

PFAS and the Mining Industry: Understanding the Challenges

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Abstract

Per- and poly-fluorinated alkyl substances (PFAS) are a group of more than 3,000 man-made chemicals including perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS). This emerging class of contaminants has been the centre of litigation settlements already worth billions of dollars across various US states. Ubiquitous at very low levels in the environment, PFAS have been measured in water supplies across the US. While the focus on PFAS to date has centred around manufacturing facilities and commonly known aqueous film forming foam (AFFF) release sites (airports and military bases), international governments have been starting to consider other types of PFAS impacts associated with a broad range of industries.

Although mining has not yet become a key focus area for concerns related to PFAS impacts, mines are beginning to be identified as sources of PFAS. For example, BHP's Mount Whaleback Iron Ore Mine in Western Australia was recently identified as the source of low level PFAS impacts to groundwater. These impacts have the potential to threaten a nearby drinking water supply, prompting BHP to evaluate PFAS use across its site. The use of PFAS within the mining industry has been long established, including use within industrial processes (e.g., use as surfactants to enhance metal recovery, within the ore flotation process, etc.), as well as use of AFFF for firefighting activities. Consequently, environmental releases of PFAS from mining facilities could occur and require consideration and management.

This paper will provide an overview of the challenges associated with PFAS in the environment, and the implications these challenges may have for the mining industry. It will review PFAS use within the mining industry, site characterization challenges, potentially relevant receptors and exposure pathways, and remedial options, as well as the status of PFAS regulation internationally.

Introduction

Per- and poly-fluorinated alkyl substances (PFAS) are a group of more than 3,000 man-made chemicals including perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS). This emerging class of contaminants has been the centre of litigation settlements worth over \$5.5 billion across the US. Ubiquitous at very low levels in the environment, PFAS have been measured in water supplies across the US. A variety of adverse health effects have been associated with PFAS exposure, including liver damage, decreased fertility, thyroid disease, cancer, decreased immunity, and more.

Mines are beginning to be identified as potential sources of PFAS release to the environment. The use of PFAS within the mining industry has been long established, including use within industrial processes (e.g., use as surfactants to enhance metal recovery, within the ore flotation process, etc.), as well as use of aqueous film forming foam (AFFF) for firefighting activities. Consequently, environmental releases of PFAS from mining facilities could occur and require consideration and management. As such, this paper will review PFAS use within the mining industry, site characterization challenges, potentially relevant exposure pathways for receptors, and remedial options, as well as the status of PFAS regulation.

PFAS Use within the Mining Industry

As outlined in Gluge et al. (2020), 1400 individual PFAS substances have been identified for more than 200 uses in 64 different categories, including the mining industry. PFAS substances are widely used due to the many properties that make them invaluable to industry, including:

- the ability to lower the aqueous surface tension
- high hydrophobicity
- high oleophobicity
- high non-flammability
- capacity to dissolve gases
- high stability
- extremely low reactivity
- high dielectric breakdown strength
- good heat conductivity
- low refractive index
- low dielectric constant
- ability to generate strong acids
- operation at a wide temperature range
- low volatility in vacuum
- impenetrability to radiation

In mining, PFAS uses include ore leaching in copper and gold mines, ore floating, separation of uranium from ore/minerals, concentration of vanadium compounds, acid mist suppressing agent, wetting agents, hydrocarbon foaming agent, and the use of fluoropolymer in pipes, cables, hoses and conveyor belts (Gluge et al. 2020, Wood 2021).

PFAS may also be present at mining sites for uses that are ancillary to the mining operation, such as PFAS-containing AFFF for fire suppression/firefighting activities, cleaning of metal surfaces, and use as a foaming agent in drilling fluids, paints and coatings, and so on. In the case of AFFF, fire suppression systems often need to be tested annually, and traditionally this has involved discharge of AFFF to the ground

surface. As noted by Hunt (2020), mining sites typically have fixed fire suppression/fighting systems that can spray suppressants for long distances from a fixed location, meaning impacts can be widespread.

Site Characterization Challenges

The characterization of PFAS at any Site, including mining sites, should consider PFAS fate and transport in the environment, requirements for adjusted field procedures during sample collection, and implementation of appropriate laboratory quality assurance and quality control (QA/QC) processes.

