Groundwater

Issue Paper/

On Per- and Polyfluoroalkyl Substances: Suggested Resources and Considerations for Groundwater Professionals

by Avram J. Frankel

Abstract

Per- and polyfluoroalkyl substances, a synthetic class of chemicals comprising thousands of compounds, are receiving increased attention over their presence in the environment, their potential effects on human health, and evolving regulation. This article summarizes suggested resources and key considerations for groundwater professionals wishing to familiarize themselves with this class of compounds. Background information, current groundwater-related regulations, risk considerations, comparison to other groundwater contaminants, and mitigation options are discussed, and a broad selection of references is supplied as a resource.

Introduction

Keeping abreast of the science, regulation, and mitigation options for groundwater contaminants can be a significant challenge for groundwater professionals. One case where this has been especially true is for the class of compounds known as per- and polyfluoroalkyl substances, or PFAS, used in a wide range of industrial and consumer product applications. While some track PFAS closely, or have some familiarity and a growing interest, others may have limited awareness of these chemicals in the area of groundwater resource management. Those delving in for the first time will encounter a rapidly increasing body of press reports, articles, technical papers, presentations, and opinion pieces on a topic that has become both a growing groundwater management issue and the subject of an advancing body of academic research and applied fieldwork. Meanwhile, PFAS regulations are evolving in the United States and internationally as key toxicology, epidemiology, and risk evaluation discussions continue, the body of environmental occurrence data expands, and PFAS-related litigation grows. This article discusses background on PFAS, summarizes a number of key issues and concerns, and provides a broad range of references, all intended as a resource for groundwater professionals trying to better understand PFAS.

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Received January 2021, accepted March 2021.

doi: 10.1111/gwat.13101

PFAS Background

So what are PFAS? PFAS are a synthetic class of chemicals, comprising thousands of compounds, some of which are not produced anymore, but many of which are currently used in a wide range of applications. The history of PFAS development and use in industrial processes, consumer and industrial products, and firefighting foams, as well as occurrence in environment and potential exposure routes, has been well documented by others (Kempisty et al. 2019; Glüge et al. 2020; ITRC 2020b; USEPA 2020b). In addition, the Interstate Technology & Regulatory Council (ITRC) has published helpful PFAS fact sheets (ITRC 2020a) and videos (ITRC 2020c) on PFAS chemistry, terminology, acronyms, naming conventions, physical and chemical properties, occurrence, environmental fate and transport, and other topics. The reader is directed to these sources for information regarding PFAS chemical structure, nature, and behavior in the environment, comprehensive presentation of which is beyond the scope of this issue article. The American Water Works Association (AWWA) also recently published a series of PFAS reference documents that summarize PFAS background information and issues related to drinking water source management (AWWA 2020b). While reliable analytical identification and quantification of individual PFAS compounds have been a challenge, in practice, for actual environmental assessment and mitigation applications, at least in the United States, laboratory analysis to meet regulatory criteria is less of an issue today based on the hard work of many over the last decade. This situation will only improve.

A subset of PFAS compounds has been detected in the environment and found to be bioaccumulative, mobile, and persistent in environmental media and may be associated with potential human health effects, although research continues in all of these areas (Kempisty et al. 2019; ITRC 2020b). Other PFAS that have been found in the environment do not bioaccumulate, and as such, do not appear to pose a potential risk to human health (Chengelis et al. 2009; Henry et al. 2018). In recent years, as more environmental data have been collected and detections in the environment have increased, most notably in drinking water, attention to this subset has risen, along with questions about the risk these compounds may pose individually and as a group, and in comparison to currently regulated compounds. This, then, begs the question of what regulation is appropriate. As groundwater professionals, many are also asking what all this means for groundwater resource management, and our respective organizations, clients, and communities.

