# Sonya Lunder

Attached are comments from Sierra Club and Earthjustice regarding the draft EIS for Washington's disposal of AFFF foams.

February 5, 2024

**Via Online Submission**
Washington State Department of Ecology
Attn: Sean Smith
P.O. Box 330316
Shoreline, WA 98133

Re: Aqueous Film-Forming Foam Collection and Disposal Program: Draft Programmatic Environmental Impact Statement

Dear Mr. Smith:

The Sierra Club and Earthjustice respectfully submit these comments on the Washington State Department of Ecology's ("Ecology") Draft Programmatic Environmental Impact Statement ("DEIS") for the planned collection and disposal of Aqueous Film-Forming Foam ("AFFF") from fire stations across the state.

To begin, we support the state's AFFF collection and disposal efforts. For much of the last century, fire stations, airports, military bases, and other facilities used AFFF made from toxic per- and polyfluoroalkyl substances ("PFAS"), a large class of dangerously persistent chemicals. The PFAS in AFFF are associated with an increased risk of cancer, developmental and reproductive harm, immune system toxicity, and other severe health effects. In 2018, the state legislature passed a law to restrict AFFF due to the dangers it poses to firefighter health and because it had contaminated drinking water across the state. Fire stations now have stockpiles of highly toxic PFAS foams. Moreover, because of PFAS' "extreme persistence … [and] mobility,"[1] many treatment and disposal technologies fail to destroy or permanently contain PFAS, but rather continue the cycle of contamination by releasing additional PFAS to the air and water. Washington's AFFF collection and disposal program allows the state to make coordinated and informed decisions about the best methods of PFAS disposal, while relieving individual fire departments of the logistical and financial burdens associated with such disposal.

We also strongly support Ecology's decision to prepare an EIS for its AFFF disposal program. As the Environmental Protection Agency has acknowledged, "significant uncertainties remain" with respect to the effectiveness and environmental impact of traditional waste disposal methods – landfilling, incineration, and deep-well injection – when applied to PFAS-containing wastes.[2] AFFF disposal presents substantial environmental and health risks, and the EIS process

[1] Carol F. Kwiatkowski et al., *Scientific Basis for Managing PFAS as a Chemical Class*, 7 Env't Sci. & Tech. Letters 532-543 (2020), DOI: 10.1021/acs.estlett.0c00255.
[2] EPA, *Interim Guidance on the Destruction and Disposal of Perfluoroalkyl and Polyfluoroalkyl Substances and Materials Containing Perfluoroalkyl and Polyfluoroalkyl Substances* at 4 (Dec. 2020), https://www.epa.gov/system/files/documents/2021-11/epa-hq-olem-2020-0527-0002_content.pdf.

offers an opportunity to carefully evaluate those impacts and to identify the safest and most effective disposal option.

However, Ecology's DEIS fails to provide the "impartial discussion of significant environmental impacts and … reasonable alternatives" that the State Environmental Policy Act ("SEPA") requires.[3] Ecology selected a private contractor with close ties to the hazardous waste incineration industry to prepare the EIS, a conflict that raises serious questions about the objectivity of the underlying analysis. The DEIS understates the harms associated with PFAS landfilling and incineration, declaring those impacts to be minimal based on a misapplication of industry test data while ignoring substantial evidence of data gaps and health risks. Ecology also understates the impacts of PFAS disposal on environmental justice communities, focusing exclusively on communities in the immediate vicinity of disposal sites even though PFAS are highly mobile and are known to cause disproportionate harms to lower income communities, Indigenous communities, and communities of color nationwide. Finally, Ecology fails to seriously consider several advanced PFAS destruction alternatives that have the potential to eliminate or reduce the impacts associated with traditional disposal technologies, such as super critical water oxidation ("SCWO") – which has been used to treat AFFF in other locations – and closed-loop Hydrothermal Alkaline Treatment ("HALT") technology developed by Washington-based Aquagga, the winner of EPA's Innovative Ways to Destroy PFAS Challenge.[4]

The impacts of Ecology's PFAS disposal decisions extend far beyond the 59,000 gallons of AFFF covered by the current collection and disposal program. In addition to fire stations, AFFF is also stored at ferry terminals, airports, refineries, and other industrial facilities across the state, and Ecology has acknowledged the potential for expanded collection and disposal efforts in the future. More broadly, other states, municipalities, and private parties are struggling with similar issues concerning PFAS disposal and are searching for better solutions. Ecology has a statutory obligation to carefully evaluate the environmental and health impacts of its PFAS disposal program, and its analysis and selection of alternatives has the potential to inform future decisions and move the nation towards more protective PFAS disposal technologies. In its final EIS, we urge Ecology to fully account for the risks associated with PFAS incineration as well as the potential benefits of alternative destruction technologies.

