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Climate change and the water quality threats posed by the emerging contaminants per- and polyfluoroalkyl substances (PFAS) and microplastics

Malcolm J. Gander

Department of Defense, Silverdale, Washington, DC, USA

ABSTRACT

Climate change affects how the emerging contaminants per- and polyfluoroalkyl substances (PFAS) and microplastics impact human health and the environment. The known and implied effects from PFAS compounds and microplastics are reviewed, followed by an overview of their occurrence, transport, degradation in fresh water and ocean water, and health impacts. PFAS and microplastics releases are increasing as a result of climate change, and the breakdown of microplastics is releasing greenhouse gases, which in turn augments climate change. Strategies are presented for reductions in the release of these emerging contaminants.

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Introduction

Per- and polyfluoroalkyl substances (PFAS) compounds and microplastics (plastics ranging in size from 1 to 5 mm, roughly the size of a grain of rice) are both very stable classes of global water pollutants. They have been detected in all humans analytically tested for their presence. Human health effects from PFAS may include ulcerative colitis, thyroid disease, high cholesterol, testicular and kidney cancers, pregnancy-induced hypertension, and reduced fertility (Di Nisio et al., 2019, 2020; Foresta et al., 2018; Swan, 2021; Waterfield et al., 2020). The science defining the toxicity and health effects from consuming water with microplastics is in its infancy. Recent studies indicate that microplastics contain chemicals that are considered endocrine disruptors, that is, chemicals interfering with the hormone-producing adrenal, pituitary and thyroid glands, while others have potential carcinogenic properties. After maternal exposure, microplastics have the propensity to cross the placental barrier and enter the foetal compartment, depositing in foetal organs; the impact on the foetus is unknown.

The purpose of this paper is to review the current knowledge of PFAS compounds and microplastics and the manner in which climate change affects – and is affected by – the behaviour of these ubiquitous materials; examine how water quality is affected by these processes; and make policy recommendations. The relationship between climate change and PFAS and microplastics is not well understood. As such, the compilation of known and implied impacts from this relationship is relatively brief, but noteworthy. Not

CONTACT Malcolm J. Gander malcolmgander@comcast.net

discussed but mentioned for completeness are pharmaceuticals, the other member of this triad of most prevalent emerging contaminants that has likewise been detected routinely in global freshwater systems, and is in need of more scientific study for protection of human health and the environment.

Per- and polyfluoroalkyl substances (PFAS)

PFAS are a large group of anthropogenic chemicals (over 6000 compounds identified) that were first synthesized in the 1930s and in use since the 1940s to make products that resist heat, stains and grease; repel water; and reduce friction in many household, industrial, aerospace and automotive applications (Interstate Technology and Regulatory Council [ITRC], 2020) (Figure 1). Examples are non-stick coatings (Teflon), textiles (Gore-Tex), stain-resistant carpets and sofas, and aqueous firefighting foams to engulf flames (AFFF). PFAS water pollution has been confirmed in the European Union (EU), Asia, Australia, the Middle East and the United States, and in most countries protective regulations are inadequate or completely lacking.

As with polychlorinated biphenyls (PCBs), PFAS are also toxic (Vandenberg et al., 2013), resistant to environmental degradation, and distributed throughout the food chain. They bioaccumulate in humans and marine and terrestrial organisms. Currently the most important and best understood classes of PFAS are perfluorooctane sulphonate (PFOS; $C_8HF_{17}O_3S$) and perfluorooctanoic acid (PFOA; $C_8HF_{15}O_2$), which are prevalent in AFFF and metal plating liquids.

PFAS is emerging now because over the last 50 years the volatile organic compounds in fuels and solvents contamination were the focus of clean-ups, and non-volatile PFAS were overlooked. Volatile contaminants are detected by the widely available gas chromatography-mass spectrometry (GC-MS) analytical instrumentation. PFAS are non-

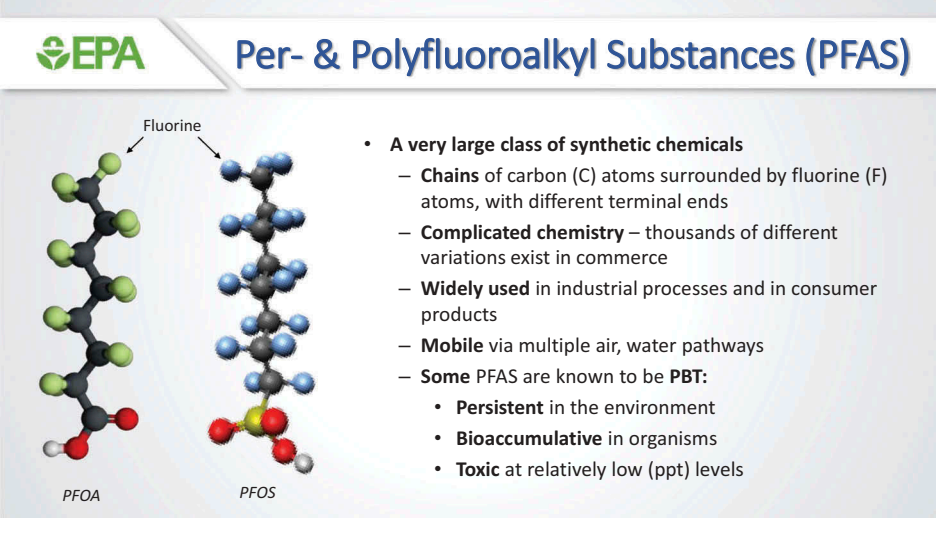

Figure 1. Per- and polyfluoroalkyl substances (PFAS) compounds: uses and characteristics. Source: Gillespie (2020).

volatile and detected by *liquid* chromatography-mass spectrometry (LC-MS), and the analytical laboratory technology to quantify environmental PFAS samples in water and soil has only been available since the early 2000s due to challenges posed by the tendency for PFAS to concentrate at water–air interfaces (Giesy & Kannan, 2002). Typical commercial laboratory methods only analyse about 30 PFAS compounds in groundwater. Given that there are over 6000 known PFAS compounds, it is acknowledged that not all that exist have been identified, nor have all the compounds that form from the breakdown of primary PFAS compounds. Moreover, toxicity studies have not been completed for most compounds.