PFAS Fate and Transport

Fate and transport of PFAS in the environment can be highly variable, given PFAS include many compounds with different physical-chemical characteristics that control their behaviour (ITRC 2021a). Carbon-fluorine chain length, functional group, charge and degree of fluorination all influence PFAS behaviour. When PFAS are discharged or spilled to ground surface, the PFAS can adsorb to soil through either hydrophobic or electrostatic interactions and remain close to the source area. PFAS can also show enhanced retention within the vadose zone, given the tendency of PFAS to accumulate at the air-water interface. Alternately, the charged functional group and associated hydrophilic properties can lead to PFAS leaching into groundwater and mobilizing with groundwater flow. Generally, the degree to which PFAS adsorb to solids or mobilize can be approximated by the chain length; longer carbon-fluorine chains tend to adsorb more strongly to solids versus shorter carbon-fluorine chains. Given the high stability of PFAS, once present in groundwater, large plumes can form that remain present for long periods of time. Transformation of commonly assessed PFAS, such as PFOA and PFOS, under typical environmental conditions is limited; however, PFAS precursors or polyfluorinated compounds may transform into more stable PFAS. Uptake of PFAS by plants and animals has been observed, with some PFAS showing bioaccumulation and biomagnification potential. Site-specific considerations cannot be omitted from assessment planning, as they do impact the fate and transport of PFAS, similar to other contaminants (ITRC 2021a).

PFAS can be found in other media, such as surface water, sediment and air (ITRC 2021a). Similar mechanisms as discussed for soil and groundwater dictate how PFAS behave in these media as well, including solid-liquid partitioning, and transformation or uptake. Given the surfactant-like properties of many PFAS and accumulation at the air-water interface, PFAS have been observed to form a foam at the top of surface water bodies when present at high concentrations. Many PFAS have low vapour pressures that limit movement of PFAS from water to air; however, there are some PFAS, such as fluorotelomer alcohols (FTOHs), that show greater volatility. Atmospheric transportation of PFAS can occur through release of volatile PFAS or PFAS adsorbed to air-borne particulate matter (ITRC 2021a).

Field Sampling Procedures and QA/QC

Although standard environmental sampling best practices should be followed, field sampling programs that include PFAS have additional considerations. PFAS are found in many commercial products, which include some of the equipment and supplies typically used to collect environmental samples, creating the potential for sample contamination. Other materials (such as glass) may adsorb PFAS, which would low-bias the collected data. Both cases should be avoided, and this can be facilitated through review of available reference documents regarding PFAS sampling, which notably include the Michigan Department of Environmental Quality (MDEC) *General PFAS Sampling Guidance* (MDEC 2018) and the Interstate Technology Regulatory Council's (ITRC's) *Sampling Precautions and Laboratory Analytical Methods for Per- and Polyfluoroalkyl Substances (PFAS)* (ITRC 2020).

Precautions outlined in MDEC (2018) and ITRC (2020) include avoiding certain clothing, materials, food packaging, and personal hygiene products that may contain PFAS when sampling. Sampling equipment and supplies should not contain Teflon, polytetrafluoroethylene (PTFE), fluorinated ethylene propylene (FEP), ethylene tetrafluoroethylene (ETFE), LDPE, polyvinylidene fluoride (PVDF), fluoropolymers or anything with “fluoro” in the name. Other materials that should be avoided during sampling include Decon-90, post-it notes, waterproof field paper or books, “blue ice” and any type of cooler pack, waterproof markers, sharpies, permanent markers, binders, spiral/ hard cover notebooks, plastic clipboards, adhesive paper products, food packaging and containers and adhesive tapes. Acceptable materials to use during sampling include materials made from high density polyethylene (HDPE), polypropylene or silicone, decontamination solutions like Alconox/ Liquinox, and field supplies that include loose plain paper, metal clipboards, ball point pens, and ice formed by water.

When executing a PFAS sampling program, PFAS sampling materials should be stored separately from sampling supplies for other parameters. Non-disposable field equipment should be decontaminated between each sample location and prior to use at a site where PFAS is being assessed. Sample collection should begin at the location where impacts are least expected (i.e., lowest anticipated PFAS concentrations) and move towards locations where impacts are most expected (i.e., highest anticipated PFAS concentrations). Eating or drinking on site during sampling should be avoided to minimize the potential for cross-contamination. Hands should be washed prior to returning to the site following any breaks.