## I. SEPA Requires Ecology to Carefully Evaluate the Environmental Impacts of Its AFFF Collection and Disposal Program, Including Alternative Disposal Options

SEPA "sets forth a state policy of protection, restoration and enhancement of the environment."[5] "The most important aspect of SEPA is full consideration of environmental values … and this policy is carried out by the EIS procedure."[6] The preparation of an EIS

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[3] Wash. Admin. Code § 197-11-400.
[4] EPA, Innovative Ways to Destroy PFAS Challenge: Winners, https://www.epa.gov/innovation/innovative-ways-destroy-pfas-challenge#Winners.
[5] *Polygon Corp. v. City of Seattle*, 578 P.2d 1309, 1312 (1978); *see also* Wash. Rev. Code § 43.21C.010; *Leschi Imp. Council v. Wash. State Highway Comm'n*, 525 P.2d 774, 781 (1974) (SEPA "indicates in the strongest possible terms the basic importance of environmental concerns to the people of this state.")
[6] *Sisley v. San Juan County*, 569 P. 2d 712, 718 (1977) (citation omitted).

"assures a full disclosure and consideration of environmental information prior to the [commencement] of the project."[7]

SEPA requires an EIS to "provide impartial discussion of significant environmental impacts and … inform decision makers and the public of reasonable alternatives, including mitigation measures, that would avoid or minimize adverse impacts or enhance environmental quality."[8] The test for significance of an environmental impact is "a reasonable likelihood of more than a moderate adverse impact on environmental quality."[9] This fact- and context-specific inquiry "does not lend itself to a formula or quantifiable test,"[10] but rather is "best determined 'on a case-by-case basis guided by all of the policy and factual considerations reasonably related to SEPA's terse directives."[11] Those factors must be considered in light of SEPA's underlying policy of maintenance, enhancement and restoration of the environment.[12]

SEPA also requires an EIS to contain a detailed discussion of reasonable alternatives to the agency's proposed action.[13] SEPA's administrative rules provide that an EIS must consider as alternatives those "actions that could feasibly attain or approximate a proposal's objectives, but at a lower environmental cost or decreased level of environmental degradation."[14] "The required discussion of alternatives to a proposed project is of major importance, because it provides a basis for a reasoned decision among alternatives having differing environmental impacts."[15]

Finally, SEPA "confers substantive authority to the deciding agency to act on the basis of the impacts disclosed."[16] SEPA is not purely an informational or procedural statute; it is intended to inform and promote decisions that further the statute's aims of environmental and health protection.

## II. Ecology Must Investigate and Disclose the Potential Conflicts Involving the Contractor It Selected to Prepare the EIS

To prepare the DEIS, Ecology retained TRC Companies ("TRC"), a private consultant with longstanding ties to the hazardous waste incineration industry.[17] By its own account, TRC represents and "produce[s] bottom-line results for our commercial, solid and hazardous waste

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[7] *Id.; see also Asarco Inc. v. Air Quality Coal.*, 601 P.2d 501, 512 (1979) (SEPA demands a "thoughtful decision-making process").
[8] Wash. Admin. Code § 197-11-400.
[9] *Id.* § 197-11-794.
[10] *Id.*
[11] *Klickitat County Citizens Against Imported Waste v. Klickitat County*, 860 P.2d 390, 398-99 (1993) (citations omitted); *Cheney v. City of Mountlake Terrace*, 552 P.3d 184, 188-89 (1976).
[12] *Polygon Corp*., 576 P.2d at 1312.
[13] Wash. Rev. Code § 43.21C.030(c)(iii).
[14] Wash. Admin. Code § 197-11-440(5)(b).
[15] *Weyerhaeuser v. Pierce County*, 873 P.2d 498, 504-05 (1994).
[16] *Polygon Corp.*, 578 P.2d at 1312.
[17] DEIS at 1-3 ("During the summer of 2021, Ecology completed a Request for Quotes and Qualification bid process and selected TRC to prepare the EIS report.")