PFAS in drinking water above established health advisory concentrations (70 parts per trillion (ppt) in the United States and 100 ppt in the EU) compels consumers to make a change to bottled water or an alternative water supply. The main sources of PFAS in groundwater are: (1) AFFF use and storage areas; (2) disposal or land application of biosolids from wastewater treatment plants (WWTP), which receive PFAS from various community sources; (3) liquid discharges from WWTP; (4) leachate from landfills; and (5) miscellaneous industrial and commercial sources (National Ground Water Association [NGWA], 2017).

PFAS compounds readily dissolve in groundwater and will not exist in the subsurface as a dense, non-aqueous phase liquid, such as gasoline, which can float on the groundwater table as an intact fuel product. The PFAS molecular structure consists of interior carbon atoms bonded to exterior fluorine atoms. The carbon–fluorine bond is the shortest and strongest bond in nature, and it is stable and resistant to both chemical and biological degradation.

After PFAS compounds are released, they are commonly highly mobile in the environment. They are known to readily infiltrate the subsurface and move to groundwater due to their relatively low surface tension. Because there are many known classes of PFAS, exceptions exist to these generalizations. For example, some larger compounds have a lower solubility and higher surface tension and are less mobile, and more susceptible to adsorption onto organic material in the vadose zone (the unsaturated zone above groundwater). Once in groundwater, the rate of transport in an aquifer varies both laterally and vertically.

Health effects from PFAS

Prolonged exposure to PFAS may result in cancer, liver damage and reduced antibody production (United States Environmental Protection Agency [US EPA], 2021b), and recent data indicate a link between the ingestion of PFAS-bearing drinking water and reduced male and female fertility.

Microplastics

Geyer et al. (2017) concluded that, since the 1950s, humankind has produced 8.3 billion tons of plastic, of which 91% has not been recycled. Plastic production has increased from 15 million tons in 1964 to 311 million tons in 2014. Although it will take centuries or even millennia for this waste to degrade, plastics will slowly degrade to increasingly smaller pieces. Clothing made from synthetic fabrics, tire dust, plastic cutlery, paints,

cosmetics and degradation of larger plastic debris items are major sources of microplastics.

There is no standard protocol to analytically isolate, quantify and characterize microplastics occurring in the soil environment. A functional and accurate analytical technique for the identification of multiple microplastic types is lacking. Devising a testing protocol that takes into account the various soil types and the heterogeneity of microplastics is currently under development, as is likewise the case for assessing microplastics in groundwater (discussed below). Depending on the origin, shape, size and composition of microplastics, it is necessary to standardize specific methods for sample collection, isolation, identification and analysis (Damania et al., 2019).

Microplastics have been detected in a broad range of concentrations in marine water, wastewater, fresh water including groundwater and drinking water, food, and bottled and tap water. Freshwater sources remain a major route of microplastic delivery to humans, through either direct consumption or the food chain (Desforges et al., 2015; Güven et al., 2017; van Cauwenberghe et al., 2015). Damania et al. (2019) compiled recent studies that have detected microplastics in 80% of global freshwater samples (Tyree & Morrison, 2017), 81% of municipal tap water samples (Kosuth et al., 2018) and even 93% of bottled water samples (Mason et al., 2018).

Microplastics have many sources and dissimilar properties. More than 5300 grades of synthetic polymers (plastics) are used in industry (Wagner & Lambert, 2018). Microplastics contain a range of chemical including pigments, ultraviolet stabilizers, water repellents and flame retardants (Damania et al., 2019). Typical microplastics compounds, known as plastics polymers, comprise products encountered in everyday activities and include not only all manner of plastic bags comprised of a variety of compounds, but also polyethylene (PE) (plastic bottles), polyurethane (furniture foam), polyvinyl chloride (PVC) (raincoats, shower curtains, window frames), and microbeads (manufactured plastic particles < 1 mm in their longest dimension) in soaps, facial scrubs and toothpastes (Figure 2).

Of central importance is determining the transport and transformation properties ('fate') of microplastics as they degrade in the environment. According to the latest report by Science Advice for Policy by European Academies (SAPEA), which forms part of the European Commission's Scientific Advice Mechanism, most studies looking at environmental toxicity have so far simulated conditions that do not reflect real-world exposure (SAPEA 2019). For human health, even less is known. Further research is required to understand the effects of different sizes, shapes and types of plastic before robust conclusions about the real risks can be drawn. This is particularly true for nanoplastics, for which much remains unknown. Evidence is emerging concerning the widespread occurrence of plastics in the human food chain, notably through seafood and salt (SAPEA 2019).

Much of the world's drinking water contains microplastics (World Health Organization [WHO], 2019). Very little sampling and assessment of microplastics in groundwater has been undertaken (Koelmans et al., 2019). Waste water treatment plants play a significant role in the collection and release of microplastics to the environment (Ziajahromi et al., 2017). Pesticides commonly contain microplastics as fillers (US EPA, 2020).

Figure 2. Generation and dispersion of microplastics in the terrestrial environment. Source: Modified from Karbalaei et al. (2018).

The potential hazards associated with microplastics come in three forms: physical particles, chemicals and microbial pathogens as part of biofilms. Based on the limited evidence available, chemicals and biofilms associated with microplastics in drinking water pose a low concern for human health. There is insufficient information to draw firm conclusions on the toxicity related to a physical human health hazard of drinking water containing plastic particles, particularly for the nano-size particles (WHO, 2019).