In order to confirm that field procedures have been effective in inhibiting sample contamination, field QA/QC blank samples should be obtained, including equipment blanks, trip blanks and field blanks. Equipment blanks are collected using laboratory-provided PFAS-free water that is passed through or over equipment used for sampling activities to assess whether the equipment represents a potential source of PFAS to the sample. Field blanks are PFAS-free water samples that are collected in separate laboratory-provided sample containers while conducting sampling in the field to monitor that field activities are not a

potential source of PFAS to the sample. Trip blanks are PFAS-free water samples prepared by the laboratory that are transported during the sampling procedure to monitor that PFAS have not been introduced to the samples through laboratory preparation or transportation. The combination of these field QA/QC blank samples will provide confidence that the collected PFAS data are representative of site conditions.

Laboratory QA/QC

Choosing a certified laboratory to complete PFAS analysis is important to maintaining the accuracy and reliability of the data. The laboratory should provide appropriate containers to collect samples (i.e., unlined and made of polypropylene or HDPE); glass containers and certain plastic bags should be avoided, wherever possible. If high PFAS concentration samples are to be submitted for analysis, these samples should be segregated during sampling and shipment, and flagged to the laboratory to support appropriate preparation for analysis. It is noted that there are only a few multi-laboratory validated and published methods for analysis of PFAS, and those released to date have generally been developed for analysis of water samples (drinking water, groundwater, surface water and wastewater). Draft laboratory methods are available for other media, such as soil, sediment, biosolids and tissue; however, these have not been validated by multiple laboratories (ITRC 2021b). Following PFAS analysis, it is important to review the laboratory certificates of analysis to confirm the reported laboratory QA/QC procedures, such as method blanks, spiked blanks and analysis of duplicates, and compare the results to the provided evaluation criteria. This review of laboratory QA/QC may help indicate whether sample matrix interference or laboratory issues could have impacted the reliability of the reported PFAS concentrations.

Relevant Exposure Pathways

Human and ecological receptors can be exposed to PFAS through various pathways both at a mining site, as well as off-site, due to fate and transport mechanisms (e.g., groundwater migration, wind erosion, deposition). The routes of exposure and the receptors exposed, particularly off-site, can be influenced by the physical location of the mining site. Figure 1 illustrates a potential mining site, the surrounding land use, and the potential routes of exposure and receptors (as indicated by the numbers [#], and explained in the text below). The main expected source of PFAS is the use of AFFF (#1). PFAS may also end up in effluent or tailings ponds through use in processing (#2). These waters are unlikely to be treated for PFAS.

Human Health

The most likely potential exposure routes to PFAS for people at a mining site (e.g., workers) are incidental ingestion of soil (#3), potable water ingestion (should the mining site rely on groundwater or nearby surface water as source water) (#4), and, to a lesser extent, direct contact with PFAS-containing products (e.g.,

exposed via impacted surface water (e.g., consumption) (#10) and via food (e.g., plants, invertebrates, mammals, birds and aquatic biota) (#10, 12, 13); however, exposure on-site for mammals and birds may be limited if measures are in place that limit their access to the mining site itself (e.g., fencing).

Remedial Options

Remediation depends on the use of treatment technologies that can exploit a contaminant's chemical and physical properties for the purpose of removing or destroying the contaminant from environmental media. PFAS are a challenge to remediate because they are typically found in the environment as mixtures composed of different PFAS with potentially very different properties. The solubility, surfactant properties, stability, and poor adsorption characteristics of different PFAS tend to complicate remediation, as common technologies are ineffective (e.g., air stripping, soil vapor extraction, biostimulation or bioaugmentation) or have limited effectiveness (e.g., chemical oxidation). There are very few field-demonstrated, cost-effective treatment technologies for PFAS on solids or in water; however, there are proven ex situ technologies that could be applicable to the situations typically encountered at a mining site and these will be reviewed here. ITRC (2021d) provides an excellent summary of other emerging technologies currently under development.

