzione (HRMS), inclusa la cromatografia liquida-spettrometria di massa (LC-MS), lo studio identifica i principali prodotti di degradazione, come gli acidi perfluoroalchilici a catena corta (PFAAs), che possono ancora rappresentare rischi ecotossicologici nonostante la degradazione parziale. La ricerca evidenzia che, sebbene l'NTP possa defluorinare significativamente i PFAS, la formazione di sottoprodotti potenzialmente nocivi richiede un attento monitoraggio. Particolare attenzione è riservata alle vie di degradazione, fornendo informazioni su come le molecole di PFAS si scompongono durante il trattamento al plasma e quali composti secondari vengono prodotti.

Inoltre, la tesi incorpora un quadro di valutazione del rischio per valutare i rischi ambientali dei PFAS e dei loro prodotti di trasformazione in base alla loro persistenza, potenziale di bioaccumulazione e tossicità (PBT). La ricerca si estende anche oltre i criteri PBT tradizionali, includendo valutazioni di persistenza-mobilità-tossicità (PMT), un approccio relativamente nuovo particolarmente rilevante per i PFAS, data la loro mobilità nei sistemi idrici e la conseguente contaminazione diffusa, che può minacciare le riserve di acqua potabile e gli ecosistemi remoti.

Lo studio discute anche le sfide normative nella gestione dell'inquinamento da PFAS, richiedendo valutazioni del rischio più complete e tecnologie avanzate di trattamento delle acque reflue per mitigare l'impatto ecologico a lungo termine di queste sostanze.

Nel complesso, questa tesi contribuisce a migliorare la comprensione di come le tecnologie avanzate al plasma possano affrontare il problema persistente della contaminazione da PFAS nei sistemi idrici. Fornisce dati preziosi sui percorsi di degradazione dei PFAS durante il trattamento al plasma e offre spunti critici sulla formazione di sottoprodotti e sui loro rischi ecologici. Integrando la tecnologia del plasma con valutazioni del rischio ambientale, la ricerca presenta una soluzione promettente per ridurre i rischi ambientali e per la salute pubblica associati ai PFAS e ad altri micropollutanti organici. Lo studio sottolinea inoltre la necessità di continuare la ricerca e lo sviluppo delle politiche per garantire che le tecnologie di trattamento delle acque possano affrontare le sfide in evoluzione della contaminazione da micropollutanti.

1. INTRODUCTION

1.1. Organic micropollutants in the aquatic environment

High demands for a better quality of life and the increasing consumption of goods have driven technological progress, development of new materials, and an overall increase in industrial production. As a result, an increasing number of anthropogenic chemicals have been detected in the aquatic environment. Among them, the main concern and awareness is about the presence of organic micropollutants (OMPs). OMPs represents a wide group of chemical compounds, including, but not limited to, pharmaceuticals, pesticides, personal care products, different household and industrial chemicals. Their sources can be diverse: industry, hospitals, private households, agricultural activities (A. Singh et al., 2024) and they can be found in various types of water including wastewater, surface water and groundwater. They have been detected in concentration range of micrograms (μg) or nanograms (ng) per litre which is considered a low range. However, it has been shown that even at these low concentrations, OMPs can have harmful effect on aquatic organisms and ultimately on humans (EEA (European Environment Agency), 2011; Rozas et al., 2016; Verlicchi et al., 2012). Various studies report that some OMPs are bioaccumulative and can cause growth inhibition and endocrine disruption in aquatic organisms (Caballero-Gallardo et al., 2016; Santos et al., 2010; Tijani et al., 2014). They have been associated with toxic effects (Shao et al., 2019), hormonal disruption (Kasonga et al., 2021), reproductive effects and physiology changes (Arnold et al., 2014). As for human health, the potential of the pollutants to cause acute or long-term effects such as immunotoxicity, neurological disorders, different types of cancers, endocrine disruption is studied (Armstrong & Gibbs, 2009; Hayman et al., 2021; Sanchez & Egea, 2018; Xue et al., 2021). In recent decades, the widespread occurrence of per- and polyfluoroalkyl substances (PFAS) in the environment and their impact on human and ecological health have raised concerns and increased social awareness.

1.1.1. Per-and Polyfluorolakyl Substances (PFAS)

These organic molecules, known as “forever chemicals”, have been produced by humans since the 1950s and are used on a daily basis for commercial and consumer purposes. PFAS, as a complex group of substances with over 4700 identified chemicals, have different properties, but one thing in common – incredibly strong and stable carbon-fluorine bond which is very difficult to break down. Fluorinated carbon chain or “tail” can vary in length chain; therefore, substances are sometimes divided into short-chain and long-chain PFAS. At one end (or both), a polar or ionizable “head” group is attached, which can also be variable, like carboxylic and sulfonic acid (Buck et al., 2011). This structure gives them unique physicochemical properties, high thermal and chemical stability, water, oil and grease repellence. Due to these properties and variability in structure, they can be used for diverse applications, such as electronics manufacturing, aqueous film-forming foams (AFFF), dust suppressions, hydraulic fluids, textile stain repellents, food containers, cleaning products, polishes, waxes, paints, cosmetics, etc (Barzen-Hanson et al., 2017; Schellenberger et al., 2022; Whitehead et al., 2021). PFAS are divided into two primary classes, polymer and nonpolymer where each class contains groups and subgroups of PFAS. Figure 1 shows the PFAS family tree which can be further divided.

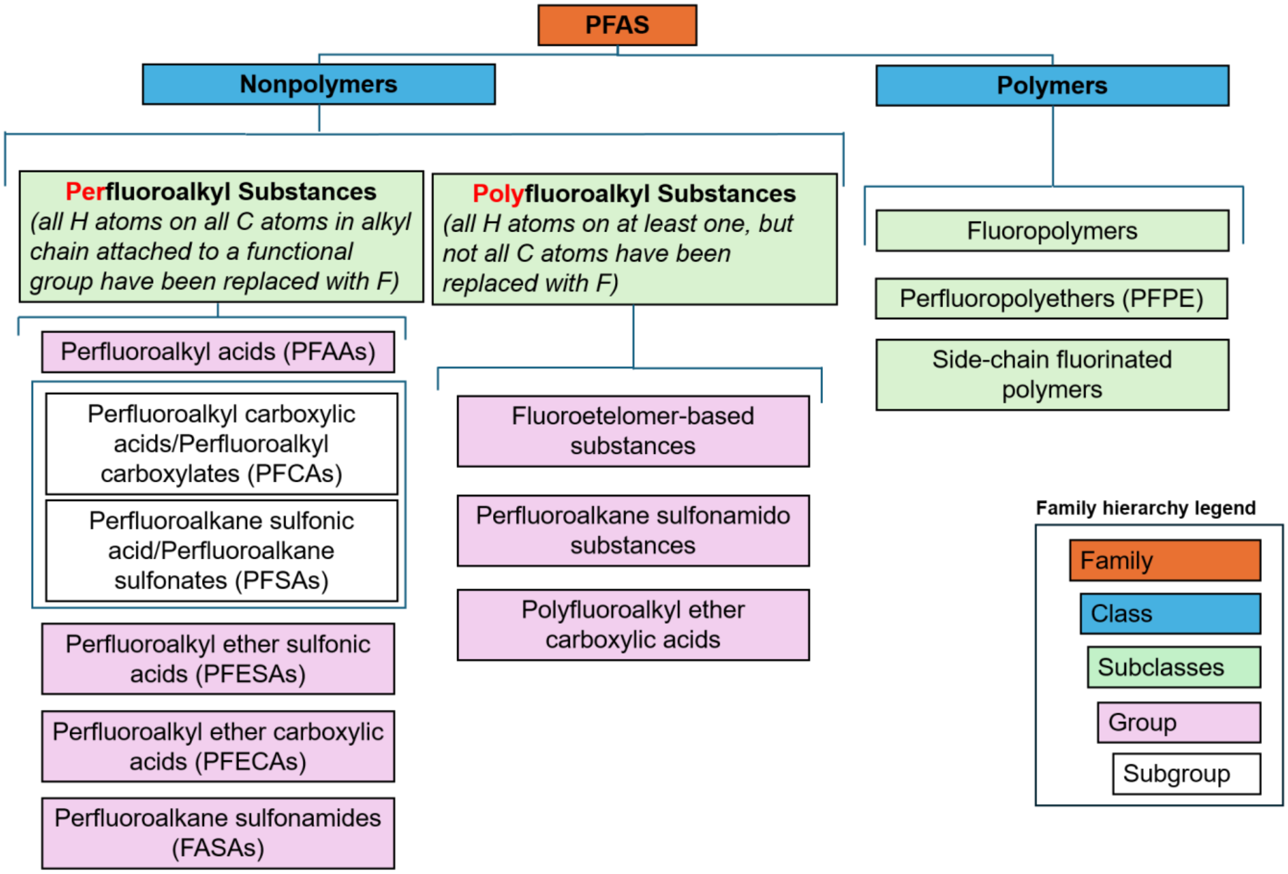
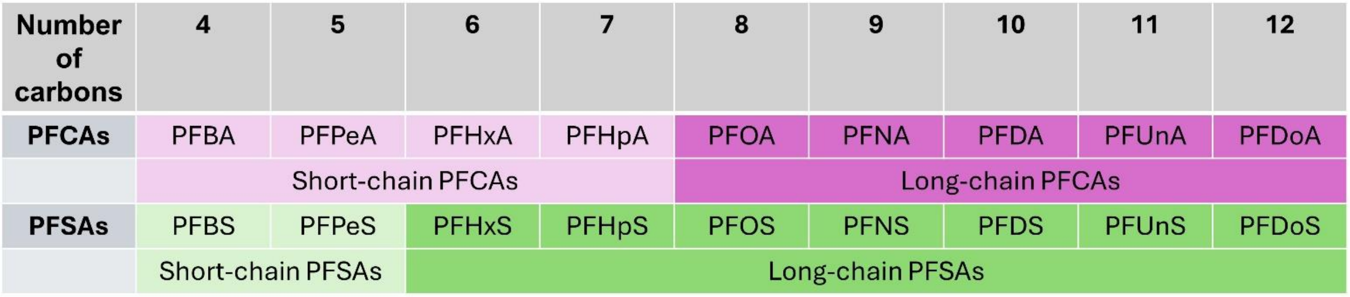


FIGURE 1. PFAS family tree, adapted from (Buck et al., 2011).

In studies PFAS are very often referred to as long-chain and short-chain, mostly to categorize PFSAs and PFCAs and to represent their behavior in different treatment processes and/or behavior in water bodies. According to (ITRC, 2019; OECD, 2018) long-chain refers to PFCAs with eight or more carbons (seven or more carbons are perfluorinated), and six or more perfluorinated carbons for PFSAs. Short chain refers to seven or fewer carbons (six or fewer perfluorinated carbons) for PFCAs and five or fewer perfluorinated carbons for PFSAs. Figure 2 illustrates the chain length of PFCAs and PFSAs.



Number of carbons	4	5	6	7	8	9	10	11	12
PFCAs	PFBA	PFPeA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA
	Short-chain PFCAs				Long-chain PFCAs				
PFSAs	PFBS	PFPeS	PFHxS	PFHpS	PFOS	PFNS	PFDS	PFUnS	PFDoS
	Short-chain PFSAs		Long-chain PFSAs						

FIGURE 2. Illustration of chain length of PFCAs and PFSAs.

Reports of the presence of PFAS in drinking water near chemical plants and in human and animal blood serum samples from areas near fluoropolymer production facilities have been known for several decades, but it is the studies of PFAS findings in remote areas that have led to global concern, and PFAS are now being monitored worldwide (Boisvert et al., 2019; Rigét et al., 2019; Sims et al., 2022). These were among the earliest pieces of evidence showing that these substances are highly persistent. While the primary source of PFAS input into the environment is direct release from industrial facilities, indirect sources are also significant. In fact, the persistence of PFAS was first evidenced by their ability to travel vast distances, proving that, in addition to direct release, indirect sources also play an important role in environmental contamination. PFAS, including various precursors and degradation products, have the potential for long-range transport and spread far from their original source. The improper disposal of PFAS-containing products and materials such as textiles, non-stick packaging and products or the use of fire-fighting foams also influence the occurrence of PFAS in the environment. Figure 3 illustrates PFAS lifecycle and significance of different exposures.

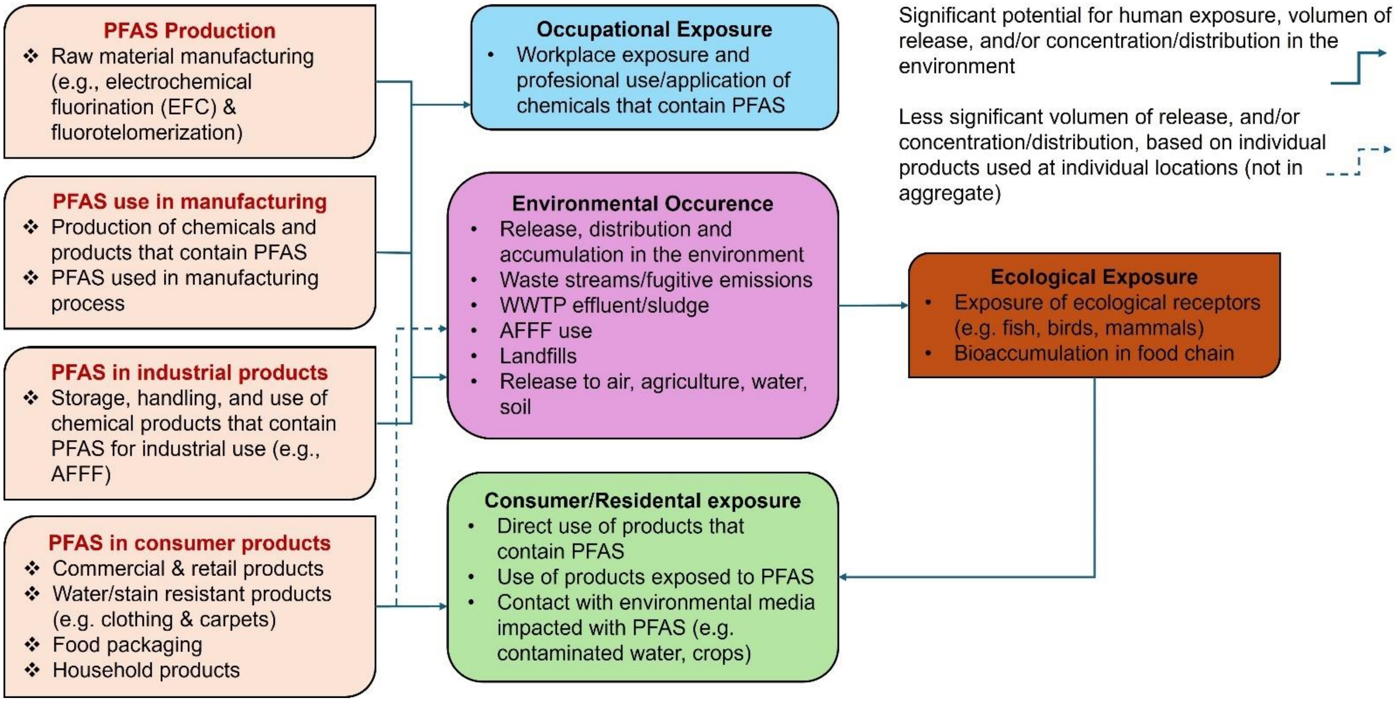


FIGURE 3. PFAS lifecycle, sources and exposure.

Typical concentrations of PFAS in water are very low, but higher concentrations (mg/L) have been found in surface and groundwater near production facilities. These findings, as well as worldwide spread, have been key factors of concern. Other studies have shown that their presence in drinking water and their potential to accumulate in food and in humans are associated with serious health effects, such as immunosuppression, thyroid disorders, cancer and significant (chronic) toxicity of some of these substances (Hayman et al., 2021; X. Li et al., 2022; Pitter et al., 2020). Since 2009, two of the most well-known compounds used and found in the environment, perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), have been recognized as potentially hazardous compounds to human health and the environment and have been regulated in the United States and Europe (European Commission, 2020a; US EPA, 2016). In 2022, the European Commission adopted the proposal to revise the list of priority substances in surface water and groundwater setting the quality standard for the sum of 24 PFAS in groundwater at 0.004 µg/L

(European Commission, 2022). Consequently, the global production of PFOA and PFOS has been restricted or banned, while new fluorinated substances have been developed as substitutes (Z. Wang et al., 2013). These new substances are mostly part of short-chain PFAS group, such as perfluorobutane sulfonic acid (PFBS) with C4 chain-length. Another interesting group are perfluropolyethers (PFPEs), or shortly ether-PFAS, which include (among others) substances named hexafluoropropylene oxide dimer acid (HFPO-DA; GenX), dodecafluoro-3H-4,8-dioxanonanoate (ADONA) and 6:2 chlorinated polyfluoroalkyl ether sulfonate (6:2 Cl-PFESA; F-53B).

GenX, which is the trade name and ammonium salt of HFPO-DA is a surfactant that has been used as a replacement for PFOA and as a chemical in polymerization processes of other perfluorinated products. Technically, the chemicals used are known as: hexafluoropropylene oxide (HFPO) dimer acid form (HFPO-DA, CAS No. 13252-13-6, also known as 2,3,3,3-tetrafluoro-2- (1,1,2,2,3,3,3-heptafluoropropoxy)propanoic acid [PFPrOPrA],FRD-903) and its ammonium salt (ammonium, 2,3,3,3- tetrafluoro-2-(heptafluoropropoxy) propanoate [CF3CF2CF2OCF(CF3)COO–NH4+, CAS No. 62037-80-3, also known as FRD -902]). ADONA, trade name for polyfluoroether carboxylate surfactant or polyfluoroalkyl ether acids, is used as replacement for PFOA in polymerization processes. More detailed discussion can be found in (Z. Wang et al., 2013) and (Munoz et al., 2019).

While the addition of an alkylether (C-O-C) group in their chemical structure may lead to higher mobility and reduced bioaccumulation, the environmental impact and toxicity of these compounds remain uncertain and concerning. Recent studies show that even though they do not have a high potency to accumulate in aquatic species, their presence in water (drinking and groundwater) has more impact on animals and humans that consume and are exposed to them (Xiao, 2017). (Pan et al., 2017) has reported GenX presence in human serum and fish muscle while ADONA has been detected in blood donor samples in Germany (Fromme et al., 2017). Levels of ADONA in surface water and its toxicity have been investigated by (Gordon, 2011), while GenX has been found in rivers of The Netherlands and Germany (Gebbink et al., 2017; Heydebreck et al., 2015). Global distribution of these substances has also been reviewed by (Pan et al., 2018). Toxicological data can be found in (Buck, 2015) as well.

1.2.Water treatment processes: Introducing new AOPs to future treatment systems

Numerous studies conducted in the past have shown that conventional biological treatment, which is used in most wastewater treatment plants (WWTPs) is only partially able to mitigate OMPs contamination with highly variable performance (Falås et al., 2016; Gros et al., 2010). Because of the recalcitrant nature of OMPs (meaning they resist degradation due to their molecular properties, such as hydrophobicity) to these types of systems, the occurrence of the pollutants has become worldwide issue. While in these processes, such as activated sludge, the reliance is on microbial degradation and adsorption to remove OMPs, its effectiveness widely depends on specific compounds and system parameters. On the other hand, improvement of removal efficiency can be done by combining biological treatment with membrane bioreactors, especially for OMPs with hydrophobic nature. More detailed discussion was presented in the review by (Grandclément et al., 2017). In summary, challenges in conventional systems are in sensitive process factors like hydraulic retention time, sludge retention time, pH, temperature, and dissolved oxygen levels. Extended retention time can enhance the breakdown of persistent contaminants, but with possible operational trade-offs. Temperature and pH can influence microbial activity and the chemical state of contaminants, affecting both biodegradation and adsorption rates. Poor elimination of more hydrophilic and poorly-to-moderately biodegradable OMPs is also well documented in (Luo et al., 2014). While conventional methods have limitations, newer methods can have potential for removal of OMPs. Among them approaches, advanced technologies to remove OMPs from wastewater are available, but in many cases, they are too costly and/or energetically unsustainable. In previous studies, different advanced oxidation processes (AOPs), such as ultraviolet (UV)/hydrogen peroxide (H_2O_2) treatment, ozonation (O_3), photo-Fenton have been recognized as successful for wastewater treatment with the ability to rapidly and efficiently degrade many different types of organic compounds (Giannakis et al., 2015; Kudlek, 2018; Wols & Hofman-Caris, 2012).

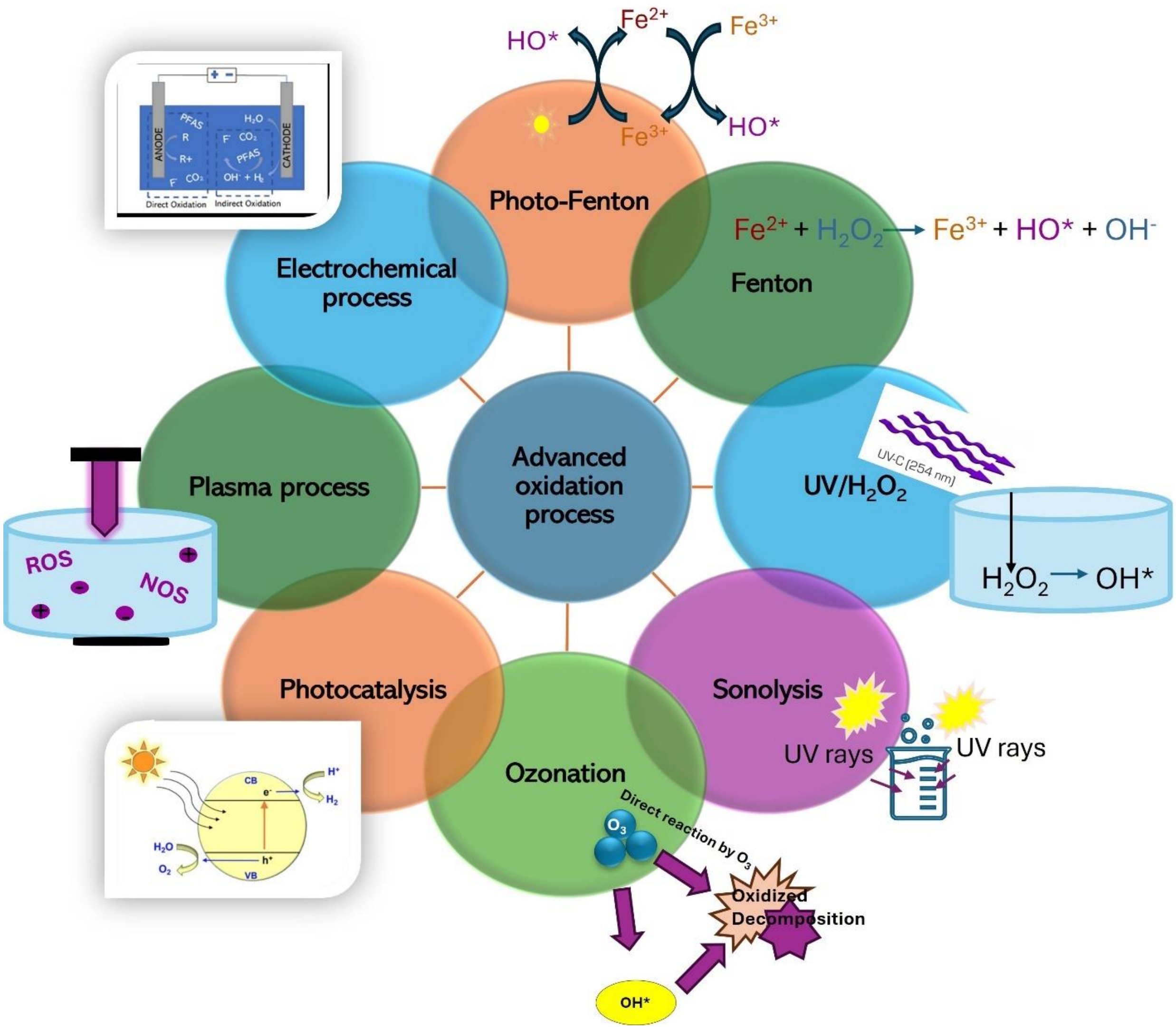


FIGURE 4. Types of AOPs.

One of the novel highly-promising AOPs is based on the use of non-equilibrium or non-thermal plasma (NTP) which produce nitrogen-containing species, hydroxyl radical, hydroperoxyl radical, atomic hydrogen and oxygen, as well as other radicals and active chemical species that are generally required for an effective water treatment (Ghime & Ghosh, 2020; Miklos et al., 2018; Ribeiro et al., 2015).

1.2.1. Fundamentals of non-equilibrium plasma for water treatment

Plasma is fully or partially ionized gas and is frequently called the fourth state of matter. Generally speaking, by applying energy to a gas, some amount of excited species and ions and electrons are produced in frequent collisions between the existing free electrons and neutral species eventually leading to the formation of plasma. The energy input required to generate plasma is mostly achieved by imposing a sufficiently high electric field. Although it contains free charge carriers, from a macroscopic point of view, plasma is electrically neutral. In thermodynamic terms plasma species (electrons, ions, and neutrals) can be characterized by their temperatures and with respect to this description plasma can be classified into two categories: equilibrium or thermal and non-equilibrium plasma. In thermal plasmas the characteristic temperatures of electrons and heavy particles (atoms, molecules, ions) are equally high, with temperature values of 10^3 K and above (Lieberman & Lichtenberg, 1994). Strictly speaking, under terrestrial conditions (i.e., in applications), these plasmas are only in a local thermodynamic equilibrium, as the temperatures of all plasma types are only the same in a limited volume of space. Thermal plasmas are realized as arcs and torches and typically used for applications where high temperatures are required, such as for cutting, spraying, welding or, as in the analytical devices, for the evaporation of an analyte material (Tendero et al., 2006).

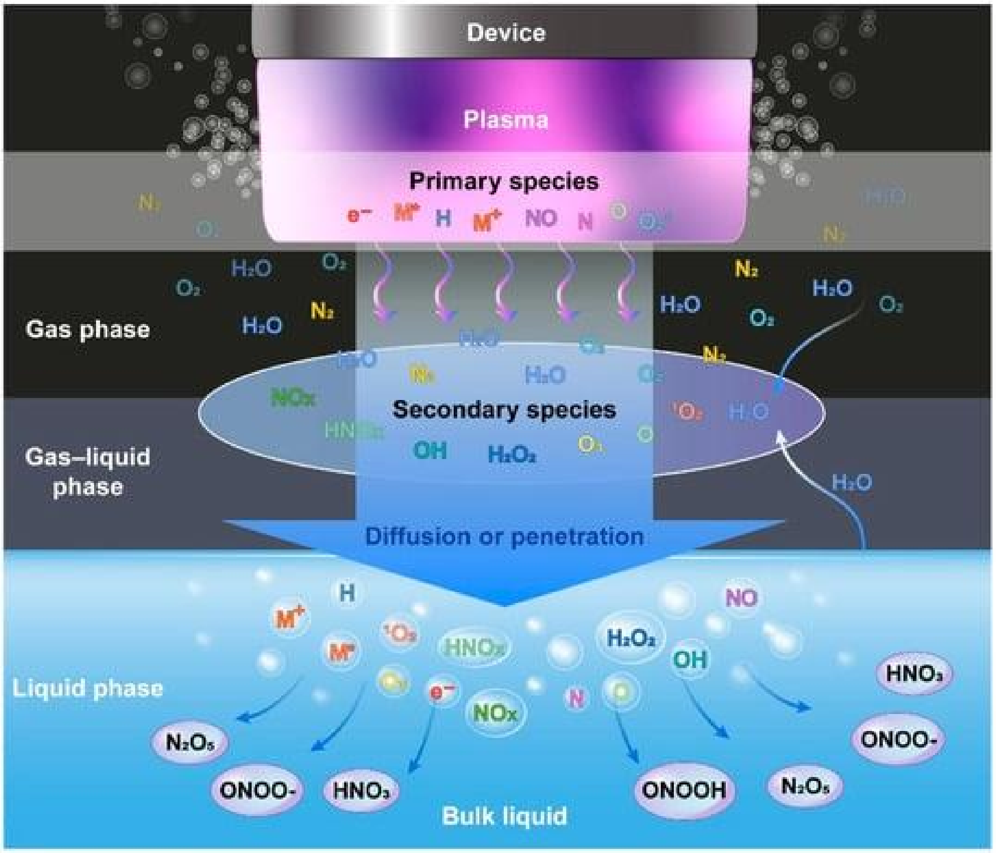


FIGURE 5. Formation of various reactive species in plasma phase, gas phase, gas-liquid phase and liquid phase, from (Kim & Kim, 2021).