As was noted for microplastics in soils, there is a fundamental challenge that is currently under intense international study and development: there are no standard sampling, extraction and laboratory analytical identification methods for microplastics in surface water or groundwater (Koelmans et al., 2019). The most common analytical techniques are either spectroscopy or GC-MS.

Sample quantification is complicated because of the difficulty of capturing all plastic particles in a given sample as material is lost or unevenly collected from containers or filters or apparatus used during analysis. In some cases, the lack of standardized analysis has resulted in false-positive identification of microplastics that were later determined to be non-plastic particles such as fibres from clothes. There is also a challenge in consistently quantifying very small or irregularly shaped particles. Different studies focus on the detection of certain particles sizes, and thus may not be representatively reporting the microplastic content of the samples under review.

Koelmans et al. (2019) analysed over 50 international drinking water sources and identified the order in globally detected plastics polymers that comprise microplastics as polyethylene (PE) > polypropylene (PP) > polystyrene (PS) > polyvinyl chloride (PVC) >

polyethylene terephthalate (PET), which probably reflects the global plastic demand and a higher tendency for PVC and PET to settle as a result of their higher densities.

Because of their adsorptive properties, microplastics readily attract and retain hydrophobic contaminants including the emerging PFAS chemicals, PCBs, pesticides or solvents. Therefore, microplastics in surface water and groundwater will tend to retain these and other contaminants. Pathogenic microbes may adsorb onto microplastics and be transported great distances and become agents of contamination in urban areas where wastewater treatment facilities are lacking (Lu et al., 2019).

WWTPs play a significant role in the release of microplastics to the environment (Ziajahromi et al., 2017). In addition to influent that contains microplastics, WWTPs have plastic componentry that help filter other contaminants, but microplastics are likely continuously leached from that componentry. Mintenig et al. (2017) sampled wastewater from WWTPs and detected microplastics and concluded the abrasion of plastic equipment used in WWTPs is a likely source, although the study did not address in detail the likely greater quantity of microplastics entering the WWTPs from influent. The study utilized Fourier transform infrared spectroscopy (FTIR), which is currently one of the principal microplastics analytical methods in use and under further refinement.

The released microplastics settle into surficial soils and variably leach to groundwater. Land application of microplastics-bearing sludge (biosolids) from WWTPs is widespread; therefore, unplanned loading to surface soils is ongoing, leading to more leaching to groundwater.

Ziajahromi et al. (2017) characterized effluent from three WWTPs using FTIR imaging. It was determined that between 22% and 90% of the suspected microplastics were found to be non-plastic particles. The lack of a standardized and applicable method to identify microplastics in complex samples, such as from wastewater, has limited the accurate assessment of microplastics and may lead to incorrect estimations. This study suggests that although low percentages of microplastics are detected in wastewater effluent, WWTPs still have the potential to act as a collection point to release microplastics given the large volumes of effluent discharged to surface water sources, which have the potential to eventually discharge to surficial soils and ultimately leach to groundwater.

Although poorly studied, residential septic systems are relatively small individually but are widespread, and they undoubtedly present an avenue for discharge of microplastics to groundwater. For example, given that karst (limestone) aquifers constitute about 25% of drinking water sources globally, Panno et al. (2019) studied microplastics in two karst aquifers in the US state of Illinois. Up to 15.2 fibres per litre of microplastics were detected, along with phosphate, chloride and triclosan, an antibacterial agent in soaps and toothpastes. This set of materials suggests septic effluent as a source.

As noted in the climate change discussion below, airborne microplastics have been identified, and adverse human health effects due to inhalation are beginning to be considered (Prata, 2017). This phenomenon also raises the non-trivial issue of ongoing dispersion to soils and a leachate to groundwater.

Pesticides commonly have microplastics as fillers; therefore, the enormous use of pesticides represents another source of microplastics to shallow soils and leachate to groundwater. Microplastics in pesticides include PVC and polyurethane (US EPA, 2020).

The US EPA consider the plastic fillers as inert, but also acknowledge they are not necessarily non-toxic.

Mintenig et al. (2019) analysed groundwater and drinking water derived from groundwater for the presence of microplastics. A total of 24 samples were taken at different locations within the drinking water supply chain: three from groundwater wells about 30 m deep; one conventional tap water sample and one water meter sample each from five different households (10 total); and one plant inlet sample and one plant outlet sample each from five different drinking water treatment plants (10 total plus one duplicate for a grand total of 11).

Laboratory analysis using FTIR did not detect microplastics in 14 of the 24 samples; less than one microplastic particle per m^3 (i.e., a trace amount) was detected in five of the samples; and the other five contained one to three particles of the following microplastics: PE, PEST, PVC or epoxy resin, and PA or polyamide/nylon particles ranged between 50 and 150 μm in size. The authors concluded the abrasion of plastic equipment used during water purification or transport (i.e., pipes, fittings and tanks in the plants), separate from the sampling for the study, was a likely source of the plastic particles detected in the water samples.

Strand et al. (2018) examined drinking water from 17 sites around Denmark, where virtually all drinking water is derived from groundwater. Of the total particles identified, 124 (44%) contained microplastic-like particles, which were further characterized by FTIR. Of the microplastic-like particles, 3% were verified as microplastic (PET, PP and PS), whereas the majority consisted of cellulose-like material (76%), with the remainder having poor spectra (10%), unknown (7%) or protein-like material (4%). This study is a good illustration of the analytical challenges posed by microplastics.

Health effects from microplastics

Phthalates, bisphenols and styrene are three classes of microplastics compounds associated with a variety of health problems, including adverse brain and organ development in children (Mersha et al., 2015; National Toxicology Program, 2011), infertility, and endocrine (hormonal) disruption (Maffini et al., 2006; Food and Drug Administration, 1996). There is evidence of adverse health effects to fish populations from microplastics (Barboza et al., 2018), and fish-carrying microplastics that are ingested by humans add microplastics to the human food web (Hossain et al., 2020; Carbery et al., 2018).

