

# **EPA Public Access**

Author manuscript

J Environ Eng (New York). Author manuscript; available in PMC 2023 August 16.

About author manuscripts

Submit a manuscript

Published in final edited form as:

J Environ Eng (New York). 2021 November 23; 148(2): 1–8. doi:10.1061/(asce)ee.1943-7870.0001957.

# Supercritical Water Oxidation as an Innovative Technology for PFAS Destruction

Max J. Krause<sup>1</sup>, Eben Thoma<sup>2</sup>, Endalkachew Sahle-Damesessie<sup>3</sup>, Brian Crone<sup>4</sup>, Andrew Whitehill<sup>5</sup>, Erin Shields<sup>6</sup>, Brian Gullett<sup>7</sup>

<sup>1</sup>US Environmental Protection Agency, Office of Research & Development, 26 Martin Luther King Dr W, Cincinnati, OH 45268

<sup>2</sup>US Environmental Protection Agency, Office of Research & Development, 109 TW Alexander Dr, Durham, NC 27709

<sup>3</sup>US Environmental Protection Agency, Office of Research & Development, 26 Martin Luther King Dr W, Cincinnati, OH 45268

<sup>4</sup>US Environmental Protection Agency, Office of Research & Development, 26 Martin Luther King Dr W, Cincinnati, OH 45268

<sup>5</sup>US Environmental Protection Agency, Office of Research & Development, 109 TW Alexander Dr, Durham, NC 27709

<sup>6</sup>US Environmental Protection Agency, Office of Research & Development, 109 TW Alexander Dr, Durham, NC 27709

<sup>7</sup>US Environmental Protection Agency, Office of Research & Development, 109 TW Alexander Dr, Durham, NC 27709

### **Abstract**

Water above 374 °C and 22.1 MPa, becomes supercritical, a special state where organic solubility increases and oxidation processes are accelerated. Supercritical water oxidation (SCWO) has been previously shown to destroy hazardous substances such as halogenated compounds. Three separate providers of SCWO technology were contracted to test the efficacy of SCWO systems to reduce per- and poly-fluoroalkyl substances (PFAS) concentrations from solutions of dilute aqueous film-forming foam (AFFF). The findings of all three demonstration studies, showed greater than 99% reduction of the total PFAS identified in a targeted-compound analysis, including perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA). PFOS was reduced from 26.2 mg/L to 240 µg/L, 30.4 mg/L to 0.310 µg/L, and 190 mg/L to 8.57 µg/L, from the Aquarden,

(corresponding author) krause.max@epa.gov.

Disclaimer

The authors declare no competing financial interest. The views expressed in this article are those of the authors and do not necessarily represent the views or policies of the U.S. Environmental Protection Agency (EPA). Any mention of trade names, products, or services does not imply an endorsement by the U.S. Government or the U.S. EPA. The EPA does not endorse any commercial products, services, or enterprises.

Supplemental Materials

Tables S1–S6, Figs. S1–S5, and files containing data for the PFAS, generated fluoride, and process are available online in the ASCE Library (www.ascelibrary.org).

Battelle, and 374Water demonstrations, respectively. Similarly, PFOA was reduced from 930 to  $0.14~\mu g/L$ , 883 to  $0.102~\mu g/L$ , and  $3,100~\mu g/L$  to non-detect in the three evaluations. Additionally, chemical oxygen demand of the dilute AFFF was shown to reduce from 4,750 to 5.17~m g/L after treatment, indicating significant organic compound destruction. In one demonstration, a mass balance of the influent and effluent found that the targeted compounds accounted for only 27% of the generated fluoride, suggesting that more PFAS were destroyed than measured and emphasizing the limitations of targeted analysis alone. As a destructive technology, SCWO may be an alternative to incineration and could be a permanent solution for PFAS-laden wastewaters rather than disposal by injection into a deep-well or landfilling. Additional investigation of reaction by-products remains to be conducted for a complete assessment of SCWO's potential as a safe and effective PFAS treatment technology.

#### **Keywords**

Supercritical water oxidation; aqueous film-forming foam; PFAS; PFOS; fluoride

#### Introduction

Water above 374 °C and 22.1 MPa becomes supercritical, a special phase of water with both liquid-like and gas-like properties. Above the critical point of water, most organic compounds are soluble, oxygen is fully miscible, and salts are insoluble (Hodes et al., 2004; Voisin et al., 2017). In the presence of an oxidizing agent, such as oxygen, supercritical water's unique properties accelerate oxidation of a broad range of organic pollutants. Since the 1980s, supercritical water oxidation (SCWO) has been used successfully to treat a variety of hazardous wastes, such as chemical warfare agents and halogenated compounds (Abeln et al., 2001; Cohen et al., 1998; Kim et al., 2010). Technical challenges have limited implementation of SCWO at scale, including the buildup of corrosive species during the oxidation reaction and salts' precipitation on the reactor body, leading to high maintenance and operation costs (Marrone, 2013; Mitton et al., 2001). These factors have historically constrained SCWO's utility to hazardous or otherwise high-cost wastes.

