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PFAS: Ecological Implications, Remedial Actions and Ethical Considerations

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Abstract

The C-F bond is one of the strongest in organic chemistry. It is responsible for the great stability of perfluoroalkyl and polyfluoroalkyl substances, commonly referred to as "PFAS", a group of man-made chemicals that include perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA). Thermal stability, surface activity, dielectric characteristics, chemical resistance, and inertness are just a few of the technical advantages that this group has over hydrocarbons, and since the 1950s, these chemicals have been largely utilized in a variety of domestic and industrial endeavors. The hydrophilic and lipophilic nature of this class of chemicals accounts for its uniqueness. Up until today, the chemistry and ecotoxicology of these chemicals continue to emerge. Issues concerning the destructive power of ignorance expedited by an ineffective regulatory institution continue to show that manufacturing chemicals are insufficient without giving serious thought to issues of openness and humanity's awareness of its own safety. When discussing the nature of humanity and how it can be defined or redefined, it is important to allude to the significance of integrating business with ethics in its various forms. This paper highlights the importance of holding polluters accountable for PFAS contamination cleanup costs while emphasizing the need for chemical manufacturers to test and disclose the health and environmental effects of PFAS compounds. In addition, the sources, types, properties, applications, distribu-

tion, toxicological implications, regulations, and analytical methods associated with PFAS (per- and polyfluoroalkyl substances) are explored. The effectiveness of the remedial methods described in this paper needs to be progressively tested while exploring other sustainable approaches.

Keywords

Emerging Contaminants, Per- and Polyfluoroalkyl Substances, Non-Polymeric Chemicals, Remediation, Ethics, Public Health

1. Introduction

Per- and polyfluoroalkyl substances (PFAS) are widely distributed across the globe and their impact on human health and the environment cannot be underestimated. Perfluoroalkyl compounds are a group of fluorinated, synthetic organic chemicals that are extremely stable [1]. The C-F bond, one of the strongest in organic chemistry (~485 kJ/mol), is responsible for the great stability associated with PFAS [2]. Thermal stability, surface activity, dielectric characteristics, chemical resistance, and physiological inertness are just a few of the properties of PFAS [1]. Since the 1950s, PFAS chemicals have been used on a large scale. They have been used to make nonstick cookware, stain-resistant fabrics and carpets, water-repellent clothing, some firefighting foams, some cosmetics, and products that resist grease, water, and oil [1]. They are used as surfactants in goods, making them stain-proof, grease-proof, water-resistant, and fire-resistant. The releases of PFAS and other emerging contaminants such as microplastics are increasing as a result of climate change [2] [3]. There are more than 6000 different forms of PFAS. However, because these chemicals are not well-known or investigated, their public-health impact is uncertain [3]. PFAS are used in a variety of domestic and industrial utilities, including paper and paints [1].

Although there are many types of PFAS, perfluorooctanoic acid (PFOA) and perfluorooctane sulfonic acid (PFOS) are the most popular (**Figure 1**). These two compounds contain at least six carbon-fluorine bonds and are termed long-chain C-F compounds, occurring mostly in groundwater [4] [5]. During production and use, PFAS can migrate into the soil, water, and air. Most PFAS are resistant to degradation, so they persist in the environment. Consequently, PFAS have been found in both human and animal blood and are present at low levels in many food products and in the environment. Water bodies that have been polluted

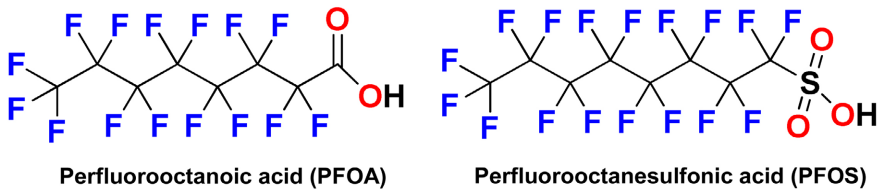

Figure 1. Molecular structure of PFOS and PFOA.

by fluorochemical industries and landfills contain a large diversity of PFAS structures [6].

PFAS are classified into two basic categories: polymeric and non-polymeric chemicals. While polymeric PFAS include widely used chemicals like Teflon and Tefzel, the majority of PFAS research focuses on non-polymeric chemicals because they are more often identified in the environment and so, more likely to be the topic of government recommendations and restrictions [7]. Perfluoroalkyl and polyfluoroalkyl compounds are two subcategories of non-polymeric PFAS. Many PFAS may break down under certain circumstances into perfluoroalkyl acids (PFAAs). Besides, precursor chemicals release PFAS indirectly contributing to global PFAS emissions in addition to direct PFAAs emissions. PFAAs are a minor subgroup of PFAS, yet they are quite persistent [1], and the perfluorocarboxylic acids (PFCAs) and perfluoroalkane sulfonic acids (PFSAs) are two major subgroups of PFAAs, each differentiated by their carboxyl and sulfonate functional groups. All available bonding sites on the carbon atoms have been replaced by fluorine in perfluoroalkyl compounds, except for one site on the terminal carbon, where a functional group is attached [8]. A non-fluorine element (usually hydrogen or oxygen) is attached to at least one, but not all, carbon atoms in polyfluoroalkyl compounds, while at least two or more of the remaining carbon atoms in the carbon chain tail are completely fluorinated [8].

The fluorine atoms that replace hydrogen throughout the PFAS carbon chains are principally responsible for the unusual characteristics. The C-F bond is one of the strongest covalent bonds due to fluorine's high electronegativity and small size [3]. The enormous energy required to break this bond is responsible for PFAS's stability in the presence of oxidants and elevated temperatures, as well as its opposition to chemical and biological disintegration [9]. As the carbon center goes progressively positive, further replacement of a carbon atom further strengthens the connection by reducing the bond length [10]. The low polarizability of fluorine contributes to the lipophilic and hydrophobic properties of PFAS [11], in addition to increasing chain length [11]. Although PFAS may be found in both aqueous and solid matrices, long-chain PFAS are more likely to adhere to soil particles owing to differences in adsorption potentials, resulting in mobility and environmental transport discrepancies [12]. Hence, the mobility of chain PFAS in the environment highly depends on chain length in addition to other determinants [8].

Functional groups including -COOH and -OH also influence PFAS chemistry. When the number of carbons is the same, more electrophilic PFCAs with carboxyls are simpler to degrade than PFSAs with sulfonates [13]. Under certain circumstances, functional groups can dissociate into ions in aqueous solutions [8]. The resulting ion might be an anion, cation, or zwitterion, with anions being more common in nature [14]. Cations are more likely to be adsorbed to soils, which have a net negative charge, while anions are less likely [15].