clients."[18] For years, TRC has also been an associate member of the Coalition for Responsible Waste Incineration ("CRWI"), a trade association created in the 1980s by Dow, 3M, Monsanto and other hazardous waste generators to promote hazardous waste incineration.[19] CRWI members currently include hazardous waste incineration companies such as Clean Harbors Environmental Services, Heritage Thermal Services, Ross Incineration Services, and Veolia ES Technical Solutions, as well as numerous chemical and pesticide manufacturers.[20] TRC is listed as an "associate member," a membership tier designed for "companies that provide goods and services to the hazardous waste combustion industry."[21]

TRC's close ties to the incineration industry raise serious concerns about the objectivity of the DEIS, and in particular Ecology's assessment of the impacts of incinerating AFFF. The mission statement of CRWI states that "high temperature combustion is an integral part of the solution to the waste management challenge facing hazardous waste generators today" and that "for many wastes … combustion remains the safest, most appropriate treatment method."[22] CRWI has openly lobbied the White House Office of Science and Technology Policy to endorse PFAS incineration, which CRWI erroneously claimed to be the "only … commercially available method for destroying PFAS compounds."[23] TRC's membership in a trade organization that exists to encourage hazardous waste incineration, and that declared has incineration to be the "only" viable option for PFAS destruction, raises serious questions about whether TRC can even-handedly assess the environmental and health impacts of PFAS incineration and other disposal methods, as SEPA requires.

Ecology must immediately disclose the extent of TRC's role in the preparation of the DEIS, as well as any screening that Ecology conducted to evaluate potential conflicts of interest before retaining TRC to work on the EIS. While SEPA authorizes Ecology to use outside consultants to prepare an EIS, Ecology remains responsible for "assur[ing] that the EIS is prepared in a professional manner."[24] Here, Ecology failed to perform that required oversight. As described in greater detail below, the DEIS's assessment of the risks from PFAS incineration rely heavily on a single test conducted by Clean Harbors, a hazardous waste incinerator and CRWI member. The DEIS also identifies two Clean Harbors incinerators as potential disposal locations, without any discussion of the substantial gaps in Clean Harbors' testing or Clean Harbors' relationship to TRC. The public has the right to know whether TRC has any current or past contractual relationship with Clean Harbors or any other hazardous waste management company, and Ecology must ensure the "impartial[ity]" of the EIS by more closely scrutinizing TRC's analysis of incineration and other disposal methods, as set forth in greater detail below.[25]

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[18] TRC, Solid Waste Management, https://www.trccompanies.com/services/remediation-and-materials-management/solid-waste-management/.
[19] CRWI: Meeting a Vital Need, https://www.crwi.org/textfiles/about.htm; *see also, e.g.,* CRWI Update: December 31, 2023, https://www.crwi.org/textfiles/updec23.pdf (listing TRC as an "associate member" of CRWA).
[20] CRWI Update: December 31, 2023, https://www.crwi.org/textfiles/updec23.pdf.
[21] CRWI, CRWI Membership, https://www.crwi.org/textfiles/why.pdf.
[22] CRWI, Meeting a Vital Need, https://www.crwi.org/textfiles/about.htm.
[23] CRWI, Comments on Request for Information; Identifying Critical Data Gaps and Needs to Inform Federal Strategic Plan for PFAS Research and Development (Aug. 29, 2022), https://www.crwi.org/textfiles/ostp22.pdf; *see also* pp. 4-9 *infra* (describing the risks associated with PFAS incineration).
[24] Wash. Admin. Code § 197-11-420(2).
[25] *Id.* § 197-11-794.

## III. Ecology Overlooks Significant Environmental and Health Risks Associated With PFAS Incineration

The DEIS badly understates the concerns regarding the safety of incineration as a disposal option for PFAS. Ecology fails to critically assess industry data effectiveness of PFAS incineration, overlooks potentially harmful byproducts of incineration, and presents an unrealistic view of the ability of compliance-plagued hazardous waste incinerators to operate at ideal conditions when incinerating PFAS stockpiles.