In non-equilibrium plasmas the temperature of the electrons is much higher than the temperatures of heavy particles. Depending on the type of plasma, temperatures of the heavy particles can be a few hundred degrees or much lower and close to the room temperature. Thus, these plasmas are also referred to as non-thermal plasma (NTP) or cold plasma. Due to pronounced non-equilibrium of particle energies, mainly electrons have sufficient energy to collide with the background gas particles and provide multiplication of charges necessary to sustain the plasma. Apart from the production of charged particles, excited species (especially metastables), fast neutrals, radicals, photons are also produced in collisions. Compared to thermal plasmas, non-equilibrium plasmas are characterized by lower energy densities, have lower degree of ionization and consequently lower particle densities (Lieberman & Lichtenberg, 1994). Nevertheless, as these plasmas work at or near room temperatures, they can be used in many different areas (Becker et al., 2004; Makabe & Petrovic, 2014).

Non-equilibrium plasmas working at atmospheric pressure have an advantage compared to their low-pressure counterparts when it comes to applications where samples cannot withstand exposures to pressures below atmospheric. Thus, many applications of plasma in the fields of biology and medicine have driven the development of atmospheric pressure non-equilibrium plasmas in the last 30 years (Fridman et al., 2008; Laroussi et al., 2017; Machala et al., 2012; Miletić et al., n.d.). Several types of electrical discharges (Figure 6.) at atmospheric pressure, such as corona, dielectric barrier discharge (DBD), gliding arc, glow discharge and streamer discharge, have been employed depending on particular treatment demands. Albeit the limited active volume of these plasmas versatility and success of their biomedical applications lies in production of suitable chemical species and their interaction with living cells (Lu et al., 2016; Privat-Maldonado et al., 2019; Tomić et al., 2021).

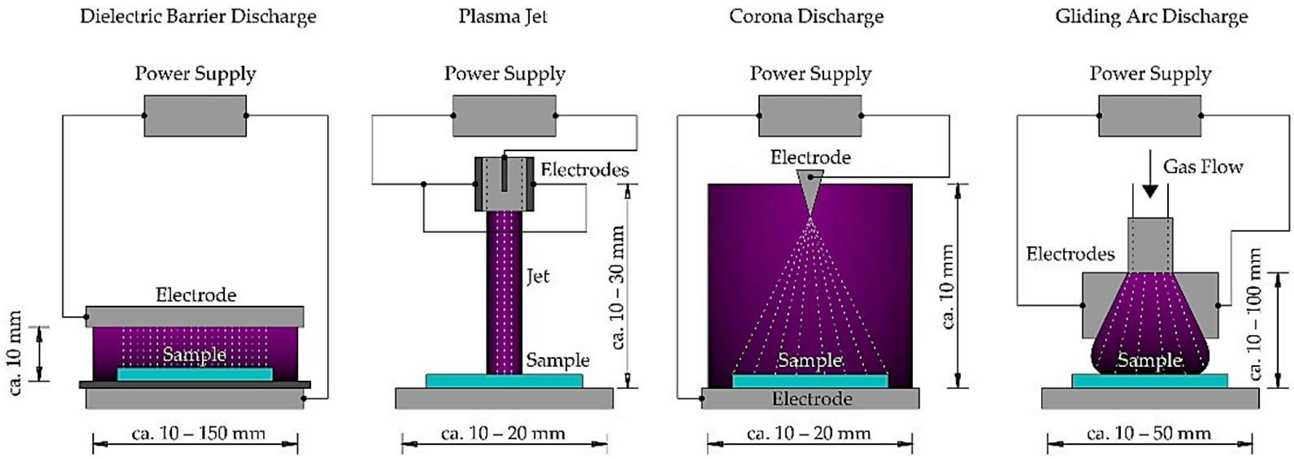


FIGURE 6. Different types of plasma discharge, from (Domonkos et al., 2021).

In recent years, the applications of non-equilibrium plasmas are expanded to wastewater treatment. According to recent papers, applications of NTP for wastewater treatment are becoming more attractive and are recognized as technological solution for OMPs which are highly recalcitrant to conventional wastewater treatment technologies. Reactive chemical species created in the plasma have already proven their capability to decontaminate water by pulverizing molecules of the pollutant in various chemical reactions (Foster, 2017; Magureanu et al., 2018). However, before reaching the auspicious situation where plasma technology is used for wastewater treatment several major obstacles should be removed. The first one is related to determination of proper parameter related to the power consumption in plasma processes that will adhere to existing wastewater technology standards and enable comparison with conventional methods. The diversity of experimental setups for water treatment, which sometimes include additional power consumption (e.g., for sample recirculation), and plasma devices that require different approaches in power measurements make this a demanding task. A comparison of data reported in review papers shows that there is no standard for specifying treatment conditions (Jiang et al., 2014; Magureanu et al., 2018; Malik, 2010; Nzeribe et al., 2019). Therefore, a paper describing the plasma treatment of wastewater should contain at least the following information: main dimensions of the experimental setup, type of discharge used, working gas flow (if any), type of power supply, electrical parameters including power delivered to the plasma, volume of sample treated (and the flow rate if it is a flowing regime), initial and final concentrations of the pollutant and duration of the treatment. A detailed description of the experimental conditions allows plasma treatments to be analyzed and compared and can be a first step towards defining appropriate power-efficiency parameter.

Another difficulty for the application of NTP as technology for water treatment comes from the rather small volume of the active plasma region which, in turn, limit the outflux of reactive species created in the plasma. Since plasma is created at atmospheric pressure, mean free paths (the mean distance between two collisions) of all particles are in the order of µm. Thus, to establish an effective interaction between the plasma and the water they should be in close contact while an increase in the transfer of reactive species requires increasing the effective interaction area. There are two different approaches for the existing experimental setups - one option is to generate plasma in water, another is to generate plasma in the gas phase adjacent to the liquid sample. In that view, we can divide atmospheric pressure non-equilibrium plasmas that can be used in wastewater treatment as discharges in liquids and in contact with liquids.

Non-equilibrium plasmas in liquids

This group of high non-equilibrium plasmas refers to the discharges where electrodes are completely immersed in liquid. There are two sub-groups:

i. discharges in liquids where no gas phase plasma is involved
ii. discharges in bubbles inside liquids.

The major challenges in these types of discharges are how to achieve a breakdown without subsequent transition into the thermal plasma, the appropriate power supply, the optimal geometry of the electrodes and their etching during the operation, heating of the liquid, the complexity of the chemical composition of the liquid etc. Until now several review papers have been published on the topics related to the discharges in liquids (Peter Bruggeman & Leys, 2009; Graham & Stalder, 2011; Locke et al., 2006; Malik et al., 2001).

The discharges with no gas phase involved can be created in the pin-to-pin, pin-to-plate or plate-to-plate electrode system with the pulsed (usually nanosecond) power supplies (Akiyama, 2000; An et al., 2007; Locke & Thagard, 2012; Petr Lukes et al., 2005; Schaper et al., 2011; Schoenbach et al., 2008; Šunka, 2001). There are several important parameters that influence the formation and propagation of the discharge such as the energy deposited in the pulse, frequency and duty cycle, inter-electrode distance, conductivity of the liquid. The discharges are streamer-like in case of non-equilibrium plasmas and the created streamers usually dissipate before reaching the grounded electrode.

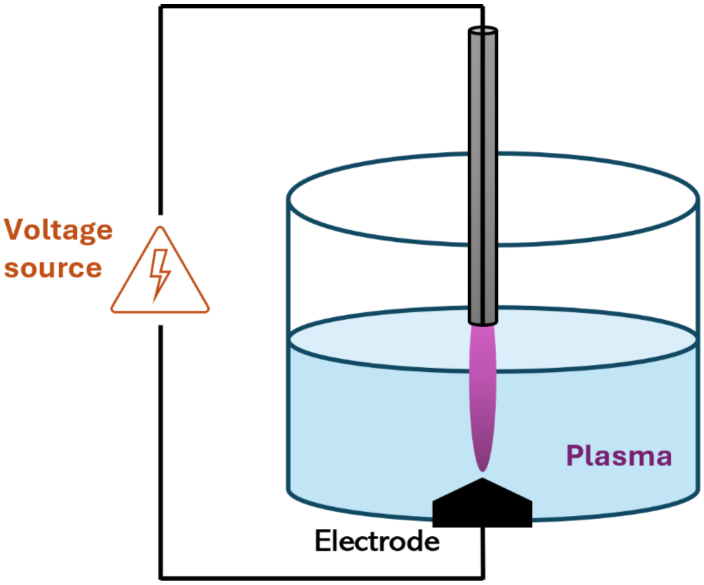


FIGURE 7. Scheme of plasma discharge in a liquid.

The second sub-type of the discharges in water involves creation of bubbles and in this case, we are dealing with gas phase surface plasmas (inside bubble) with the liquid electrode. The bubbles can be created by bubbling systems, heat wave, in capillary systems etc. (Bruggeman et al., 2008; Gershman et al., 2007). The bubbles do not need to be introduced into the liquid (for example by bubbling system) to have this type of discharge. The appearance of the micro-bubbles can be related to the breakdown of the discharge where the initial Joule heating of the liquid leads to their creation (Ceccato et al., 2010; Korobeinikov & Yanshin, 1983).

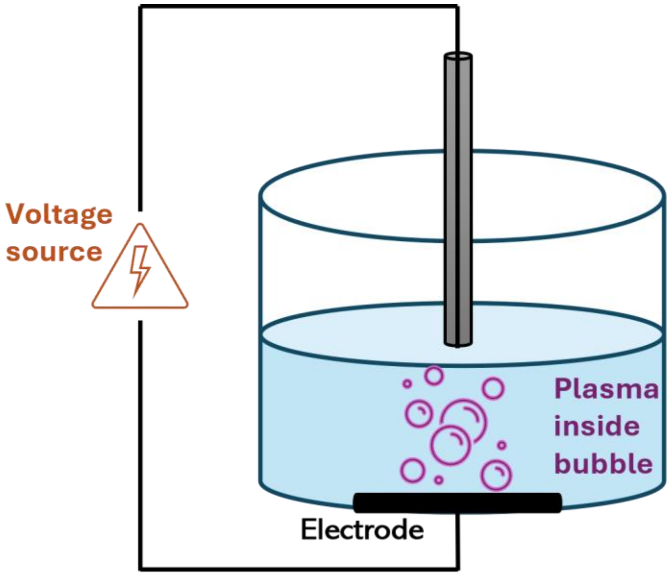


FIGURE 8 . Plasma discharge in bubbles inside a liquid.

Non-equilibrium plasmas in contact with liquid surfaces

In this case the powered electrode is not in direct contact with liquid which serves here as a grounded electrode. There are various geometries used in these type of discharges: pin-jet type, DBD-jet type, planar strip electrodes that can be in direct contact with surrounding gas or immersed in dielectric etc. (Boselli et al., 2014; Puač et al., 2012; Šimor et al., 2002; Škoro et al., 2018). The used power supplies range from nano-pulsed to a sine wave excitation voltage and the applied voltages depend on the excitation frequency, working gas used, electrode geometry and electrode gap. The applied frequencies can range from several Hz up to the MHz region. The discharge is created in the gas phase and the resulting chemistry inside the liquid is the result of gas phase and gas/liquid interface chemistry (Bruggeman et al., 2016; Parvulescu et al., 2012; Sunka et al., 1999). The gas temperature stays in the range of 300 K-400 K and usually the energy per pulse is of order of μJ. The electron temperature stays in the range of 1-3 eV and electron concentration between 10^{19}-10^{21} m^{-3}.

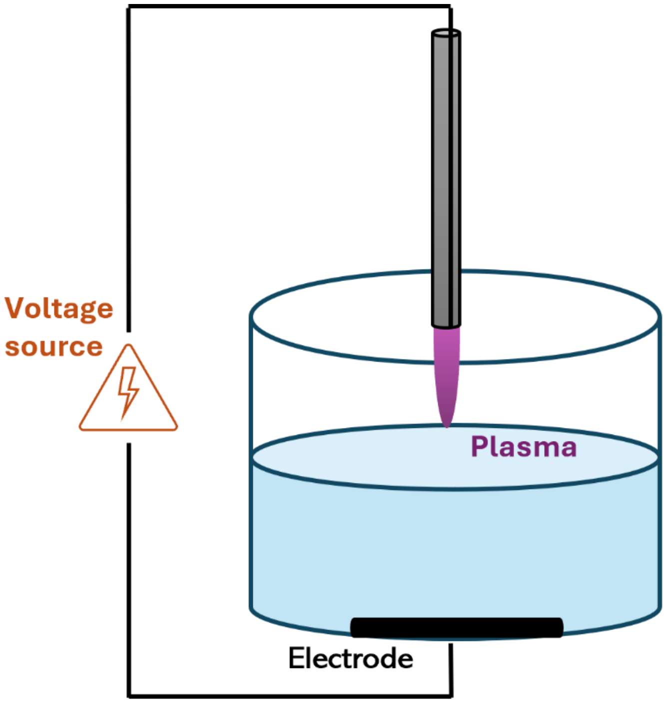


FIGURE 9. Scheme of plasma discharge above a liquid.

Many previous studies have showed successful plasma performance and removal of contaminants such as pharmaceuticals ((Iervolino et al., 2019; Magureanu et al., 2011; Sarangapani et al., 2017; Q. Zhang et al., 2018), pesticides ((Hijosa-Valsero et al., 2013; R. K. Singh, Philip, et al., 2019; Vanraes et al., 2015; Wardenier, Gorbanev, et al., 2019), phenols ((Ceriani et al., 2018; Hama Aziz et al., 2018; Marotta et al., 2011), dyes (Magureanu et al., 2013; Sarangapani et al., 2017; Yamada et al., 2020) and among them PFAS (Hayashi et al., 2015; R. K. Singh et al., 2021; Stratton et al., 2017; Takeuchi et al., 2011). However, while there are a growing number of plasma studies on water treatment, most of them have been conducted with distilled water and a single contaminant. Some have been performed in other water matrices such as tap or lake water, and very few involved mixtures. Nevertheless, further studies are needed on their degradation kinetics as well as degradation byproducts generated and their toxicity. Table 1. provides different plasma configurations used in treatemt of OMPs and their performance.

TABLE 1. Different plasma configurations in OMPs water treatment.

OMPs	**Plasma system/plasma type and configuration/working gas**	**Solution type/volume treated/treatment time/initial concentration**	**Degradation**	**Reference**
Pharmaceuticals				
Norfloxacin	DBD reactor/ discharge above liquid / Oxygen (O_2), nitrogen(N_2) or air	Ultrapure aqueous solution 3 ml 2 min 200 mg/L	O_2/air – 98 % N_2 – 50 %	(Q. Zhang et al., 2018)
Ofloxacin (OFX) and ciprofloxacin (CFX)	DBD reactor / discharge above liquid / air	Matrix solution 25 ml 5 – 25 min 10 mg/L	66 % CFX 72 % OFX	(Sarangapani et al., 2019)
Paracetamol, Caffeine, Ceftriaxone	DBD reactor / tilted cylindrical configuration, discharge above liquid / air or O_2	Ultrapure aqueous solution 100 ml 10 – 30 min 25 mg/L (parac.); 50 mg/L (caff.); 5 mg/L (ceft.)	>80 % (caff.) 89 % (parac.) >80 % (ceft.)	(Iervolino et al., 2019)
Amoxicillin, Oxacillin, Ampicillin	DBD reactor / coaxial configuration, thin falling water film / O_2	Tap water 200 ml 10 – 30 min 100 mg/L	Degradation occurred but percentage not specified	(Magureanu et al., 2011)
Ibuprofen (IBP)	DBD reactor / discharge above falling water film / air	Ultrapure aqueous solution 350 ml 15 min 60 mg/L	85 %	(Marković et al., 2015)
Diclofenac (DCF), IBP	DBD reactor / planar configuration above falling water film / argon (Ar)	Ultrapure aqueous solution 500 ml 20 – 30 min 50 mg/L	Complete degradation occured	(Hama Aziz et al., 2017)
DCF, Carbamazepine (CBZ), CFX	Corona discharge / pulsed needle-to-plane continuous flow reactor / air	Distilled, lake and river water 10 – 40 ml/min 24 min 1 ml (in mix added in equal ratio)	>99 % in distilled and lake water >91 % in river water	(R. K. Singh, Philip, et al., 2019)
Paracetamol	Corona discharge / pulsed above liquid / air or O_2	Ultrapure aqueous solution 40 000 ml 30 min 100 mg/L	Complete degradation with partial mineralization	(Panorel et al., 2013)
CBZ, diatrizoate, diazepam, DCF, IBP, 17a-ethinylestradiol, trimethoprim	Corona discharge / coaxial geometry / discharge inside water in surrounding air	Ultrapure aqueous solution 300 ml 60 min 500 mg/L	45 – 99 %	(Banaschik et al., 2015)
Perfluorinated compounds				

OMPs	Plasma system/plasma type and configuration/working gas	Solution type/volume treated/treatment time/initial concentration	Degradation	Reference
perfluorooctanoic acid (PFOA), perfluorooctane sulfonate (PFOS)	DC-plasma generated within gas bubbles/ O_2, helium (He), Ar	Ultrapure aqueous solution 50 mL 240 min 50 mg/L	92 % - decomposition ratio of fluorine ions 57 % decomposition ratio of sulfate ions	(Yasuoka et al., 2010)
PFOA, PFOS	DC-plasma generated within gas bubbles/ O_2	Ultrapure aqueous solution 20 mL PFOA: 3h 41.4 mg/L PFOS: 8h 60 mg/L	PFOA: 94.5 % defluorination ratio PFOS: 70 % deflurination ratio	(Hayashi et al., 2015)
PFOA	DC-plasma generated within gas bubbles/O_2	Ultrapure aqueous solution (single and mix with other PFAS) 20 mL 150 min 156 µM	Complete degradation in single solution ; 80 % in mix solution	(Takeuchi et al., 2014)
PFOA	Laminar jet with bubbling (LJB)/ Ar	Ultrapure aqueous solution 1.4 L 30 min 20µM	90 % (high removal rate process) 25 % (high removal efficiency process)	(Stratton et al., 2017)
PFOA, PFOS	Discharge above the liquid with bubbling/argon	Ultrapure aqueous solution 1.5 L 30-120 min 8.3 mg/L	90 % of PFOA in 60 min and PFOS in 40 min	(R. K. Singh, Fernando, et al., 2019)
Pesticides				
Lindane	DBD a) conventional batch reactor (R1)/ He b) falling water film reactor (R2)	Distilled and wastewater 175 mL 5 min 1 mg/ml	87 % in R1and 79 % in R2 for distilled water 50 % in R1 for wastewater	(Hijosa-Valsero et al., 2013)
Atrazine	pDBD, gas phase above liquid/with or without membrane/air	Water matrix 100 ml 45 min 30 µg/L	Without membrane 61.0 % With membrane 84.7 %	(Vanraes et al., 2015)
	Pulsed DBD reactor with Continuous flow falling water film over activated carbon textile/air	Deionized water 2,5 L 2500 ml 30 min 200 µg/L	93.9 %	(Wardenier, Vanraes, et al., 2019)
2,4 - D	Corona discharge, needle to plane/air	Distilled, lake and river water Not defined 24 min 0.2 – 2 mg/L	> 99 % in distilled and lake water > 91 % in river water	(R. K. Singh, Philip, et al., 2019)
	Pulsed corona discharge/O_2	Tap water 330 ml 60 min 25 mg/L	93 %	(Bradu et al., 2017)

OMPs	Plasma system/plasma type and configuration/working gas	Solution type/volume treated/treatment time/initial concentration	Degradation	Reference
	DBD reactor with planar falling water film/ pure Ar, Ar/O_2 (80:20), and air	Deionized water solution 0.5 L 90 min 100 mg/L	Degradation occurred but percentage not specified	(Hama Aziz et al., 2018)
	Multiple pin-plate corona discharge/air	Aqueous solution Not defined 6 min 1 mg/L	100 %	(R. K. Singh et al., 2017)
Alachlor	Continuous flow pulsed DBD/O_2	Deionized water solution Single pass through reactor 30 min 1mg/L	78.4 %	(Wardenier, Gorbanev, et al., 2019)
	DBD/plasma gas bubbled/ combined with activated carbon/air	Ultrapure aqueous solution 30 min 500 ml 57 µg/L	75.1 %	(Vanraes et al., 2017)
Carbofuran	Corona discharge, needle to plane/air	Distilled, lake and river water Not defined 24 min 0.2 – 2 mg/L	> 99 % in distilled and lake water > 91 % in river water	(R. K. Singh, Philip, et al., 2019)
Phenols and phenolic compounds				
2,4 dibromophenol	DBD a) conventional batch reactor (R1)/ He b) falling water film reactor, surface discharge (R2)	Ultrapure aqueous solution a) 4 ml b) 174 ml 5 min 1 mg/L	a) 98 % b) 73.5 %	(Hijosa-Valsero et al., 2013)
Bisphenol A (BPA)	Pulsed DBD reactor with Continuous flow falling water film over activated carbon textile/air	Synthetic aqueous solution in mix 2500 ml 30 min 200 µg/L	98.8 %	(Wardenier, Vanraes, et al., 2019)
Phenol	DBD reactor, surface discharge/air	Ultrapure aqueous solution 70 ml 240 min 47.05 mg/L	Almost complete removal	(Ceriani et al., 2018)
	Cylindrical DBD reactor/ O_2	Ultrapure aqueous solution 100 ml 15 min 50 mg/L	Complete mineralization after 15 min	(Iervolino et al., 2019)
	DBD reactor, surface discharge/air	Ultrapure aqueous solution 70 ml 120, 240 min 47.05 mg/L	80 % in 4h (Ni/Cr wire) Complete degradation in 2h (SS wire)	(Marotta et al., 2011)
2,4 – dichlorophenol	DBD reactor with planar falling water film/ pure Ar, Ar/O_2 (80:20), and air	Ultrapure aqueous solution 500 ml 15 min 100 mg/L	Complete degradation	(Hama Aziz et al., 2018)
Dyes				

OMPs	Plasma system/plasma type and configuration/working gas	Solution type/volume treated/treatment time/initial concentration	Degradation	Reference
Methylene blue	DBD reactor/cylindrical configuration/ air, oxygen	Ultrapure aqueous solution 100 mL 5 min; 10 mg/L	96 % (O2) 76 % (air)	(Iervolino et al., 2019)
	DC plasma, in slug flow/ gas -liquid interface with bubbles/ O_2, Ar, He	Synthetic wastewater 5 mL time specified as one-time (one lap) 15 mg/L	94.5 % O2 89.3 % Ar 75.8 % He	(Yamada et al., 2020)
	Pulsed corona discharge in multiwire-plate/air	Ultrapure aqueous solution 35 mL 10 min 50 mg/L	Almost complete degradation(decolorization)	(Magureanu et al., 2013)
Methyl orange	Surface glow discharge/air	Ultrapure aqueous solution 50 ml 15 min 10 mg/L	93 %	(W. Liu et al., 2016)
	DBD reactor/air	Aqueous solution 10 mL 60 – 180 sec 50, 75, 100 mg/L	Degradation occurred but percentage not specified	(Sarangapani et al., 2017)
	Cylinder-like reactor, DC plasma/air	Aqueous solution 200 ml 30 min 20 mg/L	Degradation occurred but percentage not specified	(He et al., 2018)
Methyl red	DBD reactor/air	Solution in deionized water 25 ml 5 min 100 mg/L	Complete degradation after 5 min at 80 kV	(Pankaj et al., 2017)
Crystal violet	DBD reactor/air	Solution in deionized water 25 ml 5 min 100 mg/L	Complete degradation after 5 min at 80 kV	(Pankaj et al., 2017)
	DBD reactor/cylindrical configuration/air	Ultrapure aqueous solution Not available 25 min 50 – 100 mg/L	> 89 %	(Reddy & Subrahmanyam, 2012)
Acid orange 7	Two formed modes-corona like discharge and streamer channels/air	Deionized water 200 ml Time not defined 20 mg/L	Degradation occurred but percentage not specified	(Ruma et al., 2013)

1.3. PFAS water treatment

In terms of PFAS elimination processes in treatment plants, many studies and practice have shown that most PFAS are highly recalcitrant to conventional wastewater treatment, but also to many AOPs due to their persistence nature. For example, (X. Yu et al., 2018) examined the effects of long-term exposure to PFOA on activated sludge in lab-scale reactor and suggested that, while extreme PFOA concentrations may be tolerated in WWTPs, long-term impacts could threaten the stability of microbial communities, especially for organic matter processing. It recommends pretreatment strategies that can reduce PFOA concentrations before standard treatment. (Lakshminarasimman et al., 2021) showed different sludge treatment types where alkaline stabilization and palletization often increase PFAS levels, while some aerobic and anaerobic systems show moderate removal. The efficiency and outcome of PFAS transformation or removal depend on conditions like sludge retention time and system design, which impact microbial activity and precursors degradation potential. It has been shown that different pretreatment methods and possible tertiary treatment methods should be implemented to degrade or completely remove PFAS (Abunada et al., 2020; Nzeribe et al., 2019). Table 2. Summarizes potential treatment technologies for PFAS with an example of the performance.

TABLE 2. Summary of potential treatment technologies for PFAS.

Mechanism	**Treatment process**	**Performance**	**Reference**
Destructive treatment	Electrochemical oxidation	16.7- 67 %	(Duinslaeger & Radjenovic, 2022)
	UV_Fenton	95 % degradation	(Tang et al., 2012)
	Sono-chemicals	99 %	(Lin et al., 2015)
	Biodegradation	Up to 60 %	(Huang & Jaffe, 2019)
	Photocatalysis	98.8 %	(Zhao et al., 2012)
Non-destructive treatment	Adsorption	Sorption rate for PFOS 15.8 mg/g at 24h	(D. Zhang et al., 2016)
	Ion exchange	88 % removal of PFOA	(Du et al., 2015)
	Nanofiltration and reverse osmosis	70-97 %	(C. Liu et al., 2022)

Removal by granular activated carbon (GAC) and ion exchange resin (IX) has been mostly used for removal of PFAS from wastewater with high efficiency for most PFAS (Chow et al., 2022; Dixit et al., 2020; Murray et al., 2021; Woodard et al., 2017). However, due to concerns about the GAC disposal, the long treatment time, the high energy input and the possible leaching of short-chain PFAS to groundwater, research into methods for complete removal has become all the more important. AOPs, such as photocatalysis (Z. Li et al., 2019), sonolysis (Gole et al., 2018), electrochemical oxidation (Duinslaeger & Radjenovic, 2022), plasma treatment technologies (Saleem et al., 2020, 2022; R. K. Singh, Multari, et al., 2019) have proven to be effective in their removal from water.

Several authors have reported the application of NTP for PFAS degradation. (Stratton et al., 2017) investigated degradation of PFOA and PFOS substances in groundwater samples. (R. K. Singh et al., 2021) used landfill leachate for the treatment of various PFAS substances with a plasma jet above the liquid with bubble formation. In (Yasuoka et al., 2011) degradation of PFOA and PFOS in solution by DC-plasma generated within gas bubbles was studied, using different gases, oxygen and argon. A similar configuration was used in (Hayashi et al., 2015), where successful degradation of PFOA and PFOS occurred after 3 and 8 hours of treatment, respectively. Defluorination ratio of 94,5% confirmed almost complete degradation of PFOA. As for the PFOS, ratio of 70% can be explained with the existence of SO_3H sulfo-group which makes PFOS less degradable. (Takeuchi et al., 2014) investigated degradation of PFOA using generated plasma inside oxygen bubbles. Initial concentration of 156 μM of PFOA was degraded after 2.5h treatment. Also, the authors investigated degradation of PFOA in a mixture with perfluoroheptanoic acid (PFHpA), another PFCA. In that case, rate constants decreased to about 80% compared to those in solutions containing single pollutant. Authors also pointed out that PFOA molecules behave differently in liquid-phase reactions than at the gas-liquid interface due to their surfactant characteristics which affects their degradation (Takeuchi et al., 2011). A few of them mentioned more complex matrices but with still limited information on PFAS byproducts after plasma treatment. (R. K. Singh, Fernando, et al., 2019) have done interesting work on breakdown products of PFAS in plasma-based water treatment processes, PFOA and PFOS compounds.

1.3.1. PFAS degradation pathways in plasma systems

For PFAS and other OMPs, the degradation mechanisms in water treatment processes have been a significant focus of the research. Understanding different systems and determining the most effective ones for removing various OMPs is crucial. It is generally known that results depend not only on the water treatment system but also on the chemical nature of the OMPs. With better understanding of degradation pathways, it is possible to determine which system is most effective for specific types of (waste)water (that contains specific OMP) as well as which transformation products may occur.

Possible degradation pathways of PFAS in a plasma-based water treatment have been proposed by several studies (Hayashi et al., 2015; Singh, Fernando, et al., 2019; Stratton et al., 2017; Takeuchi et al., 2014; Yasuoka et al., 2010). (Takeuchi et al., 2014) suggested the following degradation pathway: PFAS can adsorb on the gas-liquid interface since they have surfactant characteristics. Then, the C-C bond may break because of the interaction with electrons and ions but also as a result of a direct thermal degradation. Generated fluorocarbon radicals that are located in the bubbles may reduce and oxidize to H and O radicals, HF, CO_2 and CO gases. The authors indicated that there is more than one possible parallel pathway during degradation of PFAS, therefore, it is difficult to determine the exact degradation mechanism.