PFOA and PFOS are the most extensively manufactured and detected PFAS in

the US [16]. PFAAs have hydrophobic fluorinated tails and a hydrophilic functional group while PFOA and PFOS are innocuous, water-soluble acids that exist mostly in anionic form over a pH range [8]. PFOA is mainly dissolved, but PFOS has a greater sorption capacity [17]. The larger perfluoroalkyl chain length of PFOS makes it more bioaccumulative [18]. Most polyfluoro-compounds or partly fluorinated PFAS degrade biotically and abiotically to PFAAs [19].

2. Applications

PFAS have been used in the past in different industries whereas some are still presently available. It is important to note that the complexity and diversity of PFAS compounds contribute to variations in their environmental behavior, persistence, and potential health effects, and research in this field is ongoing, and new information continues to emerge. Therefore, specific PFAS compounds used within each industry may vary, and there may be additional uses beyond those mentioned. The information provided in **Table 1** represents common applications of PFAS in each industry [20].

Table 1. Overview of PFAS application based on industry.

Industry	Application
Aviation and aerospace	Hydraulic fluid additives to prevent evaporation, fires, and corrosion
Automotive	Surface treatment for textiles, upholsteries, carpets, leather, and exterior surfaces
Pesticides	Active ingredients such as short-chain sulfonamides in plant growth regulators and herbicides
Building and construction	Additives in paints, coatings, and surface treatments
Cosmetics	Cosmetics, shampoos, nail polish, eye makeup, denture cleaners
Electronics	Flame retardants for polycarbonate resin
Safety/firefighting	Coatings and materials used as water repellents and some Class B foam, vapor suppression for flammable liquids
Mining	Instances of surfactants used in ore mining flotation
Paper and packaging	Phosphate ester salts
Photolithography & semiconductor	Photolithography (such as using PFOS) in manufacture of semiconductor chips
Textiles, leather, and apparel	PFOA-based chromium treatment for paper and leather. Non-polymer coatings used to treat textiles to provide oil- and water-repellent and stain release finishes

3. Distribution and Toxicological Implications

The dispersion and exposure pathways of PFAS chemicals in the environment are complex. The principal sources of PFAS emissions include industrial manufacturing processes, industrial usage, and recycling. Landfilling and agricultural land use are two more indirect causes of pollution. Deposition, leaching, and runoff mechanisms control the movement of PFAS between air, soil, water, and sediment. PFAS can enter the food chain through bioaccumulation and indirect human exposure through the intake of contaminated food sources if these pathways are all used together, exposing aquatic and terrestrial ecosystems as well as humans to short- and long-term exposure. PFAS have been found in a variety of environmental media, biological species, and human populations across the world due to its physicochemical features and extensive use [21] [22]. Environmental persistence and substantial threats to ecosystems and human health are well-known effects of PFAS' high resistance to thermal, chemical, or biotic degradation [23]. The production of PFAAs, for example, can occur because of partial degradation of certain polyfluorinated PFAS under specific environmental circumstances, which can lead to the formation of additional harmful PFAS compounds [21]. According to previous research, PFOS and PFOA can appear in industrial processes or consumer items as impurities and be released in biotic or abiotic manner [19], but they can also be formed as byproducts of the breakdown or biotransformation of longer-chain PFAS molecules [24]. The amphiphilic nature of PFAS makes it possible for them to accumulate in living animals' adipose tissue or bloodstreams, and their great mobility means that they are widely dispersed in the environment by leaching into groundwater, run-off into rivers and seas, wind dispersion through dust particles, and wet/dry deposition into soils [25] [26]. **Figure 2** depicts the distribution and fate of PFAS in

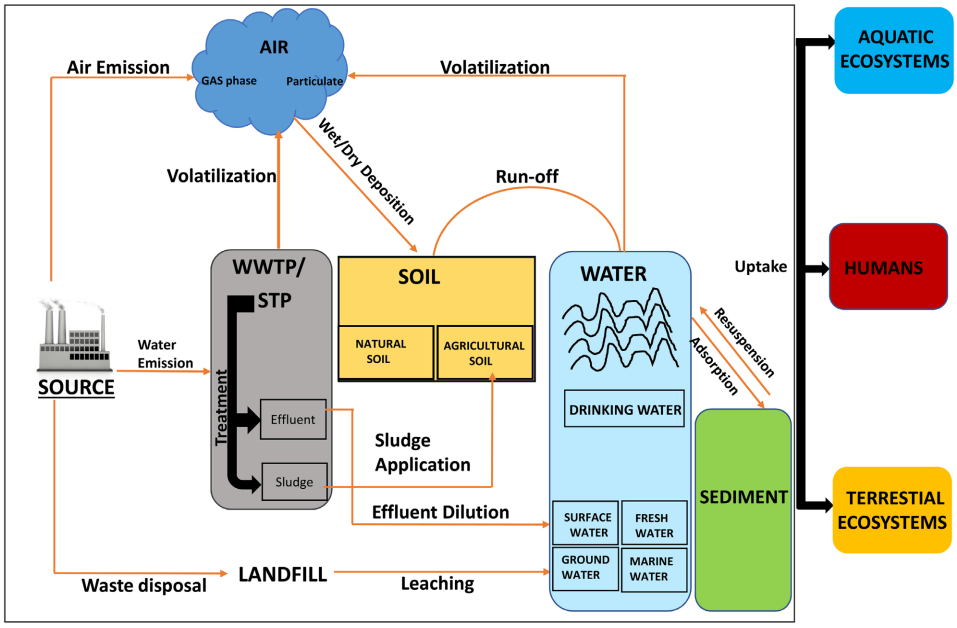

Figure 2. PFAS environmental distribution and exposure pathways.

the environment. In the sections that follow, the distribution and adverse impacts of PFAS on the environment, humans and aquatic organisms are discussed in detail.

3.1. Distribution and Adverse Impacts of PFAS on the Environment

3.1.1. Atmospheric Availability

There are some neutral species, such as polyfluoroalkanes (PFOAs) and fluorotelomer alcohols (FTOHs) that have a high boiling point but low vapor pressure and may thus partition into the atmosphere [27]. Yu and colleagues used cryogenic air samplers to gather atmospheric particle and gas phase for non-target characterization of PFAS compounds [28]. It was discovered that the particulate matter is home to a large number of PFAS as evidenced by the presence of 117 PFAS homologues spread throughout 38 classes [28].