Inadequate substitute

For both PFAS and microplastics there has been some movement by manufacturers to replace certain toxic constituents with less toxic compounds. Sadly, this had led to a disturbing trend where the substitutes have not been properly vetted scientifically, resulting in the use of substitutes that have similar toxicity to the compounds they replace (US EPA, 2021b).

With regards to PFAS compounds, 'GenX chemicals' is a trade name for a technology that substitutes the use of PFOAs and PFOS (US EPA, 2018b). Hexafluoropropylene acid (HFPO) dimer acid and its ammonium salt, and perfluorobutanesulfonic acids (PFBSs), are the main chemicals associated with the GenX technology. GenX chemicals have been

found in surface water, groundwater, finished drinking water, rainwater, wastewater, household dust and air emissions (US EPA, 2018a).

A University of Stockholm study found that GenX may be more toxic than the PFOAs they replace (Gomis et al., 2018); this finding was corroborated by a recent US EPA (2021b) study. PFOAs are used in the manufacture of non-stick coatings for cookware, water repellent garments, and other speciality agrochemicals and pharmaceuticals, and their use was phased out by US manufacturers by 2015. The GenX PFBSs are a class of chemicals that have replaced PFOS, and they are in the process of being voluntarily phased out by US manufacturers. PFBSs are used in consumer products such as carpeting and carpet cleaners, floor wax and food packaging (US EPA, 2018a).

With regard to microplastics, bisphenol A (BPA) is a widely used constituent of plastic and epoxy resin (Department of Health and Human Services, 2011). Because of a variety of adverse health effects described above, the substitutes bisphenol S (BPS), bisphenol F (BPF) and bisphenol AF (BPAF) have been developed and included in many products such as baby feeding bottles, glues, dental sealants, food packaging and personal care products (European Food Safety Authority, 2013). These are the so-called 'BPA-free' products. Because of the chemical similarities with BPA, BPS and BPF alternatives showed the same responses as BPA, for example, endocrine disruption, and increased obesity of children and adolescents (Liu et al., 2019; Moon, 2019). BPAF was shown to have a greater toxic effect (e.g., increased oestrogenic activity/endocrine disruption) than the BPA it was designed to replace (Mesnage et al., 2017).

The microplastics compounds di-isononyl phthalate (DINP) and di-isodecyl phthalate (DIDP) are both in the class of chemicals known as phthalates. Ironically, the two chemicals were used as replacements for another phthalate chemical, di-2-ethylhexylphthalate (DEHP), which the same researchers proved in previous research to have similar adverse effects (Trasande, 2019).

Climate change, PFAS and microplastics

There are a number of well-documented effects from rising global temperatures and resulting climate change that influence the movement, concentration and overall impact of the pollutants PFAS and microplastics in water bodies and groundwater.

Documented climate change effects on pollutants

More extreme storm events and resulting flooding from climate change cause the uncontrolled spread of these pollutants in surface waters and soils, and the eventual increase of leaching of these dispersed pollutants into the underlying groundwater (Intergovernmental Panel on Climate Change [IPCC], 2021).

Rising sea levels from climate change coupled with the lowering of freshwater levels in coastal drinking water wells may result in seawater intrusion into coastal aquifers (IPCC, 2021), rendering drinking water unsuitable for consumption due to high chloride concentrations. Pollutants including PFAS and microplastics entombed in coastal sediments will be released as sea levels rise and as turbulence increases in response to monsoonal rains (Galgani et al., 2015). In some areas, climate change will cause drought due to changing rainfall patterns, which will also increase the negative impact of seawater

intrusion on coastal groundwater resources because water levels in wells will drop and contaminated seawater intrusion inflow will increase.

The production of plastics by the oil and gas industry, and the attendant generation of greenhouse gases (GHGs), significantly influences climate change. According to the World Economic Forum , about 4–8% of annual global oil consumption is associated with plastics. If this trend continues, plastics will account for 10–13% by 2050 (Hamilton et al., 2019). Large oil companies have begun to increase plastic production as they realize an opportunity to increase revenue as their fuels revenue will decrease in response to the increase in electric car use (Cho, 2020; Dermansky, 2022).

The land application of biosolids from WWTPs serves as a potential leachate source of both PFAS and microplastics, as does its presence in landfills (ITRC, 2020). There is growing evidence that climate change is causing less frequent but more severe rainstorms. These extreme rainfall events will increase leaching of pollutants to groundwater and releases to surface waters, where flooding from more intense storms increases the deposition of pollutants in floodplains and low-lying urban areas. The severe flooding in summer 2021 in the German state of North Rhine-Westphalia, neighbouring Belgium and the Dutch province of Limburg is generally acknowledged as a result of climate change. Temperatures have risen, causing increased moisture in the atmosphere, which has led to more intense downpours (Pancevski, 2021). Severe flooding can overwhelm the capacity of WWTPS, resulting in overflows and unplanned releases of contaminated water into the environment.

Sparse data suggest that overlying soils or bedrock filter some microplastics before concentrating in underlying groundwater (WHO, 2019). Less frequent but more intense monsoonal rains induced by climate change have been shown to be a major contributor to aquifer recharge events in some semi-arid to arid environment aquifers (Cuthbert et al., 2019). This is counter-intuitive to conventional wisdom for most latitudes where it is acknowledged (IPCC, 2021) that recharge is diminished and runoff is increased during monsoonal rains. Therefore, in certain semi-arid to arid environments, climate change-induced monsoonal rains not only can increase recharge but also will potentially increase the leaching of microplastics (e.g., from pesticides used in agricultural areas, which use microplastics as fillers) to aquifers.

Less-studied pollutant effects on climate change

Effects from the breakdown of microplastics are contributing to global temperature increases and contributing to climate change. These effects are incompletely studied but appear profound.