Decomposition of PFOA and PFOS was also investigated by (Hayashi et al., 2015). In the degradation process of PFOA, the byproducts which are detected and measured were PFCAs ($C_nF_{2n+1}COOH$, n=1 to 6) with carboxyl group (COOH) like PFOA. Reaction formulas were suggested (Eqs.1-3) where M^+ stands for ions with the highest energy in the plasma (Hayashi et al., 2015).

$$C_nF_{2n+1}COO^- + M^+ \rightarrow C_nF_{2n+1}COO\cdot + M^+ + e^- \tag{1}$$

$$C_nF_{2n+1}COO\cdot \rightarrow C_nF_{2n+1}\cdot + CO_2 \tag{2}$$

$$C_nF_{2n+1}\cdot + 2H_2O \rightarrow C_{n-1}F_{2n-1}COO^- + 3H^+ + 2F^- + H\cdot \tag{3}$$

The hypothesis is that the PFCA are present as negative ions on the surface, and they can collide with ions with the highest energy. Similar byproducts may occur after degradation of PFOS in the treatment, but since PFOS has a sulfo-group (SO_3H), it is less likely decomposed than PFOA. Also, the formation of PFOA as a by-product of PFOS is possible by reactions (Eqs.4-6) (Hayashi et al., 2015).

$$C_8F_{17}SO_3^- + M^+ \rightarrow C_8F_{17}SO_3^{\cdot} + M^+ + e^- \qquad (4)$$

$$C_8F_{17}SO_3^{\cdot} \rightarrow C_8F_{17}\cdot + SO_3^{\cdot} \qquad (5)$$

$$C_8F_{17}\cdot + 2H_2O \rightarrow C_7F_{15}COO^- + 3H^+ + 2F^- + H \qquad (6)$$

In the study by (Yasuoka et al., 2010) it was reported that the decomposition of PFOA/PFOS may be significantly affected by the applied voltage polarity at the discharge electrode(s), regardless of the working gas. Since PFOA/PFOS in solution is an anion concentrated close to bubble-water interface, it may react with some positive plasma species approaching the surface (M^+) when a positive voltage is applied to the powered electrode. Reactions involving these species were proposed (Yasuoka et al., 2010). The ionized PFOS molecules react with M^+, resulting in the formation of shorter carbon chains than PFOS and the formation of fluoride and sulfate ions. PFOA reacts in a similar way to PFOS, with the fluorinated radical reacting with H_2O to form shorter-chain PFCA. Fluoride ions and carbon dioxide can be generated during PFCA degradation. Contrarily, if negative voltage is applied to the powered electrode, generation of oxygen and hydrogen occurs in the gas phase which may influence decomposition. Moreover, in this paper it was concluded that hydrated electrons are not significant for PFAS degradation. However, in the paper by (Stratton et al., 2017) where PFOA/PFOS degradation was studied, the hydrated electrons were reported as important species in addition to argon ions and high-energy free electrons produced in the plasma. In this investigation, the shorter-chain byproducts were quantified: PFHpA, perfluorohexanoic acid (PFHxA) and perfluoropentanoic acid (PFPnA). Although byproducts were identified, it was shown that up to 10% of PFOA and PFOS is converted into shorter-chain PFAAs. Experiments with scavenger showed that hydroxyl and superoxide radicals play no significant role. Several byproducts in plasma - based PFOA/PFOS solution treatments were also quantified by (R. K. Singh, Fernando, et al., 2019). PFOA, PFHxS and perfluorobutane sulfonate (PFBS) were found as byproducts of PFOS degradation. Also, some fluoride ions, inorganic carbon, and smaller organic acids (trifluoroacetic acid, acetic acid, and formic acid) were identified with significant concentrations. The short chain PFCAs were detected as well, which suggests that some step-wise reduction of the parent compounds has occurred. Concentrations of all byproducts increased in the first 60 minutes of treatment but by the end of experiment decreased. The authors suggested that the main species responsible for PFAS degradation are electrons from plasma/gas phase, aqueous electrons, and argon ions.

1.4. Analytical techniques for OMPs detection and monitoring

Due to the vast number of emerging contaminants, complexity of water matrices, and often, low concentrations of emerging contaminants, development of analytical techniques with high sensitivity and selectivity has always been a challenge. While the term OMPs mostly includes compounds that are known, once released in the environment, those compounds go through transformation processes, abiotic or biotic, and as a result, transformation products (TPs) occur. The formation of TPs can be through different processes such as oxidation, hydrolysis, cleavage, hydroxylation, conjugation etc. whether in the environment or during water treatment processes. To some extent, they can differ from their parent compounds in their ecotoxicological profile and environmental behavior. These unknown products represent a great challenge when it comes to the identification of contaminants in water. Nowadays, the most commonly used analytical methods for monitoring and identification of contaminants and their TPs are liquid chromatography (LC) coupled to mass spectrometry (MS) by using different mass analyzers. Most commonly mass analyzers are triple quadrupole (QdQ), ion-trap (IT), linear ion-trap Orbitrap, quadrupole-Orbitrap, quadrupole time-of-flight (Q-TOF) or quadruple-linear ion trap (Q-LIT) (Bletsou et al., 2015).

Depending on the available instrumentation, sampling, target outcome of experiments and research, identification workflows can be divided into three different types of screening:

i) Target analysis which is based on identification and determination of preselected known compounds;

ii) Suspect screening, based on the list of possible contaminants which can be compiled based on literature or prediction models;

iii) Non-target analysis, compounds are not known and are identified through supplementary analytical techniques and post-acquisition data tools with the contribution of knowledge of parent compounds (MS/MS spectrum, molecular formula, other physico-chemical data).

Figure 10 shows the flowchart of the screening procedure.

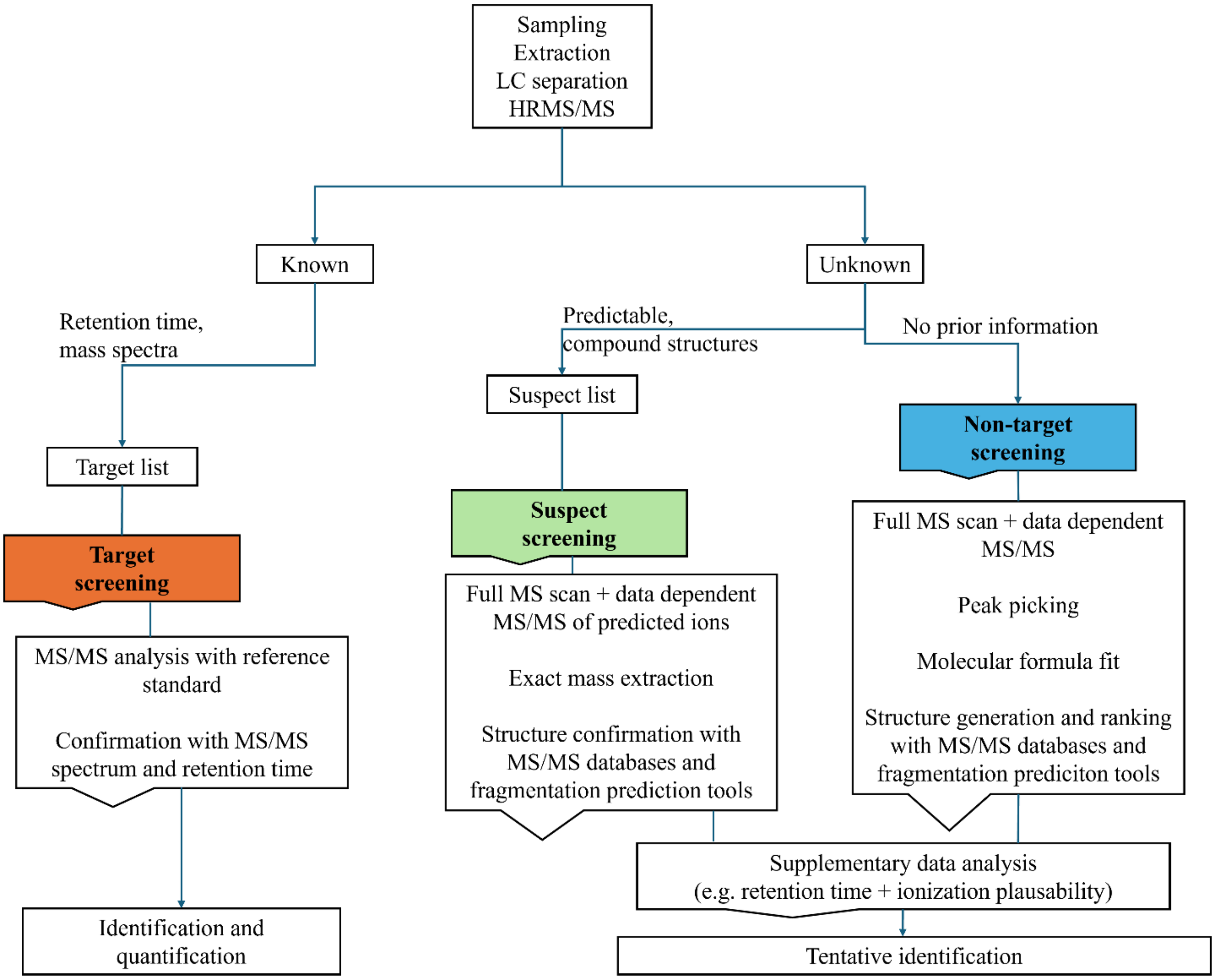


FIGURE 10. Flowchart for target, suspect and non-target screening.

Most PFASs studied nowadays are quantified by various analytical methods. The most used method is USEPA Method 537 (537.1 and 533 variants), which has been validated in several laboratories for the analysis of drinking water samples and non-drinking water matrices. Depending on the version, the methods test up to 25 PFAS analytes, while the following are always included and usually analyzed: PFOA, PFOS, PFHxA, PFHpA, PFNA, PFDA, PFBS, PFHxS and few longer-chain PFAS ((ITRC, 2019; Lallas, 2001; Llorca et al., 2010, 2012). Other well-known standard methods are USEPA SW-846 Method 8327 for analysis of groundwater, surface water and wastewater. Method 1633 also includes the analysis of sediment, soil and landfill leachate, while DOD Method AFFF01 includes the analysis of PFOA and PFOS in AFFF. Usually, all the methods require preparation of aqueous samples by using solid-phase extraction (SPE) technique and cleanup procedures for the elimination of matrix interferences in case of complex water matrices. All methods published for targeted PFAS analysis use liquid chromatography-tandem mass spectrometry (LC/MS/MS), which is especially suited for analysis of ionic compounds, such as PFSAs and PFCAs group. Even though the list of PFAS compounds exceeds 7500, standard analytical methods target only around 2% (Nason et al., 2021). Therefore, suspect screening and nontarget analysis (NTA) by using LC coupled with high resolution tandem MS (LC-HRMS/MS) are widely used approaches for identification and data collection for PFAS in environmental samples (Jamari et al., 2019; L. Liu et al., 2022; Miaz et al., 2020; Nason et al., 2021; N. Yu et al., 2018). In work of (L. Liu et al., 2022) the combination of suspect screening and NTA was applied to analyze PFAS in AFFF-contaminated water and PFAS in representative samples of fluorocarbon surfactants (FS) of two international brands, comparing PFAS composition with FS products. Suspect screening was carried out with the function of Find by Formula (FBF) which compares MS profiles of each sample with the established PFAS database (accurate mass, isotope abundance and isotope space included) while NTA analysis included mass defect filtration, -CF2- and -CF2CF2- homologues search and fragmentation verification. This combination led to great results, as 36 PFAS were identified in water contaminated by AFFF. In (Barzen-Hanson et al., 2017) 40 PFAS where discovered in AFFF-impacted groundwater by applying LC Q-TOF/MS and utilizing Kendrick mass defect in NTA. Similar suspect screening (PFAS homologue analysis with Q-TOF MS) was applied in (Y. Wang et al., 2018) to discover several PFAS classes (precursors and TPs) in wastewater of WWTP near the Yangtze River. In work of (Ng et al., 2022), a target and suspect screening of 4777 PFAS compounds in wastewater, groundwater, river water and biota samples in the Danube River basin was performed by LC-HRMS, using the NORMAN Digital Sample Freezing Platform (DSFP), generating mass spectrometry fragmentation patterns and retention time index predictions for their screening. A total of 82 PFAS were detected in the samples, of which 72 PFAS were detected by suspect screening. The LC-IMS-MS (ion mobility-MS) was used for the evaluation of PFAS in fish fillets from recreational and drinking water sources in work by (Boatman et al., 2024). They performed a suspect screening for 100 PFAS and an NTA for additional PFAS and detected a total of 36 PFAS, 19 of which with NTA. In work of (Young et al., 2022) suspect and NTA methods were used by utilizing 21 tesla (T) Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR MS) to detect PFAS in AFFF, with targeted formula database (C,H, F, N, O, P, S; ≤ Da), isotopologues and Kendrick-analogous mass difference networks (KAMDNs). Similar methods can also be found in (Cioni et al., 2024; Harris et al., 2022; Mofokeng et al., 2024). While suspect screening is quite developed and widely used, NTA is still a developing analytical approach and data processing is a major challenge (De Silva et al., 2021; Y. Li et al., 2020; Y. Liu et al., 2019; Miaz et al., 2020; Y. Wang et al., 2018). Multiple software programs are available for processing LC-HRMS/MS data, for example Compound Discoverer and FluoroMatch, however they can lack desired features for PFAS analysis, such as MS/MS libraries developed specifically for PFASs that can be used for confident structural annotation. The development of mass spectral libraries to match non-targeted analyses to source profiles is part of ongoing research.

1.5. Risk assessment

The ongoing investigation of emerging contaminants in water bodies, their fate and distribution, the identification of hotspots and sources, and the assessment of the associated risks to aquatic ecosystems are topics that are receiving considerable attention in current research and environmental discussions. Among the diverse range of OMPs, the focus is on compounds that are characterized by persistence and mobility in the water cycle. One of many challenges is the classification and prioritization of substances based on their ecotoxicological spectrum which has a great impact on bringing regulations and developing water treatment processes. In case of PFAS, for example, the question arises as to which PFAS should be completely banned from production processes and which can be used, but only after they have been completely removed in WWTP. For these reasons, environmental risk assessment (ERA) is a useful tool to point out the major concerns for certain substances. In general, various risk assessment approaches attempt to address concerns about the potential impact of individual substances on the environment by evaluating both the exposure resulting from chemical discharges and releases, and the effects of these emissions on the structure and function of the ecosystem. According to Technical Guidance Document on Risk Assessment by European Union (Commission, 2003) three approaches are used:

- Quantitative PEC/PNEC estimation for environmental risk assessment of a substance involves comparing compartmental concentrations (PEC) with the predicted no effect concentration (PNEC), which is the concentration below which unacceptable effects on organisms are unlikely to occur. This process also includes an assessment of food chain accumulation and secondary poisoning
- A qualitative procedure for environmental risk assessment of a substance is used when quantitative assessment of exposure and/or effects is not possible
- The PBT assessment of a substance involves identifying its potential to persist in the environment, accumulate in biota, and be toxic, along with evaluating its sources and major emissions

The methodologies employed aim to identify acceptable or unacceptable risk, forming the basis for regulatory decisions derived from the risk assessment. In some cases, the uncertainties in conducting the standard assessment become unacceptably high. In this instance, the methodologies focus on identifying emission sources to determine where exposures should be minimized. PECs can be derived from available measured data and/or model calculations. PNEC values are typically determined based on results from single-species laboratory tests or, in some cases, established effect or no-effect concentrations from model ecosystem tests, with appropriate assessment factors considered. The PNEC can be derived using an assessment factor approach or, when sufficient data is available, through statistical extrapolation methods. A PNEC is considered a concentration below which unacceptable effects are unlikely to occur.

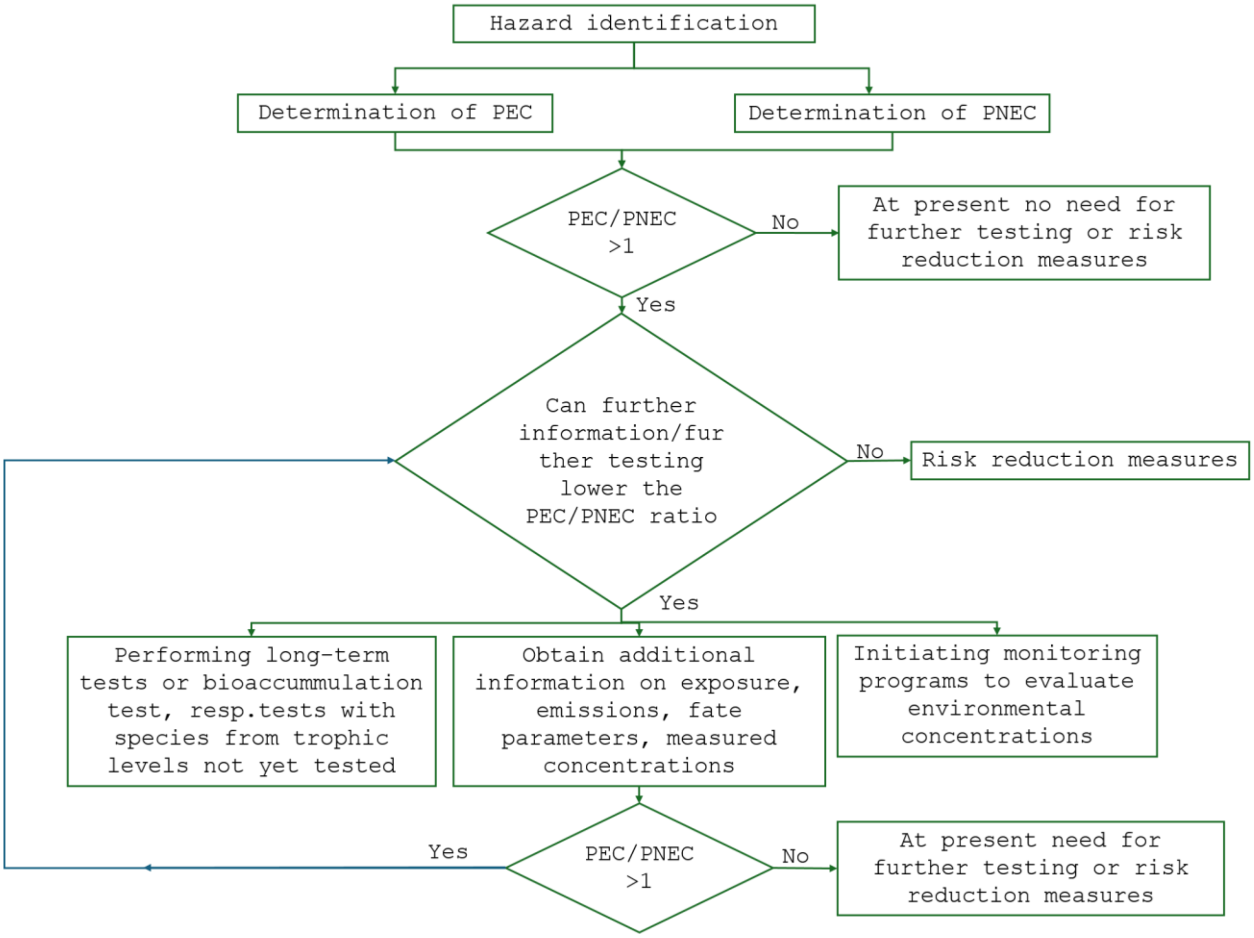


FIGURE 11. General procedure for environmental risk assessment (adapted from Technical Guidance Document on Risk Assessment by European Union)

The PBT assessment differs from local and regional assessment approaches as it aims to protect ecosystems where risks are harder to estimate. Traditional risk assessment methodologies may not adequately address these additional concerns for the marine environment, which can be summarized as:

- The concern that hazardous substances may accumulate in parts of the marine environment, leading to: (i) Unpredictable long-term effects of such accumulation. (ii) Practical difficulties in reversing such accumulation.

- The concern that remote ocean areas should remain untouched by hazardous substances resulting from human activity, preserving the intrinsic value of pristine environments.

TABLE 3. Criteria for identification of PBT and vPvB substances

Criterion	***PBT criteria***	***vPvB criteria***
P	Half-life > 60 d in marine water or > 40 d in freshwater or half-life > 180 d in marine sediment or > 120 d in freshwater sediment *	Half-life > 60 d in marine – or freshwater or > 180 d in marine or freshwater sediment
B	BCF > 2000	BCF > 5000
T	Chronic NOEC < 0.01 mg/l or carcinogenic, mutagenic or endocrine disrupting effects	Not applicable

These concerns are particularly relevant for substances that persist for long periods, bioaccumulate in biota, and cause toxic effects over long periods of time and distances. While this also applies to freshwater environments, the marine environment poses an additional challenge: once a chemical enters the open seas, stopping emissions will not necessarily reduce chemical concentrations, making any effects difficult to reverse. Furthermore, the long-term exposures and life cycles of many important marine species make early detection of effects challenging.

For PBT substances, establishing "safe" concentration in the environment is not reliable. The PBT assessment is specifically developed to address the high uncertainty in predicting reliable exposure and/or effect concentrations, which hinders quantitative risk assessment. The PBT assessment involves two main steps:

- Identification of PBT substances using specific criteria for their inherent properties.
- Evaluation of the sources, major emissions, and pathways to the marine environment to determine the most appropriate and effective measures to reduce releases.

The criteria for determining if a substance should be classified as a PBT (persistent, bioaccumulative, and toxic) substances is regulated by European Union in Technical Guidance but also based on Registration, Evaluation, Authorisation, and Restriction (REACH) (Council, 2020; EU Parliament, 2019; European Commission, 2020b; European Union Council, 2020) including European Chemical Agency (ECHA) framework criteria . For most substances, available data may not conclusively determine if they should be considered under the PBT assessment. Therefore, screening data that identify the potential for a substance to be a PBT must be utilized. In principle, substances are selected when they meet all three inherent properties: P, B, and T. However, some flexibility is required, for instance, in cases where one criterion is marginally unmet, but the others are significantly exceeded. This might include substances that do not meet the persistence criteria but bioaccumulate significantly and are found in marine biota far from anthropogenic sources.

In recent years, especially for the substances in aquatic environment, more focus is towards corresponding acronyms of PBT – PMT (which stands for Persistent, Mobile, Toxic) and vPvM (very Persistent and very Mobile) approaches (Hale et al., 2020; Jin et al., 2020; Neumann & Schliebner, 2019; Rüdel et al., 2020). Once the chemical substance enters into the environment, it can be transferred through natural barriers, soil, river banks and can pose a threat to drinking water sources. This shows that factors such as persistence and mobility of a substance in the aquatic environment, and especially their specific combination, may control the overall effect of a substance. It is evident that substances that are persistent in the environment, mobile in aquatic systems, and toxic (PMT), or those that are very persistent and very mobile (vPvM), possess specific combinations of intrinsic properties that make them inherently hazardous to drinking water resources. In 2022 (European Commision, 2022) both PMT and vPvM criteria were introduced to the Commission Delegated Regulation for the classification, labelling and packaging of substances and mixtures. The classification criteria for PMT and vPvM is as follows: for P criteria and vP criteria, the same is applied as in PBT and vPvB approaches. As for the M criteria, a substance is considered mobile when the log Koc value is less than 3. For an ionisable substance, if log Koc value is less than 3, for pH range between 4 and 9, substance is considered mobile. As for vM criteria, substance is considered very mobile when the log Koc value is less than 2 (for ionisable substance in pH range between 4 to 9) (EU, 2023). For the toxicity, the same applies in both PBT and PMT. The similarity between the acronyms is designed on purpose, to point out the equal importance of the mobile compounds as well as those that fulfill B criteria. The assessment of the PMT/vPvM is not yet regulated within EU chemicals regulation REACH. Even before REACH was established, there was widespread agreement that certain intrinsic properties should preclude a quantitative, risk-based regulatory approach. Substances that are carcinogenic, mutagenic, reprotoxic, or endocrine disruptors, for which no threshold can be determined, as well as those classified as persistent, bioaccumulative, and toxic (PBT) or very persistent and very bioaccumulative (vPvB), necessitate a reduction in human and environmental exposure and thus should be regulated based on their hazards. Unfortunately, REACH does not currently include similar criteria for intrinsic properties that might indicate a potential contaminant in drinking water. This creates a regulatory gap between the drinking water directive and REACH, undermining the precautionary protection of our drinking water sources. However, the incorporation of this approach is strongly recommended (Rudin 2023, Rudel 2020), Aggarwal 2024)) especially for the substances that show low bioaccumulation characteristics, but with high mobility, such as PFAS. According to (Hale 2020, Sjerps 2016, Aggarwal) and other studies, many substances can breakthrough artificial barriers in WWTP due to their high mobility. This suggests that when there are ongoing emissions of PMT/vPvM substances and inadequate removal during water treatment, environmental concentrations will rise over time as these substances persist in the water cycle, potentially leading to irreversible effects.

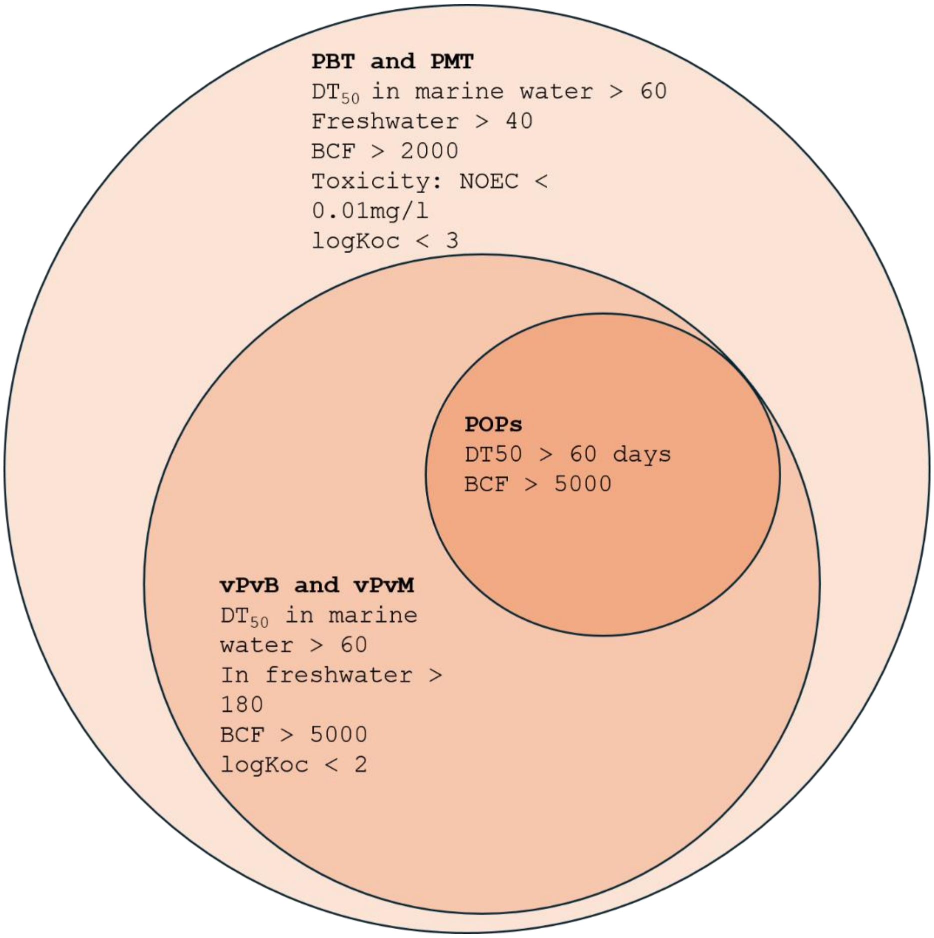


FIGURE 12. Relations of PBT/vPvB, PMT/vPvM, and POPs compounds

1.5.1. PFAS risk assessment and regulations

Even though this group of chemicals comprises more than 4,700 substances, European regulations have covered the most common such as PFOS and PFOA (EEA (European Environment Agency), 2011; European Commission, 2000). In 2018, with a European Directive (European Commission, 2018) PFOA and PFOS have been regulated with limits in drinking water at 4 μg/L and 0.4 μg/L, respectively, which are the levels that World Health Organization (WHO) recommends. Both PFOS and PFOA are now restricted under EU POPs (Persistent Organic Pollutants) Regulation (European Commission, 2020b). The Commission also proposes deviating from WHO values for the individual substances and proposes regulation for PFAS as a whole group, with suggested values (limit concentration in drinking water) of 0.1 μg/L for individual PFAS, and 0.5 μg/L for PFAS in total. Another long-chain substance, perfluorohexane-1-sulphonic acid and its salts (PFHxS) that has been widely used as a raw material or precursor in PFAS production, was assessed and considered for listing under Stockholm Convention (UNEP, 2019). In December 2019 the agreement between the European Parliament (EP) and the Council included the limit of 0.5 μg/L in drinking water for all PFAS and in December 2020 EP formally adopted the revised Drinking Water Directive which obliges Member States to transpose it into national legislation (European Union Council, 2020). Since the production of the most commonly PFAS compounds was banned, new substances have emerged as substitutes, such as hexafluoropropylene oxide dimer acid, known as GenX, dodecafluoro-3H-4,8-dioxanonanoate (ADONA) and 6:2 chlorinated polyfluoroalkyl ether sulfonate (6:2 Cl_PFESA) commercially known as F-53B (Munoz et al., 2019; Z. Wang et al., 2013). However, recent studies have shown that their global spread in aquatic environments has further implications for consumers (Brase et al., 2021; Pan et al., 2017, 2018; Xu et al., 2021) and draws attention to their toxicity (Buck, 2015; Conley et al., 2021; Coperchini et al., 2021; Gaballah et al., 2020; Gordon, 2011). As far as US regulations are concerned, the US

EPA National Primary Water Drinking Regulations set maximum levels for six PFAS in drinking water: PFOA and PFOS as individual substances and GenX, PFBS, PFNA, PFHxS as PFAS mixture. The proposed rule also requires public water systems to monitor level of PFAS, report and reduce PFAS levels when those levels exceed the proposed standards (USEPA, 2016).