Mines typically use local groundwater for drinking water and historical PFAS use may contaminate the drinking water supply to levels above recommended drinking water criteria. Beyond use of AFFF, treatment of process water at most mining sites largely does not address PFAS, meaning PFAS can be discharged to the environment in treated process water and impact drinking water supplies. As the primary concern at mining sites is drinking water, this review will focus primarily on water treatment technologies.

To date, readily available technologies for drinking water treatment have been limited to sorption and ion exchange, whereas treatment of leachates and process waters has included foam fractionation and coagulation (ITRC 2021d), depending on the composition of the solution. When considering remedial options for mining sites, it is important to note these sites are typically remote and operate under harsh environmental conditions, where power generation can be costly. Consequently, transport of PFAS-impacted treatment media off-site is expensive, sensitive specialized equipment has poor longevity, and onsite disposal of highly soluble and potentially mobile contaminants like PFAS is not practical.

Sorption and Ion Exchange

Sorption and ion exchange are two removal technologies that bind PFAS using Van der Waals and/or weak ionic forces, resulting in the accumulation of PFAS on the sorptive media. Granular activated carbon (GAC) and ion exchange resins (IX) are the most common sorptive media available used for PFAS adsorption. Various types of GAC have been tested with most PFAS and manufacturers having developed models to predict mass loading under a variety of solution conditions. Most testing has focussed on the efficacy of

GAC sorption of long-chain PFAS (Appleman et al. 2013; Ochoa-Herrera and Sierra-Alvarez 2008) and has demonstrated that GAC treatment can achieve effluent concentrations below detection limits for United States Environmental Protection Agency (USEPA) Method 537.1 (Shoemaker and Tettenhorst 2018). Although also effective with other organic contaminants such as petroleum hydrocarbons and chlorinated solvents, co-contaminants can displace PFAS from GAC, reducing treatment. Sorption efficiency is dependent on carbon chain length of the PFAS and the ionic functional group, with shorter chain PFAS and carboxylic acids having lower sorption efficiencies than longer chain and sulfonic acid types (e.g., PFOS adsorbs more effectively than PFOA [McCleaf et al. 2017] and both adsorb more effectively than perfluorobutanesulfonate [PFBS] or perfluorobutanoate [PFBA] [Appleman et al. 2013]).

GAC can be regenerated through solvent (methanol) extraction and the material reused for non-drinking water applications. The solvent extracted PFAS can be distilled to remove the solvent and the concentrated PFAS can be treated through incineration in a kiln at temperatures >1,000° Centigrade (°C).

Ion exchange has been shown to effectively sorb and treat a broad suite of PFAS at field scale to below analytical detection limits for influent concentrations in the range of several 100 micrograms per liter (µg/L) total PFAS (Kothawala et al. 2017; McCleaf et al. 2017; Woodard et al. 2017). Resins can be designed to target certain PFAS more effectively, but generally, like GAC, perfluorosulfonic acids (PFSAs) have a greater affinity than perfluorocarboxylic acids (PFCAs) for similar chain length and longer chains have a greater affinity than shorter chain PFAS. IX are also available as single use and regenerable resins, where the solvent extract can be submitted directly for incineration or distilled and the PFAS residue incinerated. Regenerable resins are better suited for removal of higher concentration PFAS (ITRC 2021d).

IX are highly susceptible to fouling and require pre-treatment for pH, inorganic and organic co-contaminants and major anions and cations. Low concentrations of dissolved organic matter, iron or manganese can significantly influence membrane performance and permeability.

Reverse Osmosis and Nanofiltration

Reverse osmosis (RO) and, to a lesser extent, nanofiltration (NF) are commonly used in mining and many industrial water treatment processes to remove ions from water by forcing impacted water through a semipermeable membrane. Both techniques can concentrate PFAS in the permeate, which can then be treated using a second technology (such as foam fractionation or advanced oxidation) and have been shown to be effective at removing longer chain (>C5) perfluoroalkyl acids (PFAAs) (Loi-Brugger et al. 2008; Tang et al. 2006). In order to preserve the RO/NF membranes for removal of PFAS, pre-treatment is required to remove interfering anions and cations, optimize pH and remove organic contaminants that might clog the membranes. The effectiveness of RO/NF at removing PFAS has been evaluated extensively in wastewater and drinking water applications where PFAS was not the target contaminant (Tang et al. 2006; Flores 2013;