Regulation

Regulation is a good starting point to consider many of the key issues. A range of viewpoints exists internationally from no regulation to an outright ban. Meanwhile, regulatory processes typically include risk evaluation, stakeholder engagement, and economic impact studies prior to promulgation of enforceable standards (Benesh and Faber 2019; USEPA 2020c; Clean Water Action 2021). Given all this, water suppliers and organizations representing water resource management organizations in the United States have urged regulators to provide clarity regarding PFAS based on appropriate scientific and economic evaluations. For example, a June 3, 2020, Joint Water Association letter to then U.S. Environmental Protection Agency (EPA) Administrator Andrew Wheeler, stated, “We ask that EPA move expeditiously to prepare the requisite analyses critical to proposing sound drinking water standards. The implications of regulating these substances will be far-reaching. A well-timed decision, based on sound science and robust analyses, is necessary to ensure effective protection of human health” (Joint Water Association 2020). Similarly, in August 2020, AWWA expressed a strong sense of urgency and range of concerns around promulgated, proposed, and pending state and federal PFAS regulation along with the following statement, “While there are considerable differences in the policy debate around PFAS, one constant is the need to make science-based decisions that provide meaningful public health protection” (Moody 2020).

The wastewater and stormwater treatment communities have also echoed these priorities to EPA, reflecting both concern over appropriately addressing PFAS, where needed, and concern over the implementation process for potential future PFAS surface water regulation (Remmel 2020). These concerns reflect issues we have seen since the onset of contaminant regulation in environmental media—balancing appropriate risk mitigation with the cost of implementation, and fears that enforceable regulations may be overly broad in some cases or not aggressive enough in others.

So what is the status of PFAS regulation of water in the United States? To start, the pace and content have varied as proposed regulations have proceeded through various state regulatory processes. It is also important to distinguish between enforceable standards versus guidance values, which some reference publications (AWWA 2020a) do better than others (ITRC et al. 2020). Terminology can also be confusing with standard, guideline, guidance value, and level, among others, being used interchangeably by some. As many of us know all too well, the difference between enforceable (e.g., maximum contaminant levels, or MCLs) and nonenforceable regulatory criteria (e.g., guidance values, health goals, notification levels) is critical, as is understanding how various nonenforceable criteria, which can vary in intent and application, are applied. For example, an exceedance of a guidance level or health goal in one state may trigger additional sampling, while exceedance of an action level in another may require public notification, additional monitoring, or other measures. Alternatively, exceedance of an MCL, an enforceable standard, can result in an enforcement order, demand to cease use of a water source, and/or fines for noncompliance.

As of February 2021, six states (MA, MI, NH, NJ, NY, VT) have enforceable drinking water standards, eight have some form of nonenforceable criteria (AK, CA, CT, IL, ME, MN, NC, OH), and one has proposed enforceable drinking water standards (WA). In addition, 12 have enforceable groundwater protection standards (AK, CO, IA, MA, MI, MT, NC, NH, NJ, RI, TX, VT), and at least four have promulgated surface water discharge standards (AK, CO, OR, MI). Currently, 36 states do not regulate PFAS in drinking water or default to EPA’s nonenforceable lifetime drinking water health advisories of 70 ng/L, or parts per trillion (ppt), for individual or combined concentrations of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS), the two most studied, well-known, and regulated PFAS compounds. About half of the states currently do not plan enforceable regulation of PFAS in ground, surface, or drinking water. Over time, we can expect the number of states regulating PFAS in some form or fashion to increase. And yes, it can be a challenge to track all of this, although many try. Caution is recommended when evaluating the accuracy of published regulatory compilations. In the end, monitoring state websites and communicating with regulators designated as PFAS points of contact in jurisdictions of interest are efficient and sensible ways to stay current.

At the federal level, EPA has said that it is considering movement towards MCLs for PFOA and PFOS (USEPA 2020a). It is also considering designation of these two compounds as hazardous substances under the Comprehensive Environmental Response, Compensation and Liability Act of 1980. Recently, the Biden administration has signaled intentions to accelerate these and other PFAS-related actions. In addition, EPA could initiate additional PFAS regulation after human health effects evaluations of perfluorodecanoic acid (PFDA), perfluorononanoic acid (PFNA), perfluorohexanoic acid (PFHxA), perfluorohexanesulfonic acid (PFHxS), perfluorobutanoic acid (PFBA), perfluorobutanesulfonic acid (PFBS), and GenX discussed in the Action Plan are completed. On the other hand, under the last two administrations, EPA has been slow to push forward new drinking water regulations (Roberson and Wilkes 2020), and it remains to be seen if the new administration will be different. In the past, EPA has declined to regulate other chemicals in groundwater that are regulated in some states (e.g., perchlorate, 1,4-dioxane, and 1,2,3-trichloropropane). If action is taken to move forward in the near term, the timeline inherent in the regulatory process suggests MCLs for PFOA and PFOS, or other PFAS likely will not be final for several years. Regardless, some states have regulated or will choose to regulate PFAS independently, which is likely to result in varying numerical limits and regulatory approaches, as has occurred to date.