3.1.2. Water Systems

Ionic PFAS with short carbon chains are extremely water-soluble and can partition at the water-air interface, whereas longer chain PFAS tend to be dispersed into the water-sediment fraction and biota. According to several investigations, PFAS have been found in freshwater across the world. Studying Lake Victoria and its tributaries led to the discovery of PFOA and PFOS from the emission of point sources including residential and industrial waste [29]. Lower concentrations were found in lake waters, with PFOA concentrations in the range of 0.04 - 12.0 ng/L and PFOS concentrations ranging between 0.04 - 2.5 ng/L, respectively [29]. Sedimentary PFOS concentrations ranged from 1.0 - 22.6 ppb, with a gradual decline from summer to winter [29]. PFOS and PFHxS dominated the PFAS composition in both cases [30]. The greatest concentration of PFSAs, PFCAs, and PFPIAs was found in the sediment cores of the Ontario Lake (13 ppb), with PFOS accounting for more than 80 percent of the overall content [31]. Small-mouthed salamanders were found to be more susceptible to PFAS at later stages of development than gray tree frogs, showing that species-specific effects can affect the susceptibility of biota to PFAS chemicals separate from type and ambient concentration [32]. PFAS chemicals produced and disseminated via diverse routes have been extensively recorded in seawater and seas, making them important environmental receptors [33]. Subsequent research by the same authors looked at the many sources of PFAS entering the Bohai Sea, including river and coastal wastewater as well as other effluents that run directly into the ocean. PFBS, PFOA, and PFOS were the most prevalent chemicals in river samples, with total PFAS values ranging from 0.013 to 69.2 ppb, indicating the existence of heavily contaminated locations. On the other hand, PFOA was the most prevalent chemical in coastal wastewater and effluents, with PFAS concentrations ranging from 0.02 - 7.5 parts per billion and 0.013 - 0.3 parts per billion, respectively [34]. The authors discovered that riverine inputs were responsible for most of the PFAS pollution in Bohai Sea, whereas coastal wastes and effluents

played a smaller contribution. PFAS levels in surface rivers and nearby groundwater were examined by Yao and lab members in two industrialized cities in northern China on a regional scale. PFAS concentrations were found at levels as high as 0.1 ppb at certain sample locations, with considerable contributions from PFOS, PFOA, PFBA, and N-EtFOSAA [35]. River water infiltration, agricultural soil leaching, municipal, industrial, and landfill wastewater have all been identified as potential sources of PFAS contamination in groundwater [35]. The discharge of AFFFs containing PFAS or its precursors from firefighting training facilities is another well-documented source of groundwater contamination [15]. Drinking water is a major source of exposure to PFAS since even modest levels of PFAS in water can lead to large loads in blood serum over the course of a lifetime [36]. Compared to other non-human animals, it has been anticipated that the extended absorption of PFOA through drinking water will result in blood concentrations up to 100 times greater than those detected in the ingested drinking water. Many public water systems serving millions of people have PFAS levels exceeding the national environmental agencies' safe standards, and long-term exposure to water with PFAS concentrations as low as 70 parts per trillion (ppt) may have harmful impacts on human health [37] [38]. The Yangtze River tributary system in China's Jiujiang Province was studied by Tan and colleagues for the presence of PFAS. Total PFAS levels were found in tap water samples in the range of 2.40 - 300 ng/L, with Jiujiang City reporting the highest values.

3.1.3. Soils and Plants

Since PFAS have been shown to be more prevalent in soils from developed nations like Japan and China, total PFAS levels in soil have been estimated to range from 13,000 to 36,000 parts per billion (ppb) [39]. Particulate matter can be dispersed in the air, and PFAS with high affinity for the particulate matter might possibly move from the originating emission source to distant locations and finally be deposited on the soil [40]. Surface water and soil samples from a region in Ohio and West Virginia near a fluoropolymer manufacturing plant were studied by Galloway *et al*., and the soil samples taken in 2016 and 2018 contained measurable amounts of PFOA, which suggests that the soil matrix has been contaminated for some time [41]. There is evidence to show that the usage of groundwater contaminated with fluorochemicals, such as at the FIP in China, can have a negative influence on home-grown vegetables and eggs, resulting to high concentrations of fluorochemicals in the soil. Another major cause of soil contamination by PFAS that might directly affect human food sources is the application of biosolids [21]. PFAS concentrations in soil samples were compared in the presence and absence of sludge application in a location near Decatur, Alabama, USA. It has been shown that contaminated sludge can cause greater PFAS concentrations in the surface soil samples that receive it, with total values up to 5.0 mg/kg [42].

3.2. Adverse Impacts on Humans and Aquatic Organisms

PFAS exposure parameters and target characteristics such as, but not limited to age and sex, can have a wide variety of unfavorable health effects [43]. Female and male reproductive systems are being affected by PFAS at an increasing rate [21]. The thyroid and mammary glands, as well as other endocrine organs, have been shown to be adversely affected by endocrine disruption. It has been shown to have developmental impacts in children, such as altered behavior or an earlier onset of puberty; nevertheless, birth weight loss has also been shown in neonates [21]. Long-term exposure to PFAS has been linked to an increased risk of kidney, prostate, and testicular cancer in the general population, as well as changes in cholesterol metabolism or a decreased ability of the immune system to fight off infections. Using a modified version of EPA Method 537, water testing carried out from May through to December 2019, by Environmental Working Group (EWG) in a sample of 31 states found PFAS availability in tap water, prevalent in North Carolina and Iowa, but with Mississippi having no detection of the chemical [44]. **Figure 3** shows that North Carolina and Iowa samples were above the 70 ppt EPA advisory limit.