While regulations and proposals already exists for some PFAS substances, the challenge - one of many – is to classify and prioritize individual substances from the large group based on their ecotoxicological spectrum. The knowledge of the PFAS substances profile has great impact on the regulations and on developing water treatment processes. An important issue is also the lack of toxicity data for their byproducts, which raises the question of which PFAS should be completely banned from production processes and which can be used, but with a higher effort for excellent removal (ideally mineralization) in WWTPs (Brase et al., 2021; Fenton et al., 2021; Nian et al., 2020). For these reasons, ERA is a useful tool to point out the major concerns for certain substances. PBT assessment of PFAS based on REACH (ECHA, 2013; EEA (European Environment Agency), 2011; EU Parliament, 2019; European Commission, 2020a) including ECHA framework criteria can be useful tool to evaluate the prioritization of chemicals needed to be monitored or potentially banned from production chain (Ankley et al., 2021; Rüdel et al., 2020). In the study by (Vierke et al., 2012), the PBT assessment of the substance PFOA was evaluated using the following criteria under REACH, showing how the PBT criteria for PFOA are fulfilled. Environmental risk of 17 PFAS in marine sediment and water in the Gulf of Gdansk was presented in (Gałęzowska et al., 2021) while (Hale et al., 2020) presented case studies of PFBS and GenX and their persistence and mobility. A more comprehensive analysis of PFAS data identified under REACH is provided by (Rudin et al., 2023).

2. OBJECTIVES

The main research hypothesis of this thesis was that the use of new advanced technological processes, such as plasma water treatment, weather as a pretreatment method or post-treatment (tertiary treatment) or, potentially as a part of the hybrid systems, can improve the degradation and removal of very persistent and recalcitrant OMPs such as PFAS. More important, the implication of different approaches when assessing the environmental risk of the PFAS contaminants may be of significant value to conclude about the impact of parent compounds and their transformation products, to the aquatic environment (and consequently humans). Therefore, the overall objective of this thesis is divided into two streams: (i) to study elimination of PFAS compounds in different water matrices, behavior of water matrices during plasma treatment and (ii) environmental risk assessment of PFAS compounds in different water sources.

Specific objectives are:

- Study of NTP in gas-liquid environment generated with pin-type electrode setup at a laboratory scale for the removal of six substances selected as representatives of the different groups of perfluorinated compounds: carboxylates, sulfonates, and ethers
- Evaluation of the removal efficiency of each substance in three different matrices: distilled water (DW), tap water (TW), and secondary effluent (SE), under same experimental conditions
- To investigate various working parameters of NTP treatment and to identify byproducts in the liquid phase using HRMS, with a focus on novel substances such as ADONA, whose degradation mechanism was also investigated

- Environmental risk assessment of PFAS substances in fresh water (drinking water, river and groundwater), worldwide, to determine the occurrence of parent compounds and their transformation products, as well as novel compounds such as GenX and ADONA;
- To propose and evaluate approach in PBT and PMT methods, and to indicate which substances are of very high concern and what further steps are to be taken accordingly

3. METHODOLOGY

3.1. Plasma treatment of PFAS

Plasma source configuration

The treatments of PFAS-polluted water samples were performed using a non-thermal plasma (NTP) treatment with an atmospheric pressure plasma jet (APPJ) source. Electrical characterization of this device is presented in (JOVANOVIĆ et al., 2022) and (Kumar et al., 2022). Laboratory-scale APPJ source configuration is shown schematically in Figure 13. The APPJ consisted of a stainless-steel high-voltage (HV) electrode (1 mm in diameter) inserted inside a ceramic tube, which was then inserted in a glass tube with outer and inner diameters of 6 and 4 mm, respectively. The electrode was connected to a commercial HV RF power source (T&C Power Conversion AG0201HV) with a frequency of 332 kHz. In the experiments, argon was used as a working gas, with a flow rate of 1 standard liter per minute (slm). The argon flow rate was controlled by mass flow meter (OMEGA, FMA5800/5500). Time-variable current and voltage signals were monitored with a Tektronix oscilloscope (MDO3024 model), and a HV probe (Tektronix 6015A) was used to determine the voltage at the HV electrode. The glass sample vessel (φ= 55°mm) had copper tape at the bottom and it was grounded via a resistor of R= 1 kΩ for current monitoring. The streamer type discharge was generated above the liquid in a 10 mm gap between the tip of the powered electrode and the surface of the liquid sample. Simultaneously, the data from the oscilloscope was transferred to a laptop for further analysis. The power delivered from the power supply to the plasma source and the power in the grounded line, i.e. the power deposited from the plasma passing through the sample, were calculated.

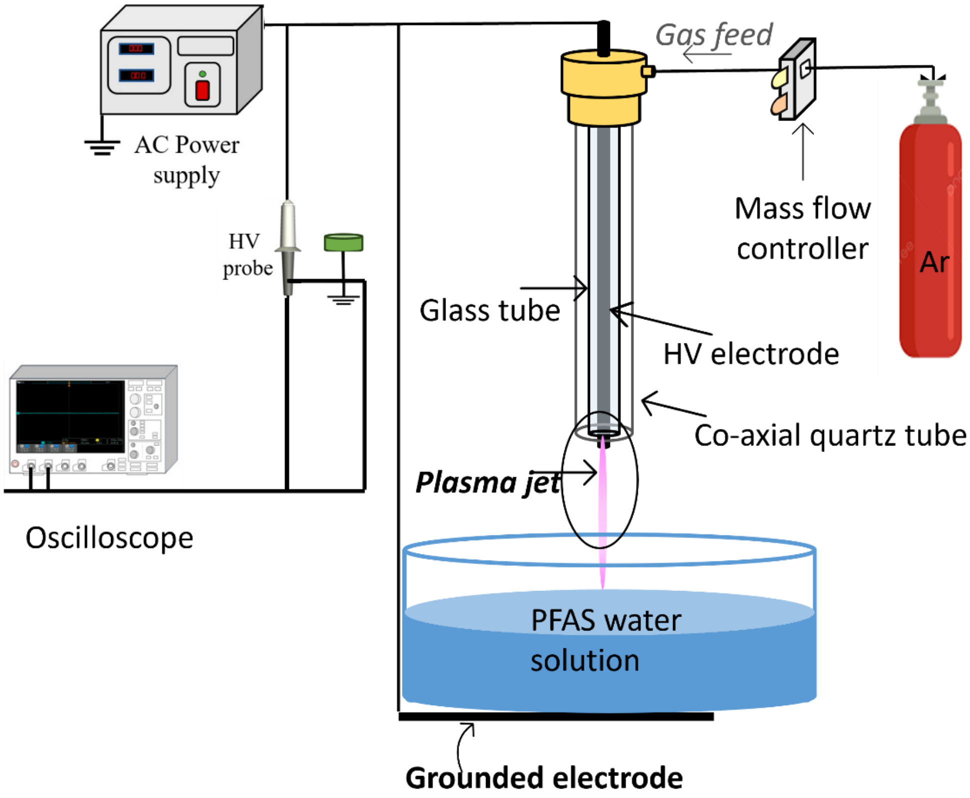


FIGURE 13. Plasma configuration scheme

Water samples treatment experiments

Standards for substance used in experiments, perfluorooctanesulfonic acid (PFOS), nonfluorobutane-1-sulfonic acid (PFBS), perfluorobutyric acid (PFBA), undecafluorohexanoic acid (PFHxA) were purchased from Sigma Aldrich. Hexafluoropropylene acid (HFPO - DA or GenX) and dodecafluoro-3H-4,8,-dioxanoate (ADONA) were purchased from Wellington laboratories. All solutions were prepared in high purity methanol (Thermo Fischer Scientific) as a solvent at room temperature (≈ 25°C) with a bulk concentration of 1000 mg/L and stored at ≈ 4 °C. Details of the compounds can be found in Table 9 of Annex.

From the standards bulk of 1000 mg/L, individual solutions of 6 different compounds, PFOS, PFBS, PFBA, PFHxA, GenX, ADONA were prepared in different types of water matrices: distilled water (DW), tap water (TW) and secondary effluent (SE) with initial concentration of 100 μgL^{-1}. Solutions were prepared in polypropylene flasks and used immediately in the experiments. The TW was obtained in Belgrade (Serbia) and filtered before the PFAS compounds were added. The SE was obtained from WWTP in Manresa (Spain) and was also filtrated prior to spiking. The characteristics of the TW are listed in Table 12 in the Annex, which is derived from public information on the quality of TW and Table 13 shows some physico-chemical parameters of the SE.

The experiments were done for each compound individually in 2 different volumes, 5 mL and 10 mL in different time intervals. For the 5 mL solutions, which were prepared with DW only, time intervals of 1, 1.5, 3, 3.5, 5 min and 3,5,7,10 min, using the same initial concentration with argon as working gas. As for 10 mL, individual PFAS solutions were subjected to plasma treatment for time intervals of 3, 5, 7 and 10 min, in all three matrices. Each experiment (each time interval) was done separately. After the plasma treatment, samples were taken in polypropylene vials of 1 mL to avoid any glass materials (due to PFAS tendency to "stick" on the glass wall of bottles) to investigate the degradation profile through target analysis and for the study of byproducts through non-target analysis. Additionally, all samples of TW and SE were filtered using Clarify-PP 13mm Syringe Filters 0.22 μm prior to injection to instruments QTRAP and Orbitrap. Measurements of pH, conductivity, and temperature for both control samples and each plasma – treated sample were conducted. Control samples consisted of untreated solutions in DW, TW and SE. DW served as a model to explore optimal removal without matrix interference. TW and SW allowed us to assess PFAS behavior and degradation efficiency in more complex environments. Additionally, the impact of plasma treatment on various parameters under the same initial concentration and treatment duration as in DW were examined. Furthermore, the volume of all samples was measured after each treatment. All experiments were tripled, and all measurements were taken as average value for the calculations of the results. In cases where the values differed significantly, those were not taken into calculations. For the experiments of DW, TW and SE treatment of 10 mL, both target and non-target analysis was utilized.

Analytical methods

For target PFAS analysis, a 5500 QTRAP hybrid triple quadrupole-linear ion trap mass spectrometer (QqLIT-MS) with a turbo Ion Spray source (Applied Biosystems, Foster City, CA, USA) coupled to a Waters Acquity Ultra-Performance^{TM} liquid chromatograph (UPLC) (Milford, MA, USA) was used, based on a method that was previously published (Llorca et al., 2012). The optimized compound-dependent parameters of the MS are summarized in Table 10 of Annex. For the chromatographic separation, an Acquity UPLC C18 column (50 mm x 2.1 mm, 1.7 µm) was used coupled with Phenomenex Luna 5 µm precolumn C8 (50 mm x 3 mm, 100 Å) to minimize contamination from mobile phases. The mobile phase used for the chromatographic separation consisted of aqueous ammonium acetate 5 mM (A) and methanol (B) with final flow rate of 0.4 ml min^{-1}. The elution gradient condition started at 10 % B, rose to 50 % B in 2 min, then linearly increased to 70 % B in 4 min and finally increased to 90 % B in 8 min. The sample injection volume was 10 µL. Limit of detection (LOD) for this method was 0.1 µg/L. Calibration curves of 5, 10, 25, 50 and 100 µg/L were done for each analytical batch. In case of TW and SE, samples were filtered prior to injection. High purity methanol and Mili-Q water used for mass spectrometry analysis were purchased from Thermo Fischer Scientific, while ammonium acetate used for mobile phases was obtained from VWR. The chemicals used were of either analytical grade or high purity (>98 %).

Liquid chromatography – high resolution mass spectrometry (LC-HRMS) on Orbitrap Exploris 120 (OE120) was used to identify possible degradation byproducts of all compounds. EPA Method 57 was adapted from the EPA Thermo Scientific source with some minor modifications. The mobile phases were 5 mM ammonium acetate in water (A) and methanol (B). In the final conditions, 90 % of (A) and 10 % of (B) were used at a flow rate of 0.4 mL/min and a pressure was 195 bar. The injection volume was 5 µL. Compound Discoverer (CD) version 3.1.0.3 (Thermo Scientific) was used for the data analysis. The .RAW files produced by the instrument were used directly in CD and FreeStyle (Thermo Fischer) software to confirm the reliability of TPs results. Workflow was based on the pre-generated "Environmental w Stats Unknown ID w Online and Local Database Searches" option (Figure 20, Annex), with few alterations within workflow nodes. The search for the exact mass matches in the samples was performed using the list of compounds in the EPA CompTox Dashboard PFAS Masterlist available August 30, 2022 (ComTox, s.f.) and the "Compound Class Scoring" feature. For tis purpose, two classes were created manually, "PFSAs" with fragments $[SO3]^-$, $[FSO3]^-$ and "PFAS general" with seven characteristic fragments: [C2F5]-, [C3F7]-, [C4F9]-, [C5F11]-, [FSO3]-, [FSO2]-, [CF3O]- General instrument parameters can be found in Table 11 of Annex.

3.2. Risk assessment

PFAS selection

A full list of PFAS with CAS number, molecular formula and molecular mass that have been studied in this part of work can be found in Table 14 of Annex. List contains PFAS substances that have been considered under the REACH, European Directive 2020/2014, USEPA list of contaminants and are of current interest in many studies and regulations. Additionally, list was updated with other substances in order to cover different PFAS structures, mostly carboxylates, sulfonates and ether-PFAS, as well as to cover both long and short-chain PFAS. The list contains various parent compounds, their transformation products, intermediates and metabolites that have been detected in water sources in the last 7 years. CompTox Chemicals Dashboard v2.2.1 database was used for the collection of PFAS chemical formula, structure, molar mass, Simplified Molecular Input Line Entry System (SMILES) and other chemical and physical properties.

HQ/RQ – Hazard assessment

According to the EU guidelines (Commission, 2003) the hazard quotient (HQ) approach is used to obtain toxicological risk level of each compound. Individual HQs were calculated as the ratio between the measured environmental concentration (MEC_1) and the Predicted No Effect Concentration (PNEC) (7).

$$HQ = MEC_1/PNEC \tag{7}$$

An exhaustive literature review was conducted to collect measured concentrations of PFAS compounds in drinking water, groundwater and river water (Boone et al., 2019; Campo et al., 2016; EPA Office of Water, 2024; Gebbink et al., 2017; Kurwadkar et al., 2022; X. Li et al., 2022; T. Liu et al., 2022; McMahon et al., 2022; Pan et al., 2018; Sadia et al., 2023). In addition, another set of concentration data was collected based on highest concentration reported wastewater effluents (MEC_2) from the comprehensive and detailed review by (Lenka et al., 2021) to predict risk quotient (RQ), which was calculated using a similar equation as for HQ and the same PNEC values (8).

$$RQ = MEC_2/PNEC \tag{8}$$

From the studies that are well summarized in (Lenka et al., 2021), the highest concentration found was used to predict the worst case scenario. The PNEC values were taken as the lowest recorded toxicity data - fresh water, where possible, and biota fish from NORMAN database (NORMAN, 2022). If available, the PNEC values were taken from experimental data for more accurate reflection of actual toxicological impact and real-world relevance. Otherwise, predicted values were derived from Quantitative Structure-Activity Relationship (QSAR) models. Some of the target compounds were not available via input of their CAS numbers, therefore, SMILES notations were used. The environmental risk characterization was performed by following ranking criteria from (Gałęzowska et al., 2021; Mendoza et al., 2015) with some modifications. If the HQ (RQ) values are below 0.01, it is classified as insignificant level. If $0.01 \leq HQ(RQ) < 0.1$, the risk is low; if $0.1 \leq HQ(RQ) \leq 1$ the risk is moderate, if $1 < HQ(RQ) \leq 10$, the risk is high. All HQ(RQ) values above 10 are considered extreme risk level. Scores from 1 to 5 were then assigned accordingly: 1 as the lowest score (lowest risk) and 5 the highest score (the highest risk). In case data has not been found, the score of the high risk (5) has been given.

OPB(M)T environmental Hazard

According to the current legislation of PFAS in water, the use and manufacturing of a few PFAS compounds are being restricted under European Chemicals Regulation REACH (EU Parliament, 2019) (Stockholm, 2019). In this work, a method has been proposed to identify environmental hazard of a substance by following the criteria set in REACH regulations with few alterations and suggestions. The identification of P, B, T, M and O was carried out for total of 37 compounds, including transformation products and precursors, from perfluoroalkyl carboxylic acids (PFCAs), perfluoroalkane sulfonic acids (PFSAs) and perfluoropolyethers (PFPEs) subgroup of PFAS and some others. Each of the criteria has been assigned with corresponding variable, with set thresholds and assigned score (Sx) which will be explained below.

For the P criteria, according to REACH, the half-life data should be considered under adequate conditions. It is very difficult to measure the biodegradation half-life (DT50) of PFAS, as they take years to degrade and are therefore considered very persistent (Cousins et al., 2020). Another possible approach to evaluate the persistence of a compound is through its removal efficiency in wastewater treatment plants (WWTP) and/or laboratory experiments (Castaño-Trias et al., 2024; Daouk et al., 2015; Verlicchi et al., 2023). In this work, literature data of the removal efficiency from WWTP has been collected (Lenka et al., 2021). The proposed threshold was modified from (Daouk et al., 2015) and the P criteria is given with corresponding variable - removal efficiency (r.e.) 100-R. The assigned scores were accordingly from 1 to 5, and if no data were available, a score of 5 was assigned, according to (Verlicchi et al., 2023).

For the B criteria, the assessment of the substances can be done based on the bioconcentration factor (BCF) values. According to the European guidelines (Council, 2020), if BCF is higher than 2000, the compound is considered as bioaccumulative and if it is greater than 5000, the compound is very bioaccumulative. However, since the BCF values in the database vary greatly, B is evaluated in this work using the octanol/water partition coefficient (log Kow) (Ankley et al., 2021; Verlicchi et al., 2023). If the log Kow is lower than 1, the risk is considered insignificant, if it is higher or equal to 1, the risk is low, if it is between 2 and 3, the risk is medium, if it is higher than or equal to 3, the risk is high and all log Kow values higher than or equal to 4.5 correspond to extreme risk. The values of log Kow were modeled with QSAR and EPISUITE KOWWIN (https://qsartoolbox.org/https://www.epa.gov/tsca-screening-tools/download-epi-suitetm-estimation-program-interface-v411, last access 03/02/2024).

As for the T criteria, the evaluation is in general related to the endpoints. If the long-term-no-observed effect concentration (NOEC) for marine and freshwater organisms is less than 0.01 mg/L, the substance is classified as a toxic compound. However, due to the lack of data and consistency of the NOEC values, some compounds may be scored as of high or non-significant risk, depending on which NOEC value was taken (measured by hours or days). To avoid inconclusive results, another possible approach was considered in this paper. The PNEC data found in the scientific literature and/or through NORMAN database were used to predict the toxicity of the compounds. Where possible, the lowest experimental data available was taken, otherwise, it was modeled. The score from 1 to 5 was based on (Ankley et al., 2021; Verlicchi et al., 2023). If the PNEC value (µg/L) is above 100, the risk is considered insignificant, if the PNEC is between 10 and 100 (equal), the risk is low, a PNEC above 1 and lower than or equal to 10 corresponds to a medium risk, if the PNEC is above 0.1 and lower than or equal to 1, the risk is considered high. If the PNEC is below 0.1 or no data is available, the score is 5, which corresponds to an extreme risk.

In addition to that, for each substance M criteria (measured by means of log K_{oc}) and O criteria (measured by the concentration of the compound in the water compartment) have also been added.

To simplify the method, the same concentrations are used for the O criteria as for the calculation of the HQ. The concentration ranges (ng/L) of below 1, 1-10, 10-50, 50-100 and over 100 were defined and the corresponding scores assigned. In parallel, a further set of concentrations was collected by different regions to compare the occurrence of different PFAS substances. The Swedish National Food Agency has recommended limits for drinking water based on the presence of 11 PFAS (European Commission, 2020a; Kurwadkar et al., 2022) and if the sum of the concentrations of these PFAS compounds is greater than 90 ng/L, this is considered a pollution of drinking water. On the other hand, USA has health advisory levels for PFOA and PFOS of 70 ng/L. The Organization for Economic Co-operation and Development (OECD) has suggested vales of 0.1µg/L for individual PFAS (OECD, 2018). Therefore, the above-mentioned concentration limits were taken into account when defining the thresholds and the concentrations of 70 and 90 ng/L were classified as high and extreme risk. For the compounds where no data has been found, the score of 5 has been given precautionally.

According to (Hale et al., 2020; Rudin et al., 2023) the mobility is not mandatory and currently not regulated under REACH but more attempt for mobility assessment for the substances such as PFAS have attracted attention (Hale et al., 2022). For the evaluation of the substances mobile (M) criteria, the lowest organic carbon-water coefficient (log Koc) is used as a corresponding value, at pH around 7. If the coefficient is less than 4.0, in the pH range of 4-9, the substance is considered mobile according to proposal from (Neumann & Schliebner, 2019) . Therefore, this work considers and scores (for the first time) mobility in the risk methodology to assess the risk of each compound. For PFAS substances with a log Koc value greater than or equal to 5, the risk is considered insignificant or low. If the log Koc is 4, the compound is classified as medium risk. All compounds with a log Koc of less than 4 and 3 are considered mobile (which corresponds to a high risk) and very mobile (extreme risk), respectively.

In this way, each compound is characterized by 5 properties (criteria). For each of them, thresholds were set, according to literature suggestions and evidence, as it will be explained below. The thresholds define the intervals to which a score from 1 to 5 is assigned (Table 4). The lower the score, the lower the expected environmental impact. Table 4 summarizes thresholds and scores for each property and the corresponding risk level characterization. The behavior of a compound is related to the combination of the selected properties.

TABLE 4. Criteria thresholds for OPB(M)T ranking

Criteria	**O**	**P**	**B**	**T**	**M**	Score (Sx)	Risk
Corresponding variable	***Concentration range (ng/L)***	***Removal efficiency %***	***logKow***	***PNEC water (ug/L)***	***logKoc***		
	0-1	100	<1	PNEC > 100	>5	**1**	Insignificant
	1-10	60-80	≥1	10 <PNEC ≤ 100	4.1-5	**2**	Low
	10-50	40-60	≥2	1 < PNEC ≤ 10	4	**3**	Moderate (medium)
	50-100	20-40	≥3	0.1 < PNEC ≤ 1	3-3.9	**4**	high
	Above 100	<20	≥4.5	PNEC ≤ 0.1, or no data avaliable	logKoc<3	**5**	extreme

Sx – index for individual score where x stands for corresponding criteria (O, P, B, M or T)

Two approaches are taken below: the OPBT and OPMT approaches, in which the sum of the individual scores assigned to the five properties (S_{OBPT} and S_{OPMT} indices) is considered as the total score; the higher the total score, the higher the concern and potential negative impact of the compound.

$$S_{OPBT} = S_O + S_P + S_B + S_T \tag{9}$$

$$S_{OPMT} = S_O + S_P + S_M + S_T \tag{10}$$

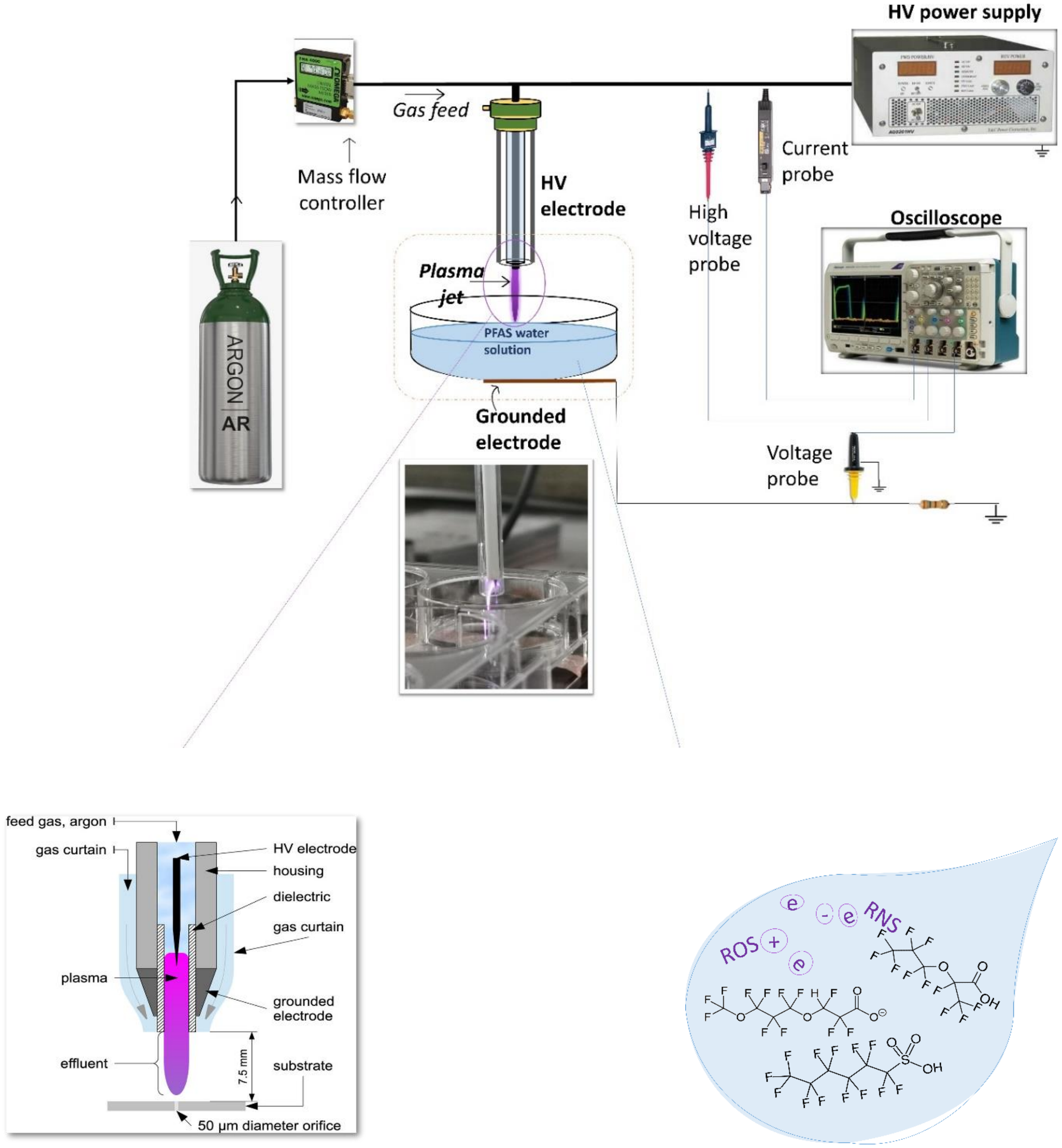
For the ranking of the substances based on their environmental risk, there will be the OPBMT criteria which is the sum of all individual assigned scores and also sum of the weighted scores ($OPBMT_W$).

$$OPBMT_w = S_O{*}w + S_P{*}w + S_B{*}w + S_M{*}w + S_T{*}w \tag{11}$$

According to (Verlicchi et al., 2023) the quality factor (or weight *w*) can be added as an individual criterion and data quality can be taken into account when ranking the substances. This step can be useful when the collected data contain different sources, both experimental and model data, as well as data that have not been found and have been assigned a high value, potentially leading to a "false" risk. Therefore, each score for each criteria (O,P,B,M,T) was multiplied by a factor *w*, as follows: if data is not available, the factor *w* is equal to 1; if the PNEC or logKow and logKoc were modeled with QSAR approach, the factor *w* is 2; factor *w* is 3 if experimental value is available. As a final result, all the criteria, OPBMT were calculated with and without adding factor *w* in order to demonstrate the difference in ranking.

4. RESULTS AND DISSCUSION

Chapter 1. Degradation of PFAS



Chapter is based on publication (Topolovec et al., 2024): “Plasma water treatment for PFAS: Study of degradation of perfluorinated substances and their byproducts by using cold atmospheric pressure plasma jet, Journal of Environmental Chemical Engineering, 12(3),1129

Degradation of PFAS in distilled water

The degradation of the individual PFAS compounds was studied in DW samples for two different volumes and time intervals. First, experiments were carried out in a volume of 5 mL for 5 minutes and 10 minutes to investigate the degradation kinetics and to determine the parameters and experimental conditions. Once the optimal conditions were settled for successful degradation of all compounds, the removal efficiency of each PFAS in DW was investigated during 10 min of plasma treatment at an initial concentration of 0.1 µg/L. The results are shown in Figure 14.