In the US, aqueous film-forming foam (AFFF) has been used for over 50 years for certain firefighting applications and associated training exercises. The vast majority of AFFF in use or stockpiled contains fluorosurfactants, which are made up of per- and poly-fluoroalkyl substances (PFAS) (Barzen-Hanson et al., 2017; Place & Field, 2012). It is estimated that there are millions of liters of AFFF in private, public, and military custody (Darwin, 2011). Many PFAS are stable and resistant to natural destruction in the environment, leading to their pervasive presence in groundwater, surface waters, and drinking water in some localities (Boone et al., 2019; Houtz et al., 2013; Houtz et al., 2016; Hu et al., 2016; Munoz et al., 2017). The US Environmental Protection Agency (EPA) and Department of Defense (DoD) identified PFAS destruction as a priority research area, and several states have promulgated or drafted individual PFAS limits for drinking water and soils (Coyle et al., 2021; ITRC, 2021). Due to the bioaccumulative nature and adverse health effects of some PFAS, many states have restricted or prohibited the use of fire-fighting foam containing PFAS. Millions of liters of highly concentrated material now must be disposed

of or destroyed in a manner that is protective of human health and the environment (EPA, 2020). The cost and method of AFFF disposal in the US are of interest to nearly every state and the federal government. The state of Michigan recently paid \$1.4M to dispose of 194,585 liters (51,404 gallons) of PFAS-containing AFFF in a hazardous waste landfill, a \$7.19/L (\$28/gallon) disposal cost (MI EGLE, 2020). The typical method of destruction of hazardous wastes in the US has been incineration. Several states and the US Navy have paused incineration of AFFF until its efficacy has been proven, and so alternative and safe methods must be found (Carignan & Clukey, 2020). The potentially high cost for disposal and the desire to do so in a safe manner presents an opportunity for innovative technologies like SCWO (Hori et al., 2008; Pinkard et al., 2021; Wu et al., 2019).

SCWO's previous applications to destroy chemical warfare agents, polychlorinated biphenyls, and halogenated compounds makes it a potential, but unproven, alternative for PFAS destruction -especially for waste streams like AFFF that contain significantly greater concentrations of PFAS than landfill leachate or wastewater (Barzen-Hanson et al., 2017; Houtz et al., 2018; Houtz et al., 2016; Loganathan et al., 2007; Masoner et al., 2020; Moody & Field, 2000; Ruyle et al., 2020; Yu et al., 2009). With the goal of evaluating SCWO as an innovative technology to destroy PFAS, demonstration studies were conducted independently by three providers of SCWO systems. This case study highlights the results of the three experiments comparing influent and effluent liquid-phase concentrations of targeted (i.e., identified and quantified) PFAS and other parameters, identifies current limitations of the study's findings, and discusses issues for technological development.

#### **Materials and Methods**

Three different organizations were contracted to independently test their respective SCWO systems for the potential to destroy PFAS in AFFF: Battelle (Columbus, USA), Aquarden Technologies (Skaeving, Denmark), and 374Water (Durham, USA). As shown in Table 1, the three experiments used similar PFOS-based AFFF material: 3M Lightwater<sup>TM</sup> produced prior to 2002. Lightwater<sup>TM</sup> produced before 2002 contains both short-chain and long-chain PFAS, including the C8 compounds perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA), along with up to 15% by volume of other non-fluorinated organic molecules (Barzen-Hanson et al., 2017; Houtz et al., 2016; Moody & Field, 2000). At this time, PFOS and PFOA are the primary PFAS of concern in the US and represent a particular point of interest by the US EPA. Product images are presented in Figures S1–S3 of the SI.

The three demonstrations were conducted similarly, and all were continuous flow systems, but some differences are noted here. Battelle's PFAS Annihilator<sup>™</sup> was used to conduct duplicate experiments with influent and effluent samples collected and analyzed in triplicate. A 100x dilute solution of AFFF and an oxidant (confidential) were fed through the SCWO reactor in a single pass with a residence time of <10 s. An alkaline solution (confidential) was added to the effluent, post-treatment to neutralize acid formation. Battelle's samples underwent targeted analysis for 28 PFAS by its Environmental Laboratory Accreditation Program (ELAP) accredited laboratory (Norwell, USA). For the demonstration, Aquarden used a feed flow of 1 L/h and a reactor residence time of 60 s. AFFF was diluted with

distilled water and an alkaline buffer (potassium hydroxide 0.5% w/w) to a final dilution of 100x. Throughout this test, the maximum reactor temperature was maintained at 590 °C, and reactor operation pressure was set at 24 MPa. ALS Environmental Lab analyzed a single effluent sample for 12 PFAS (Copenhagen, Denmark). For the 374Water demonstration their SCWO unit located at Duke University was used. A desired influent PFAS concentration was set to 200–300 ppm (See Table S2), and so a 30x dilution was determined. The maximum reactor temperature was 595 °C with a feed rate of 0.35 kg/min and reactor residence time of 6–8 s. Influent and effluent from the 374Water system were analyzed for 28 PFAS by TestAmerica (West Sacramento, USA). Table S5 shows which of the PFAS were analyzed for by each vendor, indicating which compounds were similarly or uniquely investigated. The various test parameters are highlighted in Table 2. Some of the test parameters have been shielded by the vendors under confidential business information (CBI) but taken together, an evaluation of the SCWO technology is still possible.

The analysis of PFAS in the liquid influent and effluent was conducted by high performance liquid chromatography followed by tandem mass spectrometry (HPLC/MS/MS) (Shoemaker & Tettenhorst, 2020). Chemical oxygen demand (COD), a measure of oxidizable pollutants in water, was measured by colorimetry for the Aquarden and 374Water AFFF samples (Hach Company, Colorado, USA). Fluoride was measured by an ion-selective electrode (ISE; YSI, Ohio, USA) and Ion Chromatography (IC; Thermo Scientific, Massachusetts, USA) by EPA 9056A for the Battelle influent and effluent samples only. ISE data are presented in the main text and comparable IC data are presented in the SI. As discussed later, the purpose of performing both was to evaluate the accuracy of the ISE. Destruction efficiency (DE) is defined here as unity minus the ratio of sum of targeted PFAS in the liquid effluent and influent material, as shown here:

% Destruction Efficiency = 
$$100 * \left(1 - \frac{\sum PFAS_{Effluent}}{\sum PFAS_{Influent}}\right)$$

Target PFAS compounds detected below their respective method detection limits were assumed to be zero. This assumption was taken because assigning a value to a non-detect measurement would bias the DE (i.e., destroying material that was not detected). Although DEs calculated on an individual basis are discussed below, the primary performance criteria were the cumulative DE of the targeted compounds. DE here assumes gas-phase PFAS emissions are negligible, which were not investigated in this study.