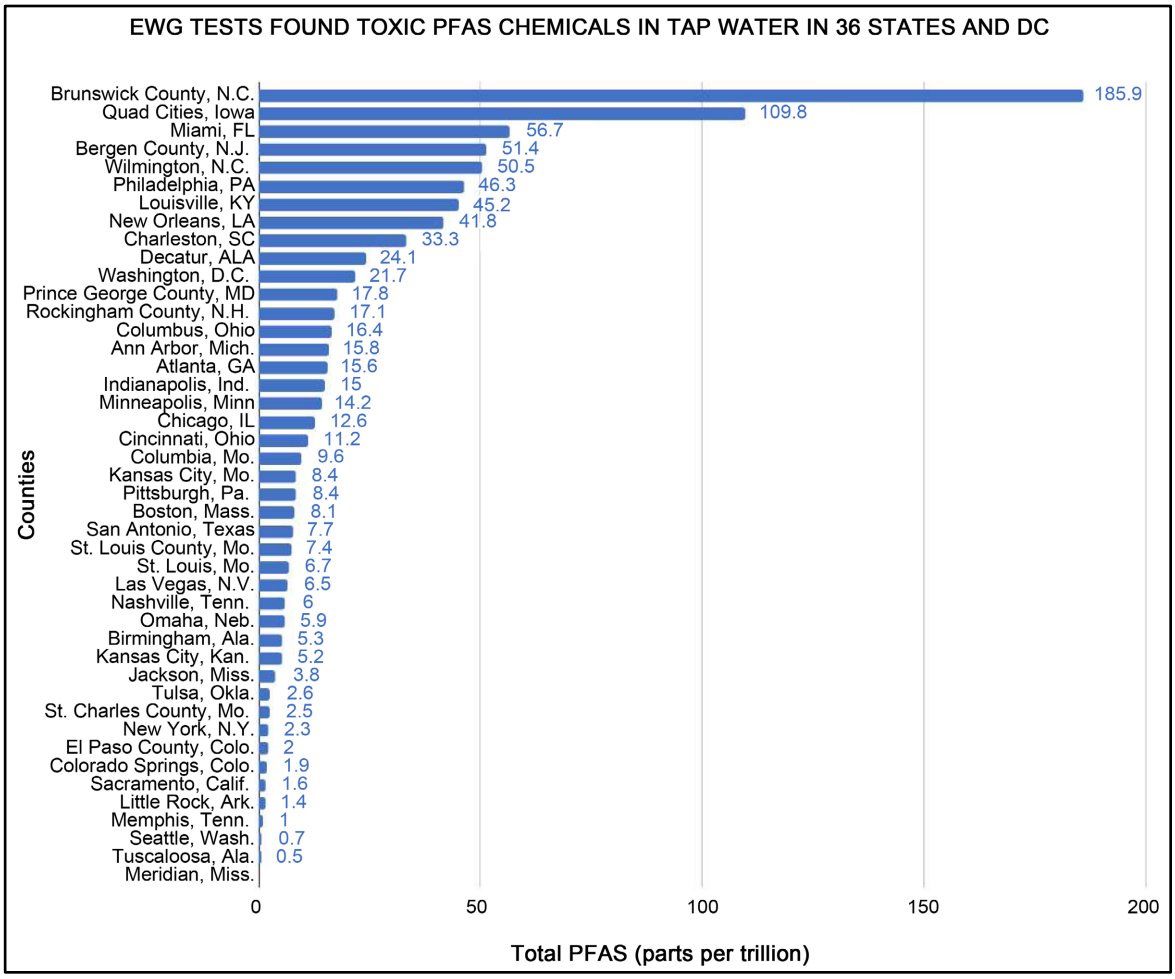

Figure 3. EWG tests found toxic PFAS chemicals in tap water in 31 states and D.C., USA.

From less than 1 ppt in Seattle and Tuscaloosa, Alabama, to over 180 ppt, PFAS were found in 43 samples across the United States. Meridian, Mississippi, draws its drinking water from wells more than 700 feet deep, and this was the only sample that did not contain any detectable PFAS. There was an average of six or seven distinct chemicals found in the samples that tested positive for PFAS. Thirteen distinct PFAS were found in varied quantities in one sample.

Generally, compounds in the aquatic environment can be either agonists or antagonists, depending on the other chemicals present [45] [46]. It is possible that PFAAs might alter cell membrane permeability, which may lead to an increase in chemical entry [47]. In water, salt can alter the physicochemical characteristics of chemicals such as PFAAs, which can have an impact on their toxicology [47]. With artificial saltwater (30 percent), the hatching enzyme activity and the hatching rate of *O. melastigma* were increased [48]. *O. melastigma* larvae (at 12 dph) demonstrated a lower survival rate and body width, as well as substantial changes in oxidative stress, immunological and inflammatory response-related genes, in response to PFOS in saline water [49]. In 30 percent salty water, PFOS dramatically altered *O. melastigma*'s cardiac development-related genes [50]. On condition of blackish Sea water, *G. crenularis* showed oxidative stress and DNA methylation under a semi-static condition [51], and *T. japonicus* showed oxidative stress and induction of the CYP enzyme with a loss in fertility and developmental delay [52]. **Table 2** displays the exposure conditions of different PFAS on fish and other aquatic organisms.

4. Regulations and Analytical Methods

4.1. Regulations and Standards

Factors that influence PFAS guideline threshold values include societal, political, and economic ones. As long as the PFAS regulation levels are consistent across recommendations, the problem can be solved. A new set of guidelines from the US Environmental Protection Agency (EPA) referred to PFAS as a serious hazardous chemical in 2019 [53]. Because of this, PFAS legislation and regulations are hindered by the fact that there is a wide range of PFAS compounds and a lack of knowledge that can be used to construct consistent laws around the globe [54].

The US Environmental Protection Agency (USEPA) has produced non- regulatory PFAS concentrations to address the health effects of PFAS exposure time. The Environmental Protection Agency (EPA) has examined and regulated about 191 PFAS chemicals since 2006 through a series of directives [54]. The EPA has set a threshold for PFOA and PFOS in drinking water at 70 parts per trillion (ppt).

There are two ways in which this lifetime health advisory applies to PFOA and PFOS: individually and additionally in the case of accidental high levels as in Australian standards [54]. Another issue with rapidly changing rules is the need for quickly created analytical methodologies [53]. Toxicological data varies

Table 2. Exposure conditions of different PFAS on fish and other aquatic organisms (Source: Lee *et al*., 2020 [47]).

Test system	Exposure method (exposure method, concentration, vehicle, solution exchange time, and the others)	Organism characteristics (age, developmental stages)	PFAA type	Exposure time (sampling time, refresh time, generation)	Effects
		Fish			
Fathead minnow (*Pimephales promelas*)	Flow-through exposure; 45 ml/min solution supply; 0, 0.03, 0.1, 0.3, 1 mg/L PFOS	F0: Six-to-seven-month adult fish F1: From embryo to fry 24 dpf	PFOS	14 d (at 1 mg/L), 21 d, and 24 d	Reproductive toxicity, endocrine disruption, PFOS accumulation
Juvenile atlantic salmon (*Salmo salar*)	Dietary exposure; 0.2 mg/kg PFOA, PFOS; 0.01% methanol solvent	Juvenile fish (sexually immature), average mass of 70 ± 20 g	PFOA, PFOS	Sampling at 0, 2, 5, 8, and 14 d 0, 3, 6 d food spike exposure and 7 d recovery 315	Beta-oxidation, oxidative stress
Rainbow trout (*Oncorhynchus mykiss*)	Dietary exposure; PFC mixture exposure (in the ratio of 1:1:1:1, mix A composed of 5 mg/L individual PFC (PFOA, PFNA, PFDA, PFUnDA), mix B composed of 50 mg/L individual PFC, mix C composed of 250 mg/L individual PFC). For VTG, PFOA and PFDA exposure, 0.026, 0.128, 0.64, 3.2, 16, 80, 400, 2000 mg/L PFOA or PFDA; DMSO vehile (≤0.05 mg/L)	Subchronic PFC exposure: 11 month old juvenile trout; PFOA and PFDA exposure for VTG analysis: 5 month old juvenile trout	PFOA, PFNA, PFDA, PFUnDA, PFPA, PFHxA, PFHpA, PFDoDA, PFTrDA, PFTDA, PFBS, PFOS, PFDS, E2	14 d (feeding every 5 d per a week)	Endocrine disruption
Zebrafish (*Danio rerio*)	Static-exposure; 0.1% DMSO(v/v); 8, 16, 32 μM PFOS for sensitive period screening; 16 μM PFOS for histological examination, transmission electron microscopic examination, NimbleGen microarray	Embryo within 0.5 h of spawning	PFOS	0 to 48 hpf or 48 - 96 hpf for sensitive period screening; 48 - 96 hpf for histological examination and transmission electron microscopic examination; from 48 hpf during 48 h for NimbleGen microarray	Developmental toxicity, microassay gene profiles