Ecology erroneously asserts that "[i]ncineration is one of only a few technologies that can potentially destroy PFAS … reducing future risks to public health and adverse effects on the environment."[26] The only cited support for that claim is a study conducted by a hazardous waste incinerator, without any government oversight, that purportedly found "destruction of 99.9999 percent of common legacy PFAS compounds."[27] But that study did not, and could not, establish the safety of PFAS incineration, since it did not measure the PFAS and other byproducts that are most likely to be produced during the incineration process.

Destruction and removal efficiency ("DRE") compares the levels of certain target PFAS in the feedstock waste with the levels of those chemicals in stack emissions following incineration. But it doesn't account for the formation of harmful byproducts that may be generated as result. The incineration of PFAS releases highly reactive fluorine molecules that can form a variety of harmful fluorinated compounds, including but not limited to new PFAS. As the Department of Energy and U.S. Environmental Protection have acknowledged, "incineration can result in the formation of other PFAS compounds in [stack] emissions," as well as other harmful products of incomplete combustion ("PICs") "which may become problematic in their own right."[28] A "destruction" method that merely converts one PFAS to another or generates toxic PICs does not "reduc[e] future risks to public health and adverse effects on the environment."[29]

### A. The EIS Relies Exclusively on an Industry-Funded Study That Didn't Examine Harmful Byproducts of Incineration

The incineration destruction figure cited by Ecology comes from a single test conducted at Clean Harbors' Aragonite, Utah incinerator in July 2021.[30] This study measured PFAS emissions using EPA Other Test Method 45 ("OTM-45") for air, which is capable of detecting

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[26] DEIS at 2-21.
[27] *Id.*
[28] *See* Dep't of Energy, DOE Commercial Potential Evaluation (CPE) Report: PFAS in Wastewater at 30 (Aug. 2023), https://science.osti.gov/-/media/sbir/pdf/Application_Resources/2023/CPE-PFAS-Final-Report.pdf; EPA, Technical Brief: Per- and Polyfluoroalkyl Substances (PFAS) Incineration to Manage PFAS Waste Streams (Feb. 2020), https://www.epa.gov/sites/default/files/2019-09/documents/technical_brief_pfas_incineration_ioaa_approved_final_july_2019.pdf (findings that PFAS "can result in the formation of smaller PFAS products, or products of incomplete combustion (PICs), which may not have been researched and thus could be a potential chemical of concern.")
[29] DEIS at 2-21.
[30] *See* EA Eng'g, Sci. & Tech. and Montrose Envt'l Gr., *Report on PFAS Destruction Testing Results at Clean Harbors' Aragonite, Utah Hazardous Waste Incinerator* (Nov. 2021) ("Clean Harbors Test Report").

approximately 50 semi-volatile and polar PFAS, less than 1% of the PFAS class.[31] But PFAS incineration is also expected to produce a variety of volatile, nonpolar PFAS, which are not detected by OTM-45.[32] Clean Harbors thus cannot say whether its alleged destruction of PFOA and PFOS is actually creating new PFAS that it failed to measure its pilot study.[33]

Notably, while Washington presents the data on PFAS incineration as clear cut, a PFAS incineration scientist commissioned by Clean Harbors to review its study data raised concerns about the formation of breakdown products and the low recovery of fluorine in the form of hydrofluoric acid.[34] The challenges of documenting the ultimate fate of the fluorine molecules released during incineration led the scientist to conclude, "[i]n summary, development of better analysis methods organic and inorganic fluoride are needed to support PFAS-performance testing at the full scale."[35]

EPA recently released a new draft test method for air, OTM-50, which will capture up to 30 highly volatile, nonpolar PFAS, the very type of breakdown products expected to be produced by PFAS incineration. This method will allow future experimental and observational studies to more fully report products of incomplete combustion of PFAS materials.[36] But it was not used by Clean Harbors or in any of the studies referenced in the DEIS, precluding a full assessment of the effectiveness and impacts of PFAS incineration.