#### **Results and Discussion**

PFOS-based AFFF contains high concentrations of fluorine and sulfur, which under supercritical conditions have the potential to form hydrofluoric and sulfuric acids, respectively. These are both corrosive to the equipment and potential health hazards to operators. Without prior knowledge of the material behavior or emission potential, dilution of the AFFF was deemed necessary. Additionally, the AFFF was characterized for COD as a measure of energy within the material to estimate an appropriate influent concentration. COD was found to be  $467,000 \pm 9,000$  mg/L for the AFFF sample sent to 374Water and 475,000 mg/L for the Aquarden sample. The Battelle sample was not tested for COD but

was characterized by estimated PFAS influent concentration. All groups supplemented an oxidant (either liquid or gas) into the system to provide sufficient oxygen to the system. And all groups supplemented -either to the influent or effluent- an alkaline material (e.g., sodium bicarbonate) to reduce the potential for hydrofluoric or sulfuric acid formation within the effluent stream. 374Water also used an alcohol-based fuel supplement (isopropyl alcohol) to boost calorific value of the dilute AFFF waste stream. Targeted PFAS analysis of the influent showed relatively good agreement among the groups and taken along with the COD values, suggested that the three different Lightwater samples were manufactured similarly despite different production years and locations (See Table 1).

In the Aquarden experiment, the reactor temperature was maintained at 590 °C, and reactor operation pressure was 24 MPa. A single test was conducted with influent and effluent samples analyzed for 12 compounds, as shown in Figure 1A and reported in Table S3. The effluent pH and COD were measured periodically from the continuous flow system. As shown in Figure 2, over the entire treatment process, COD decreased by 99.9% from 4,750 to 5.17 mg/L and pH decreased from 12.75 to 3.26 despite the alkaline buffer, indicating oxidation and acid formation. The overall DE was found to be greater than 99%. PFOS and PFOA were reduced from 26,200  $\mu$ g/L to 240  $\mu$ g/L and 930 to 0.14  $\mu$ g/L, respectively. As reported in Table S2, PFOS accounted for 67% of the influent and 98% of the effluent PFAS.

In the Battelle experiment, duplicate tests were conducted to test the repeatability and performance of Battelle's PFAS Annihilator™ system. Results shown in Figure 1B are averages of triplicate sample analyses and duplicate experiments (i.e.,  $3 \times 2 = 6$ measurements). The error bars are the standard deviation of replicates. The averages and standard deviations for targeted PFAS analysis of the influent and effluent are reported in Table S4. PFOS was reduced from 30,599 to 0.33 µg/L in Test 1 and from 30,251 to 0.29 µg/L in Test 2, showing reduction over 99.99% (Table S3). Average total targeted PFAS concentration was reduced from 40,454 to 8.64 µg/L with PFOS, perfluoroheptanoic acid (PFHpA), and perfluorododecanoic acid (PFDoA) being the primary contributors to the effluent concentration. The presence of PFDoA was attributed to the neutralizing agent, added after SCWO treatment to prevent the formation of hydrofluoric acid. As shown in Figure 1B, Sulfonates appear to have been more effectively destroyed than carboxylates. However, these observed concentrations appear to be due to more precise method sensitivity from the Battelle analytical laboratory (i.e., lower reporting limits). Interestingly, perfluorodecanoic acid (PFDA) concentration increased in the effluent of the second test and perfluorotridecanoic acid (PFTrDA) and 6:2 Fluorotelomer sulfonic acid (6:2FTS) were below the method detection limit (MDL) in the influents and above the MDL in the effluent. The 6:2 FTS measured in the effluent is likely due to small background levels in the SCWO system and/or the alkaline neutralization solution. It is critical to note that the analysis by HPLC/MS/MS for PFAS is in the ng/L to µg/L calibration range and so the limit of quantitation (LOQ) for influent samples is many orders of magnitude greater than for the effluent samples (See Tables S2–S4). Thus, detection of compounds in the effluent does not necessarily indicate chemical formations or transformations, though this also cannot be ruled out.

In the 374Water demonstration, a single influent sample and triplicate effluent samples were collected after the system reached a steady-state. The results presented in Figure 1C reflect the average and standard deviation of those triplicates. PFOS was reduced over 99.99%, from 190,000  $\mu$ g/L to 8.57  $\mu$ g/L. Total targeted PFAS decreased from 243,000  $\mu$ g/L to 9.63  $\mu$ g/L over the course of the experiment. PFOS constituted 78% of the influent PFAS and 88% of the effluent concentration. The reactor residence time was 6–8 s, and 25 L of dilute AFFF was processed. Only 9 compounds of the 28 analyzed were detected in the influent (Table S4), similar to other reported studies (Barzen-Hanson et al., 2017; Houtz et al., 2016; Ruyle et al., 2020). This difference in comparison to the other demonstrations is likely due to a combination of different sample materials (Table 1), and variations in analytical laboratory techniques and method detection limits (Tables S2–S4).

In all cases, the effluent ΣPFAS concentrations were greater than EPA drinking water health advisory limit (70 ng/L) or state-level limits (ITRC, 2021). Final disposal of the effluent may require multiple treatments in a circular or re-concentrated stream. Figure 3A presents a conceptual full-scale process, which would recycle the SCWO effluent as the makeup water for AFFF dilution in successive runs until the material has been fully treated. In this scenario, a combination of AFFF material and perhaps AFFF-impacted groundwater could be simultaneously treated. Alternatively, as shown in Figure 3B, SCWO liquid effluent could be sent through a high pressure or reverse osmosis (RO) membrane with the concentrate being sent back for further treatment. RO has previously been shown to remove 99% of PFAS from drinking water (Crone et al., 2019; Flores et al., 2013). Permeate would be free of PFAS (and other pollutants) and so could be discharged.