Continued

Zebrafish (*Danio rerio*)	Semi-static exposure (50% renewals every 5 d, except for initial 5 d when embryo hatching occur); 0.01% DMSO; 0.5 μM PFOS (250 μg/L)	8 hpf	PFOS	From 8 hpf to 120 dpf	Thryoid toxicity
Marine medaka (*Oryzias melastigma*)	Semi-static exposure (25‰ saline water); 1, 3, 10 μg/L PFBS; daily exchange	Eggs	PFBS	From egg state to sexual maturity state (6 month old)	Ocular toxicity, neuronal toxicity, protein profilings
Zebrafish (*Danio rerio*)	Semi-static exposure (50% renewals every 5 d, except for initial 5 d when embryo hatching occur); 0.01% DMSO; 0.5 μM PFOS	Developmental stage from 8 h dpf to 150 dpf	PFOS	5 month exposure (from 8 h dpf to 150 dpf), followed by 5 d spawning time, hatching, and others	Lipid metabolism change, ATP content, gross index, histological changes, endocrine disruption
Pseudokirchneriella subcapitata, *Daphnia magna*, *Oncorhynchus mykiss*	Acute toxicity test: Static exposure; APFO (PFOA + NH_4^+ salt); to *D. magna*, 0, 100, 178, 316, 562, 1000 mg/L APFO; to *O. mykiss*, 0, 31.3, 62.5, 125, 250, 500, 1000 mg/L APFO; to *P. subcapitata*, 5.76, 11.37, 22, 70, 46.33, 95.87, 180, 67, 369.67 mg/L APFO); Chronic toxicity test: To *D. magna* (Semi-static exposure: 0, 4.31, 9.16, 20, 44.2, 88.6 mg/L); to *O. mykiss* (Flow-through exposure (5.76 replace-ment per day, ELS test, 0, 2.18, 4.48, 10.7, 20.9, 40 mg/L)-OECD 201, 202, 203; EU commission directive 92/69 EEC, OECD 210, 211	Acute test: 6 h - 24 h neonate *D. magna*, 40 mm - 50 mm *O. mykiss*, 104 cells/ml inoculation *P. subcapitata*, Chronic test: 6 h - 24 h neonate *D. magna*, Fertilized egg to 85 d *O. mykiss*	APFO (PFOA + NH_4^+ salt)	Acute toxicity test: *D. magna*: 48 h, *O. mykiss*: 96 h, *P. subcapitata*: 96 h; Chronic toxicity test: *D. magna* 21 d, *O. mykiss* 85 d	Acute toxicity, reproductive toxicity(ex. 95 d-*O. mykiss* ELS test)
Zebrafish (*Danio rerio*)	Semi-static exposure, replaced 50% at every 5 days; 8 hpf to 180 dpf exposure period; 0.01% DMSO; 0, 0.02, 0.1, 0.5 μM PFOS	8 hpf embryo	PFOS	8 hpf to 180 dpf	Lipid metabolism disturbance, oxidative stress

Continued

Thicklip grey mullets (*Chelon labrosus*),	Static exposure; 2 mg/L PFOS dissolved in seawater	Juvenile fish	PFOS	2 and 16 d	Transport gene expression change
European bullhead (*Cottus gobio*)	Semi-static exposure; a half of water was replenished every 24 h; 0.1 and 1 mg/L PFOS	Adult fish, 10.4 ± 4.1 g; catching organism in Samson river and acclimated in tap water	PFOS	96 h	Enzyme activity, protein expression change (ex.: HSPA4, HSC70-2 etc.)
Zebrafish (*Danio rerio*)	Semi-static exposure, replenished half every day, 0.002% DMSO; 0, 10, 50, 250 μg/L PFOS	F0 fish: 14 dpf zebrafish fry	PFOS	F0 fish: 70 d PFOS exposure and 30 d only water exposure, (100 d) F1 fish: Offspring of PFOS treated female and nonchemical treated male fish	F0: Gross index, thyroid toxicity, endocrine disruption F1: Reproductive toxicity endocrine disruption

from one standard to the next, and there is no global consensus on PFAS toxicity estimates. While the European Union has just recently begun developing a preliminary set of standards for the maximum permissible quantities of PFAS, the drinking water commission of the Ministry of Health in Germany has recommended a health-based advice for the maximum PFAS level. The recommended value is based on PFOA and PFOS lifetime exposure limits of 300 ng/L for all demographic categories [54]. In Germany, the German Drinking Water Commission (TWK) issued the first health-based lifetime PFOA and PFOS exposure limit of 0.3 g/L in drinking water in mid-2006 after PFOA was found in drinking water at quantities up to 0.64 g/L [55]. After an extremely high concentration of polyfluoroalkyl substances (PFAS) was found in the Veneto region's water supply, Italy implemented PFAS regulations [56]. When it comes to PFAS levels in drinking water, the Italian National Health Institute has set the bar at no more than 30 ng/L for PFOS and 500 ng/L for all others. Water samples in Spain were routinely analyzed for various PFAS substances as part of periodic PFAS monitoring activities and findings show that PFAS concentrations showed differences throughout Spain, leading to the determination that there is an improbable health concern based on the identified levels of PFOS and PFOA [57]. The highest mean concentrations for PFOS and PFOA were 1.81 and 2.40 ng/L, respectively [57].

4.2. Analytical Methods

Chromatography and mass spectrometric detection are the most often used

analytical procedures for PFAS measurement. Liquid and gas chromatography techniques have been used for the study of PFAS, including high performance liquid chromatography (HPLC) as well as capillary liquid chromatography (CLC) and gas chromatography (GC) [58]. GC is a useful technology for PFAS analysis of volatile and semi-volatile materials, whereas classical HPLC is employed for ionic PFAS analysis [59]. The sensitivity and detection limit of capillary electrophoresis (CE) for ionized and polar PFAS measurement are not comparable to HPLC [60]. In order to use LC-MS to sensitively and selectively detect PFAS, US EPA and the American Society for Testing and Materials (ASTM) created EPA 537, EPA 537.1 and ASTM D7979-17, ASTM D7968-17a. In addition to PFAS analysis, either sample preparation or pre-treatment technique is often necessary before conducting any instrumental test. For example, several extraction techniques such as solid phase extraction (SPE), liquid-liquid extraction (LLE), solid phase micro extraction (SPME), and dispersive liquid-liquid micro extraction (DLLME) are commonly used to improve selectivity, sensitivity, and clean-up of target analytes from the sample background [61]. Chromatography, often paired with mass spectrometric detection, predominantly governs the analytical techniques employed for the determination of PFAS [62].