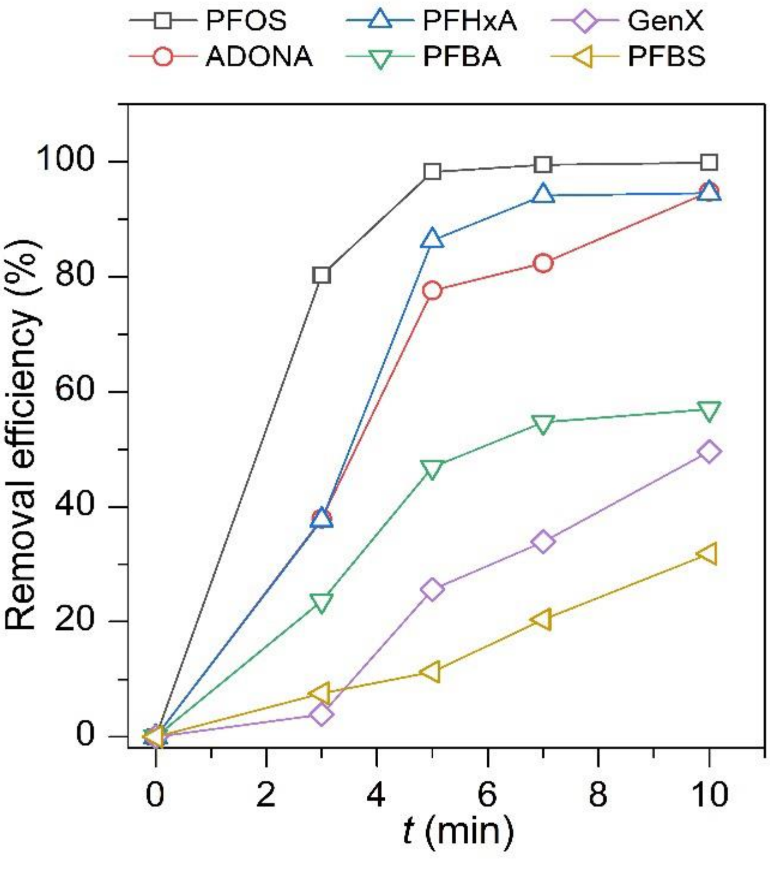


FIGURE 14. Removal efficiency of PFAS in DW (drinking water).

As it can be seen, the removal efficiency of PFOS, PFHxA and ADONA reached over 90% after 10 minutes of treatment. The removal efficiency trend for all compounds is as follows: PFOS (C8) > PFHxA (C6) > ADONA (C7) > PFBA (C4) > GenX (C6) > PFBS (C4). It can be observed that the longer the chain-length of the compound, the higher the efficiency for the same treatment time. As a result of the structure of PFAS compounds, surface activity increases with chain length, which means that long-chain PFAS will have better contact with the plasma at the plasma-liquid interface and faster degradation. Short-chain PFAS tend to accumulate less at the surface and therefore longer treatment time is needed. The fastest degradation occurred at the beginning (between 3 and 6 min) for all studied PFAS, followed by a slow increase. It is possible that slow degradation is due to the presence of byproducts and depending on the compound, those byproducts are produced in different treatment times. The trend of rapid degradation is more pronounced for three compounds with longer chain length (PFOS, ADONA, PFHxA) when compared to GenX, PFBA and PFBS. The lowest degradation was observed for PFBS with only around 30 % removal efficiency in 10 min. For the same treatment time, the removal of PFBA, which has the same chain length as PFBS, was 57 %. Compared to sulfonates, carboxylates are harder to degrade which has been shown in previous studies (R. K. Singh et al., 2021; R. K. Singh, Multari, et al., 2019). Most of the results in this work show the same consistency, except for PFBS and PFBA. However, it seems that the hydrophobicity of PFBA, based on the log Kow values, is slightly higher than of PFBS, which can explain the higher removal efficiency of PFBA. According to the results, high removal efficiency occurred in the case of ADONA (around 95% in 10 min) while for GenX was 50% for the same treatment time. The compound properties (Table 9 and Table 14 in the Appendix) show that ADONA has an additional CF_3O group that can give the molecule a higher surface activity.

A few parameters were measured during the treatment of the solutions. Figures 15a and 15b show the pH, conductivity, and temperature measurement results (average values). Additionally, the treated water volume was also measured at the end of each treatment. The same change in pH was observed for each compound in all experiments. The initial pH was between 6 and 7.5, while after 10 min of treatment time, the pH value decreased to around 3. The pH decreased drastically at the beginning of the treatment (in the first two min), and then varied around 3 for the rest of the treatment. The reduction in the pH value could be attributed to a generation of some reactive species. Although argon was used as a working gas, some nitrogen species could occur in the solution due to plasma contact with ambient air (Kumar et al., 2022; Marotta et al., 2011). Additionally, byproducts resulting from the degradation such as sulfuric acids and the production of few other plasma species, H^+ and hydrogen peroxide, could contribute to an acidic environment and lead to decrease in pH (Marotta et al., 2011).

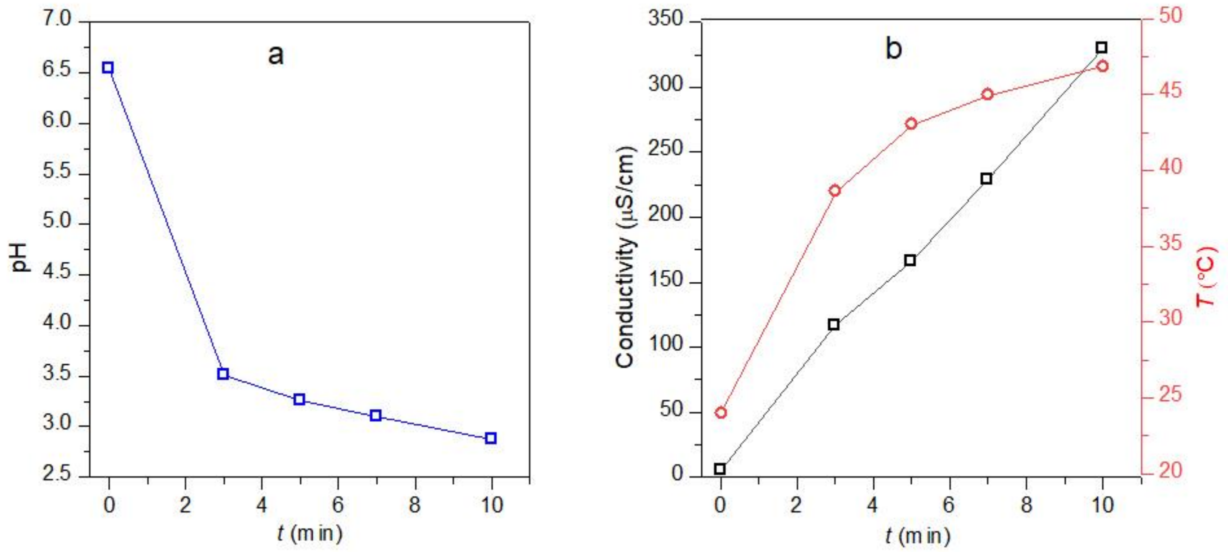


FIGURE 15A AND 15B. Dependency of pH, conductivity and temperature during treatment time of PFAS (total average value) in DW (drinking water).

The measured initial conductivity of solutions was around 4 μS/cm and it increased linearly in all experiments. After 10 min of treatment, it was around 400 μS/cm. The trend suggests that conductivity is likely to increase with increasing treatment duration. Some previous works (R. K. Singh et al., 2021; R. K. Singh, Multari, et al., 2019; H. Wang et al., 2018) have indicated that in plasma-liquid systems, the conductivity of water tends to increase due to the interaction with the electrons formed in the discharge, which can break water molecules into ions. The ionic species generated in the plasma are transferred into the liquid, resulting in more ions in the water. While some authors indicated a negative correlation between the degradation rate of PFAS and an extremely high conductivity (above 20 mS/cm) and assumed that a high ion concentration reduces the contact area with contaminated water (R. K. Singh, Multari, et al., 2019), others indicated that conductivity does not significantly affect the degradation or even has a positive impact (H. Wang et al., 2018). For an accurate assessment, the type of discharge and the level of conductivity should therefore be taken into account. In these experiments, the degradation rate for all compounds decreased over time and this was probably caused by the competition between byproducts and parent compound to react with plasma species and not due to the changes in conductivity which reached 400 μS/cm and could be considered as low.

Volume of the samples was measured after the treatment to observe possible loss due to evaporation. The volume loss after 10 min of treatment was 10% and this was taken into account by normalizing the data for all samples. To investigate the evaporation, the temperature inside the solution was measured. The temperature of the solution gradually increased under plasma exposure, with a maximum of 45°C in some cases. The increase in temperature over treatment time indicates that surface processes were dominantly governing the evaporation and not the heating of the sample volume. One of the possible mechanisms was the local heating at the point of contact of the plasma streamer and water due to the higher local temperature (still below 100°C). Another mechanism was the change in the partial pressure in the interface gas/liquid region due to argon flow and the plasma. This localized change in the partial pressure leads to evaporation of the treated liquid sample. The rise in the temperature, as shown in Figure 15b, is not linear and the heating slows down never going above 50°C, which indicates that degradation of contaminants is purely due to non-thermal processes.

Degradation of PFAS in complex matrices

Regarding the degradation of PFAS in NTP treatment with a gas-liquid interface, previous studies have shown promising results, but most of them have been conducted in pure water matrices, with PFOS and PFOA as representatives. However, in a recent study (Groele et al., 2021) PFAS removal from groundwater (already contaminated with PFAS) using plasma has been investigated. (R. K. Singh et al., 2021) investigated the removal of PFAS using landfill leachate samples and showed the potential of plasma technology for treatment of PFAS contaminated water. In this work, the removal efficiency in TW and SE has been assessed for all 6 substances as in DW, as a function of the treatment time. Results are given in Figure 16a and 16b.

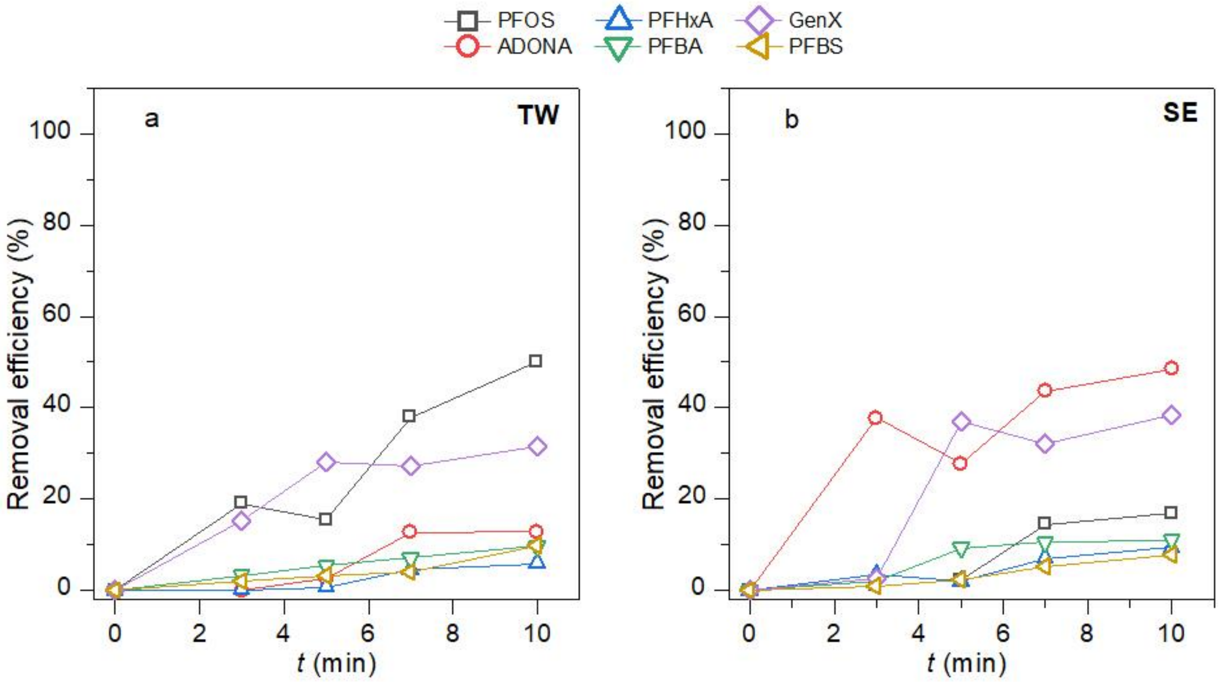


FIGURE 16A AND 16B. Removal efficiency of PFAS in TW (tap water) and SE (secondary effluent).

A lower removal efficiency was observed in both types of matrices compared to experiments in pure water. Short-chain PFAS (PFBS, PFBA and PFHxA) showed almost linear degradation and very low percentage of removal efficiency (less than 10%) compared to PFOS, GenX and ADONA. A major difference was in the case of PFHxA where efficiency was around 94% in DW while in TW and SE it was around 6% and 9%, respectively. The removal efficiency decreases with the complexity if the matrix, especially for compounds that do not easily migrate to the liquid surface.

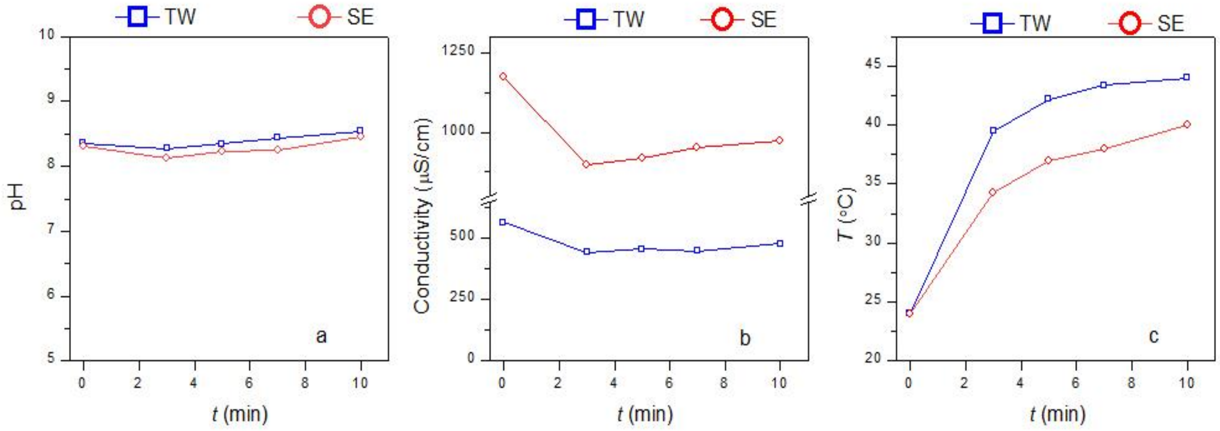


FIGURE 17A, 17B AND 17C. Dependency of pH, conductivity and temperature during treatment time of PFAS in TW (tap water) and SE (secondary effluent), (averaged values obtained from all samples).

Figure 17a. shows trend of the pH (average values) of the TW and SE samples during NTP treatment. The initial pH was around 8.3 for both TW and SE matrices, and this value did not significantly change with plasma treatment even for the longest treatment time of 10 min. It should be noted that pH is not necessarily dependent on the main compounds that were investigated. In fact, the pH did not drastically change when PFAS compounds were added to all solutions. Considering the chemistry of water samples, it is possible that in real water samples the concentration of basic species such as carbonate anions calcium and potassium (which were not present in DW) is much higher compared to the expected acid products of PFAS, hence the neutral to basic pH.

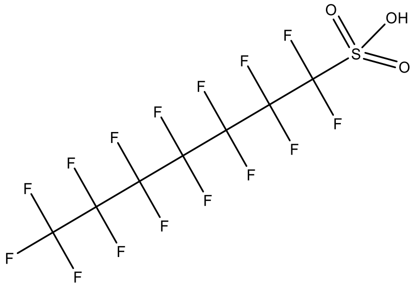
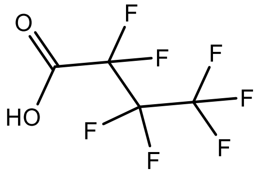
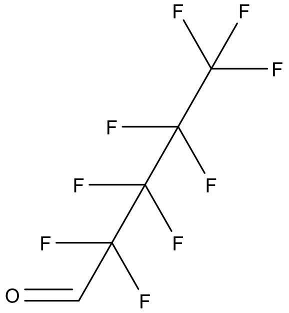
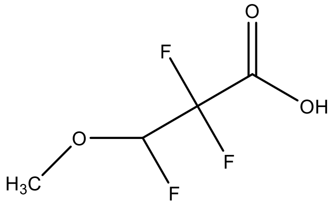
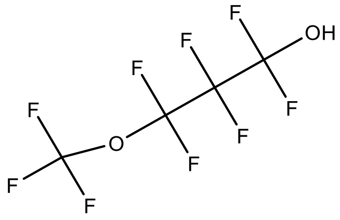
The changes of the solutions conductivity (Figure 17b) were also diverse when compared to DW. Generally, the conductivity was higher in TW (initial around 500 μS/cm) and SE (initial around 1200 μS/cm) than in DW (5 μS/cm). In the case of all compounds, the trend shows a small decrease at the beginning of the treatment followed with a slight increase in the end of the treatment, in both

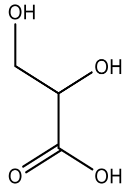
TW and SE. However, the decrease in SE is more significant than in TW. Since the solutions are much more complex from the chemical point of view, the matrix definitely impacts their conductivity. Also, it can be concluded that plasma treatment did not significantly affect the water conductivity in real water samples. As for the temperature, it can be seen (Figure 17c) that the trend was very similar to that in DW. At the end of the treatment, the maximum volume loss was around 7%, which indicates that the same conclusion related to evaporation mechanisms could be drawn as for DW samples.

PFAS byproducts

Some previous studies have discussed possible byproduct of PFOA and PFOS using different plasma configurations and proposed degradation pathways (Hayashi et al., 2015; R. K. Singh, Fernando, et al., 2019; Stratton et al., 2017; Takeuchi et al., 2014). Here, the analysis of the transformation products (TP) was performed using the LC-Orbitrap HRMS for all compounds in all 3 matrices. In total, 6 different byproducts have been found. Table 5 shows proposed structures and observed masses of byproducts as well as their parent compounds and type of matrices in which they were detected. TP_212 has also been reported in (R. K. Singh, Fernando, et al., 2019), while others are reported for the first time in this work. Figures 21-25 in Annex shows byproducts masses extracted from TIC.

TABLE 5. PFAS byproducts

Parent compound (matrix type)	Byproduct TP mark	Name	Molecular formula	RT (min)	Observed mass m/z	Structure
PFOS (TW)	TP_448	1,1,2,2,3,3,4,4,5,5,6,6,7,7,7-pentadecafluoroheptane-1-sulfonic acid (PFHpS)	$C_7HF_{15}O_3S$	9.87	449.9333	
PFOS (TW)	TP_212	2,2,3,3,4,4,4-heptafluorobutanoic acid (PFBA)	$C_4HF_7O_2$	4.89	212.9793	
PFHxA (DW)	TP_246	2,2,3,3,4,4,5,5,5-nonafluoropentanal	C_5HF_9O	4.80	246.9815	
PFBA (TW) ADONA (TW)	TP_157	2,2,3-trifluoro-3-methoxypropanoic acid	$C_4H_5F_3O_3$	0.54	157.0117	
ADONA (DW, TW)	TP_250	1,1,2,2,3,3-hexafluoro-3-(trifluoromethoxy)propan-1-ol	$C_4HF_9O_2$	6.35	250.9758	

ADONA (TW)	TP_105	2,3-dihydroxypropanoic acid	$C_3H_6O_4$	0.86	105.0192	

The NTP jet generates highly reactive species, including e_{aq}^{-}, $^{\bullet}OH$, and $^{\bullet}H$. In water with a neutral pH, PFOS exists in its anionic form, capable of swiftly reacting with e_{aq}^{-} to create the corresponding radical anions. Subsequently, the reactive species could induce the cleavage of C-C, resulting in the formation of TP_448 (*m/z* 449.9333). Also, the subsequent reactions with e_{aq}^{-} and/or $^{\bullet}OH$ can led to the formation of perfluoric acid intermediates, such as TP_212 (*m/z* 212.9793) or PFBA. Both have been detected after 10 min of treatment. According to the previous literature, degradation of long-chain PFAS during plasma treatment involves interaction of argon ions, aqueous and plasma electrons and hydroxyl radicals which lead to the formation of short-chain PFAS. PFBA is known as a common byproduct of PFOS, and based on this hypothesis, it should degrade further by losing another ($-CF_2$) group. Then, the interaction with reactive species degrades it into short chain organic acids with the possibility to reach mineralization. In this case, it can be concluded that electrons and argon ions indeed play an important role in initiation reaction by attacking the C-S bond, followed by propagation reaction that result in the formation of short – chain PFBA. A longer treatment time would be needed to determine whether PFBA was still present after 10 minutes and/or degraded to some degree. In DW samples, no byproducts were detected, which means either PFOS was completely degraded, or the level of byproducts was very low. Regarding PFHxA, the -COOH group was targeted by electrons, leading to the creation of unstable perfluoroalkyl radicals through an electron-mediated chain initiation process.

After 10 minutes of reaction in TW, a byproduct identified as TP_157 (m/z 157.0117) originating from PFBA was detected. This byproduct arises from H/F exchange process. Moreover, the C-C breaks within the molecule can interact with $^{\bullet}$OH through intramolecular reaction, ultimately resulting in the formation of an ether compound. The same TP was identified in ADONA samples in TW, which correspond to C-C breaks and defluorination. Since both TW and SE are complex matrices, electrons and ions needed for degradation of PFAS have less ability to react with target compound due to the presence of scavengers such as NO_3^-. This could be a possible explanation for why the same byproducts are not found in different solutions at the same treatment time. The rest of the byproducts found in other solutions was TP_246 DW in the case of PFHxA and was defined as radical form which was present in 3-10 min treatment time, with slowly decreasing trend after 3 minutes. Attack of the electrons or argon ions and the OH radical resulted with PFHxA molecule losing ($-CF_2O$) group.

The byproducts TP_250 (m/z 250.9758) and TP_105 (m/z 105.0192), originating from ADONA, were identified. TP_250 was detected in DW within the 3 to 7-minute treatment, though its presence was no longer detectable after a 7-minute treatment. In TW, on the other hand, TP_250 persisted from the third minute, with a slight decrease until the end of treatment. Additionally, the presence of TP_105 was noted in TW, with its concentration progressively increasing between 3 to 10 minutes of treatment time.

These results point to several possibilities: *i)* same types of byproducts can be found in different cases, but the higher the complexity, it takes longer times for the detection/formation of byproducts; *ii)* more than one reaction is possible during treatment time; *iii)* level of byproduct concentration is too low in the certain treatment time and does not exclude the presence of the byproduct; *iv)* in DW, byproduct was also degraded during treatment since there was no complex interferences with reactive species. Figure 18a and 18b compare ion intensity trend of ADONA as parent compound with detected byproducts in DW and TW.

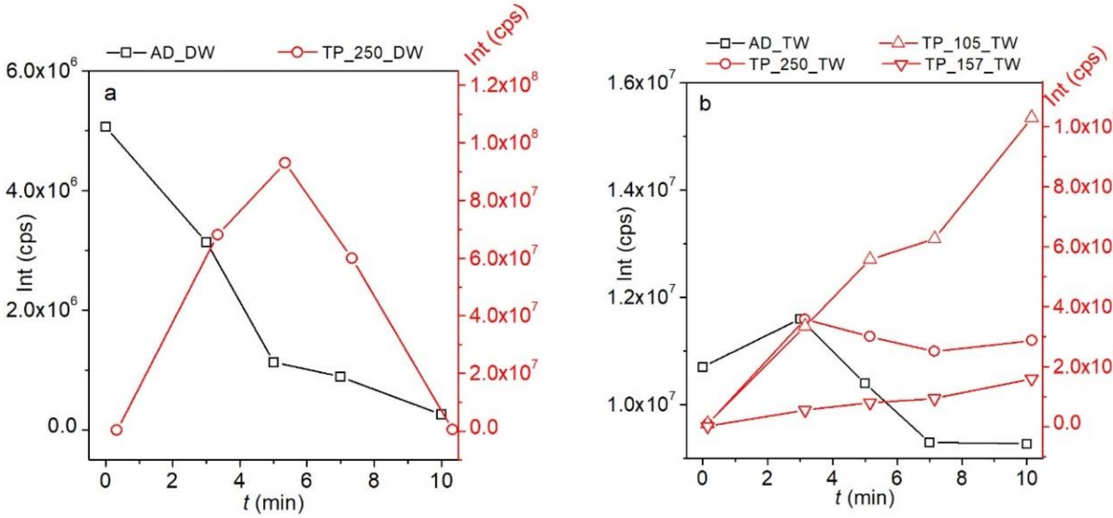


FIGURE 18A AND 18B. Ion intensity (counts per second - cps) of MS signals of ADONA and byproducts : TP_250 in DW (drinking water) (a) and TP_250, TP_105 and TP_157 in TW (tap water) (b).

It was found that a possible byproduct in GenX sample was trifluoroacetic acid TFA ($C_2F_3O_2H$). But since the same byproduct was detected in some blank samples, it was impossible to conclude whether TFA is a product or was trapped in the MS system. Therefore, the degradation pathway was proposed only for ADONA (Figure 19), although there is a possibility that the same degradation pathway applies to GenX, as the structure of these compounds is similar.