Table 3 presents a hypothetical scenario of Figure 3A as an example of how the process could work to ultimately reduce PFAS concentrations. In the example, 1,000 L of AFFF are treated at 100x dilution ( $\Sigma PFAS_{influent} = 40,000 \, \mu g/L$ ) at an assumed rate of 10,000 L per day. The dilution is assumed to be with clean water initially, and then a combination of clean water and recycled SCWO effluent is used as the makeup in successive days. Clean water is used in the final two days to flush the system and reduce PFAS levels to a value below the health advisory limit. This scenario does not account for the additional volumes of an alkaline treatment or oxidant. And the scenario assumes 5% water volume loss of the influent (to gas-phase emissions and solids formation) as well as 99% DE, even in Days 12 and 13 where influent PFAS concentrations are much lower. Decreasing the dilution factor to 30 from 100 brings the conclusion of treatment at Day 7 (not shown, Table given in Supplemental Materials Excel file). While reducing the dilution factor would reduce the total volume of material to be treated and shorten treatment time, it may come at costs of decreased reactor lifespan, increased maintenance, and/or increased potential for emissions or by-products. This simple exercise highlights the potential for SCWO as a treatment alternative but neither short- nor long-term evaluations have been published to date.

As described in the PFAS data, Battelle performed two replicate tests of their SCWO system and so, for each test, 7 grab samples of influent and effluent were collected and analyzed for fluoride as an indirect measure of mineralization of organoflourine. ISEs offer rapid analysis but may be subject to interferences by other ions in solution and other matrix effects. To verify the ISE readings, fluoride was also measured by IC. Both ISE and IC

sample data, including quality control and calibration data are given in the Supplemental Materials Excel file. ISE was calibrated at 1, 10, and 100 mg/L according to user manual instructions. Measurements of the fluoride influent and effluent were compared to IC and ISE, where a low bias in the ISE data was observed. To reduce matrix effects, the effluent samples were diluted by 20 times for both ISE and IC. The influent samples, which would be expected to have less fluoride, were not diluted. IC measurements were -1–22% greater than respective ISE measurements of the influent grab samples and 1–29% greater than effluent grab samples. ISE measurements require an ionic strength adjustor (ISA) to dilute the effect of other ions within the solution, which may partially explain the discrepancies observed between the two analytical approaches shown in Figures S4 and S5. The relative standard deviation of the ISE measurements alone were between 3 and 5% for both tests and so the ISE data are shown here in Figure 2. All data are presented in the Excel Supplemental Materials file.

As shown in Figure 2, fluoride increased from  $2.78 \pm 0.14$  mg/L in the influent to  $97.5 \pm 4.04$  mg/L in the effluent, suggesting successful mineralization of organofluorine. A stoichiometric accounting of fluorine in the influent based on the composition and concentrations of the PFAS identified in the targeted analysis was estimated to be 25.9 mg/L. Thus, the total measured fluorine in the dilute AFFF influent was 28.7 mg F/L (2.78 + 25.9 mg F/L). In reality, this would underestimate fluorine because the targeted analysis quantified only 28 compounds, whereas there may be dozens of additional compounds at varying concentrations including other organofluorine compounds that are not PFAS (Barzen-Hanson et al., 2017; Houtz et al., 2016; Place & Field, 2012; Ruyle et al., 2020). The value of this assessment comes from the mass balance comparison to the respective effluent concentrations. In the effluent, ΣPFAS<sub>effluent</sub> = 0.011 mg/L, meaning the fluorine content was 0.006 mg F/L based on the specific PFAS concentrations and molecular weights. The calculations for this stoichiometric mass balance are provided in the Supplemental Materials Excel file. Based on an equimolar (1:1) conversion of fluorine to fluoride, only 25.9 mg F/L would be expected in the effluent due to the detected PFAS in the influent. However, this accounts for only 27% of the 97.5 mg/L measured in the effluent. This indicates a large fraction of the total fluorine in the dilute AFFF was not quantified as either fluoride or contained within one of the 28 targeted PFAS. This speaks to the importance of gathering additional data from assays of total organofluorine analyses, total oxidizable precursors, and/or semi-quantitative non-targeted analyses to more comprehensively assess fluorine content within wastes to be treated/disposed (Dubocq et al., 2019; McDonough et al., 2019; Robel et al., 2017; Weiner et al., 2013). This shows SCWO effectively mineralized fluorine compounds that were not identified, meaning SCWO may effectively treat a range of organofluorine compounds.

Understanding the total cycle and transformative nature of these compounds in a supercritical environment will be helpful in developing this technology and addressing potential operational issues. The generation of fluoride salts is a positive indicator of oxidation but scaling along the reactor walls and tubing can clog the effluent lines. This could become a significant issue to maintain process efficiency as full-scale systems will be required to operate for periods of days, weeks, or perhaps continuously (Marrone, 2013). As these were time-limited studies, long-term reactor performance could not be assessed.

It is known that the step-wise PFAS destruction mechanism of SCWO can produce small volatile organofluorine by-products, such as trifluoromethane, a greenhouse gas, and smaller perfluorocarboxylic acids which can have detrimental health effects (Hori et al., 2008). Likewise, oxidation of PFAS drives the formation of both hydrofluoric and sulfuric acid gases, which are corrosive to SCWO systems (Mitton et al., 2001). Hydrofluoric acid is also highly toxic, which can cause health and safety concerns for workers, as well as the need for emissions control technologies to limit release.

#### **Conclusions**

The intent of this research was to assess the efficacy of SCWO as a technology that could reduce PFAS concentrations from water containing unused AFFF. Three SCWO systems were independently contracted to demonstrate their technology for this purpose. This research was not intended to compare different SCWO systems to each other, as each operated under different conditions, used similar but different PFOS-based AFFF, and employed different analytical labs. Each of the three SCWO systems achieved greater than 99% destruction efficiency of  $\Sigma PFAS$  from dilute AFFF, including 99% destruction of PFOS and PFOA in the liquid phase. The effluent concentrations were still higher than the EPA's drinking water health advisory limit (i.e.,  $0.070~\mu g/L$ ) and state-level limits, and so, repeated treatments may be needed before final disposal. The study quantified specific PFAS and select wastewater characteristics such as fluoride, pH, conductivity, and COD, limiting the conclusions drawn here. The targeted analyses of the liquid-phase, before and after treatment, offer a useful assessment of the technology, which showed positive results. More rigorous examinations of the influent and effluent composition, including gas-phase products are needed.