### B. A Recent Study by EPA Scientists Confirms the Potential Generation of PFAS and Toxic Byproducts During PFAS Incineration

In July 2023, a publication by EPA scientists ("Shields et al.") reviewed the safety and efficacy of PFAS incineration in a trial study at EPA's Rainbow research combustor.[37] This study also used EPA method OTM-45 to measure the destruction of PFAS from AFFF

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[31] *See* Suzanne Yohannan, *EPA Eyeing Paired Issuance of PFAS Disposal Guidance, Air Test Method*, Inside PFAS Policy (Dec. 11, 2023) ("OTM-45 … measures approximately 50 semi-volatile per- and polyfluoroalkyl substances (PFAS) and polar PFAS in air emissions"); Nat'l Inst. of Env't Health Sci., *Per- and Polyfluoroalkyl Substances (PFAS)*, https://www.niehs.nih.gov/health/topics/agents/pfc ("PFAS are a group of nearly 15,000 synthetic chemicals").

[32] Suzanne Yohannan, *EPA Eyeing Paired Issuance of PFAS Disposal Guidance, Air Test Method*, Inside PFAS Policy (Dec. 11, 2023); *see also* Jeff Ryan, EPA Off. of Res. and Dev., Presentation to EPA Region 4 Spring Grants/Planning Meeting at Slide 13 (May 23, 2019), https://cfpub.epa.gov/si/si_public_file_download.cfm?p_download_id=538634&Lab=NRMRL

[33] *See, e.g.,* Clean Harbors Test Report at 7-3 ("Given that laboratory standards enabling targeted analysis exist for only about 50 of the thousands of extant PFAS, other analytical tools such as non-targeted PFAS analysis and Total Organic Fluorine … could be employed in the future to more completely characterize the PFAS profiles in the waste and other process streams, as well as in the stack gas.")

[34] Phil Taylor & Associates, LLC, *Final Report: Assessment of a Report on PFAS Destruction Testing Results at Clean Harbors' Aragonite, Utah Hazardous Waste Incinerator. Prepared for Clean Harbors Environmental Services, Inc.* (Jan 26, 2022) (a copy of this report is attached to these comments as **Exhibit A**).

[35] *Id.*

[36] EPA, Other Test Method 50 (OTM-50): Sampling and Analysis of Volatile Fluorinated Compounds from Stationary Sources Using Passivated Stainless-Steel Canisters (2024), https://www.epa.gov/system/files/documents/2024-01/otm-50-release-1_0.pdf

[37] Erin P Shields et al., *Pilot-Scale Thermal Destruction of Per-and Polyfluoroalkyl Substances in a Legacy Aqueous Film Forming Foam*, 3 Env't Sci. & Tech Eng'g. 1308-1317 (2023), DOI:10.1021/acsestengg.3.c00098 (a copy of this study is attached to these comments as **Exhibit B**).

compounds, while using but nontarget analysis of OTM-45 cannisters to identify about 10 fluorochemicals as breakdown products. These include fluoroform, pentafluoroethane, 1H-hepafluoropropane, and 1H perflouroheptane, which are greenhouse gases with long residency times in the atmosphere. Of particular importance was the observation that PFAS breakdown and byproduct formation is highly temperature dependent, with notable performance declines below experimental temperatures of 1000° C. At 970° C less than 99.99% of two shorter chain PFAS chemicals (PFBA and PFPeA) were destroyed. At 870° C cannisters included at least 15 measurable breakdown products at concentrations ranging from 0.4 to 903 mg/m$^3$. The authors conclude: "These results suggest that [destruction efficiency] alone may not be the best indication of total PFAS destruction, and additional PIC characterization may be warranted."[38]

The Shields study also focused on steady-state combustor operations, noting that the real-world operating conditions of a hazardous waste incinerator will inevitably include temporary disruptions to oxygen and temperature depressions.[39] The authors state the "time dependent behavior of PFAS in [hazardous waste incinerators] and other batch fed systems will depend on the system's ability to smooth these transients and maintain high temperatures," concluding, "[m]ore research into rotary kiln systems and full-scale incinerators is needed."[40] Multiple studies have detected elevated PFAS concentrations in the vicinity of operating incinerators or thermal oxidizers designed to destroy gaseous PFAS waste, raising further concerns about the impacts of PFAS incineration.[41] Ecology failed to consider those studies or address those potential impacts in its DEIS.