4.2.1. Liquid Chromatography

HPLC with a UV (ultraviolet) detector was previously utilized to identify both long and short chain PFAS in the liver samples of rat using a fluorescence-based 3-bromo-acetyl-7-methoxycoumarin [63]. Soon after, LC-MS/MS was established to identify trace amounts of PFOA, PFOS and PFHxS by Hansen *et al.* [64]. After homogenization, samples were extracted by liquid phase extraction (LPE), with PFAS identified in the ranges of 2 - 8.5 ppb in liver and 1 - 2 ppb in blood serum [64]. Higgins *et al.* employed LC-MS/MS to identify 12 PFAS in sediment and household sludge, in the ranges of 0.04 - 0.25 ppb and 0.7 - 2.2 ppb, respectively [65]. Analytes were extracted by solid-liquid extraction (SLE) in ultra-sonication with methanol: water (9:1) and 0.1 percent acetic acid [65].

Bao *et al.* utilized HPLC-MS/MS with negative electrospray ionization (ESI) for the detection of 8 PFAS in river sediments [66]. The material was extracted using tetrabutylammonium hydrogensulfate and sodium carbonate (1:5). Concentration was calculated from 0.1 - 3.6 ppb and the recoveries reached up to 108 percent [66]. Li *et al.* conducted UPLC/ESI-MS/MS to test PFAS in sediment collected from various lakes [67]. PFAS were recovered from dry sediment by ultra-sonication in methanol and getting the total concentration of PFAS from 0.61 - 26 ppb [67]. Additionally, strong spike recoveries (90% - 100%) without matrix effects confirmed the method's validity and acceptance.

When Tittlemier *et al.* used LC-MS/MS to verify the existence of PFSAs and PFCAs in various food webs, the compounds of interest were isolated using SLE with methanol and the LOD ranged from 0.5 to 6 ppb after homogenization and centrifugation, respectively [68]. 13C4-PFOS and 13C4-PFOA were used as ISs to analyze a wide range of PFAS in raw and cooked fish samples using a

UHPLC-MS/MS instrument [69]. PFAS were discovered in raw samples, however, ultra-trace level detection was difficult from cooked samples, which suggests that PFAS are released when materials are cooked.

Many nations' food samples were evaluated for the presence of polyfluoroalkyl substances [70]. The QuEChERS technique was used to extract samples after they had been homogenized, filtered, and purified. Additionally, C18 silica and ENVI-carb sorbents were utilized in the cleanup process to ensure adequate recoveries (70% - 130%).

By inhaling PFAS-contaminated dust, dust mites, and other goods that contain PFAS, humans may be exposed. PFAS from a large volume of air were enhanced on XAD-2 resin/PUF and extracted with methanol by Yao *et al*. [71]. A dispersive ENVI-carb clean-up process was used to purify the extracts and mass spectrometer and quantitative analyses were conducted using SIM and PCI, respectively. An extraction method known as solvent extraction was used to maximize the amount of PFSAs and PFCAs (C4, C6-C8) found in the test samples [71].

4.2.2. Gas Chromatography

In analyzing PFAS in air, gas chromatography-mass spectrometry (GC-MS) is employed to execute concurrent separation and detection of volatile, semi-volatile and neutral PFAS [60], and PFAS from other matrixes as well. One of the earliest analyses of PFAS by GC was conducted by Ylinen and colleagues for urine and plasma samples [72]. The first validation of an analytical method for the analysis of extractable PFCAs, PFSAs and FOSA associated to textiles was carried out by Van der Veen *et al*. [73]. The researchers used methanol and acetone/acetonitrile at 80:20 volume-volume. The findings revealed that conducting two consecutive extractions using 5 mL of methanol for 30 minutes resulted in the best performance, achieving an extraction efficiency of over 90%. The impact of the sample matrix on the quantification of PFAAs was investigated, revealing ion suppression caused by various matrix effects or sorption behavior specific to different textile samples. The method was validated, demonstrating overall recoveries exceeding 80% and low relative standard deviations (RSDs) of less than 9% (n = 3) for repeatability and less than 20% (n = 3) for reproducibility. Analysis of ionic PFAS performed with a high-performance liquid chromatograph-tandem mass spectrometer (HPLC-MS/MS) has been recorded [73].

4.2.3. Nano-Based Sensor

Different types of nano sensors, particularly nanoparticle (NP)-based sensors, have been developed for PFAS identification, as summarized in **Table 3**.

5. Remedial Tecniques

5.1. Soil Remediation

Remediating PFAS-contaminated solid and aqueous media can be extremely difficult. PFAS soil decontamination may be made logistically and economically feasible using soil additives in two general ways: mobilization and immobilization.

Table 3. Nanoparticle-based sensor and sources of PFAS detected.

Identified PFAS	Nanoparticles with modified groups	Sensing types	Sensitivity	Sources	References
PFOS	Quantum dots nanoparticles (QDNPs)	Optical	2.5 ppt	River, lake and bottled water	Zhang *et al.* [74]
PFOA, PFOS, PFHA	Molecularly imprinted polymer modified TiO_2 nanotube arrays	Photoelectrochemical	85 ng/L	Tap, river and mountain water	Li *et al.* [75]
PFOA	Glass-chip-AIE	Fluorescence	41 ppb	Water	Fang *et al.* [49]

Both abiotic and biotic degradation mechanisms can be used to remove PFAS from soil using these methods [76].

5.1.1. Mobilization

Solubilization, desorption, and complexation processes are important mechanisms for contaminant mobilization in soils and sediments. Mobilization techniques, such as soil washing and phytoremediation (absorbing contaminants through plant roots), can be used to remove toxicants from soil. These techniques aim to enhance the mobility and/or bioavailability of contaminants, facilitating their removal or degradation. However, the effectiveness of these techniques can vary depending on the specific contaminants, soil/sediment characteristics, and environmental conditions. Site-specific assessments and considerations are necessary for successful implementation.