Moving past regulatory implementation considerations, we see differences in the number and type of PFAS compounds regulated, a wide range of regulatory criteria concentrations, and regulation both individually and as a class. Using drinking water regulations as an example, of the 15 states with established and proposed regulatory criteria, five include PFOA and PFOS only (AK, CA, CT, ME, NY), six include five or more PFAS compounds (MA, MI, MN, OH, VT, WA), three are in between (IL, NH, NJ), and one regulates a single compound (NC). Six regulate a combination of short- and long-chain PFAS (IL, MA, MI, MN, OH, WA), while seven regulate only long chains (AK, CA, CT, NH, NJ, NY, VT) and one regulates a single short-chain compound (NC). (Short-chain PFAS are defined as perfluoroalkane sulfonates with five fluorinated carbons or fewer and perfluoroalkyl carboxylates with six fluorinated carbons or fewer.) In all, of the more than 600 PFAS known to be used in the United States (85 FR 14098), 10 are currently regulated in drinking water. Some of this regulatory variability is seen in international regulations as well. While a summary of international regulatory information is beyond the scope of this article, many of the issues presented above are common to international regulations. For example, the inconsistencies in which PFAS are of concern, how they are regulated, and to what degree (OECD n.d.).

Which compounds are regulated and where can depend on many factors, but one is regional occurrence. To assess occurrence in the United States, numerous PFAS sampling efforts have been completed, including the 2013–2015 national water supply sampling of six PFAS in 4920 public water supply systems under the Third Unregulated Contaminant Monitoring Rule (UCMR3). UCMR3 has been followed by public water supply, domestic well, groundwater, wastewater, and other sampling efforts in more than 20 states, with many ongoing and planned additional programs. In some cases, state sampling efforts have spurred regulation such as in Michigan, while the results from others, like Kentucky, have backed decisions not to pursue PFAS regulation (Commonwealth of Kentucky 2019). In addition, it appears that the future UCMR5 national public water supply survey may include approximately 30 PFAS using updated analytical methods with lower detection limits than UCMR3 (USEPA 2019). Overall, regional and national data sets will expand to further inform stakeholders.

Regulated concentrations and approaches for PFAS compounds also vary considerably across states. For example, Michigan's seven MCLs range over five orders of magnitude from 6 (PFNA) to 400,000 (PFHxA) ppt. Looking more closely, we find a range of 6 (PFNA) to 70 (PFOA, PFOA, PFHxS) ppt for long-chain PFAS and from 140 (GenX) to 400,000 (PFHxA) ppt for short chains. In addition, five states have chosen to regulate long-chain PFAS as a class (AK, CT, MA, NY, VT), while none regulate short chains in this fashion. Six states regulate PFAS exclusively as individual compounds (CA, MI, MN, NH, NJ, WA). Massachusetts has an MCL of 20 ppt combined for PFOA, PFOS, PFNA, PFHxA, PFHxS, and PFDA, whereas New Hampshire has separate MCLs for PFOA, PFOS, PFNA, and PFHxS. One state combines class and individual approaches (OH). To many, the range of regulated concentrations and differing approaches at the state level are confusing.