### C. Commercial Incinerators, including Clean Harbors Aragonite, Do Not Routinely Operate the Under the Ideal Combustion Conditions Tested by Clean Harbors and Shield

The Shields study highlights the role that temperature and residency time of incinerators play in the effectiveness of thermal destruction of PFAS. Thermal breakdown is dependent on proper residency time, temperature and turbulence inside the incinerator chamber. But neither Shields nor Clean Harbors tested incinerators during their real world, commercial operations. Instead, those tests were conducted under carefully controlled conditions; EPA and Clean Harbors aimed for temperatures and retention times at the upper edge of commercial operating efficiency and manipulated the feedstock and operating conditions to attain desired temperature ranges and retention times. Notably, both of the Clean Harbors incinerators referenced in the EIS

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[38] *Id.* at 1308.
[39] *Id.* at 1314-15.
[40] *Id.* at 1315.
[41] *See* Kaitlin V. Martin et al., *PFAS Soil Concentrations Surrounding a Hazardous Waste Incinerator in East Liverpool, Ohio, An Environmental Justice Community*, 30 Env't Sci. Pollution Res. Int'l 80643-80654 (June 10, 2023), doi: 10.1007/s11356-023-27880-8 (detecting elevated PFAS levels in the soil surrounding the Heritage Thermal Services incinerator in East Liverpool, OH); Bennington College Press Release, *First in the Nation Testing Reveals Toxic Contamination in Soil and Water Near Norlite Incinerator* (Apr. 27, 2020), https://www.bennington.edu/sites/default/files/sources/docs/Norlite%20News%20Release%20%5Bdb%20final%20updated%5D.pdf (detecting elevated PFAS levels in the soil and groundwater surrounding Norlite incinerator in Cohoes, NY); Jiaqi Zhou et al. *Legacy and Emerging Airborne PFAS Collected on PM2.5 Filters in Close Proximity to a Fluoropolymer Manufacturing Facility.* 12 Env't Sci.: Processes & Impacts 2272-2283 (2022), https://pubs.rsc.org/en/content/articlelanding/2022/em/d2em00358a/unauth (measuring PFAS in the air near the Chemours Fayetteville NC facility, which uses a thermal oxidizer to treat gases containing PFAS)

– in Aragonite, Utah and Kimball, Nebraska – have already received and incinerated large volumes of AFFF and other PFAS-containing waste, but they did not measure their releases of PFAS during those operations.[42]

Ecology states that hazardous waste incinerators have administrative controls like permit conditions, operating and maintenance procedure and trained personnel to ensure incineration happens under carefully controlled conditions.[43] In reality, however, incinerators like Clean Harbors' Aragonite facility routinely violate permit requirements.

The Aragonite facility has a long history of environmental non-compliance, including "incinerating mercury-containing wastes that are prohibited from incineration," "incinerating lead-containing wastes that are prohibited from incineration," "failing to properly categorize wastes and/or document the categorization of wastes," "failing to calibrate monitoring instruments," and dozens of other violations.[44]

The other Clean Harbors incinerator considered by Ecology, in Kimball, Nebraska, has a similarly checkered compliance history, as documented in the accompanying analysis of several hazardous waste incinerators' environmental violations.[45] In 2020, EPA and Clean Harbors reached a settlement agreement resolving alleged violations related to emissions limits and reporting, including "failure to manage and contain hazardous wastes; failure to comply with air emission limits; failure to comply with chemical accident prevention safety requirements; and failure to timely report use of certain toxic chemicals.[46] Our analysis of publicly available records also indicated the facility had at least 105 total violations of emission limits, operating permit limit ("OPLs"), or other permit terms.[47] The facility reported at least 57 instances where it exceeded the emissions standard for total hydrocarbon content ("THC").[48] Of these, two were expressly linked in the facility's reports to problems maintaining adequate minimum temperature for the combustor.[49] There was one additional reported violation during this span where the facility violated its minimum temperature requirement.[50] The facility also documented ten exceedances of the particulate matter standard.[51]

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[42] According to EPA, Clean Harbors Aragonite burned more than 60,000 kg of PFAS between January 2023 and September 2023, at least 460,000 kg since 2018, while Clean Harbors in Kimball burned at least 237,000 kg of PFAS waste between 2018 and 2023. *See* EPA, PFAS Analytical Tools (2024), https://awsedap.epa.gov/public/extensions/PFAS_Tools/PFAS_Tools.html.