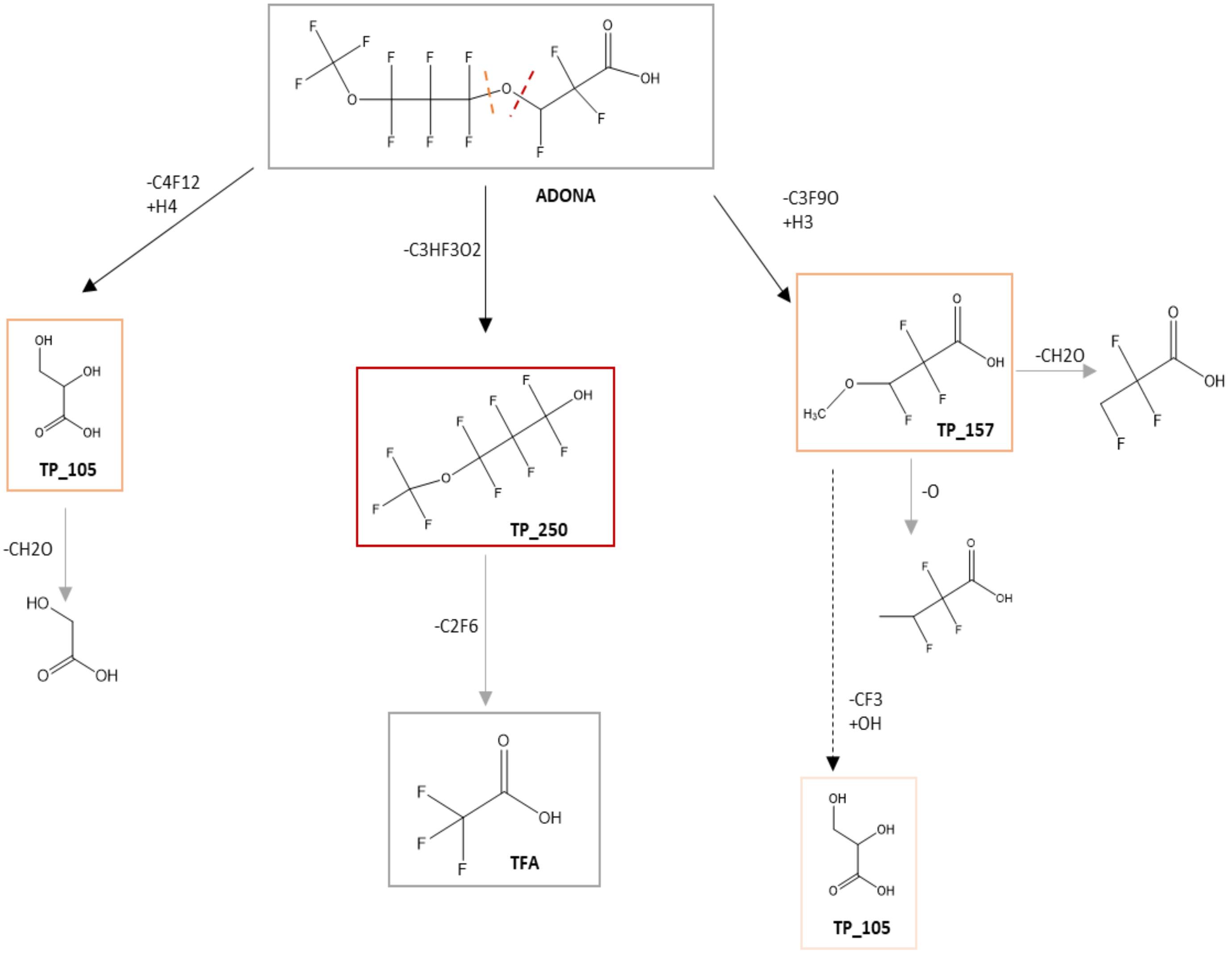
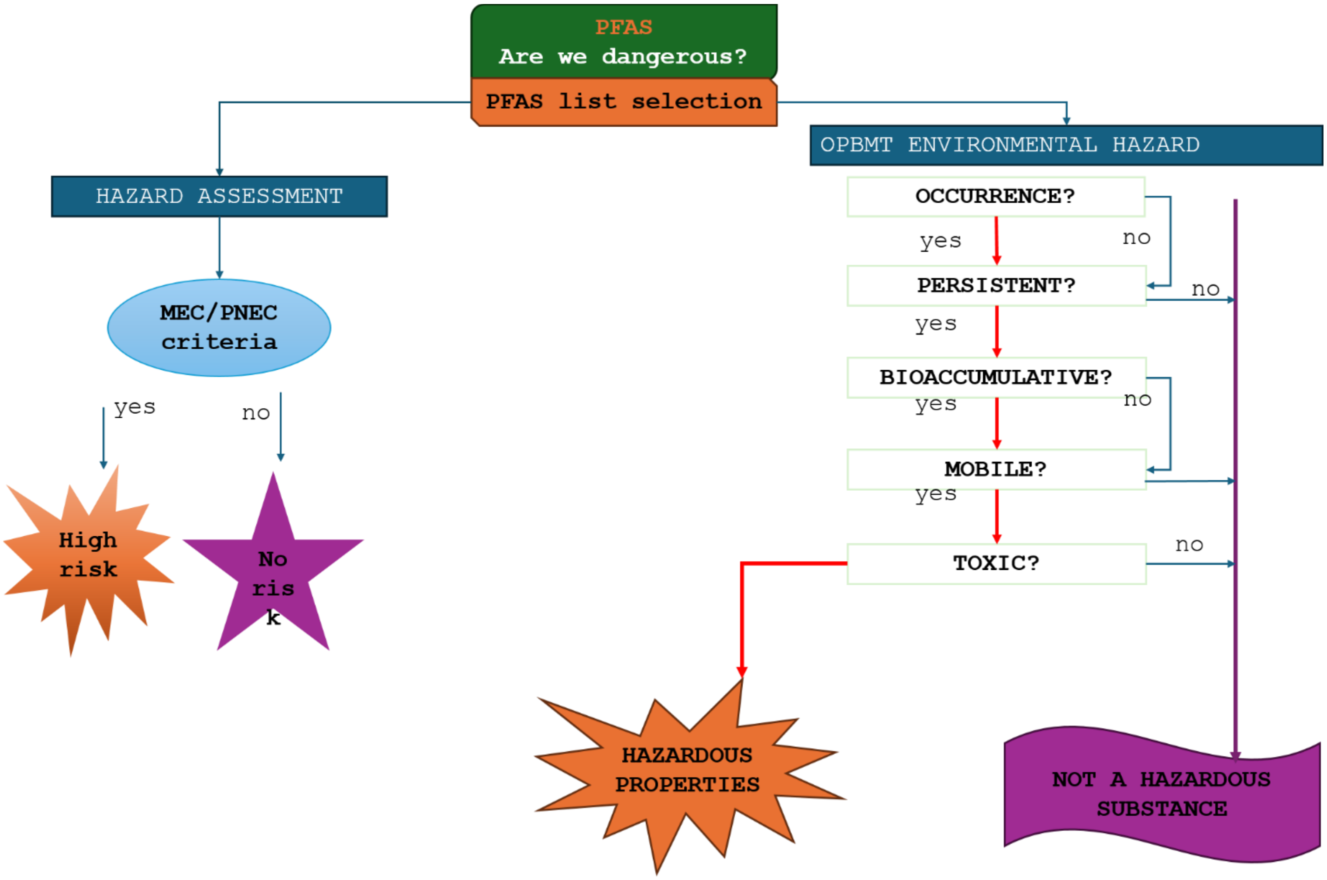


FIGURE 19. Proposed degradation pathway for ADONA

While the carboxylic or sulfonic group is favoring site for direct electron transfer, causing a cleavage of C-C or C-S bond in other PFAS, here, oxidative degradation occurs which causes split of ether-bond (C-O cleavage). With further reactions of decarboxylation, defluorination, HF exchange, TP-250 is converted into TFA. Based on the structure of the parent compound and the byproducts, it can be seen that the C-O cleavage in TP_157 takes place at a different carbon. TP_105 was defined as a third possible by-product.

Based on the elucidation of byproducts resulting from PFAS treatment using CAP, it can be outlined that the degradation of PFAS in water occurs through electron transfer, leading to the formation of corresponding radical anions which means that reactive species trigger chain reactions leading to the cleavage of C-F, C-C, or C-S bonds within PFAS molecules.

Chapter 2. PFAS risk assessment



Chapter 2. is based on work in paper : “The “Forever Chemicals” in water – assessment of PFAS contaminants and proposed methodology approach for risk hazard evaluation”, B.Topolovec, P.Verlicchi – in preparation

Hazard and Risk Quotient

As indicated before, the calculations of the HQ and RQ were done by following equations (7) and (8) respectively. Table 6 shows the selected PFAS compounds, their ecotoxicological data together with their selected concentration values, PNEC, calculated HQ and RQ and the corresponding score for the environmental risk level assessment.

Out of 37 compounds, 8 compounds are considered high and extreme risk in fresh water. It should be noted that 4 compounds, mostly long-chain PFSAs, are scored with 5 due to unavailable data which can mean that they have not been a subject of investigation or on the list of monitoring substances. Among these substances, PFOS received the highest score, leading to the conclusion that, despite its ban, it is still present in freshwater and poses a great threat to aquatic species. Compounds PFOA, PFHxS and PFDA are scored with value 4 and are thus considered of high risk. The new substances considered as substitutes for banned PFAS, HFPO-DA, F-53B, ADONA, are scored with 3 and 1 respectively, which means they pose medium risk (HFPO-DA, F-53B) and insignificant risk (ADONA). Most of the compounds pose low risk, especially compounds from PFSAs subgroup, regardless of their chain length. The insignificant risk is considered for some short-chain PFAS, such as PFPA, PFPS, PFHpS, PFMPA, PFMBA, which are mostly transformation products of corresponding long-chain PFAS or intermediates. As for the RQ, which was calculated based on the concentration of compounds in wastewater, in total they pose higher or equal risk level when compared to HQ. For example, PFOA is classified as an extreme risk if the concentration in wastewater is considered, while the risk is classified as medium if a concentration in freshwater is taken into account. PFHpA, 6:2 FTS, PFHpS, 8:2 FTS show high risk level while they were considered low or insignificant risk in fresh water. The risk posed by

PFOS is extreme, while the other compounds are rated 5 as no data are available. In view of the results obtained, it is clear that the need for advanced monitoring and the upgrading of existing WWTPs with suitable processes is of great importance. Future actions should consider prioritizing the compounds that pose a high and extreme risk, but also the compounds for which no data are available, in order to draw more appropriate conclusions.

OPB(M)T assessment

Table 6 reports the values of the 5 criteria for each substance, the corresponding variables and the score Sx assigned according to Table 4 (where x refers to O, P, B or T), and the final score in the case of OPBT (S_{OBPT}) and OPMT (S_{OPMT}), which summarizes the environmental risk classification. The threshold for environmental risk (ERy, where y refers to the corresponding approach, OPBT or OPMT) is as follows: if the sum $S_{OPB(M)T}$ is 4, the compound is considered of no concern, $S_{OPB(M)T}$ equal to 5 and below 10 is low risk, $S_{OPB(M)T}$ equal to 10 and below 15 is medium risk, $S_{OPB(M)T}$ equal to 15 and below 20 is high risk and if $S_{OPB(M)T}$ equal to 20 is extreme risk.

TABLE 6. OPB(M)T criterion of PFAS substances

No	Compound	Max C(ng/L)	S_O	r.e.%	S_P	logKow	S_B	logKoc	S_M	PNEC (μg/L)	S_T	S_{OPBT} score	EROPBT	S_{OPMT} score	ER	Reference Max C
1	PFOS	128	**5**	57	**3**	4.49	**5**	3.4080	**4**	0.002	**5**	18	HIGH	17	HIGH	(Campo et al., 2016)
2	PFOA	1500	**5**	0	**5**	4.81	**5**	2.8163	**5**	0.18	**4**	19	HIGH	19	HIGH	(McMahon et al., 2022)
3	PFHxA	198	**5**	0	**5**	3.48	**4**	2.0806	**5**	140.00	**1**	15	HIGH	16	HIGH	(Pan et al., 2018)
4	PFHxS	1434	**5**	n.d.	**5**	3.16	**4**	2.6730	**5**	0.87	**4**	18	HIGH	19	HIGH	(Pan et al., 2018)
5	PFBA	644	**5**	20	**4**	2.14	**3**	1.3394	**5**	27.80	**2**	14	MEDIUM	16	HIGH	(Campo et al., 2016)
6	PFBS	544	**5**	33	**4**	1.82	**2**	1.9318	**5**	372	**1**	12	MEDIUM	15	HIGH	(T. Liu et al., 2022)
7	ADONA p.a.	0.2	**1**	n.d.	**5**	5.74	**5**	1.9437	**5**	1.75	**3**	14	MEDIUM	14	MEDIUM	(Sadia et al., 2023)
8	HFPO-DA	812	**5**	n.d.	**5**	8.12	**5**	1.9236	**5**	1.35	**3**	18	HIGH	18	HIGH	(Gebbink et al., 2017)
9	PFHpA	177	**5**	n.d.	**5**	4,15	**4**	2.4512	**5**	0.50	**4**	18	HIGH	19	HIGH	(Boone et al., 2019)
10	PFPEA	514	**5**	50	**3**	2.81	**3**	1.7100	**5**	3.91	**3**	14	MEDIUM	16	HIGH	(Boone et al., 2019)
11	PFPA	9.2	**2**	18	**5**	1.47	**2**	0.9688	**5**	176.00	**1**	10	MEDIUM	13	MEDIUM	(Gebbink et al., 2017)
12	F-53B	52.2	**4**	n.d.	**5**	5.24	**5**	2.5492	**5**	0.33	**4**	18	HIGH	18	HIGH	(Pan et al., 2018)
13	6:2 FTS	17	**3**	n.d.	**5**	2.66	**3**	2.3964	**5**	0.62	**4**	15	HIGH	17	HIGH	(McMahon et al., 2022)
14	PFNA	38.6	**3**	n.d.	**5**	5.48	**5**	3.1869	**4**	1.00	**4**	17	HIGH	16	HIGH	(Boone et al., 2019)
15	PFDA	213	**5**	n.d.	**5**	6.15	**5**	3.5575	**4**	0.17	**4**	19	HIGH	19	HIGH	(Campo et al., 2016)
16	PFUNDA	3.06	**2**	n.d.	**5**	6.82	**5**	3.9281	**4**	0.13	**5**	17	HIGH	16	HIGH	(Pan et al., 2018)

17	PFDODA	3	**2**	n.d.	**5**	7.49	**5**	4.2987	**2**	0.11	**5**	17	HIGH	14	MEDIUM	(EPA Office of Water, 2024)
18	PFTrDA	7	**2**	n.d.	**5**	8.16	**5**	4.6693	**2**	0.10	**5**	17	HIGH	14	MEDIUM	(EPA Office of Water, 2024)
19	PFPS	12	**3**	n.d.	**5**	2.49	**3**	2.3024	**5**	2.03	**3**	14	MEDIUM	16	HIGH	(McMahon et al., 2022)
20	PFHpS	2.9	**2**	51	**3**	3.82	**4**	3.0381	**4**	0.48	**4**	13	MEDIUM	13	MEDIUM	(McMahon et al., 2022)
21	PFNS	n.d.	**5**	n.d.	**5**	5.16	**5**	3.7793	**4**	0.22	**4**	19	HIGH	18	HIGH	/
22	PFDS	0.13	**1**	n.d.	**5**	5.83	**5**	4.1498	**2**	0.16	**4**	15	HIGH	12	MEDIUM	(T. Liu et al., 2022)
23	PFUNDS	n.d.	**5**	n.d.	**5**	7.27	**5**	4.5204	**2**	n.d.	**5**	20	EXTREME	17	HIGH	/
24	PFDODS	n.d.	**5**	n.d.	**5**	8	**5**	4.8910	**2**	0.12	**4**	19	HIGH	16	HIGH	/
25	PFTrDS	n.d.	**5**	n.d.	**5**	8.75	**5**	5.2616	**1**	n.d.	**5**	20	EXTREME	16	HIGH	/
26	11Cl-PF3OUdS	5	**2**	n.d.	**5**	8.44	**5**	4.4741	**2**	0.045	**5**	17	HIGH	14	MEDIUM	(EPA Office of Water, 2024)
27	9Cl-PF3ONS	2	**2**	n.d.	**5**	6.93	**5**	3.7329	**4**	0.039	**5**	17	HIGH	16	HIGH	(EPA Office of Water, 2024)
28	NFDHA	2	**2**	n.d.	**5**	4.89	**5**	1.6831	**5**	4.32	**3**	15	HIGH	15	HIGH	(EPA Office of Water, 2024)
29	8:2 FTS	1.58	**1**	53	**3**	5.22	**5**	3.1376	**4**	0.25	**4**	13	MEDIUM	12	MEDIUM	(Sadia et al., 2023)
30	PFEESA	3	**2**	n.d.	**5**	3.56	**4**	2.0790	**5**	3.03	**3**	14	MEDIUM	15	HIGH	(EPA Office of Water, 2024)

31	4:2 FTS	3	**2**	n.d.	**5**	2.04	**3**	1.6552	**5**	2.97	**3**	13	MEDIUM	15	HIGH	(EPA Office of Water, 2024)
32	PFMPA	4	**2**	n.d.	**5**	3.15	**4**	1.3263	**5**	4.61	**3**	14	MEDIUM	15	HIGH	(EPA Office of Water, 2024)
33	PFMBA	3	**2**	n.d.	**5**	4.18	**4**	1.6969	**5**	3.66	**3**	14	MEDIUM	15	HIGH	(EPA Office of Water, 2024)
34	NEtFOSAA	0.32	**1**	n.d.	**5**	7.35	**5**	3.7141	**4**	0.3	**4**	15	HIGH	14	MEDIUM	(T. Liu et al., 2022)
35	NMeFOSAA	0.3	**1**	n.d.	**5**	6.63	**5**	3.4430	**4**	0.41	**4**	15	HIGH	14	MEDIUM	(T. Liu et al., 2022)
36	PFTA(PFTeDA)	3.15	**1**	n.d.	**5**	9.95	**5**	5.0399	**2**	0.083	**5**	17	HIGH	14	MEDIUM	(Sadia et al., 2023)
37	TFA	1104.6	**5**	n.d.	**5**	0.50	**1**	0.5093	**5**	110	**1**	12	MEDIUM	16	HIGH	(Sadia et al., 2023)

Occurrence

Based on the reported maximum concentrations, 15 out of 37 compounds are considered of extreme risk with concentrations above 100 ng/L in different types of fresh water (river, groundwater, drinking water) which exceed already established regulations. One compound, F-43B, has a score of 4, which makes it a high risk. The majority of the other PFAS are classified as low risk. However, according to the literature, the occurrence can also vary from region to region. Table 7 shows the reported maximum concentrations in different regions (Boone et al., 2019; Campo et al., 2016; Gebbink et al., 2017; Kurwadkar et al., 2022; Pan et al., 2018). As it can be seen, the occurrence of one and the same compound can vary, e.g. PFOS – while values close to and above 100 ng/L are reported for rivers in the USA and Europe, values above 30 ng/L have been reported in Asia. Compounds such as PFHxA, PFHxS, PFBS were found in medium to high range of concentrations, while in Asia they are in an extremely high range. On the other hand, according to the literature, most of the long-chain compounds reported in low concentration ranges in the USA have not been detected in Europe.

TABLE 7. Reported concentrations and score for different regions

COMPOUND	USA max conc. ng/L	Score USA	Europe max conc	Score Europe	Asia max conc	Score Asia	Reference (USA, Europe, Asia)
PFOS	98	**4**	128	**5**	29.7	**3**	(McMahon et al., 2022)**,**(Campo et al., 2016)**,**(Pan et al., 2018)
PFOA	1500	**5**	52.2	**4**	244	**5**	(McMahon et al., 2022)**,**(Campo et al., 2016)**,** (T. Liu et al., 2022)
PFHxA	55.1	**4**	18.7	**3**	198	**5**	(Boone et al., 2019)**,**(Campo et al., 2016)**,**(Pan et al., 2018)
PFHxS	81	**4**	36.7	**3**	1434	**5**	(McMahon et al., 2022)**,**(Campo et al., 2016)**,**(Pan et al., 2018)
PFBA	96.8	**4**	644	**5**	143	**5**	(Boone et al., 2019)**,** (Campo et al., 2016)**,** (T. Liu et al., 2022)
PFBS	24	**3**	27	**3**	544	**5**	(McMahon et al., 2022)(Campo et al., 2016)**,** (T. Liu et al., 2022)

ADONA	3	**2**	0.2	**1**	1.55	**2**	(EPA Office of Water, 2024), (Sadia et al., 2023), (Pan et al., 2018)
HFPO-DA	5	**2**	812	**5**	144	**5**	(EPA Office of Water, 2024),(Gebbink et al., 2017),(Pan et al., 2018)
PFHpA	177	**5**	24	**3**	32.8	**3**	(Boone et al., 2019), (Llorca et al., 2012), (T. Liu et al., 2022)
PFPeA	501	**5**	9.4	**2**	38.2	**3**	(Boone et al., 2019), (Llorca et al., 2012), (T. Liu et al., 2022)
PFPA	Nd	**5**	9.2	**2**	n.d.	**5**	/, (Gebbink et al., 2017), /
F-53B	Nd	**5**	n.d.	**5**	52.2	**4**	/,/, (Pan et al., 2018)
6:2 FTS	17	**3**	1.19	**2**	13.9	**3**	(McMahon et al., 2022), (Sadia et al., 2023), (Pan et al., 2018)
PFNA	41.4	**3**	19.8	**3**	27.9	**3**	(Boone et al., 2019), (Campo et al., 2016), (T. Liu et al., 2022)
PFDA	31.1	**3**	213	**5**	5.75	**2**	(Boone et al., 2019), (Campo et al., 2016), (Pan et al., 2018)

PFUnDA	2.90	**2**	0.62	**1**	3.06	**2**	(Boone et al., 2019), (Campo et al., 2016), (Pan et al., 2018)
PFDoDA	0.28	**1**	0.16	**1**	2.30	**2**	(Boone et al., 2019), (Sadia et al., 2023), (Pan et al., 2018)
PFTrDA	7	**2**	0.04	**1**	1.56	**2**	(EPA Office of Water, 2024), (Campo et al., 2016), (Pan et al., 2018)
PFPS	12	**3**	0.62	**1**	4.42	**2**	(McMahon et al., 2022), (Sadia et al., 2023)/, (T. Liu et al., 2022)
PFHpS	2.9	**2**	0.13	**1**	n.d.	**5**	(McMahon et al., 2022), (Sadia et al., 2023)/
PFNS	Nd	**5**	n.d.	**5**	n.d.	**5**	/
PFDS	Nd	**5**	n.d.	**5**	0.13	**1**	/, /, (T. Liu et al., 2022)
PFUnDS	Nd	**5**	n.d.	**5**	n.d.	**5**	/
PFDoDS	Nd	**5**	n.d.	**5**	n.d.	**5**	/
PFTrDS	nd	**5**	n.d.	**5**	n.d.	**5**	/
11Cl-PF3OUdS	5	**2**	n.d.	**5**	n.d.	**5**	(EPA Office of Water, 2024)

9Cl-PF3ONS	2	**2**	n.d.	**5**	n.d.	**5**	(EPA Office of Water, 2024)
NFDHA	2	**2**	n.d.	**5**	n.d.	**5**	(EPA Office of Water, 2024)
8:2 FTS	5	**2**	1.58	**2**	0.28	**1**	(EPA Office of Water, 2024)**,** (Sadia et al., 2023)**,** (Pan et al., 2018)
PFEESA	3	**2**	n.d.	**5**	n.d.	**5**	(EPA Office of Water, 2024)**, //**
4:2 FTS	3	**2**	n.d.	**5**	0.11	**1**	(EPA Office of Water, 2024)**, /,** (Pan et al., 2018)
PFMPA	4	**2**	n.d.	**5**	n.d.	**5**	(EPA Office of Water, 2024)
PFMBA	3	**2**	n.d.	**5**	n.d.	**5**	(EPA Office of Water, 2024)
NEtFOSAA	5	**2**	n.d.	**5**	0.32	**1**	(EPA Office of Water, 2024)**, /,** (T. Liu et al., 2022)
NMeFOSAA	6	**2**	n.d.	**5**	0.3	**1**	(EPA Office of Water, 2024)**, /,** (T. Liu et al., 2022)
PFTA(PFTeDA)	8	**2**	3.15	**2**	134	**5**	(EPA Office of Water, 2024)**,** (Sadia et al., 2023)**,** (Pan et al., 2018)
TFA	n.d.	**5**	1104.6	**4**	n.d.	**5**	/**,** (Sadia et al., 2023)**,** /

Persistence

Out of 9 compounds with reported removal efficiency, 3 compounds, PFOA, PFHxA, PFPA exhibit a removal efficiency of less than 20% and thus a score of 5 was assigned corresponding to an extreme risk. PFBA and PFBS were removed between 20 and 40% and thus the score was 4 corresponding to a high risk, while PFOS and PFPeA showed higher removal, around 50% (score equal to 3, corresponding to a medium risk). Most compounds were given a score of 5 as no data was available, however, it should be noted that some authors (Lenka et al., 2021) reported removal efficiency of PFAS mixture. This work can also be useful for the evaluation of the water treatment performance by using concentrations of measured PFAS mixture in effluent. However, demonstrating the persistence of individual compounds is of great importance in order to classify compound risk which would lead to the definition of maximum concentration in water bodies.

Bioaccumulation and Mobility

As mentioned before, for the B criteria, BCF is considered when evaluating weather compound can bioaccumulate or not. The BCF values of PFAS can be quite low due to their mobility and give the impression of a low environmental risk. In this work, according to Table 6, almost all compounds (29 in total) are classified as extreme or high risk (scores 5 and 4, respectively) if we consider log Kow as the corresponding value for the B criteria, with the exception of PFBA, PFPeA, PFPS, 6:2 FTS, 4:2 FTS, which score was 4 (moderate), PFBS and PFPA, which score was 2 (low risk), and TFA, which leads to an insignificant risk (score equal to 1).

As mentioned previously, PFAS are quite mobile in the aquatic environment and the use of the mobility criterion in their case could be a better approach than bioaccumulation when assessing risk in the aquatic environment. Compounds that are very persistent and difficult to degrade in treatment processes, along with high mobility, have more chances to be found in drinking water from different aquatic sources. In the current study, the score is assigned according to the values of log Koc shown in Table 4. According to the results in Table 6, most of the PFASs pose a high risk: 18 received a score of 5 (extreme risk) and 10 a score of 4 (high risk). Only 8 compounds have an insignificant risk. As expected, compounds with high molar mass (g/mol) have insignificant mobility, in this case all the compounds whose molar mass exceeds 600 g/mol. It should be noted that some compounds with longer perfluorinated chain, namely C10, C11 and C12 are very mobile compared to compounds with the same number of carbon atoms in the chain, but with lower molar mass. When comparing two different approaches, OPBT and OPMT, the resulting environmental risk changed for 15 compounds: 8 compounds are considered of high risk when the criterion M is considered (medium risk if the B criteria is considered instead of M), 4 compounds are considered of medium risk (high risk with B criterion) and 3 compounds result of high risk (extreme risk when B criterion is considered).

Toxicity

The toxicity criterion, as shown in Table 4, is based on the PNEC values, preferably on experimental data, but when data is missing, QSAR was used for modelled PNEC. With the highest scores of 4 and 5, 23 compounds have a high to extreme risk, including PFOS, PFUNDA, PFDODA, PFTrDA, PFUNDS, PFTrDS, 11Cl-PF3OUdS and 9Cl-PF3ONS with the highest score. 9 compounds lead to a moderate risk and 5 compounds, PFHxA, PFBA, PFBS, PFPA, TFA present a low /insignificant risk. As expected, compounds with the lowest PNEC have potentially higher environmental risk.

As for the ranking substances, Table 8 shows on the left the list of compounds ranked according to OPBMT score without applying weighting criteria and on the right side with applying weighting criteria (OPBMT$_w$). It turns out that 6 compounds remain among the first 10 compounds, PFOA, PFOS, PFHxS, HFPO-DA, PFDA and F-53B and should be considered of high risk. The compounds PFBA, PFBS, PFHxA, PFPEA increases their final score (thus their final risk) being included in the first 10 positions. On the other hand compounds such as PFNS, PFDODS, PFDS, PFTrDS, PFUNDS after the weighting phase, reduce their final score and thus their risk. ADONA, which is considered as new substitute compound for PFOA, remains among the first compounds. It can also be observed that short chain PFAS which are transformation products are of high risk as well as parent compounds. This underlines the need to improve the efficiency of PFAS removal and to try to ensure extremely high or even complete removal.

TABLE 8. Obtained ranking before and after weighting criteria applied and OPBMT score

Compound	O	P	B	M	T	OPBMT score		Compound	O	P	B	M	T	OPBMT score
PFOA	5	5	5	5	4	24		PFOA	15	15	10	10	12	62
PFHxS	5	5	4	5	4	23		PFOS	15	9	10	8	15	57
HFPO-DA	5	5	5	5	3	23		PFHxA	15	15	8	10	3	51
F-53B	4	5	5	5	4	23		PFHxS	15	5	8	10	8	46
PFDA	5	5	5	4	4	23		HFPO-DA	15	5	10	10	6	46
PFNS	5	5	5	4	4	23		PFDA	15	5	10	8	8	46
PFHpA	5	5	4	5	4	23		PFPEA	15	9	6	10	6	46
PFOS	5	3	5	4	5	22		PFHpA	15	5	8	10	8	46
PFUNDS	5	5	5	2	5	22		PFBA	15	12	6	10	2	45
PFDODS	5	5	5	2	4	21		F-53B	12	5	10	10	8	45
PFNA	3	5	5	4	4	21		PFBS	15	12	4	10	3	44
PFUNDA	2	5	5	4	5	21		PFNA	9	5	10	8	12	44
PFTrDS	5	5	5	1	5	21		PFUNDA	6	5	10	8	10	39
9Cl-PF3ONS	2	5	5	4	5	21		PFHpS	6	9	8	8	8	39
PFHxA	5	5	4	5	1	20		9Cl-PF3ONS	6	5	10	8	10	39
6:2 FTS	3	5	3	5	4	20		6:2 FTS	9	5	6	10	8	38
NFDHA	2	5	5	5	3	20		8:2 FTS	3	9	10	8	8	38
NEtFOSAA	1	5	5	4	4	19		PFPA	6	15	4	10	2	37
NMeFOSAA	1	5	5	4	4	19		NFDHA	6	5	10	10	6	37
ADONA p.a.	1	5	5	5	3	19		PFNS	5	5	10	8	8	36
PFBA	5	4	3	5	2	19		PFPS	9	5	6	10	6	36
PFPEA	5	3	3	5	3	19		PFDODA	6	5	10	4	10	35
PFDODA	2	5	5	2	5	19		PFTrDA	6	5	10	4	10	35
PFTrDA	2	5	5	2	5	19		11Cl-PF3OUdS	6	5	10	4	10	35
11Cl-PF3OUdS	2	5	5	2	5	19		PFEESA	6	5	8	10	6	35
PFEESA	2	5	4	5	3	19		PFMPA	6	5	8	10	6	35
PFMPA	2	5	4	5	3	19		PFMBA	6	5	8	10	6	35
PFMBA	2	5	4	5	3	19		ADONA p.a.	3	5	10	10	6	34
PFPS	3	5	3	5	3	19		NEtFOSAA	3	5	10	8	8	34
PFTA(PFTeDA)	1	5	5	2	5	18		NMeFOSAA	3	5	10	8	8	34
4:2 FTS	2	5	3	5	3	18		TFA	15	5	2	10	2	34
8:2 FTS	1	3	5	4	4	17		4:2 FTS	6	5	6	10	6	33

PFDS	1	5	5	2	4	17		PFDODS	5	5	10	4	8	32
PFBS	5	4	2	5	1	17		PFTA(PFTeDA)	3	5	10	4	10	32
PFHpS	2	3	4	4	4	17		PFDS	3	5	10	4	8	30
TFA	5	5	1	5	1	17		PFUNDS	5	5	10	4	5	29
PFPA	2	5	2	5	1	15		PFTrDS	5	5	10	2	5	27

5. CONCLUSION

In summary, this research highlights the interconnected roles of degradation experiments and risk assessment in enhancing our understanding of organic micropollutant (OMP) transformation and its environmental impact. Plasma treatment experiments demonstrate promising potential for breaking down persistent compounds, such as PFAS, by revealing specific degradation pathways and identifying resulting transformation products. These processes, however, underscore the importance of a comprehensive risk assessment framework to address the potential ecotoxicological impacts of byproducts formed during degradation. By combining these insights, the study emphasizes that an interdisciplinary approach—merging experimental degradation effectiveness with risk evaluation—is crucial for developing sustainable and safer water treatment methods. This integrated perspective not only advances pollutant degradation science but also supports policy and regulatory measures, addressing both the immediate and long-term ecological risks linked to OMPs in water systems.