1) Soil Flushing and Soil Washing

To remove contaminants from the soil, a flushing solution is injected into the ground during the process of soil flushing [77]. The key advantage of soil flushing is that enormous amounts of soil can be treated without the requirement for excavation and transport [78]. Some organic/inorganic acids/bases and solvents, including MeOH or EtOH, may be useful in flushing PFAS from soils. Schröder used organic solvents to test the extraction abilities of a solvent or a combination of solvents for sludge PFAS extraction, EtOAc, DMF, and MeOH Modified with Phosphoric Acid were shown to be the most effective solvents for extracting PFAS from pressurized solvent extraction at 150˚C (143 bar) and 150˚F (59˚C) [79].

2) Photoremediation

As opposed to other POPs, PFAS are easily absorbed by plants and removed via phytoremediation because they are so easily soluble [76]. As stated previously, the chain length of PFAS chemicals and the sorption behavior of soils both influence plant uptake. The bioconcentration factor (BCF) was a critical parameter used by Huff *et al.* to evaluate the suitability of plant species for contaminated site phytoremediation [80]. They also found that a proprietary soil addition increased plant uptake of PFOA and PFOS by 40% - 340%. Similarly, Gobelius *et al.* found that plants exposed to uptake contaminated with PFAS com-

pounds near a Stockholm firefighting training facility successfully absorbed 26 of the substances [81]. Although phytoremediation of a PFAS-contaminated site is a lengthy procedure, it is low-cost and requires essentially no upkeep [76]. As a result, phytoremediation is the most cost-effective and long-lasting green remediation method for PFAS-contaminated locations [76].

5.1.2. Immobilization

The immobilization approach redistributes PFAS pollutants from the solution to solid phase, thereby lowering their mobility and bioavailability [76].

1) Sorption

Carbon- and clay-based materials, ionic surfactants, and anion exchange resins are the primary sorbents utilized to remove PFAS from soil and water [82]. PFOA and PFOS could be effectively removed from soil and water using granulated activated carbon (AC), whether it was powdered or granulated [83]. In order to immobilize PFAS in contaminated soils, Hale *et al.* evaluated AC, compost soil, and montmorillonite [77]. AC, compost, and montmorillonite additions all reduced PFAS leaching by 94% - 99.9%, 29% - 34%, and 28% - 40%, respectively. Many aspects including medium qualities, PFAS features, and adsorbent characteristics would influence the overall efficiency of PFAS remediation via sorption treatments [84]. Adsorbents with tiny pore size and high specific surface area can lead to high PFAS sorption capacity. Similarly, adsorbents having a basic or positively charged surface tend to demonstrate significant PFAS sorption capacity through the combined mechanism of hydrophobic contact and electrostatic attraction [85].

2) Stabilization and Solidification

Stabilization and solidification (S/S) of PFAS can be done by the application of cementitious binders and additives into the contaminated environmental media, including soil [86]. Sörengård *et al.* assessed seven additives, including powdered activated carbon, Rembind®, pulverized zeolite, chitosan, hydrotalcite, bentonite, and calcium chloride at 2.0% application rate, for stabilizing a total of 14 PFAS chemicals in a soil that has been polluted for an extended period of time [87]. The activated carbon and Rembind® additives performed the best, reducing leaching by 70% and 90%, respectively, for all PFAS compounds except perfluorobutane sulfonate.

5.2. Water and Groundwater Remediation

5.2.1. Membrane Technologies

A wide range of applications, including desalination and wastewater treatment, can benefit from membrane technologies that can be easily tailored [88]. According to Boonya-Atichart *et al.*, the removal capacity of PFOA using nanofiltration (NF) membrane was 99.5%, and the membrane can reject soluble neutral and charged organic molecules with molecular weight > 200 Da because of the pore size restriction [89]. It is therefore possible to eliminate 414-g/mol of PFOA by using NF.

5.2.2. Chemical Redox Reaction

Activated persulfate was utilized by Yin and coworkers under very acidic settings and 90% of PFOA was degraded [90]. PFOA breakdown was facilitated by the production of radicals by protons, according to their discussion.

5.2.3. Nano-Sorption

Activated carbon, carbon nanotubes, polymeric resins, and biomaterials have all been employed as adsorbents. Though there were certain problems, some of which were: limited adsorption capacity; long equilibrium time; expensiveness; and the possibility of secondary contamination, these adsorbents offered some advantages [91]. Magnetite nanoparticles with a maximum adsorption capacity of 63 mg/g were used by Gong's team to remove PFOA from water [92].

5.2.4. Electrochemical Treatment

Because of its ease of use and minimal energy consumption, electrocoagulation has become a popular treatment option [93]. A 200 ppm PFOA solution treated with stainless steel cathode and Zn anode by Wang and colleagues removed 99.7% of the contaminant [94].

5.2.5. Photocatalysis

Many materials have been explored as catalysts for photodegradation of PFAS via photocatalysis, which is a cost-effective treatment method [95]. An entirely new (BOHP) microparticle was used by Sahu's group to rapidly degrade and mineralize PFOA when exposed to UV light [96]. As a result of the preferential adsorption of deprotonated PFAS to the hydroxylated BOHP surface and the associated greater attraction, BOHP disintegrated nearly 100% of the PFOA in just one hour.

5.2.6. Hybrid Treatment Processes

Membrane filtration and photocatalysis could be combined to remove PFOA from groundwater, according to Boonya-Atichart *et al.* [89]. Upon filtering, nZVI photocatalyzed the degradation of the concentrated PFOA. The nanoparticles were then removed from the photocatalytic process using UF. The removal effectiveness of PFOA was 99.6% in the application for real groundwater treatment, and the rejected part was destroyed by photocatalysis at 60% efficiency. As a result, this demonstrates that photocatalysis and membrane filtration can be combined to remove unwanted contaminants effectively before they are released into the environment.

5.3. Destruction of PFAS

For PFAS-contaminated soils, the eradication of PFAS molecules via biotic/abiotic degradation processes can enable total cleanup [76]. Organic contaminants in soils and groundwater can be degraded by microorganisms, and hence soil microbial composition affects PFAS biodegradation [97] [98]. To give just one example, researchers found that *E. coli* could not biodegrade PFOS or PFOA while

studying the bacteria [99]. However, considerable reduction in the concentration of PFOS was achieved by the addition of *Acidimicrobium* sp. [100] and *P. parafulva* [101]. Yi *et al.* have identified PFOA-degrading bacteria. In the study, a PFOA-degrading strain was isolated from the soil near a perfluorinated compound production plant through acclimation and enrichment culture, using PFOA as the sole carbon source [101].

In most cases, standard water oxidative/disinfection procedures failed to destroy PFOS and PFOA [102]. Chemical and thermal redox processes, on the other hand, can be used to remove PFAS chemicals from soil, waste, and water [103]. In water systems, electrochemical oxidation process—which encompasses the concept of "separate, concentrate, destroy" as illustrated in **Figure 4**—systematically breaks down PFAS, transforming it from a hazardous material into carbon dioxide, water, and fluoride. Thermal treatments for PFAS-contaminated soil include thermal desorption and full destruction of PFAS, both of which need high temperatures (~1000˚C) [104] [105] [106].