Breakdown of microplastics

The uncontrolled dumping of plastics in oceans is increasing. Global temperatures in both the atmosphere (IPCC, 2021) and the global ocean water (International Union for Conservation of Nature [IUCN] 2021) are increasing. Higher temperatures increase the breakdown of plastics, which increases the release of GHGs, particularly methane and ethylene (Royer et al., 2018; World Wildlife Fund , 2021). Thus, the increased dumping and breakdown of plastics adds additional GHGs and likely contribute to increases in global temperatures, which is altering the climate (Ford et al., 2021), although large-scale

quantification of the impact from releases of methane and ethylene from plastics is lacking (Royer, 2018). One consequence of climate change that is apparently exacerbated by the degradation of plastics is more extreme rainstorms in most regions of the globe (IPCC, 2021), resulting in more runoff and less recharge to drinking water aquifers. Thus, there is a strong connection between the breakdown of microplastics in the oceans and drinking water resources.

Low-density polyethylene (LDPE) plastic is one of the most prevalent forms of plastic in the ocean, resulting from its use in many products including common grocery bags, sandwich bags, plastic wrap and beer six-pack rings. LDPE is estimated to account for 36% of all plastic types (Geyer et al., 2017). Laboratory studies using seawater and various common varieties of plastic indicate that LDPE is the most prolific emitter of methane and ethylene (Royer et al., 2018).

It has been verified that Arctic sea ice contains microplastics, and it is inferred that the Arctic has collected vast amounts of microplastics (Obbard et al., 2014; Peeken et al., 2018). Therefore, as temperatures increase, the ice melts and releases microplastics, which then triggers the breakdown of these microplastics and adds to the GHGs influencing the climate. Another example of increased microplastics loading into the ocean is found in data collected from the Ganges River, which results from increased rainfall associated with monsoons.

It was estimated that the Ganges releases approximately 1 billion microplastic particles into the Bay of Bengal per day during non-monsoonal periods, whereas 3 billion microplastic particles are released during post-monsoonal periods (Napper et al., 2021).

Phytoplankton

The two major types of plankton are phytoplankton and zooplankton. Phytoplankton are photosynthesizing plants, and zooplankton are very small animals. Phytoplankton are consumed by zooplankton, which are consumed by fish and crustaceans (e.g., crabs, crayfish, shrimp, krill), which are in turn eaten by larger predators, etc. Thus, plankton are the foundation of the entire marine food web.

The ocean absorbs about 30% of global atmospheric CO_2 (Gruber et al., 2019), and phytoplankton are known to be the primary processors of CO_2 (Lindsey & Scott, 2010). This fact makes phytoplankton the most essential component of the marine habitat from a climate change (i.e., CO_2-consuming) perspective, alongside the fact that phytoplankton produce as much as 50% of the Earth's oxygen (Spencer, 2019) (Figure 3).

It has recently been documented that plankton are increasingly ingesting microplastics, resulting in reduced growth and lowering their ability to photosynthesize (Kvale et al., 2021). This reduction in photosynthetic activity is related to microplastic particle size (Zhang et al., 2017; Setälä et al., 2014). Microplastics penetrate the phytoplankton cell wall and this results in a reduction in the ability of the green pigments (chlorophyll) in phytoplankton cells to absorb sunlight (Nerland et al., 2014) and convert light energy to chemical energy, which is photosynthesis (Bryant & Frigaard, 2006). This impacts the effectiveness of processing CO_2 and producing oxygen.

This effect from microplastics in the oceans may contribute to an increase in global warming because the plankton are increasingly underperforming in their ability to absorb the typical amount of CO_2 they would otherwise be processing. The impact of microplastics exacerbates a recognized condition of variable reductions of the

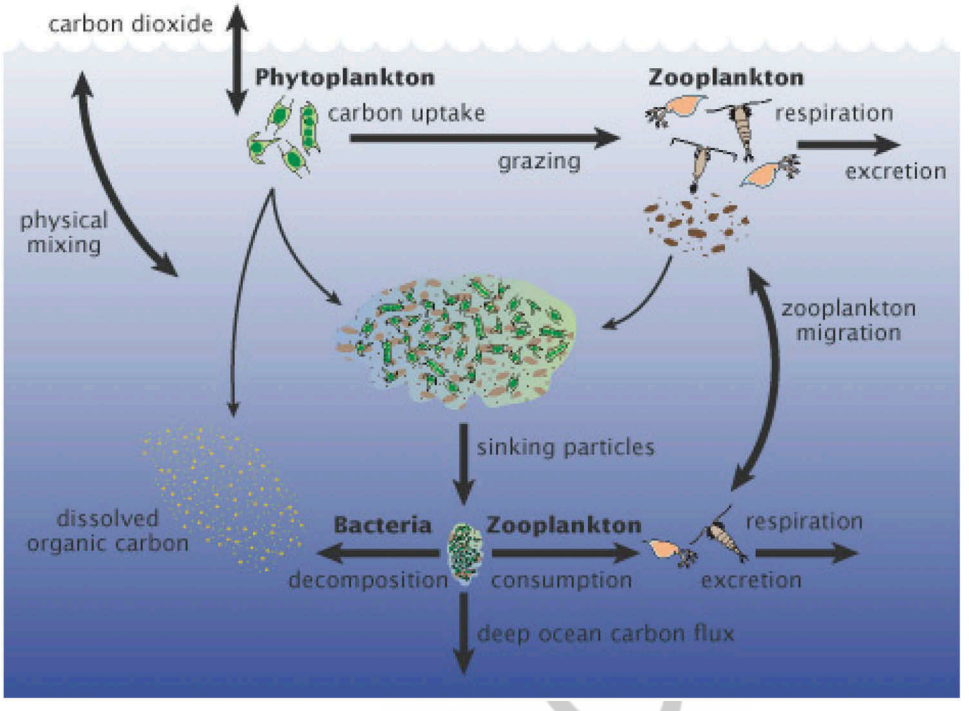

Figure 3. Phytoplankton primarily reside in the shallow oceans and photosynthesize most of the atmospheric CO_2 to the ocean, generating about half of the Earth's oxygen. Source: Modified from 2010).

phytoplankton populations and productivity brought about by two significant global warming effects (Lindsey & Scott, 2010; Osman et al., 2019; Rousseaux & Gregg, 2015; Spencer, 2019):

- Acidification of the ocean by formation of carbon acid ($H_2O + CO_2 = H_2CO_3$).
- Warming of surface ocean temperatures since the 1950s.