Glover et al. 2018; Dickenson 2016; Merino et al. 2016). Tang et al. (2006 and 2007) studied PFAS from various wastewaters using various RO and NF membranes and achieved >99% removal at PFOS concentrations ranging from 0.5 to 1,500 milligrams per liter. Although RO/NF have high treatment efficiencies at high PFAS concentrations and reliably remove the bulk of PFAS from highly impacted waters (e.g., PFAS-AFFF impacted groundwater where concentrations can be in the high $\mu\text{g/L}$ range), they still require a polishing treatment using GAC or IX to reliably achieve regulatory criteria for effluent limits.

Foam Fractionation

As a result of their non-polar tail and polar head, PFAS tend to accumulate at the air-water surface which facilitates removal via foam fractionation by bubbling air or reactive gases (e.g. ozone) through a water column to form foam. The foam, which is composed predominantly of PFAS and other similar co-contaminants, is then skimmed off the water surface. One application used by the Australian Department of Defence, Army Aviation Centre Oakey (AACO) (base near Toowoomba, Queensland) is referred to as surface activation foam fractionation (SAFF) and uses hundreds of columns to progressively strip PFAS off the top of the water columns (ITRC 2021d). Various studies have shown that C6 PFAS and greater can be removed effectively with this technology; however, it is less effective on shorter chain PFAS. The treatment rates that can be achieved with foam fractionation depend on the degree of foaming and contaminant load. At high foaming rates, throughput is reduced significantly, but the technology is very useful for removal of longer chain PFAS from concentrated mixed contaminant streams and RO/NF reject.

Developing Destructive Technologies

There are many destructive technologies in development showing promise for the destruction of short and long chain PFAS using oxidation approaches (ITRC 2021d). Ozonation (in combination with persulfate), activated persulfate, electrochemical oxidation, sonochemical oxidation, supercritical water oxidation, photochemical oxidation (UV-Ox) and other advanced oxidation technologies are in various stages of development. While these technologies are promising, the PFAS concentrations need to be in the range where oxidation is cost effective. At remote sites, like mining sites, where disposal of PFAS can be challenging due to transportation costs, these destructive technologies may be better options for onsite destructive treatment of concentrated waste in combination with a GAC or IX polishing post treatment.

Status of PFAS Regulation

To date, internationally, there appears to be no official guidance or guidelines produced regarding PFAS that are specifically directed to the mining industry; however, many jurisdictions have produced screening values for environmental media that would be potentially applicable to mining sites. Standards and

guidelines for surface water, drinking water, groundwater, and soil have been developed for up to 20 PFAS in the jurisdictions of Canada, the United States (US), and internationally. The majority of these standards and guidelines are for PFCAs and PFSAs, with only a few jurisdictions preparing standards and guidelines for select fluorotelomer sulfonic acids (FTSAs) and GenX (a trade name for a group of shorter chain PFAS, e.g., less than six carbons). Some of these values are regulated. Select jurisdictions have also developed criteria for other types of media (e.g., sediment, ambient air, fertilizer, fish tissues, eggs, other food products, etc.); however, these values are often unregulated. Given the primary exposure pathway of concern at mining sites is expected to be ingestion of potable water, this review will focus on standards and guidelines that have been produced for water.

North America

In the US, no federal maximum contaminant level (MCL) has been released by the USEPA for any PFAS; however, the USEPA did define a lifetime health advisory for drinking water concentrations of PFOA and PFOS as 70 nanograms per litre (ng/L) in 2016, which applies to PFOA and PFOS individually and as a sum (USEPA 2019a). The USEPA has also released a screening level of 40 ng/L to determine if PFOA and/or PFOS are present in groundwater and warrant further investigation, but the preliminary remediation goal for contaminated groundwater remains as the USEPA drinking water health advisory (USEPA 2019b). In 2020, the PFAS Action Act was passed by the House of Representatives to classify certain PFAS as hazardous substances, which is expected to lead to enforceable MCLs in future (Library of Congress, 2020).