6. Science, Trascience, and Conscience

DuPont scientists discovered in the 1960s that PFOA might expand the size of the livers of animals [107]. In other records, the firm was aware of the link between PFOA and malignant tumors by the 1990s. Workers at the corporation were exposed to the risk of high levels of cancer and the chance of giving birth to children with birth defects, among other health problems [108], but the company did not share this information with the public, regulators, or even a huge

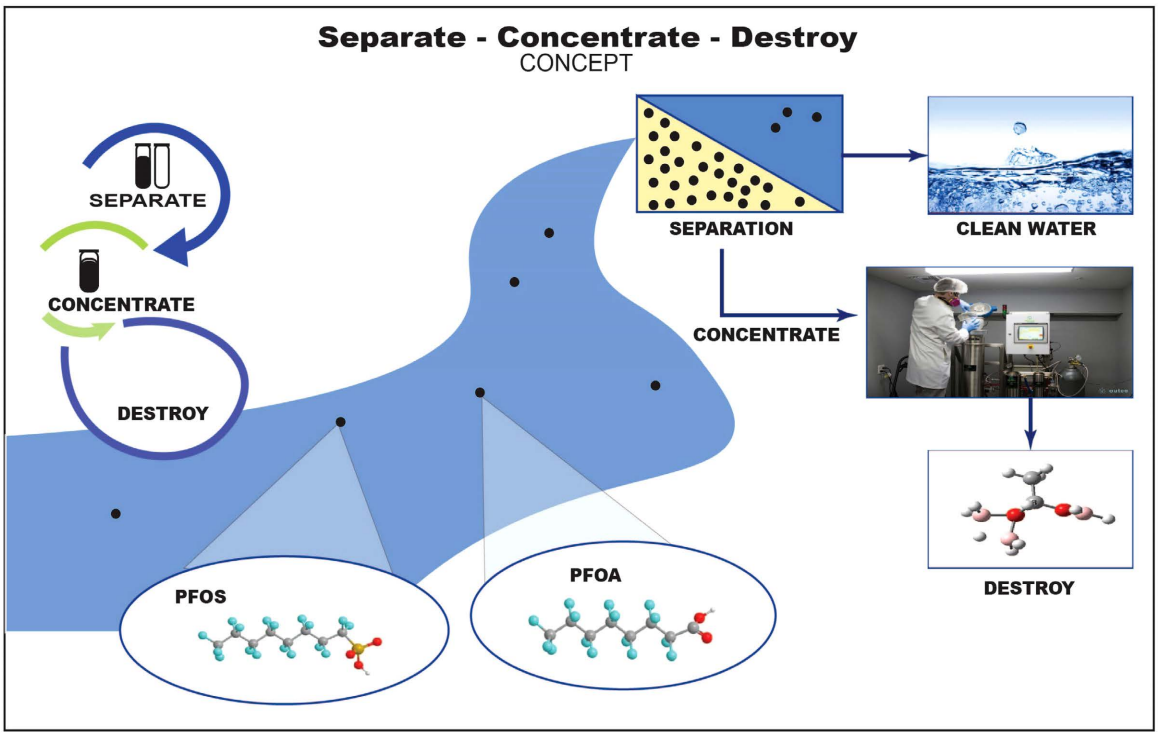

Figure 4. Emerging PFAS destruction concept.

percentage of its own employees [109]. This corporate misrepresentation was not unique to DuPont. 3M, a chemical firm, also suppressed and minimized the dangers of PFAS for decades, according to records provided by the Minnesota Attorney General's Office in early 2018 [110]. It was 3M, the company that invented PFOA that also employed PFOS in one of its most popular products. Despite decades of scientific studies showing the harm of the chemicals, 3M did not turn over any of its research to the EPA for more than 20 years. While both 3M and DuPont are paying out large sums of money in court settlements, scientific research has shown that PFOA and PFOS have been related to health impacts such as testicular cancer, kidney disease, and an increased risk for asthma and thyroid problems [111] [112]. Science as a body of knowledge aims at contributing to the development of human society, particularly in terms of medical and technological advancement. However, from time immemorial, misconduct has been a major component of virtually all human societies, evident in the resulting backwardness that exists and metastasizes across the world. The act of shortcutting, to go through the right process in a bid to reduce stress, yet receive relief, accolades, money, trust, and any sort of prestige has for many years been part of the research community, and only very few of the overwhelming majority have been caught red-handed and subsequently sanctioned. While Humans are transient beings, simple actions made can lead to ample destructions, as in the case study of the consultant assigned by 3M. When presented with specific situations in his lifetime, Mahatma Gandhi demonstrated an attitude that was consistent with his principles connected to universal values such as love for his fellow human beings, justice, peace, non-violent tolerance, and freedom [113]. In his lifetime, he posited seven deadly sins that can fast-track the destruction of the world. All are related to the conscience of man, and the theory and practice of ethics. Of a fact, the criminal acts demonstrated by DuPont and 3M, and perhaps other unpopular chemical manufacturers, allows for the review of some of these "sins" in a bid to save and redirect the focus of humans and humanity. The most relevant unethical actions exhibited by these companies and their allies are knowledge without character, commerce without morality, and science without humanity. Not only should the focus be on PFAS going forward, heavy metals, microplastics and other emerging contaminants should also be explored as each group has its own chemistry and environmental impact [114] [115] [116]. Therefore, it is not enough to want to produce chemicals if transparency and the consciousness of safety of humanity are not deeply considered. Coupling business with ethics in all its forms must be alluded to, in defining and redefining humanity. Because not addressing issues as this is compounding the problem of the world, scientists, legal practitioners, policymakers, and individuals and groups in influential positions must strive to not compromise ethical values in the face of inducement and corrupt practices.

7. Conclusion and Recommendations

While it is pivotal for polluters to be held accountable for the costs associated

with remediating the PFAS contamination, increasing requirements for chemical manufacturers to test and disclose health and environmental effects from numerous PFAS will help alleviate the destructive effects of the emerged contaminant in various environmental segments. Thus, relevant global agencies including US EPA, WHO, and the United Nations should develop policies governing sustainable, ethical manufacturing and application of PFAS chemicals. Although sample preparation methods have been designed to extract PFAS, and considering their low quantities in the environment, the chemistry of PFAS and their precursors are still unclear, complex, and ambiguous. Further work is still needed to overcome constraints associated with their analysis. Also, the effectiveness of the remedial techniques and destruction methods described in this review requires progressive testing while inventing or exploring other sustainable ways.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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