Risk Considerations

So why the differences? Decisions on which compounds to regulate and to what concentration, and whether to regulate individually or as a class, fundamentally come down to differences in interpretation of the available technical information, the approaches used to address the uncertainty in those interpretations, and the level of risk that is considered acceptable when factoring in health, economic, and other considerations prioritized by a given regulatory body. In evaluating human health as an example, technical evaluations of the potential health risks posed by PFAS should consider how a person can become exposed; the amount of exposure that can occur; the age, sex, and susceptibility of the exposed person; the toxic effects that exposure could have; and if those toxic effects exceed a level of risk that is considered acceptable by the regulatory agency (Post 2020). Each of these steps requires consideration of a significant amount of available data related to occurrence, chemical fate and transport, resource use, modes of action, critical effects, dose–response, causality, relative potency, and myriad other factors. Though research has and continues to add considerably to our knowledge base, the bottom line is that uncertainty still exists. A recent meeting of U.S. government scientists on PFAS noted important data gaps and studies under way to resolve some of them (National Academies of Sciences, Engineering, and Medicine 2021). The approaches regulatory agencies use to address this uncertainty are an important source of variation in proposed or promulgated values.

In the end, some argue for regulation as a class (Kwiatkowski et al. 2020), while others argue for consideration of some PFAS individually, with emphasis on resolution of key data gaps to support a more consistent, defensible, and comprehensive evaluation approach (Goodrum et al. 2020). These considerations also reflect differences in opinion on priorities, such as additional regulation now versus waiting on further studies. These factors, along with each state's regulatory process, including various degrees of economic analysis and political considerations, inform the current regulatory environment, as does the reality that once promulgated, enforceable regulations are difficult and time-consuming to modify.

Comparative Risk Perspectives

But how do the risks from PFAS compare to other compounds we have been addressing for years? A number of us have been asking this question, which is made even more relevant as we work with aquifers containing mixes of PFAS, volatile organic compounds (VOCs), and other chemicals. Trichloroethene (TCE) is one of the most studied and frequently detected groundwater contaminants in the United States (Toccalino and Hopple 2010), if not the world. Unlike PFAS, consensus exists on mitigating the risks from TCE exposure, which for drinking water, is reflected in a long-standing MCL of 5 μg/L, or parts per billion (ppb). Comparing the lowest state drinking water regulatory criteria for PFAS (5.1 ppt notification level for PFOA in California) to the TCE MCL could imply to some stakeholders that PFOA presents a thousand times more risk to human health than TCE. A related question is why many PFAS are regulated to low parts per trillion (i.e., 0 to 100 ppt) criteria when chlorinated solvents, such as TCE, are allowable up to 5 ppb, or 5000 ppt, in drinking water. It is not difficult to find publicly available Consumer Confidence Reports that document myriad regulated chemicals compliant with applicable enforceable drinking water criteria, most in the parts per million and parts per billion range and thus many orders of magnitude greater in concentration than most PFAS regulatory criteria (e.g., City of Fresno 2019). While we know uncertainty is a big factor in development of PFAS regulatory criteria in the low parts per trillion range, questions like these, and their technical and financial implications for PFAS mitigation (which in the drinking water world can fall disproportionately on smaller and less well-funded utilities) are spurring comparative evaluations of regulatory approaches for PFAS to more long-standing and better understood environmental contaminants.

A recent article by Newell et al. (2020) moves this discussion forward. The article is also timely given concerns of many in the environmental remediation community that addressing PFAS may be a far greater challenge than for prior contaminants (Simon et al. 2019) versus the measured optimism of others (Suthersan et al. 2016). Newell et al. (2020) compares and contrasts PFAS to chlorinated VOCs (including TCE), BTEX (benzene, toluene, ethylbenzene, and xylenes), 1,4-dioxane, and methyl *tert*-butyl ether (MTBE), all organic contaminants that have affected groundwater and drinking water sources around the world, and resulted in decades of lessons learned from mitigation efforts. The paper considers a range of comparative metrics including total chemical production (i.e., potentially releasable mass to the environment), number of estimated impacted sites, frequency of detection in drinking water aquifers, median plume length, degree of hydrophobic sorption in the aquifer matrix, regulatory criteria stringency, required remediation efficiency, anticipated in situ remediation performance, and intensity of applied research. Four of the criteria (production, impacted sites, detection frequency, and remediation efficiency) indicate the overall scale of PFAS groundwater remediation may be less of a challenge than the other contaminants. One metric, median plume length, suggests the scale of PFAS remediation at affected sites may be slightly larger than for chlorinated solvents. Another metric, hydrophobic sorption, was inconclusive. Finally, three metrics (regulatory criteria, in situ remediation, and research intensity) suggest that PFAS will likely present a greater challenge where mitigation is required.