This variable annual reduction of phytoplankton population and productivity was indicated between 1997 and 2008 (Behrenfeld et al., 2009), for example, due to warmer-than-average ocean temperatures. When warmer ocean surface temperatures continue for longer periods, temperature layers, or stratification, of the water column persists. This phenomenon inhibits mixing and thus inhibits the movement of nutrients from deeper levels to the surface where phytoplankton will benefit from the nutrients (Behrenfeld et al., 2009). Less available nutrients will reduce the phytoplankton population.

The resulting excess CO_2 will increase ambient temperatures, which leads to evapotranspiration increases, all caused by global warming. In most latitudes, increasing temperatures have been shown to cause more precipitation and less snowfall, leading to less snowmelt and less groundwater recharge in the spring (IPCC, 2021).

Microplastics and sunlight absorption

Black carbon particles, produced by the incomplete combustion of fossil fuels, have been shown to be the second-largest driver of climate warming after CO_2 since the Industrial Revolution that began in the mid-1700s (Myhre et al., 2013). Much of black carbon's role in climate warming results from the melting of snow and ice. The melting results in: (1) the darkening of the Earth's surface; (2) decreasing the amount of sunlight the planet reflects; and (3) increasing the amount of sunlight that it absorbs. To date, estimates quantifying the effect of black carbon particles have not taken into account the role of possible significant amounts of microplastics in the melting of snow and ice (Ming & Wang, 2021).

Like black carbon, microplastics have the ability to absorb sunlight and, consequently, melt snow and ice, which also darkens the Earth's surface and thus decreases the amount of land surface that has reflective snow and ice. Most plastic products are dyed or painted (Andrady et al., 2016; Marti et al., 2020) (Figure 4).

The subordinate amount of clear or translucent plastics would not normally absorb consequential amounts of sunlight; however, the absorption levels increase after wear and tear in the form of, for example, scratched surfaces (Ishaq, 2019). In addition to mechanical breakdown, microplastics typically degrade by oxidation, photooxidation, biological degradation or hydrolysis, which is breakdown due to reaction with water (Niaounakis, 2017). Therefore, in total, whether microplastics are coloured, translucent or clear, they will absorb sunlight to varying degrees and contribute to darkening of the Earth's surface. Microplastics have been detected in many remote snow-packed and/or high-altitude areas worldwide, including the United States. Switzerland (Swiss Alps),

Figure 4. The many colours of microplastics. Each colour absorbs light differently. Source: Florida Sea Grant (2021)/Flickr (2017).

Germany, the Arctic and Antarctica (Allen et al., 2019; Bergmann et al., 2019; Brahney et al., 2020). These occurrences are the result of long-distance atmospheric deposition (Zhang et al., 2020), which are facilitated by the fact that microplastics are lighter than dust and become airborne more easily (Evangeliou et al., 2020).

It is hypothesized that microplastics and black carbon have been deposited together since the 1950s when both microplastics and petroleum products began to be widely used (Geyer et al., 2017). The mass of microplastics compared with that of black carbon has only been assessed in one study (Dubaish & Liebezeit, 2013). Here, an evaluation was conducted of seawater samples from the vicinity of the north-western coast of Germany, and from land-based freshwater sources. There were five times as many microplastics particles observed in a microscope slide compared with black carbon particles from seawater. Microplastics were detected in all nine freshwater samples, which included samples from effluent emanating from a sewage treatment plant, whereas black carbon particles were only detected in two of the nine samples.

Given the volume of microplastics produced in parallel with the production of black carbon emissions since the 1950s, the evidence for microplastics dispersion throughout worldwide high-altitude areas dominated by snow and ice, and the volumetric dominance of coloured microplastics that have the ability to absorb sunlight in a manner similar to black carbon, then it is likely that microplastics may also be providing an important contribution to the increase in global temperatures by causing the melting of snow and ice that would otherwise be reflecting sunlight (Ming & Wang, 2021). The sheer volume of known worldwide microplastics suggests a significant link with regard to the consequences of the melting of snow and ice by the inferred action of microplastics at higher elevations.

Aside from microplastics in snow and ice, another aspect of this poorly understood issue of microplastics' ability to absorb sunlight comes from a recent study of airborne microplastics (Revell et al., 2021). The study investigated how airborne microplastics behave in the atmosphere and whether they contribute to warming or cooling. It is known that airborne particles (aerosols), including dust, sea spray and soot (black carbon), may both reflect or absorb sunlight (IPCC, 2021), and thus cool or warm ambient temperature, respectively, depending on specific characteristics of the particle in question. The study concluded that airborne microplastics can behave the same way, that is, they may reflect or absorb sunlight – and thus cool or warm the ambient temperature, respectively, based on specific characteristic (particularly colour) of the microplastics particles.

The study showed that airborne microplastics' cooling effect dominates over a warming effect and, overall, their influence on global climate is currently very small. The authors noted that given the projected doubling of plastic waste in the next three decades (Geyer et al., 2017), the influence of airborne microplastics on the global climate will continue to increase.