The presence of PFAS in the effluent not accounted for by the targeted compound analysis affirms that non-targeted analyses, including total oxidizable precursors or total organic fluorine, would be informative understanding potential byproducts and SCWO destruction efficiency (McDonough et al., 2019; Weiner et al., 2013). The potential for air emissions of PFAS and other by-products from SCWO systems requires further study (Horst et al., 2020; Winchell et al., 2020). Understanding operation and maintenance costs, wastewater and air pollution control requirements, and other lifecycle factors would help provide evidence for SCWO's utility as a PFAS treatment technology that is a viable alternative to incineration or landfilling.

# Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

# **Acknowledgements**

The authors wish to thank Aquarden, Battelle, and 374Water for conducting these experiments at the direction of EPA's Office of Research & Development PFAS Innovative Treatment Team. The authors thank Matthew Magnuson of EPA for supplying the AFFF used in the Battelle experiments. The authors thank the Naval Research Laboratory for supplying the AFFF used in the 374Water experiment.

# **Data Availability**

All data, models, and code generated or used during the study appear in the submitted article.

#### References

- Abeln J, Kluth M, Petrich G, Schmieder H.2001. Supercritical Water Oxidation (SCWO): A process for the treatment of industrial waste effluents. International Journal of High Pressure Research, 20(1–6), 537–547.
- Barzen-Hanson KA, Roberts SC, Choyke S, Oetjen K, McAlees A, Riddell N, McCrindle R, Ferguson PL, Higgins CP, Field JA 2017. Discovery of 40 classes of per-and polyfluoroalkyl substances in historical aqueous film-forming foams (AFFFs) and AFFF-impacted groundwater. Environmental science & technology, 51(4), 2047–2057. [PubMed: 28098989]
- Boone JS, Vigo C, Boone T, Byrne C, Ferrario J, Benson R, Donohue J, Simmons JE, Kolpin DW, Furlong ET 2019. Per-and polyfluoroalkyl substances in source and treated drinking waters of the United States. Science of the Total Environment, 653, 359369.
- Carignan S, Clukey K.2020. Destroying Forever Chemicals Ignites N.Y.

  Town's 'Worst Fears' https://news.bloomberglaw.com/environment-and-energy/destroying-forever-chemicals-ignites-n-y-towns-worst-fears. Accessed on: 11/20/2020.
- Cohen LS, Jensen D, Lee G, Ordway DW 1998. Hydrothermal oxidation of Navy excess hazardous materials. Waste Management, 18(6–8), 539–546.
- Coyle C, Ghosh R, Leeson A, Thompson T.2021. US Department of Defense–funded research on treatment of per-and polyfluoroalkyl substance–laden materials. Environmental Toxicology and Chemistry, 40(1), 44–56. [PubMed: 32744747]
- Crone BC, Speth TF, Wahman DG, Smith SJ, Abulikemu G, Kleiner EJ, Pressman JG 2019.

  Occurrence of Per- and Polyfluoroalkyl Substances (PFAS) in Source Water and Their Treatment in Drinking Water. Crit Rev Environ Sci Technol, 49(24), 23592396.
- Darwin RL 2011. Estimated Inventory of PFOS-based Aqueous Film Forming Foam (AFFF). 2011 update to the 2004 report entitled "Estimated Quantities of Aqueous Film Forming Foam (AFFF) in The United States". https://www.informea.org/sites/default/files/imported-documents/UNEP-POPS-POPRC13FU-SUBM-PFOA-FFFC-3-20180112.En.pdf. Accessed on: 08/23/2011.
- Dubocq F, Wang T, Yeung LW, Sjöberg V, Kärrman A.2019. Characterization of the chemical contents of fluorinated and fluorine-free firefighting foams using a novel workflow combining nontarget screening and total fluorine analysis. Environmental science & technology, 54(1), 245–254. [PubMed: 31789512]
- EPA. 2020. Basic Information on PFAS. https://www.epa.gov/pfas/basic-information-pfas. Accessed on: 09/14/2020.
- Flores C, Ventura F, Martin-Alonso J, Caixach J.2013. Occurrence of perfluorooctane sulfonate (PFOS) and perfluorooctanoate (PFOA) in NE Spanish surface waters and their removal in a drinking water treatment plant that combines conventional and advanced treatments in parallel lines. Science of the Total environment, 461, 618–626. [PubMed: 23764674]
- Hodes M, Marrone PA, Hong GT, Smith KA, Tester JW 2004. Salt precipitation and scale control in supercritical water oxidation—Part A: fundamentals and research. The Journal of Supercritical Fluids, 29(3), 265–288.
- Hori H, Nagaoka Y, Sano T, Kutsuna S.2008. Iron-induced decomposition of perfluorohexanesulfonate in sub-and supercritical water. Chemosphere, 70(5), 800–806. [PubMed: 17720216]
- Horst J, McDonough J, Ross I, Houtz E.2020. Understanding and Managing the potential by-products of PFAS destruction. Groundwater Monitoring & Remediation, 40(2), 17–27.
- Houtz E, Wang M, Park J-S 2018. Identification and fate of aqueous film forming foam derived per-and polyfluoroalkyl substances in a wastewater treatment plant. Environmental science & technology, 52(22), 13212–13221. [PubMed: 30339382]