Relatedly, while we continue to expand our knowledge about PFAS fate and transport, studies have indicated that some PFAS show significant physical attenuation in the vadose zone (Anderson et al. 2019; Schaefer et al. 2019), including partitioning and sequestration at the air–water interface (Costanza et al. 2020). In addition, a few recent studies have documented biological degradation of PFAS in laboratory environments (Huang and Jaffé 2019; Yu et al. 2020), a fact that reminds us that many formerly emergent contaminants (e.g., TCE, perchlorate, 1,4-dioxane, MTBE, and others) were initially thought not to bioattenuate in the subsurface, but then were later found to both biologically degrade under certain conditions and be amenable to engineered biological treatment including combined remedy approaches. Perhaps this will be the case for some PFAS. Despite the challenging chemical nature of PFAS, similar to our experience with other groundwater contaminants, our understanding of PFAS in groundwater will increase, leading to refined understandings of the fate and transport of these compounds in groundwater.

Mitigation

What mitigation options exist for PFAS? Key drinking water mitigation options include use of alternate sources, source blending, retirement or replacement of supply wells, and treatment. While most of the PFAS mitigation literature focuses on treatment, the other options are often significantly more cost-effective, are faster to implement, and have been successful, often in high-profile efforts (Michigan 2019, 2020). Proven and emerging drinking water treatment technologies have been summarized well by others (AWWA 2020c), with full-scale applications of granular activated carbon (GAC), ion exchange resin, and membrane filtration (e.g., reverse osmosis and nanofiltration), and some designs combining technologies. All proven in application, these three technologies have important pre-treatment, performance, and residuals management (e.g., membrane filtration concentrate, and spent GAC and ion exchange resin disposal) considerations, which are critical to evaluate against project-specific design criteria to comprehensively assess effectiveness, implementability, and lifecycle cost. As with the removal of other drinking water contaminants, especially considering the common occurrence of co-contamination in drinking water sources, combinations of technologies appear promising and will likely see greater application (Franke et al. 2019). In addition, a number of developing technologies (e.g., alternate adsorptive media) may become commercially viable for water treatment or have residuals management applications (e.g., electrochemical oxidation and plasma), with much emphasis on the latter given concerns over the ultimate fate of removed PFAS (Horst et al. 2018).

ITRC has summarized field-proven, limited application (e.g., field pilot) and developing soil and groundwater remediation technologies (ITRC 2020c). An important application for both established and evolving groundwater remediation technologies is pre-treatment of high concentration influents, a key difference from drinking water treatment applications. Another important area is in situ treatment, where initial results from field testing of colloidal activated carbon for groundwater and thermal treatment for soil have shown some promise. Finally, similar to consideration of nontreatment mitigation options for PFAS in drinking water, engineered remediation is not always the answer. As with all soil and groundwater contamination, comprehensive risk evaluation is critical to ensuring resources are applied where receptor risk reduction is most needed. This is especially true given the regulatory discussion above and evolving nature of PFAS remediation goals.

Closing

Given these considerations, it is important to remember, and take heart in, the fact that PFAS are not the first environmental contaminants we have addressed. Much has been achieved and we have many lessons learned from decades of mitigation efforts, lessons we should harness to wisely focus our resources on appropriate risk reduction. New data from a range of studies will continue to become available and can better inform current and future decision-making. If we are honest about contaminant mitigation efforts to date, many could have happened faster and with more effect, while others were not justified from the outset from a risk reduction standpoint. Striking a balance between action and informed decision-making is always a challenge. It is as important as ever to commit to science-based and equitable approaches and build on our collective experience addressing anthropogenic chemicals.

Acknowledgments

This work was supported by Integral Consulting Inc. The author thanks three anonymous reviewers for their comments, and his colleagues at Integral who made important contributions to earlier versions. He also thanks Dr Anthony Luz for his input while he was at Integral.

Author's Note

The author does not have any conflicts of interest or financial disclosures to report.

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