Conclusions and policy recommendations

There is an as-yet poorly defined link between global warming, microplastics and freshwater/drinking water, particularly groundwater resources. One aspect of this link is an evaluation of the breakdown of microplastics in ocean water. The way in which the

enormous and increasing volumes of microplastics in the oceans degrade and release GHGs requires more scientific quantification. The build-up of these gases adds to the existing concentrations of GHGs in the atmosphere, all of which increases global warming. This warming contributes to climate change, and one consequence of climate change is more extreme rainstorms in most regions of the globe (IPCC, 2021), resulting in more runoff and less recharge to drinking water aquifers. Thus, there is a strong connection between the breakdown of microplastics in the oceans and drinking water resources.

Microplastics are widespread in sea ice and in glaciers. As global temperatures increase, more of these microplastics are released and then break down, releasing GHGs. This addition of these GHGs adds to the observed cumulative heat-trapping, but this phenomenon is poorly understood and more research is warranted to define not only the current extent of this mechanism but also to model how this mechanism will increase as plastic production ramps up. The release of more microplastics will lead to their degradation and increase GHGs, which further warm the planet and again contribute to the extreme storm events that results in more runoff (in most latitudes; IPCC, 2021) and less recharge to drinking water aquifers.

More research is needed to assess the radiative effects of both black carbon and microplastics on global warming. Coloured microplastics have the ability to absorb sunlight in a manner similar to black carbon; thus it is likely that microplastics may also be providing an important contribution to the increase global temperatures by causing the melting of snow and ice that would otherwise be reflecting sunlight (Ming & Wang, 2021).

Another area of applied research worthy of funding is the need to better understand how the ingestion of microplastics by phytoplankton inhibits their growth and ability to carry out photosynthesis (Zhang et al., 2017). Phytoplankton are vital because they consume about 30% of global CO_2 and produce up to 50% of the Earth's oxygen, and they serve as the foundation of the aquatic food web by feeding a staggering array or organisms, from animal-like zooplankton to whales. Given the enormous benefits we receive from phytoplankton, it behoves us to define more precisely the impact of microplastics on their function.

The physical harm to aquatic creatures by ingestion of microplastics is well-documented. The toxic effects to humans from long-term exposure/ingestion of compounds that comprise plastics are coming into focus, but are as yet incompletely understood. Removal of microplastics from drinking water or ocean water is currently cost-prohibitive. Therefore, source control and reduction of releases can be pursued by a coherent international strategy promoted by organizations such as the WHO, an agency of the United Nations. This organization can also provide guidelines to promote more extensive collection and recycling of used plastic items, which can be reused in new production in many cases (Rhodes, 2018).

The trend of increasing global plastics production – particularly single-use plastics – could be reversed by the passage of statutory requirements in individual countries that mandate gradual reduction of plastics production. The EU member states accomplished this in 2019 by passing the 'single-use plastics (SUP) Directive' (EU, 2019). A primary objective of the legislation is to limit the 10 most commonly found single-user plastics found on European beaches, as they represent 70% of all marine litter in the EU (Plastic Solutions Fund, 2019). These items are straws, drink

stirrers, balloon sticks, cotton buds, coffee cups and lids, other cups, cutlery, and containers. Progressively phasing out these common plastic items will result in a significant reduction in the overall mass of plastic waste. It has been estimated that reusing just 10% of our plastics products could reduce by half the amount of plastic waste released into the ocean (World Economic Forum, 2021). Reuse will be more effective if educational programmes are implemented to raise awareness about the benefits of consumption reduction as well as recycling. Education should ideally be expanded to include labelling requirements, where there is disclosure of the known toxic effects from some of the compounds commonly added to plastics (Plastic Solutions Fund, 2019).

As plastics production ramps up due to demand, there is an opportunity to establish controls that promote reuse and reduce disposal in landfills and the oceans. In December 2021, Exxon Corporation opened a large facility in Texas whose main products are polyethylene (PE) and ethylene (Dermansky, 2022). Given that PE accounts for one-third of the plastics found in the oceans (Royer, 2018), statutory requirements that are not cost-prohibitive could be phased in that prominently label PE plastic products to promote sorting during recycling. Interestingly, a recently completed study at a hospital in Rotterdam, the Netherlands, showed that common PE-based surgical wrapping plastic can be successfully collected and sorted within a facility, sterilized, melted and poured into bars that can be turned into granules, ready for injection moulding (Van Straten et al., 2021).

Manufacturers could also subsidize establishing infrastructure to reprocess used PE plastic, which is commonly used in products including grocery bags, squeeze bottles, packaging film and toys (*Encyclopaedia Britannica*, 2022). It is acknowledged that although PE is the main ingredient in many plastic applications, there are many different percentages of additives that comprise the PE-dominant products. Therefore, requirements should include a standardization of these additives to support more efficient reprocessing.

Countries should move towards a policy of full-cost accounting to ensure the market price of plastics reflects the cost of production as well as life cycle management (clean-up, recycling, reuse, etc.). This recommendation is akin to the extended producer responsibility (EPR) approach under which producers are given a significant responsibility – financial and/or physical – for the treatment or disposal of post-consumer products (Organisation for Economic Co-operation and Development [OECD], 2001).

Unlike microplastics, the deleterious health effects from PFAS have been well proven and the regulatory activity towards minimizing release to the environment and uptake by humans is underway in countries in the EU and the United States. For both PFAS and microplastics, the EU is developing a Sewage Sludge Directive (EurEau Newsletter, 2021) aimed at reducing releases of these contaminants via biosolids generated from WWTPs, which are collection points where these particles of emerging concern are not currently filtered or otherwise treated and discharging to freshwater bodies or wetlands or offshore (Burns & Boxall, 2018; Tyree & Morrison, 2017; Wagner & Lambert, 2018) (Figure 5). This Sewage Sludge Directive is an update of a 30-year-old directive that of course originally had no mention of these materials. This activity serves as a model for other countries to follow in the gradual reduction of the use and uncontrolled release of PFAS compounds and microplastics.