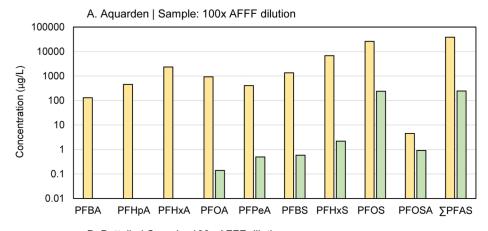
Houtz EF, Higgins CP, Field JA, Sedlak DL 2013. Persistence of perfluoroalkyl acid precursors in AFFF-impacted groundwater and soil. Environmental science & technology, 47(15), 8187–8195. [PubMed: 23886337]

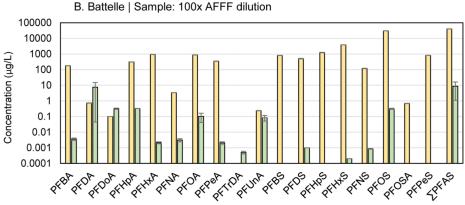
- Houtz EF, Sutton R, Park J-S, Sedlak M.2016. Poly-and perfluoroalkyl substances in wastewater: Significance of unknown precursors, manufacturing shifts, and likely AFFF impacts. Water research, 95, 142–149. [PubMed: 26990839]
- Hu XC, Andrews DQ, Lindstrom AB, Bruton TA, Schaider LA, Grandjean P, Lohmann R, Carignan CC, Blum A, Balan SA, Higgins CP, Sunderland EM 2016. Detection of Poly- and Perfluoroalkyl Substances (PFASs) in U.S. Drinking Water Linked to Industrial Sites, Military Fire Training Areas, and Wastewater Treatment Plants. Environ Sci Technol Lett, 3(10), 344–350. [PubMed: 27752509]
- ITRC. 2021. PFAS Technical and Regulatory Guidance Document and Fact Sheets. https://pfas-1.itrcweb.org. Accessed on: 08/12/2020.
- Kim K, Son SH, Kim K, Kim K, Kim Y-C 2010. Environmental effects of supercritical water oxidation (SCWO) process for treating transformer oil contaminated with polychlorinated biphenyls (PCBs). Chemical Engineering Journal, 165(1), 170–174.
- Loganathan BG, Sajwan KS, Sinclair E, Senthil Kumar K, Kannan K.2007. Perfluoroalkyl sulfonates and perfluorocarboxylates in two wastewater treatment facilities in Kentucky and Georgia. Water Res, 41(20), 4611–20. [PubMed: 17632203]
- Marrone PA 2013. Supercritical water oxidation—Current status of full-scale commercial activity for waste destruction. The Journal of Supercritical Fluids, 79, 283–288.
- Masoner JR, Kolpin DW, Cozzarelli IM, Smalling KL, Bolyard SC, Field JA, Furlong ET, Gray JL, Lozinski D, Reinhart D.2020. Landfill leachate contributes per-/poly-fluoroalkyl substances (PFAS) and pharmaceuticals to municipal wastewater. Environmental Science: Water Research & Technology, 6(5), 1300–1311.
- McDonough CA, Guelfo JL, Higgins CP 2019. Measuring total PFASs in water: the tradeoff between selectivity and inclusivity. Current opinion in environmental science & health, 7, 13–18. [PubMed: 33103012]
- MI EGLE. 2020. Michigan program to collect and dispose of PFAS-containing firefighting foam nets 51,000 gallons. https://www.michigan.gov/egle/0,9429,7-135-3308\_3323-541554--,00.html#:~:text=The Michigan PFAS Action Response,gallons of AFFF for disposal. Accessed on: 09/20/2020.
- Mitton D, Eliaz N, Cline J, Latanision R.2001. An overview of the current understanding of corrosion in SCWO systems for the destruction of hazardous waste products. Materials Technology, 16(1), 44–53.
- Moody CA, Field JA 2000. Perfluorinated surfactants and the environmental implications of their use in fire-fighting foams. Environmental science & technology, 34(18), 3864–3870.
- Munoz G, Labadie P, Botta F, Lestremau F, Lopez B, Geneste E, Pardon P, Devier MH, Budzinski H.2017. Occurrence survey and spatial distribution of perfluoroalkyl and polyfluoroalkyl surfactants in groundwater, surface water, and sediments from tropical environments. Sci Total Environ, 607–608, 243–252.
- Pinkard BR, Shetty S, Stritzinger D, Bellona C, Novosselov IV 2021. Destruction of perfluorooctanesulfonate (PFOS) in a batch supercritical water oxidation reactor. Chemosphere, 279, 130834. [PubMed: 34134433]
- Place BJ, Field JA 2012. Identification of novel fluorochemicals in aqueous film-forming foams used by the US military. Environmental science & technology, 46(13), 7120–7127. [PubMed: 22681548]
- Robel AE, Marshall K, Dickinson M, Lunderberg D, Butt C, Peaslee G, Stapleton HM, Field JA 2017. Closing the mass balance on fluorine on papers and textiles. Environmental science & technology, 51(16), 9022–9032. [PubMed: 28712295]
- Ruyle BJ, Thackray CP, McCord JP, Strynar MJ, Mauge-Lewis KA, Fenton SE, Sunderland EM 2020. Reconstructing the Composition of Per-and Polyfluoroalkyl Substances in Contemporary Aqueous Film-Forming Foams. Environmental Science & Technology Letters, 8(1), 59–65.

Shoemaker J, Tettenhorst D.2020. Method 537.1 Determination of Selected Per- and Polyflourinated Alkyl Substances in Drinking Water by Solid Phase Extraction and Liquid Chromatography/ Tandem Mass Spectrometry (LC/MS/MS). https://cfpub.epa.gov/si/si\_public\_record\_Report.cfm? dirEntryId=343042&Lab=NERL. Accessed on: 08/23/2021.