In the absence of federal MCLs, pressure from citizens and politicians has led some states to develop their own standards (Zemba et al. 2019). Many states have developed their own guidelines and criteria, especially for PFOA and PFOS, at a range of values more conservative than the USEPA (ITRC 2021e). Illinois (2 ng/L PFOA and 14 ng/L PFOS) and California (5.1 ng/L PFOA and 6.5 ng/L PFOS) have some of the most conservative values for drinking water (ITRC 2021e). Hawaii has set criteria for the largest number of PFAS parameters, with groundwater protective concentration levels for 18 PFAS. The range of guidelines and standards available from the States for the six PFAS for which standards and guidance values are most commonly defined are summarized in **Error! Reference source not found.**1. Soil guidelines and standards for the protection of drinking water or groundwater have also been released by 12 States for up to 18 PFAS (ITRC 2021e).

In Canada, Health Canada (HC) has established drinking water guidelines (DWGs) for PFOA and PFOS, as well as drinking water screening values (DWSVs) for nine additional PFAS (HC 2019). The DWGs and DWSVs for the same six PFAS included in Table 1 are detailed in Table 2. The DWGs and DWSVs were defined to protect human exposure from drinking water sources. The DWGs for PFOA and PFOS are presented as Maximum Acceptable Concentrations (MACs) that are based on a study that

referenced hepatocellular hypertrophy in rats as a result of exposure to PFOA and PFOS (HC 2018a and 2018b). Health Canada suggested that an additive approach using the ratio of PFOA and PFOS to their respective DWG should also be considered in cases where PFOA and PFOS occur concurrently in drinking

Table 1: Sample PFAS Water Guidelines and Standards (United States) (ITRC 2021e)

PFAS Analyte	Drinking Water (ng/L)	Groundwater (ng/L)	Surface Water (ng/L)
PFOA	2 - 667	2 – 40,000,000	70 – 24,000
PFOS	6.5 - 667	2 – 500,000	6 – 300,000
Perfluorononaote (PFNA)	6 - 70	4.4 – 40,000,000	70 – 1,000
PFBS	345 – 667,000	420 - 400,000	400,000
Perfluorohexanesulfonate (PFHxS)	18 - 140	18 – 500,000	700
Perfluoroheptanoate (PFHpA)	20 - 70	2 – 40,000,000	300

water sources (HC 2018a and 2018b). In 2021, the Canadian Council of Ministers of the Environment (CCME) produced a federal environmental quality guideline for PFOS in groundwater protective of ecological receptors and human health (CCME 2021). The CCME value is also summarized in **Error! Reference source not found.** None of the federal guidelines developed in Canada are currently regulated. The only Canadian province to produce regulated values is British Columbia (BC) (BC 2019); these values are included in Table 2.

Table 2: Sample PFAS Water Guidelines and Screening Values (Canada)

PFAS Analyte	DWG (MAC, ng/L) (HC 2019)	DWSV (ng/L) (HC 2019)	CCME, Groundwater (ng/L) (CCME 2019)	BC Contaminated Sites Regulation, Drinking Water (ng/L) (BC 2019)
PFOA	200			200
PFOS	600		600	300
PFNA		20		
PFBS		15,000		80,000
PFHxS		600		
PFHpA		200		

International

The Australian government completed a literature review for PFAS toxicity and indicated the evidence of human health impacts directly related to PFAS exposure is limited and does not indicate an increase in overall cancer risk (Zemba et al. 2019); however, this government still released health-based PFAS guidelines for drinking water, residential water, and soil for PFOA, PFOS, and PFHxS (ITRC 2021e).

For other areas known for mining sites, such as South America, Indonesia, Asia, Russia and the Middle East, country-specific regulatory frameworks for PFAS are unknown; however, many of the countries in these regions are part of the Stockholm Convention (Brennan et al. 2021) which has been regulating select PFAS as Persistent Organic Pollutants since 2009.

Conclusion

PFAS can be found at mining sites both due to their use in industrial processes, as well as in AFFF. The assessment, management, and remediation of environmental releases of PFAS from mining facilities needs to consider the unique receptors and exposure pathways associated with these remote sites, as well as the related logistical challenges for assessment and remedial approaches. As a number of jurisdictions are advancing regulation around the use of PFAS and its presence in environmental media, mining facilities will need to consider the potential impacts and liabilities associated with PFAS use at their operations.

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