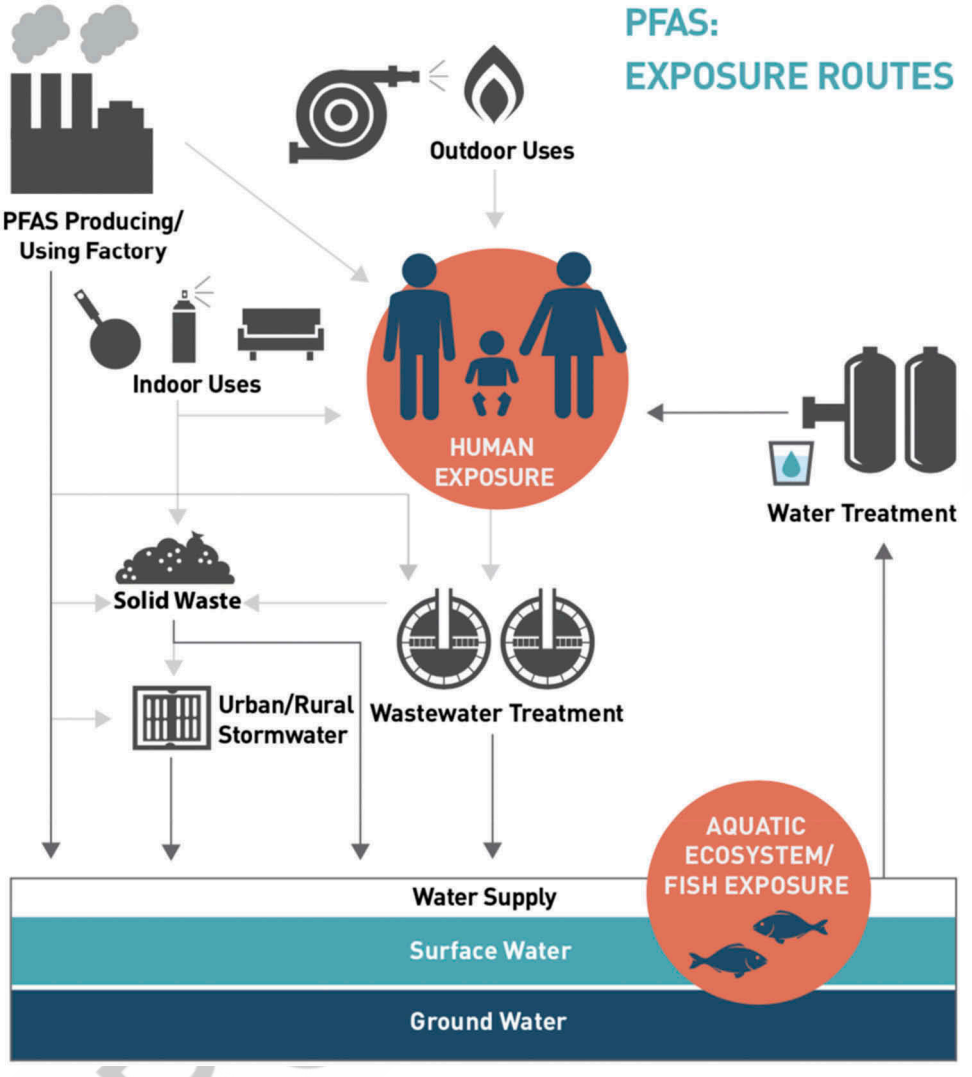

Figure 5. Per- and polyfluoroalkyl substances (PFAS) exposure routes, including contaminant movement through wastewater treatment plants. These same exposure pathways apply to the movement of microplastics. For indoor uses, PFAS may occur as coatings in cookware, in anti-fog sprays for glasses, and in fire-retardant coatings on furniture and rugs. Source: Water Research Foundation (2021).

A relatively inexpensive public health policy to manage PFAS pollution could involve baseline monitoring (sampling/laboratory analysis) in WWTPs, which could verify the presence and concentration of PFAS in effluent as well as in biosolids. This would guide the control of effluent or restrict or prohibit land application of biosolids generated by the WWTPs if lifetime health advisory concentrations are exceeded (e.g., 70 ppt in water in the United States and 100 ppt (provisional) in the EU). The industrial facilities generating the PFAS can be tapped to allocate funds to conduct the monitoring in the WWTPs along with testing before wastewater effluent is released from their facilities.

Wholesale infrastructure changes are prohibitively expensive, so incremental changes, such as monitoring (periodic sampling and analytical testing), is a way to manage a large-scale problem. Analytical testing for PFAS, in particular, given the fact that microplastics laboratory analysis is still somewhat unreliable, is one efficient use of a nominal amount of funding. PFAS monitoring will aid in the management and ultimately the improvement of water quality of irrigation water from surface water or groundwater sources, and the monitoring of groundwater from production wells used for drinking water. The results can aid in identifying particularly poor-quality incoming water and redirecting at least some of this undesirable water.

The effectiveness of PFAS compounds in AFFF, and household products, for example, has been a boon for corporations. Because of the backlash from PFAS causing cancer and birth defects, there has been some progress in the United States to force manufacturers curb and even stop the use of some PFAS compounds. However, this has led to the substitution of the banned PFAS compounds with other as-yet unregulated PFAS compounds. As noted above, it has been shown that these substitutes likewise have similar toxicity signatures as the PFAS compounds they are replacing. In light of this, there needs to more ambitious global regulatory involvement in halting the use of PFAS compounds in (at least) products that have widespread consumer use. Some PFAS-bearing products such as AFFF are capable of saving property and human life by its unique ability to rapidly halt fires, including large industrial fires. Therefore, whereas these products currently have an appropriate function when used judiciously, the search for substitute PFAS compounds – with verifiably less toxic constituents – should be encouraged and the overall use of PFAS should be reduced.

Disclosure statement

No potential conflict of interest was reported by the author.

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