Overview of achieved results:

This doctoral thesis consists of two parts:

(i) study and evaluation of PFAS degradation in PFAS-contaminated water matrices by applying non-thermal atmospheric pressure plasma

(ii) comprehensive environmental risk assessment of 37 PFAS compounds, encompassing both legacy and emerging substances, including a proposal for methodological approach to risk assessment

The conclusions are as follows:

- The results obtained demonstrate the success of application of NTP-APPJ for PFAS-contaminated water treatment on laboratory scale, for three different water matrices.
- In DW, high removal efficiency (>90%) was achieved for longer chain PFAS; PFOS, PFHxA and ADONA in 10 minutes of treatment time while other compounds showed lower removal efficiency, but still high for short treatment time.
- In TW and SE, which represent real water samples, the percentage of degradation was lower overall, between 8 and 50%, depending on the compound and matrices. However, while the short chain PFAS in SE showed almost the same percentage as in TW, the PFOS removal was about 16 % and that of GenX and ADONA about 39 % and 49 %, respectively.
- The degradation is compound-depending and is influenced by various matrix effects.
- PFAS substances ADONA and GenX have shown promising results and successful removal in plasma system used in this work.
- The focus of this thesis was also investigation of byproduct - in total, 7 different byproducts were detected. The results confirmed one of the earlier hypothesis that for PFSAs and PFCAs compounds, electron transfer was important initiation step of PFAS degradation, breaking of the C-C bond or C-S bond on the head group. Degradation was then followed by decarboxylation, defluorination, hydrolysis and reaction with OH radical. As for ADONA and GenX, initial break of the bond is on the ether group, possibly followed by process of defluorination and decarboxylation. Degradation mechanism of ADONA is proposed

- Both reduction and oxidation processes are involved in PFAS degradation, although, the mechanism may be different for different types of compounds.
- The findings of ERA of 37 PFAS highlight substantial risks associated with several PFAS. In particular PFOS, despite being banned, remains a severe threat to aquatic ecosystem (and eventually human health risk) due to its high bioaccumulation and mobility potential.
- Compounds like PFHxS and PFDA also present high risk which underlines the need for stringent regulatory measures and targeted remediation efforts.
- Emerging new substances, such as HFPO-DA and F-53B pose high environmental risks which suggests that replacements are not entirely risk-free and still require monitoring and regulation. ADONA on the other hand, exhibit lower risk compared to other substitutes, yet its presence and potential should not be overlooked.
- Considering that the compounds of similar structure and transformation products of parent compounds can pose similar risks, and based on HQ and RQ results, it can be concluded that PFAS originating from wastewater effluents present significantly higher risk than those in freshwater. This emphasizes the need for advanced wastewater treatment processes capable of efficiently removing PFAS avoiding their emission and spread in the environment (natural water bodies).
- the high mobility of PFAS substances may play key role in assessing their environmental impact and should be taken into consideration as part of PMT criteria rather than PBT.

Key future steps and research gaps for addressing challenges ahead

While the results of this work have shown promising removal efficiency of PFAS, to effectively utilize plasma technology for wastewater treatment, several key challenges should be addressed:

- Parameter Determination: Establish appropriate parameters for power consumption in plasma processes to align with existing wastewater treatment standards and allow comparisons with conventional methods.
    - Variations in experimental setups often add to power requirements (e.g., sample recirculation).
    - Plasma devices may have unique power measurement requirements, complicating standardized evaluation.
- For meaningful analysis and comparison of plasma treatment methods, research publications should include:
- Detailed reporting of the parameters such as dimensions of the experimental setup, type of plasma discharge and working gas flow, power supply type and parameters, including power delivered to the plasma, volume of the treated sample and flow rate (if applicable) would be a first step towards defining a suitable power-efficiency metric.

Moreover, key challenges and recommendations for better understanding of PFAS degradation mechanism and their impact on the aquatic environment are as follows:

- More research towards detailed degradation mechanisms to demonstrate pathway step by step
- Further investigation and developing of non-target analysis
- Investigation of compound toxicity, both parent compounds and transformation products

- Future research and regulatory efforts should prioritize compounds identified as high and/or extreme risk. Besides there should be an evaluation and potential revision of regulatory frameworks to include newer PFAS and more restricted concentrations, as well as the development of policies for phasing out high-risk PFAS.
- emerging substances and those with incomplete data profiles require targeted studies to elucidate their environmental behavior and potential impacts.
- development and implementation of monitoring programs for both legacy and emerging PFAS compounds, with a focus on high-risk areas such as wastewater treatment plants and downstream waterbodies is recommended as well as research and development of advanced water treatment technologies specifically designed to target persistent OMPs, such as PFAS.

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ANNEX

Supplementary Material for Chapter 1

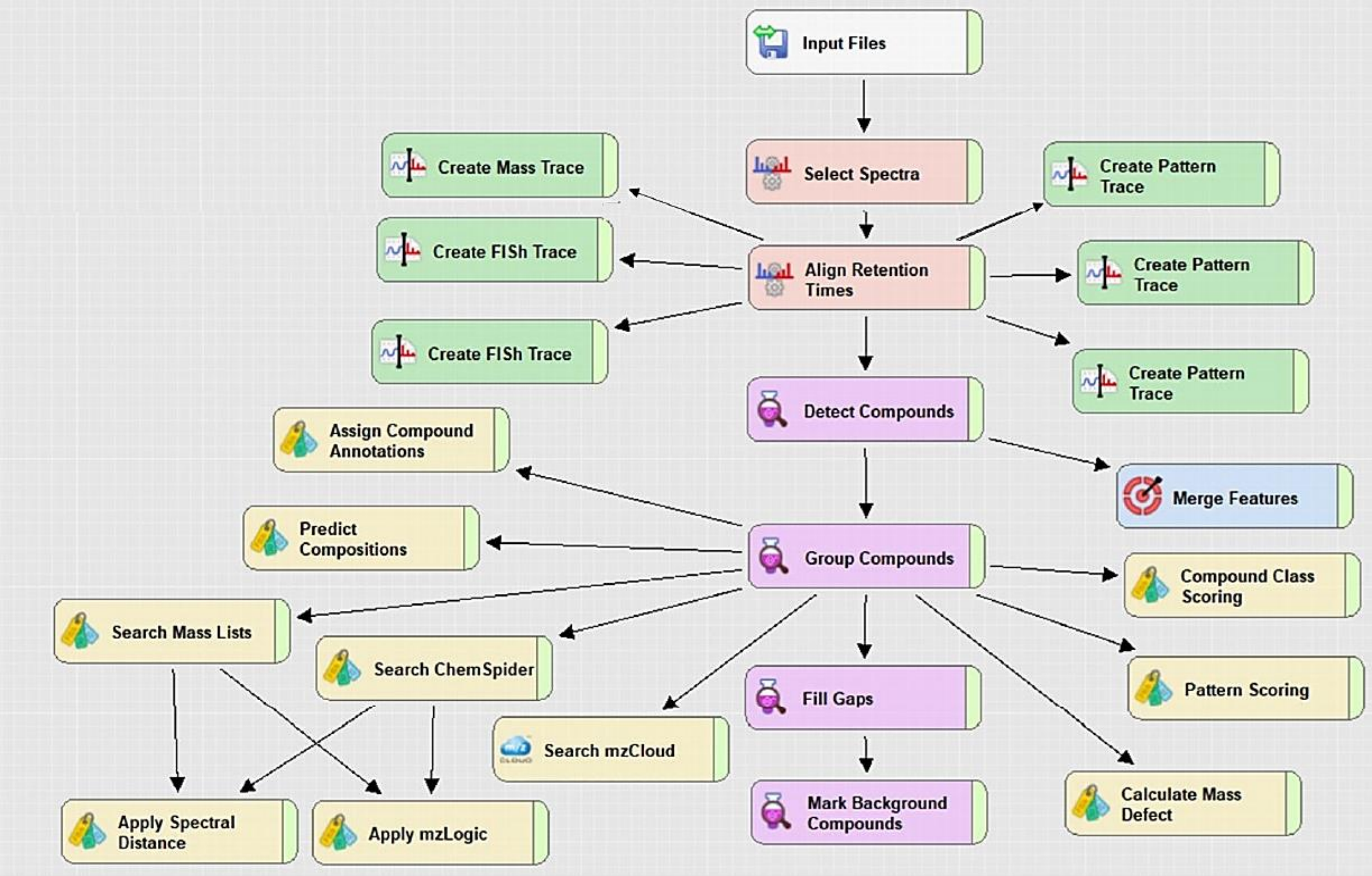


FIGURE 20. Workflow tree showing Compound Discoverer components (screenshot)

TABLE 9. Summary of the physico-chemical properties of the selected PFAS, including molar mass (MW, g/mol), theoretical octanol-water partition coefficient (log Kow), predicted acid dissociation constant (pKa))

Compound	**CAS No.**	**Molecular Formula**	**MW (g/mol)**	**Log Kow**	**pKa**
PFOS	1763-23-1	$C_8HF_{17}O_3S$	500.13	-0.57-7.03	-3.41-0.14
PFHxA	307-24-4	$C_6HF_{11}O_2$	314.05	2.02-5.97	-0.17-0.84
PFBA	375-22-4	$C_4HF_7O_2$	214.04	2.08-3.93	0.05-1.07
PFBS	375-73-5	$C_4HF_9O_3S$	300.10	0.732-3.67	-3.94-0.14
ADONA	958445-44-8	$C_7H_2F_{12}O_4$	378.07	5.74	0.8-1.5
HFPO-DA (GENX)	13252-13-6	$C_6HF_{11}O_3$	330.05	3-8.12	-0.77

TABLE 10. The optimized compound-dependent MS parameters: declustering potential (DP), collision energy (CE) and cell exit potential (CXP) for each compound and each transition of the negative mode.

Compound	**Q1 Mass (Da)**	**Q3 Mass (Da)**	**DP**	**CE**	**CXP**
PFBA	213.114	169.00	-25	-14	-9
	213.114	119.00	-25	-32	-9
PFBS	299.070	80.00	-15	-66	-7
	299.070	98.80	-15	-36	-11
PFHxA	313.000	269.00	-5	-12	-17
	313.000	119.00	-25	-40	-10
PFHxS	398.924	79.90	-30	-74	-9
	398.924	99.10	-30	-76	-7
PFOA	412.953	368.90	-15	-14	-17
	412.953	169.10	-15	-28	-7
PFOS	498.895	79.90	-15	-104	-11
	498.895	98.90	-15	-88	-9
HFPO-DA(GENX)	328.974	285.00	-20	-8	-11
	328.974	168.800	-20	-18	-25
ADONA	376.910	251	-55	-18	-11

TABLE 11. General instrumental parameters in non-target analysis using HRMS.

Instrument	Thermo Scientific SII coupled with Orbitrap Exploris 120
Analytical column	Thermo Scientific Hypersil GOLD aQ, 2.1 x 150 mm (3µm)
Mobile phase	A: 5 mm ammonium acetate in water, B: methanol Final gradient: 90% A, 10% B
Injection volume/ flow rate	5 µL/ 0.4 mL/min
Method duration	9 min
Mass parameters	Ion source type: H-ESI Spray voltage: Static Positive Ion (V): 3500 Negative Ion (V): 2500 Gas Mode: Static Sheath Gas (Arb): 50 Aux Gas (Arb): 10 Sweep Gas (Arb): 0 Ion transfer tube temp. (°C): 325 Vaporizer temp. (°C): 350 Orbitrap resolution 300 000 Scan range (m/z): 100-1000 RF Lens (%): 70

Table 12. Water composition of tap water in Belgrade

Parameter	Concentration in regular occasion (mg/L)
Ammonia	0.5
Antimony	0.003
Arsene	0.01
Copper	2.0
Barium	0.7
Boron	1
Cyanides	0.05
Zinc	3.0
Fluorides	1.2
Total Chromium	0.05
Chlorides	250
Cadmium	0.003
Calcium	200.0
Potassium	12.0
Magnesium	50.0
Molybdenum	0.07
Sodium	200.0
Nickel	0.02
Nitrates	50.0
Nitrites	0.03
Lead	0.01
Selenium	0.01
Manganese	0.05
Mercury	0.001
Water hardness	16-18 ° dH
TOC	5.76

TABLE 13. Physico-chemical parameters of SE

pH	7.6
Conductivity µS/cm	1413
BOD5 mgO2/l	5
N total mgN/l	8
P total mgP/l	0
TOC mg C/l	2.5

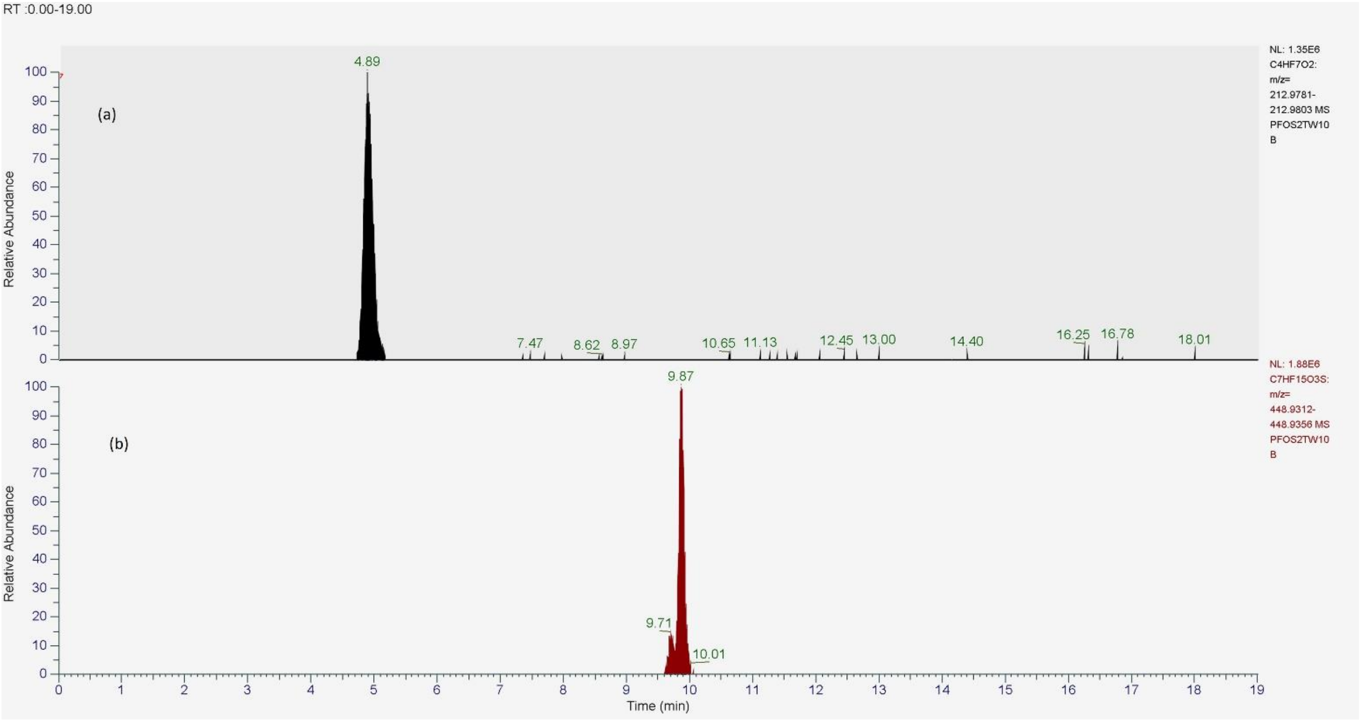


FIGURE 21. Different byproducts masses extracted from TIC of PFOS in TW, (a) TP_212 and (b) TP_448.

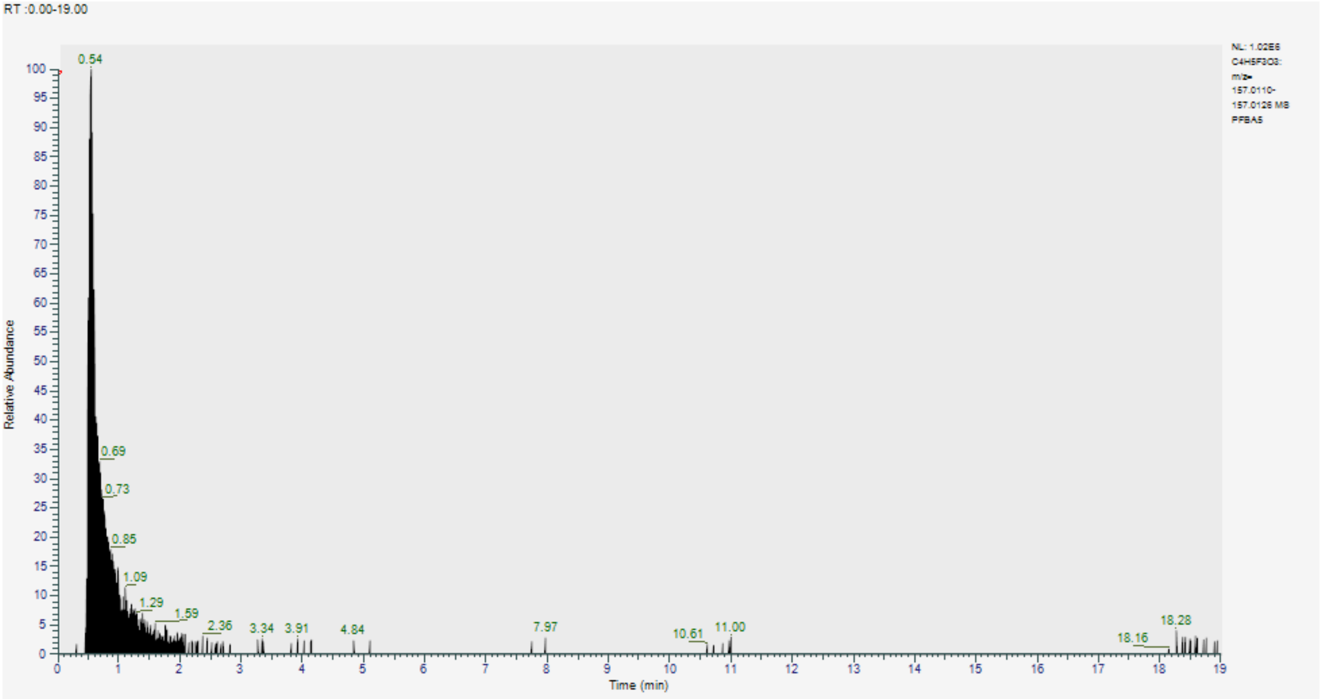


FIGURE 22 . Byproduct mass extracted from TIC of PFBA in TW, TP_157.

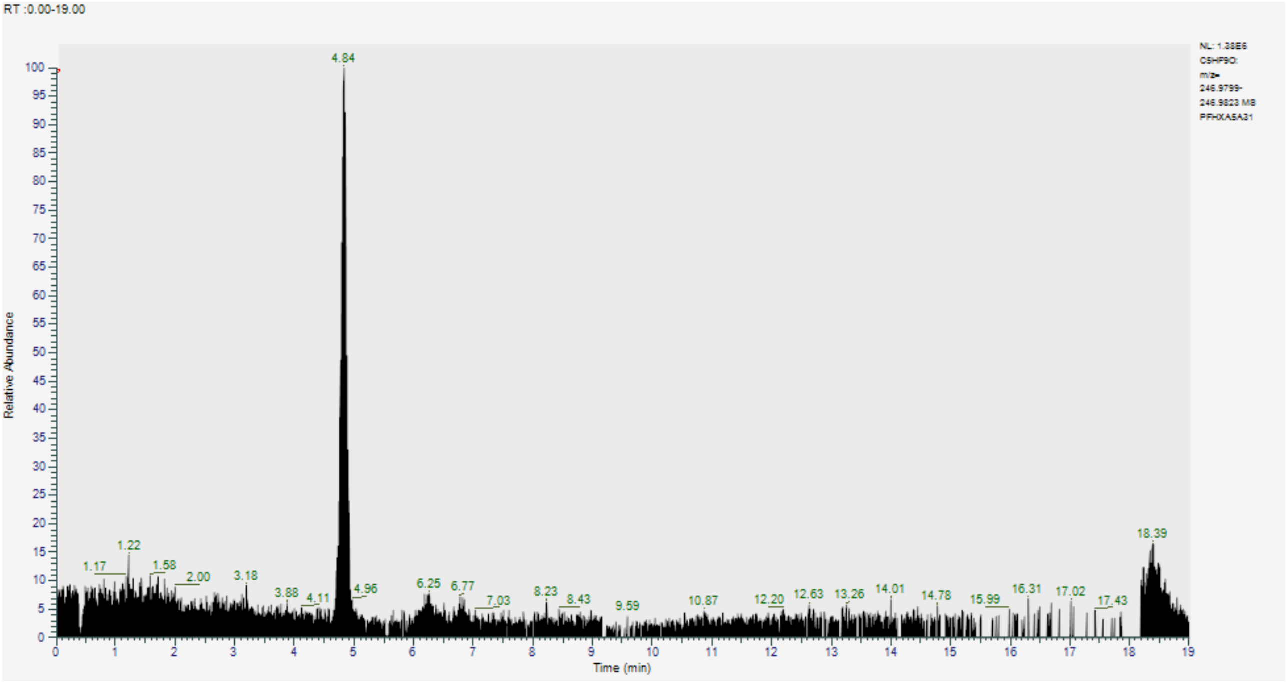


FIGURE 23. Byproduct mass extracted from TIC of PFHxA in DW, TP_246.

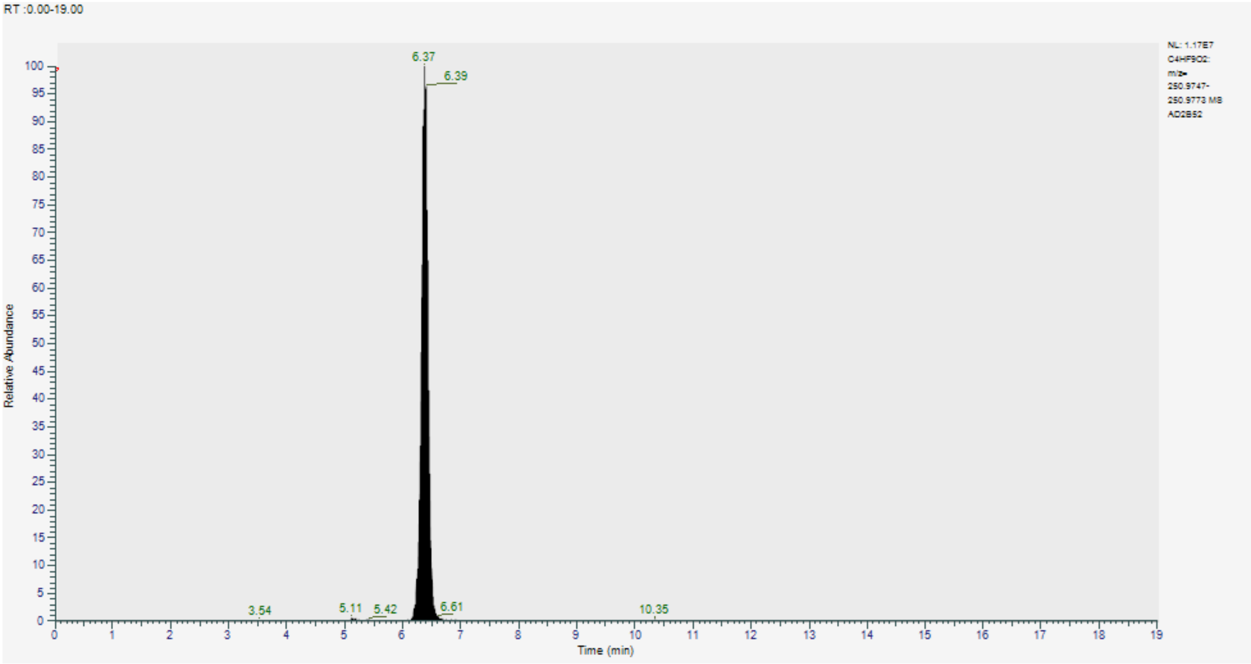
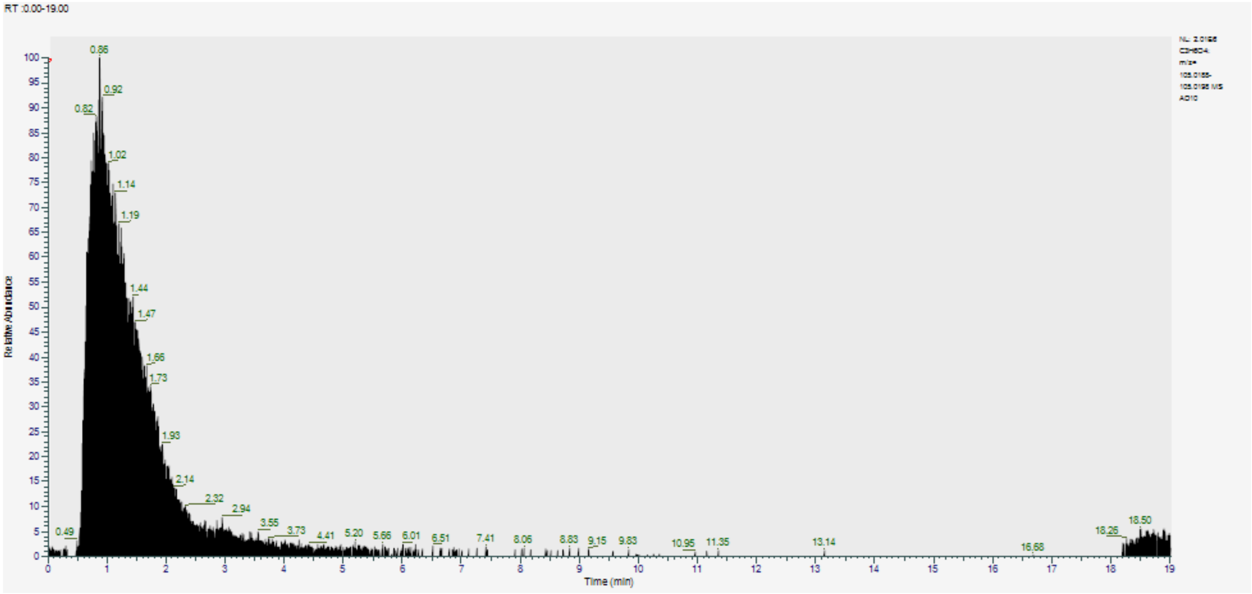
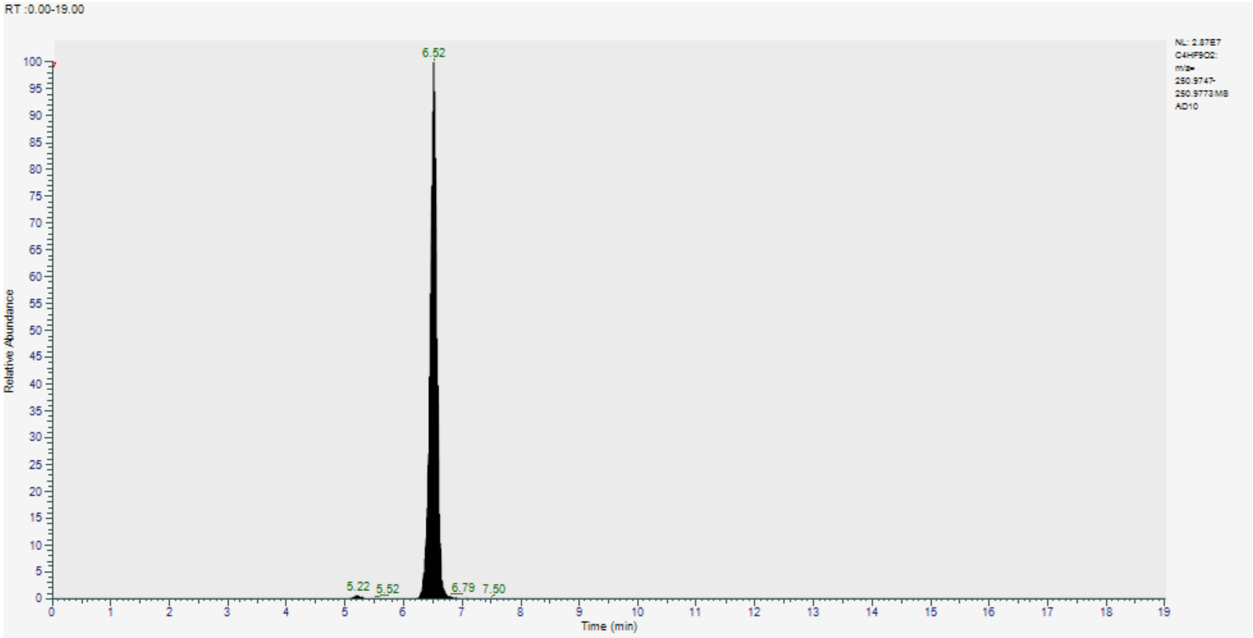


FIGURE 24. Byproduct mass extracted from TIC of ADONA, in DW, TP_250.