- Voisin T, Erriguible A, Ballenghien D, Mateos D, Kunegel A, Cansell F, Aymonier C.2017. Solubility of inorganic salts in sub-and supercritical hydrothermal environment: Application to SCWO processes. The Journal of Supercritical Fluids, 120, 18–31.
- Weiner B, Yeung LW, Marchington EB, D'Agostino LA, Mabury SA 2013. Organic fluorine content in aqueous film forming foams (AFFFs) and biodegradation of the foam component 6: 2 fluorotelomermercaptoalkylamido sulfonate (6: 2 FTSAS). Environmental Chemistry, 10(6), 486– 493.
- Winchell LJ, Ross JJ, Wells MJ, Fonoll X, Norton JW Jr, Bell KY 2020. PFAS Thermal Destruction at Wastewater Treatment Facilities: A State of the Science Review. Water Environment Research: a Research Publication of the Water Environment Federation.
- Wu B, Hao S, Choi Y, Higgins CP, Deeb R, Strathmann TJ 2019. Rapid destruction and defluorination of perfluorooctanesulfonate by alkaline hydrothermal reaction. Environmental Science & Technology Letters, 6(10), 630–636.
- Yu J, Hu J, Tanaka S, Fujii S.2009. Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) in sewage treatment plants. Water Res, 43(9), 2399–408. [PubMed: 19359027]

■Influent
■Effluent





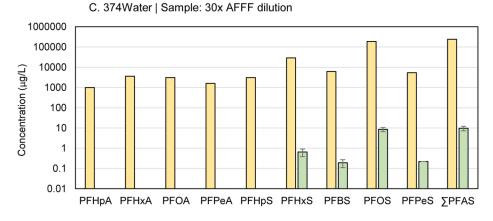


Figure 1.

PFAS quantified in the influent or effluent of the SCWO experiments performed by (A)

Aquarden, (B) Battelle, and (C) 374Water. PFAS are organized alphabetically by detected carboxylic acids and then sulfonic acids. Refer to the supplemental materials for a full list of analyzed PFAS.

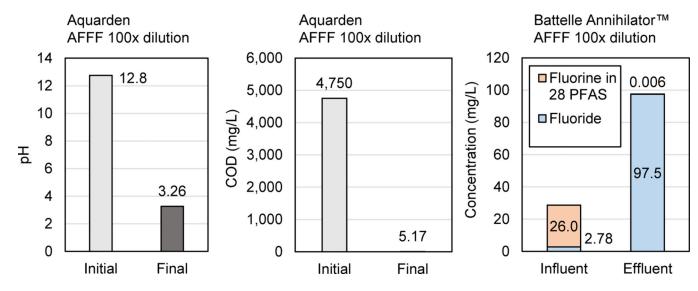


Figure 2.

The observed decrease in pH and COD in the Aquarden samples indicate acid formation but also significant oxidation and organics destruction. Separately, the increased presence of fluoride in the Battelle experiment effluent indicates fluorine mineralization beyond the identified PFAS.

Krause et al. Page 14 Α В Clean Clean water water

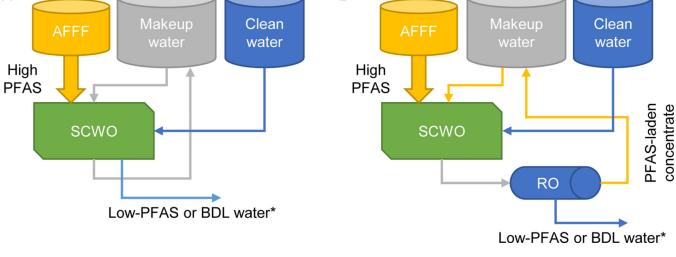


Figure 3. The treatment of AFFF could require successive treatments by SCWO to fully reduce concentrations of PFAS. In proposed scenario A, clean water is used initially and then treated SCWO effluent is used to dilute the next batch to reduce makeup water requirements. In proposed scenario B, a reverse osmosis (RO) system is used to concentrate the PFAS and recycled for further treatment, with the clean effluent free for final disposal. \*BDL – below detection limit.

Table 1.

Details of the AFFF tested in the demonstrations.

SCWO Providers	Product Name	Product Type	Lot Number	Manufacture or Pack Date	Chemical oxygen demand* (mg/L)
374Water	3M Lightwater <sup>™</sup>	FC-203CF	30040	October 1998	467,000
Aquarden	3M Lightwater <sup>™</sup> Alcohol-type concentrate (ATC-plus <sup>™</sup> )	ZF-0002050B	040007	February 1996	475,000
Battelle	3M Lightwater <sup>™</sup>	FC-203CF	30076	May 2001	Not tested

st Chemical oxygen demand (COD) measured from a 1000x dilute sample by Hach colorimetry test.

 Table 2.

 SCWO reaction parameters from the three demonstrations

SCWO Providers	Temperature (°C)	Pressure (MPa)	Reaction residence time (s)	Oxidizer	Alkaline treatment type	Alkaline treatment location
374Water	595	CBI	6–8	Air	СВІ	Influent
Aquarden	590	24	60	Air	КОН	Influent
Battelle	590	CBI	10	CBI	СВІ	Effluent

CBI - confidential business information

**EPA Author Manuscript** 

Table 3.

A hypothetical scenario of SCWO treatment of 100x dilute AFFF.

Effluent/Makeup**	PFAS Concentration (μg/L)	400	384	384	384	384	384	384	384	384	384	384	3.64	0.035
	Volume (L)	005'6	6,500	6,500	9,500	005,6	9,500	6,500	9,500	6,500	9,500	9,500	9,500	9,500
Total Mixture	PFAS Concentration (μg/L)	40,000	38,380	38,365	38,364	38,364	38,364	38,364	38,364	38,364	38,364	38,364	364	3.46
	Volume (L)	10,000	10,000	10,000	10,000	10,000	10,000	10,000	10,000	10,000	10,000	10,000	10,000	10,000
Influent Makeup water  Clean water	PFAS Concentration (µg/L)	0	0	0	0	0	0	0	0	0	0	0	0	0
	Volume (L)	006'6	405	405	405	405	405	405	405	405	405	405	500	500
	PFAS Concentration (µg/L)	0	400	384	384	384	384	384	384	384	384	384	384	3.64
	Volume (L)	0	9,500	9,500	9,500	9,500	9,500	9,500	9,500	9,500	9,500	9,500	9,500	9,500
AFFF	PFAS concentration (µg/L)	$4 \times 10^{6}$	4×10 <sup>6</sup>	4×10 <sup>6</sup>	4×10 <sup>6</sup>	$4 \times 10^{6}$	4×10 <sup>6</sup>	4×10 <sup>6</sup>	4×10 <sup>6</sup>	4×10 <sup>6</sup>	4×10 <sup>6</sup>	4×10 <sup>6</sup>	4×10 <sup>6</sup>	4×10 <sup>6</sup>
	Volume (L)*	100	95	95	95	95	95	95	95	95	95	95	0	0
	AFFF to treat (L)	1,000	006	805	710	615	520	425	330	235	140	45	0	0
	Schedule (Day)	1	2	3	4	5	9	L	8	6	10	11	12	13
	Makeup water Clean water Total Mixture	AFFF to Volume treat (L) * (µg/L) (L) (L) (µg/L) (L) (L) (µg/L) (L) (L) (µg/L) (L) (L) (L) (µg/L) (L) (L) (L) (L) (L) (L) (L) (L) (L) (	AFFF to treat (L)         Volume treat (L)         PEAS (upd.)         PFAS (upd.)	AFFF to treat (L)         Volume (L)*         PEAS (H)         Concentration (H)         Volume (L)*         Concentration (H)         Volume (H) <th>AFFF to treat (L)         Volume (L)         Concentration (L)         Volume (L)         Concentration (L)         Volume (L)         Volume (L)         PFAS (L)         Volume (L)         PFAS (L)         Volume (L)         PFAS (L)         Volume (L)         Volume (L)         Volume (L)         Volume (L)         PFAS (L)</th> <th>AFFT to treat (L)         Volume treat (L)         PEAS         PEAS</th> <th>AFFF to treat (L)         Volume (L)*         PFAS (μg/L)         Volume (L)*         PFAS (L)*&lt;</th> <th>AFFT to treat (L)         Volume (L) (L)*         PEAS (L) (L)         PEAS (L)         PEAS (L) (L)         PEAS (L</th> <th>AFF to treat (L)         PFAS (hg/L)         Volume (hg/L)         Concentration (hg/L)         Volume (hg/L)         PFAS (hg/L)         PFAS</th> <th>AFFF to treat CL)         Concentration treat CL)         PFAS (ug/L)         Volume (ug/L)         PFAS (ug/L)         Volume (ug/L)         PFAS (ug/L)         Volume (ug/L)         FFAS (ug/L)         PFAS (ug/L)         &lt;</th> <th>AFFF to treat CL)         AFFF (math)         AFFF (math)         Volume (concentration)         Volume (mg/L)         Volume (mg/L)         Volume (mg/L)         Volume (mg/L)         Volume (mg/L)         ACCONCENTRATION (L)         Volume (mg/L)         Volume (mg/L)</th> <th>AFFF to treat (L)         Online (reat (L))         AFFF to (lig(L))         Online (lig(L))         Concentration (lig(L))         Volume (lig(L))         PFAS (lig(L))         Volume (lig(L))         PFAS (lig(L))         Volume (lig(L))         PFAS (lig(L</th> <th>AFPF In Load         Per Pass (volume treat)         Per Pass (volume treat)&lt;</th> <th>AFFF to treat trait         Volume (concentration)         Volume (concentration)         Concentration (L)*         Volume (L)*         Concentration (L)*         Volume (L)*         PFAS (L)*</th>	AFFF to treat (L)         Volume (L)         Concentration (L)         Volume (L)         Concentration (L)         Volume (L)         Volume (L)         PFAS (L)         Volume (L)         PFAS (L)         Volume (L)         PFAS (L)         Volume (L)         Volume (L)         Volume (L)         Volume (L)         PFAS (L)	AFFT to treat (L)         Volume treat (L)         PEAS         PEAS	AFFF to treat (L)         Volume (L)*         PFAS (μg/L)         Volume (L)*         PFAS (L)*<	AFFT to treat (L)         Volume (L) (L)*         PEAS (L) (L)         PEAS (L)         PEAS (L) (L)         PEAS (L	AFF to treat (L)         PFAS (hg/L)         Volume (hg/L)         Concentration (hg/L)         Volume (hg/L)         PFAS	AFFF to treat CL)         Concentration treat CL)         PFAS (ug/L)         Volume (ug/L)         PFAS (ug/L)         Volume (ug/L)         PFAS (ug/L)         Volume (ug/L)         FFAS (ug/L)         PFAS (ug/L)         <	AFFF to treat CL)         AFFF (math)         AFFF (math)         Volume (concentration)         Volume (mg/L)         Volume (mg/L)         Volume (mg/L)         Volume (mg/L)         Volume (mg/L)         ACCONCENTRATION (L)         Volume (mg/L)         Volume (mg/L)	AFFF to treat (L)         Online (reat (L))         AFFF to (lig(L))         Online (lig(L))         Concentration (lig(L))         Volume (lig(L))         PFAS (lig(L))         Volume (lig(L))         PFAS (lig(L))         Volume (lig(L))         PFAS (lig(L	AFPF In Load         Per Pass (volume treat)         Per Pass (volume treat)<	AFFF to treat trait         Volume (concentration)         Volume (concentration)         Concentration (L)*         Volume (L)*         Concentration (L)*         Volume (L)*         PFAS (L)*

Assumed as 10,000 L/d based on discussions with vendors regarding a field-scale system and 100x dilution factor.

\*\* Effluent volumes are based on 5% mass loss to gas-phase emissions and solids precipitation. Effluent concentrations assume 99% DE of PFAS. Effluent volumes and concentrations from Dayn are used for the makeup volumes and concentrations on Dayn+1.