RT :0.00-19.00
NL: 2.01E6
C3H5O4:
m/z=
105.0188-
105.0198 MS
AD10
Relative Abundance
Time (min)
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
0.86
0.82
0.92
1.02
1.14
1.19
1.44
1.47
1.66
1.73
1.93
2.14
2.32
2.94
3.55
3.73
4.41
5.20
5.66
6.01
6.51
7.41
8.06
8.83
9.15
9.83
10.95
11.35
13.14
16.68
18.26
18.50
0.49


RT :0.00-19.00
NL: 2.87E7
C4HF9O2:
m/z=
250.9747-
250.9773 MS
AD10
Relative Abundance
Time (min)
0
5
10
15
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100
0
1
2
3
4
5
6
7
8
9
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11
12
13
14
15
16
17
18
19
6.52
5.22
5.52
6.79
7.50

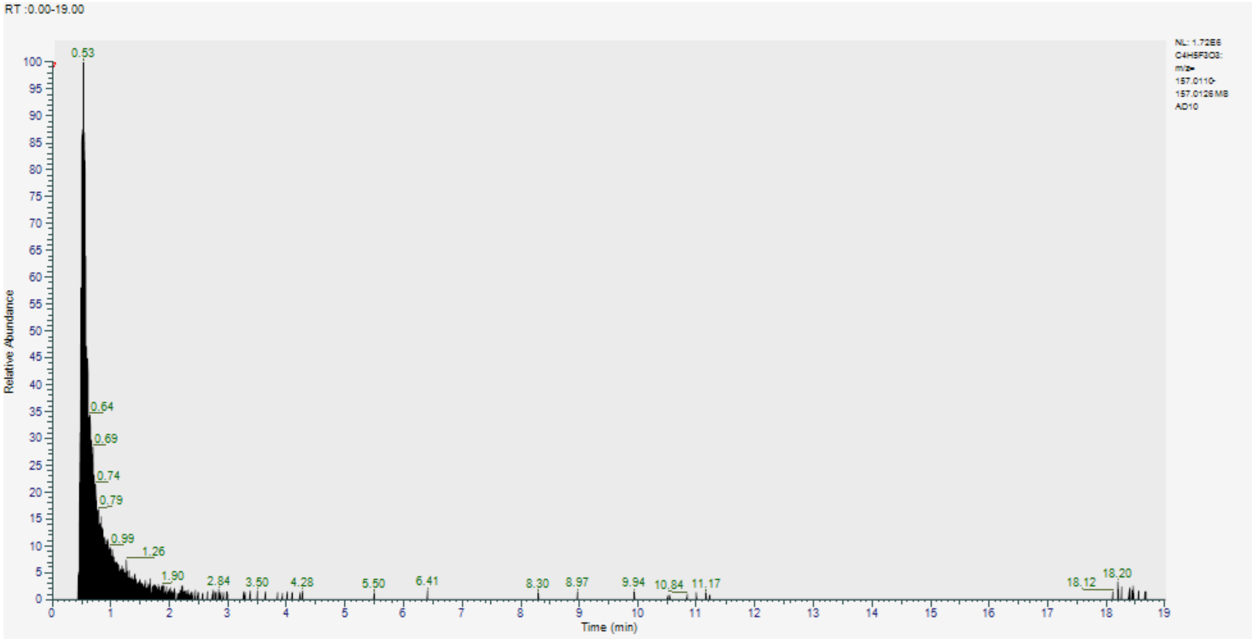
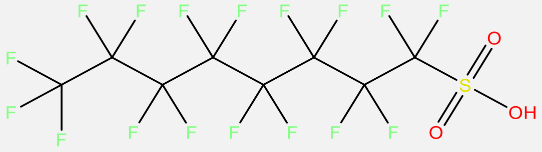
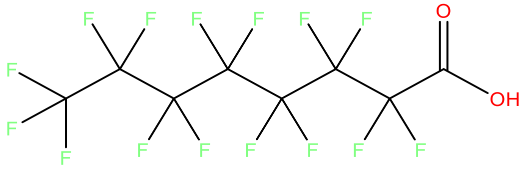
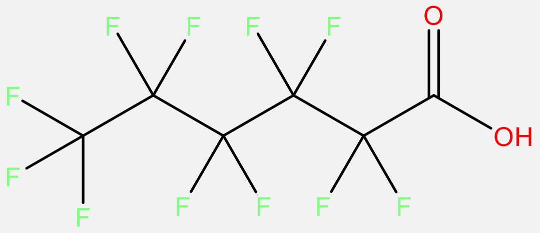
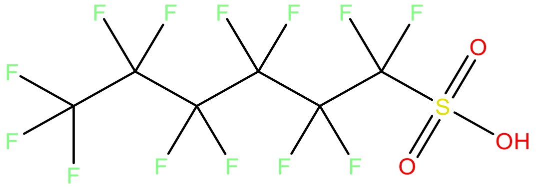
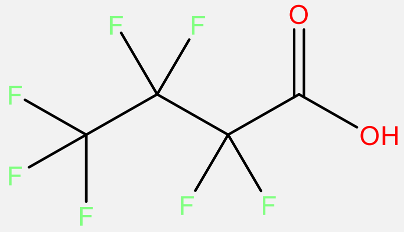
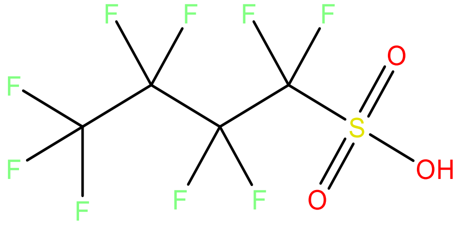
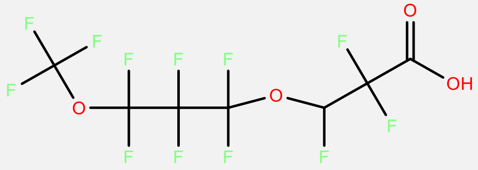
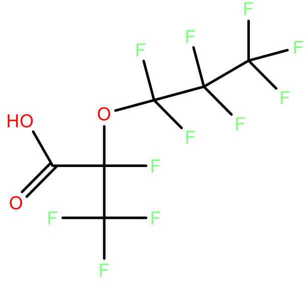


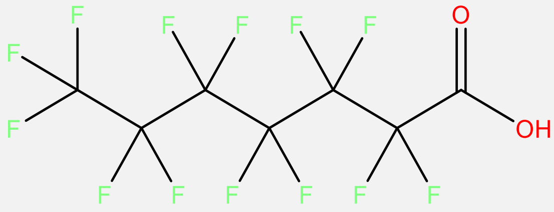
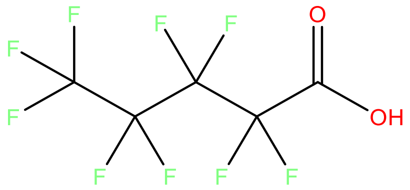
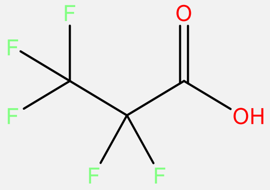
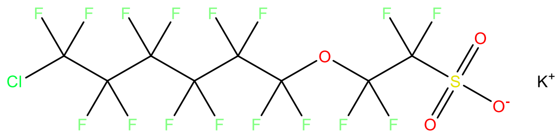
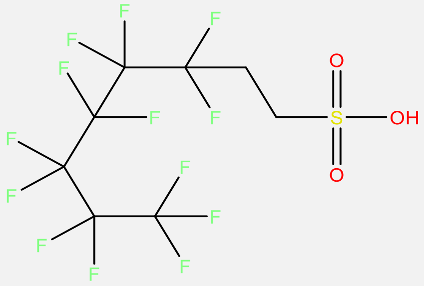
FIGURE 25. Byproducts masses extracted from TIC of ADONA in TW, (a) TP_105, (b) TP_250, (c) TP_157.

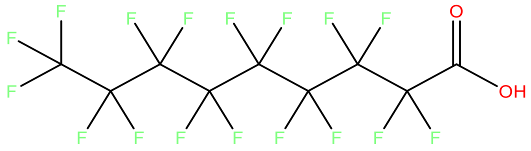
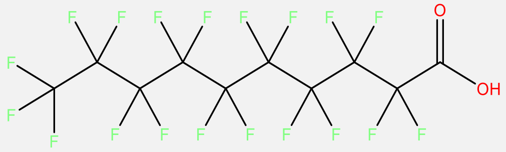
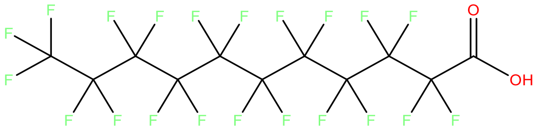
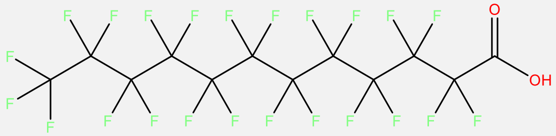
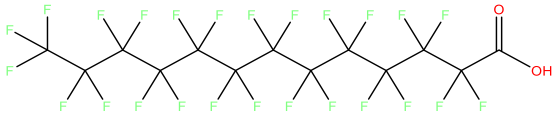
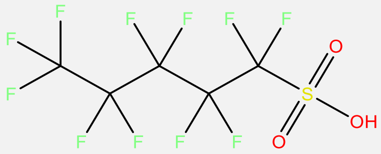
Supplementary material for Chapter 2

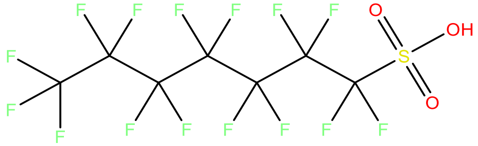
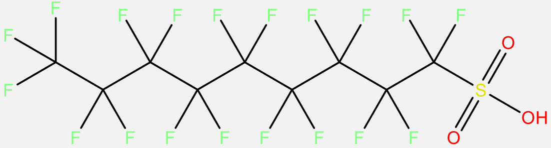
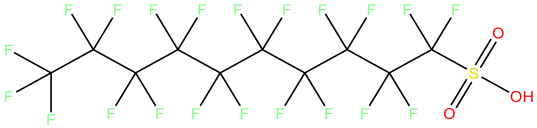
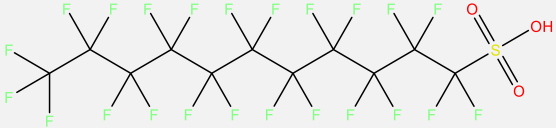
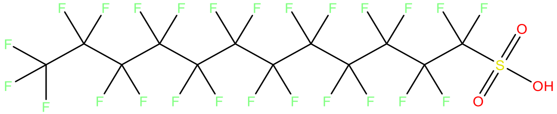
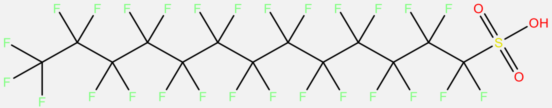
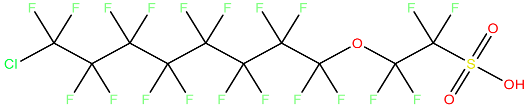
TABLE 14. List of PFAS compounds

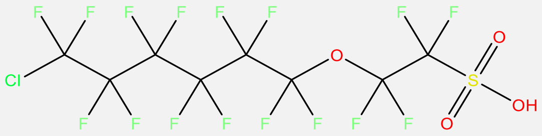
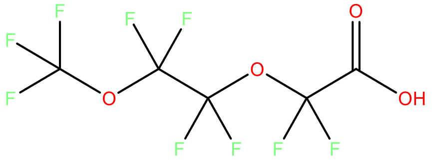
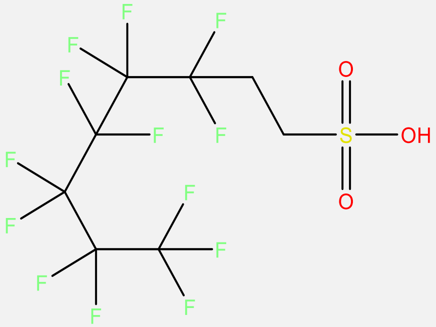
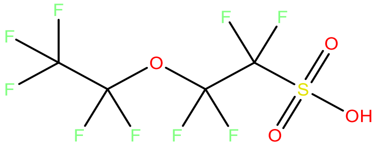
Compound	**Acronym (Abbrevation)**	**CAS number**	**Chemical formula**	**Molar mass g/mol**	**Chemical structure**
Perfluorooctanesulfonic acid	PFOS	1763-23-1	$C_8HF_{17}O_3S$	500.13	
Perfluorooctanoic acid	PFOA	335-67-1	$C_8HF_{15}O_2$	414.07	
Perfluorohexanoic acid	PFHxA	307-24-4	$C_6HF_{11}O_2$	314.05	
Perfluorohexanesulfonic acid	PFHxS	355-46-4	$C_6HF_{13}O_3S$	400.11	

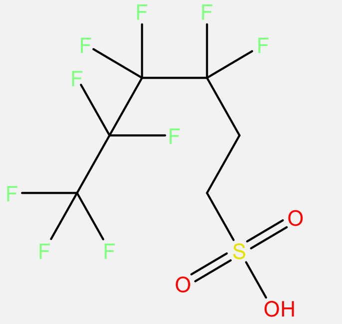
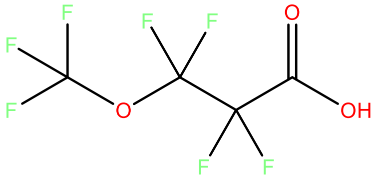
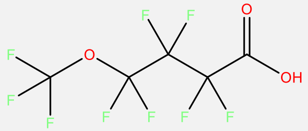
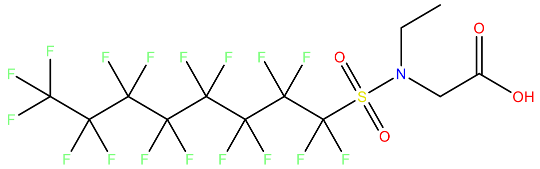
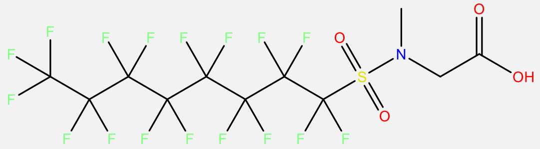
Perfluorobutanoic acid	PFBA	375-22-4	$C_4HF_7O_2$	214.03	
Perfluorobutanesulfonic acid	PFBS	375-73-5	$C_4HF_9O_3S$	300.09	
4,8-dioxa-3H-perfluorononanoic acid (parent acido f ADONA)	ADONA	919005-14-4	$C_7H_2F_{12}O_4$	378.07	
Perfluoro-2-methyl-3-oxahexanoic acid (parent acid of Gen-X)	HFPO-DA	13252-13-6	$C_6HF_{11}O_3$	330.05	

Perfluoroheptanoic acid	PFHpA	375-85-9	$C_7HF_{13}O_2$	364.06	
Perfluoropentanoic acid	PFPeA	2706-90-3	$C_5HF_9O_2$	264.05	
Perfluoropropanoic acid	PFPrA	422-64-0	$C_3HF_5O_2$	164.03	
Potassium 9-chlorohexadecafluoro-3-oxanonane-1-sulfonate	F-53B (6:2 Cl-PFESA)	73606-19-6	$C_8ClF_{16}KO_4S$	570.67	
6:2 Fluorotelomer sulfonic acid	6:2 FTS	27619-97-2	$C_8H_5F_{13}O_3S$	428.16	

Perfluorononanoic acid	PFNA	375-95-1	$C_9HF_{17}O_2$	464.08	
Perfluorodecanoic acid	PFDA	335-76-2	$C_{10}HF_{19}O_2$	514.09	
Perfluoroundecanoic acid	PFUnDA	2058-94-8	$C_{11}HF_{21}O_2$	564.09	
Perfluorododecanoic acid	PFDoDA	307-55-1	$C_{12}HF_{23}O_2$	614.10	
Perfluorotridecanoic acid	PFTrDA	72629-94-8	$C_{13}HF_{25}O_2$	664.10	
Perfluoropentanesulfonic acid	PFPS	2706-91-4	$C_5HF_{11}O_3S$	350.10	

Perfluoroheptanesulfonic acid	PFHpS	375-92-8	$C_7HF_{15}O_3S$	450.12	
Perfluorononanesulfonic acid	PFNS	68259-12-1	$C_9HF_{19}O_3S$	550.13	
Perfluorodecanesulfonic acid	PFDS	335-77-3	$C_{10}HF_{21}O_3S$	600.14	
Perfluoroundecanesulfonic acid	PFUnDS	749786-16-1	$C_{11}F_{23}SO_3H$	650.15	
Perfluorododecanesulfonic acid	PFDoDS	79780-39-5	$C_{12}F_{25}SO_3H$	700.16	
Perfluorotridecanesulfonic acid	PFTrDS	791563-89-8	$C_{13}F_{27}SO_3H$	750.16	
11-Chloroperfluoro-3-oxaundecanesulfonic acid	11Cl-PF3OUdS	763051-92-9	$C_{10}HClF_{20}O_4S$	632.59	

Perfluoro(2-((6-chlorohexyl)oxy)ethanesulfonic acid)	9Cl-PF3ONS	756426-58-1	$C_8HClF_{16}O_4S$	532.58	
Perfluoro-3,6-dioxaheptanoic acid	NFDHA	151772-58-6	$C_5HF_9O_4$	296.04	
8:2 Fluorotelomer sulfonic acid	8:2 FTS	39108-34-4	$C_{10}H_5F_{17}O_3S$	528.18	
Perfluoro-2-ethoxyethanesulfonic acid	PFEESA	113507-82-7	$C_4HF_9O_4S$	316.09	

4:2 Fluorotelomer sulfonic acid	4:2 FTS	757124-72-4	$C_6H_5F_9O_3S$	328.15	
Perfluoro-3-methoxypropanoic acid	PFMPA	377-73-1	$C_4HF_7O_3$	230.03	
Perfluoro (4-methoxybutanoic acid)	PFMBA	863090-89-5	$C_5HF_9O_3$	280.05	
2-(N-Ethylperfluorooctanesulfonamido) acetic acid	NEtFOSAA	2991-50-6	$C_{12}H_8F_{17}NO_4S$	585.23	
2-(N-Methylperfluorooctanesulfonamido) acetic acid	NMeFOSAA	2355-31-9	$C_{11}H_6F_{17}NO_4S$	571.20	

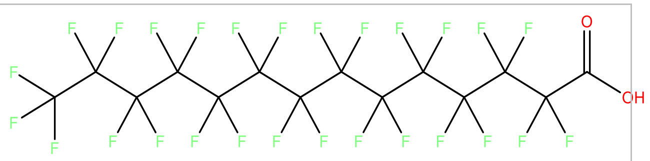
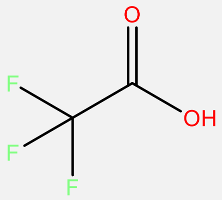
Perfluorotetradecanoic acid	PFTA(PFTeDA)	376-06-7	$C_{14}HF_{27}O_2$	714.12	
Trifluoroacetic acid	TFA	76-05-1	C2HF3O2	114.02	

TABLE 15. Maximum concentrations for HQ and RQ calculations and type of water source

COMPOUNDS	MEC1 (ug/L)	Water source	MEC2 (ug/L)	Water source	Reference (MEC1, MEC2)
PFOS	0.128	River	0.075	Effluent	(Campo et al., 2016), (Lenka et al., 2021)
PFOA	1.5	Groundwater	28	Effluent	(McMahon et al., 2022), (Lenka et al., 2021)
PFHxA	0.198	Lake	10.3	Effluent	(Pan et al., 2018), (Lenka et al., 2021)
PFHxS	1.434	Lake	0.43	Effluent	(Pan et al., 2018), (Lenka et al., 2021)
PFBA	0.644	River	0.8	Effluent	(Campo et al., 2016), (Lenka et al., 2021)
PFBS	0.544	Groundwater	1.5	Effluent	(T. Liu et al., 2022), (Lenka et al., 2021)
ADONA	0.0002	Surface wáter	n.d.	/	(Sadia et al., 2023), /
HFPO-DA	0.812	River	n.d.	/	(Gebbink et al., 2017), /
PFHpA	0.177	Drinking water	0.94	Effluent	(Boone et al., 2019), (Lenka et al., 2021)

PFPeA	0.514	Drinking water	1.69	Effluent	(Boone et al., 2019), (Lenka et al., 2021)
PFPA	0.0092	River	0.014	/	(Gebbink et al., 2017),/
F-53B **(6:2 Cl-PFESA)**	0.0522	Lake	n.d.	/	(Pan et al., 2018), /
6:2 FTS	0.017	Groundwater	4.79	Effluent	(McMahon et al., 2022), (Lenka et al., 2021)
PFNA	0.0386	Drinking water	0.009	Effluent	(Boone et al., 2019), (Lenka et al., 2021)
PFDA	0.213	River	0.003	Effluent	(Campo et al., 2016), (Lenka et al., 2021)
PFUnDA	0.00306	River	n.d.	/	(Pan et al., 2018), /
PFDoDA	0.003	Drinking water	n.d.	/	(EPA Office of Water, 2024), /
PFTrDA	0.007	Drinking water	n.d.	/	(EPA Office of Water, 2024), /
PFPS	0.012	Groundwater	n.d.	/	(McMahon et al., 2022),/
PFHpS	0.003	Groundwater	2.95	Effluent	(McMahon et al., 2022) (Lenka et al., 2021)
PFNS	n.d.	/	n.d.	/	/,/
PFDS	0.00013	Groundwater	n.d.	/	(T. Liu et al., 2022), /
PFUnDS	n.d.	/	n.d.	/	/,/
PFDoDS	n.d.	/	n.d.	/	/,/
PFTrDS	n.d.	/	n.d.	/	/,/
11Cl-PF3OUdS	0.005	Drinking water	n.d.	/	(EPA Office of Water, 2024),/
9Cl-PF3ONS	0.002	Drinking water	n.d.	/	(EPA Office of Water, 2024),/
NFDHA	0.002	Drinking water	n.d.	/	(EPA Office of Water, 2024),/
8:2 FTS	0.002	Surface water	0.33	Effluent	(Sadia et al., 2023), (Lenka et al., 2021)
PFEESA	0.003	Drinking water	n.d.	/	(EPA Office of Water, 2024),/

4:2 FTS	0.003	Drinking water	n.d.	/	(EPA Office of Water, 2024),/
PFMPA	0.004	Drinking water	n.d.	/	(EPA Office of Water, 2024),/
PFMBA	0.003	Drinking water	n.d.	/	(EPA Office of Water, 2024),/
NEtFOSAA	0.0003	Groundwater	n.d.	5	(T. Liu et al., 2022)
NMeFOSAA	0.0003	Groundwater	n.d.	5	(T. Liu et al., 2022)
PFTA(PFTeDA)	0.003	Surface wáter	n.d.	5	(Sadia et al., 2023)
TFA	1.105	Drinking water	n.d.	5	(Sadia et al., 2023)

TABLE 16. MAXIMUM REPORTED CONCENTRATIONS IN DIFFERENT REGIONS AND WATER SOURCE TYPE

COMPOUND	USA max conc. ng/L	Source water USA	Europe max conc	Source water Europe	Asia max conc	Source water Asia	Reference (USA, Europe, Asia)
PFOS	98	Groundwater	128	River	29.7	Lake	(McMahon et al., 2022),(Campo et al., 2016),(Pan et al., 2018)
PFOA	1500	Groundwater	52.2	**River**	244	**Groundwater**	(McMahon et al., 2022),(Campo et al., 2016), (T. Liu et al., 2022)
PFHxA	55.1	**Surface water**	18.7	**River**	198	**Lake**	(Boone et al., 2019),(Campo et al., 2016),(Pan et al., 2018)
PFHxS	81	**Groundwater**	36.7	**River**	1434	**Lake**	(McMahon et al., 2022),(Campo et al., 2016),(Pan et al., 2018)
PFBA	96.8	**Surface water**	644	**River**	143	**Groundwater**	(Boone et al., 2019), (Campo et al., 2016), (T. Liu et al., 2022)
PFBS	24	**Groundwater**	27	**River**	544	**Groundwater**	(McMahon et al., 2022)(Campo et al., 2016), (T. Liu et al., 2022)
ADONA	3	**Drinking water**	0.2	**Surface water**	1.55	**River**	(EPA Office of Water, 2024), (Sadia et al., 2023), (Pan et al., 2018)
HFPO-DA	5	**Drinking water**	812	**River**	144	**Lake**	(EPA Office of Water, 2024),(Gebbink et al., 2017),(Pan et al., 2018)
PFHpA	177	**Drinking water**	24	**Surface water**	32.8	**Groundwater**	(Boone et al., 2019), (Llorca et al., 2012), (T. Liu et al., 2022)
PFPeA	501	**Surface water**	9.4	**Surface water**	38.2	**Groundwater**	(Boone et al., 2019), (Llorca et al., 2012), (T. Liu et al., 2022)

PFPA	Nd	/	9.2	**River**	n.d.	/	/, (Gebbink et al., 2017), /
F-53B	Nd	/	n.d.	/	52.2	**Lake**	/,/, (Pan et al., 2018)
6:2 FTS	17	**Groundwater**	1.19	**Surface water**	13.9	**River**	(McMahon et al., 2022), (Sadia et al., 2023), (Pan et al., 2018)
PFNA	41.4	**Surface water**	19.8	**River**	27.9	**Groundwater**	(Boone et al., 2019), (Campo et al., 2016), (T. Liu et al., 2022)
PFDA	31.1	**Surface water**	213	**River**	5.75	**Lake**	(Boone et al., 2019), (Campo et al., 2016), (Pan et al., 2018)
PFUnDA	2.90	**Surface water**	0.62	**River**	3.06	**River**	(Boone et al., 2019), (Campo et al., 2016), (Pan et al., 2018)
PFDoDA	0.28	**Surface water**	0.16	**Surface water**	2.30	**Lake**	(Boone et al., 2019), (Sadia et al., 2023), (Pan et al., 2018)
PFTrDA	7	**Drinking water**	0.04	**River**	1.56	**Lake**	(EPA Office of Water, 2024), (Campo et al., 2016), (Pan et al., 2018)
PFPS	12	**Groundwater**	0.2	**Surface water**	4.42	**Groundwater**	(McMahon et al., 2022), (Sadia et al., 2023)/, (T. Liu et al., 2022)
PFHpS	2.9	**Groundwater**	0.13	**Drinking water**	n.d.	/	(McMahon et al., 2022), (Sadia et al., 2023)/
PFNS	Nd	/	n.d.	/	n.d.	/	/
PFDS	Nd	/	n.d.	/	0.13	**Groundwater**	/, /, (T. Liu et al., 2022)
PFUnDS	Nd	/	n.d.	/	n.d.	/	/
PFDoDS	Nd	/	n.d.	/	n.d.	/	/
PFTrDS	nd	/	n.d.	/	n.d.	/	/

11Cl-PF3OUdS	5	**Drinking water**	n.d.	/	n.d.	/	(EPA Office of Water, 2024)
9Cl-PF3ONS	2	**Drinking water**	n.d.	/	n.d.	/	(EPA Office of Water, 2024)
NFDHA	2	**Drinking water**	n.d.	/	n.d.	/	(EPA Office of Water, 2024)
8:2 FTS	5	**Drinking water**	1.58	**Surface water**	0.28	**River**	(EPA Office of Water, 2024), (Sadia et al., 2023), (Pan et al., 2018)
PFEESA	3	**Drinking water**	n.d.	/	n.d.	/	(EPA Office of Water, 2024), //
4:2 FTS	3	**Drinking water**	n.d.	/	0.11	**River**	(EPA Office of Water, 2024), /, (Pan et al., 2018)
PFMPA	4	**Drinking water**	n.d.	/	n.d.	/	(EPA Office of Water, 2024)
PFMBA	3	**Drinking water**	n.d.	/	n.d.	/	(EPA Office of Water, 2024)
NEtFOSAA	5	**Drinking water**	n.d.	/	0.32	**1**	(EPA Office of Water, 2024), /, (T. Liu et al., 2022)
NMeFOSAA	6	**Drinking water**	n.d.	/	0.3	**1**	(EPA Office of Water, 2024), /, (T. Liu et al., 2022)
PFTA(PFTeDA)	8	**Drinking water**	3.15	**Drinking water**	1.34	**Lake**	(EPA Office of Water, 2024), (Sadia et al., 2023), (Pan et al., 2018)

TFA	n.d.	/	1104.6	**Drinking water**	n.d.	/	/**,** (Sadia et al., 2023)**,** /