[43] DEIS at 3.1-8.

[44] Utah Dep't of Env't Quality, *Compliance History, for the Clean Harbors Aragonite, LLC Facility* (Aug. 25, 2021), https://documents.deq.utah.gov/waste-management-and-radiation-control/facilities/clean-harbors/aragonite/DSHW-2014-018229.pdf.

[45] *See* Sierra Club and Earthjustice, *Incineration is Not a Safe Disposal Method for PFAS* (2022) (a copy of this analysis is attached as **Exhibit C**).

[46] EPA Press Release, *United States and State of Nebraska Reach Settlement with Clean Harbors Environmental Services Inc. for Violations of Multiple Environmental Laws* (Aug. 31, 2020), https://www.epa.gov/newsreleases/united-states-and-state-nebraska-reach-settlement-clean-harbors-environmental-services

[47] Exhibit C at 9.

[48] *Id.*

[49] *Id.*

[50] *Id.*

[51] *Id.*

Those reports may actually underrepresent the facility's compliance problems. A separate report related to leak-detection also included reporting of startup/shutdown events, revealing incidents that are not reflected in the list of OPL and emission limit violations reported for 2019. Summary reports filed by the facility show that, during 2019, the facility was in "upset" mode and reporting excess THC emissions for a total of 45.7 hours. Of this total, 27.25 hours were attributable to "startup/shutdown" events with the remaining being attributable to "process problems." The facility reported an additional 0.4 hours of excess emissions related to O2-related upset conditions. EPA has characterized the Kimball, NE incinerator as a "significant noncomplier" with the Resource Conservation and Recovery Act ("RCRA") in every quarter since 2021.[52]

Those violations are not unique to Clean Harbors; other hazardous waste incinerators have similar number and types of permit violations, including explosions and major malfunctions.[53] It is common for air permits to exempt pollutant limits during periods of Start-up, Shut-down, and Malfunction ("SSM") events.[54] Given the gaps in the available test data, the potential releases of PFAS and other toxic byproducts from hazardous waste incinerators, and the long history of permit violations by Clean Harbors and others, Ecology cannot reasonably conclude that PFAS incineration presents "minimal" impacts on public health and the environment.

## IV. Ecology Overlooks Significant Environmental and Health Risks Associated With Landfill Disposal of PFAS

Ecology also understates the impacts associated with the disposal of AFFF at hazardous waste landfills in Idaho and Nevada. Without considering the latest research on potential PFAS releases from landfills, Ecology asserts that "[t]he risk of PFAS release [from landfills] is very low" and "[t]he consequences [of such releases] would be insignificant."[55] These conclusions are not supported by the record.

Due to their volatility and mobility in water, substantial volumes of PFAS are projected to be lost from landfills each year. A recent review paper authored by EPA scientists ("Tolaymat et al") estimated that 1,233 kg of landfills are released annually via leachate and landfill gas, or approximately 15 percent of the quantity of PFAS shipped to U.S. landfills on a given year.[56] More than 130 kg of those PFAS releases are projected to be uncontained and released directly to environment.[57]

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[52] EPA, Enforcement and Compliance History Online, *Detailed Facility Report*: *Clean Harbors Environmental Services Inc. 2247 S. Highway 71, Kimball, NE*, https://echo.epa.gov/detailed-facility-report?fid=110041638458&ej_type=sup&ej_compare=US (last visited Feb. 4, 2024).

[53] *See* Earthjustice et al., *Vestiges of Environmental Racism* (2021) https://earthjustice.org/wp-content/uploads/earthjustice_ca-incinerator-report_20211108.pdf; EPA, *Complaint and Notice of Opportunity to Request a Hearing*, Docket No. CAA-02-2020-1004 (2020), https://dec.ny.gov/environmental-protection/waste-management/hazardous-waste/norlite-llc/enforcement-history

[54] *See* 40 C.F.R. §§ 60.2918, 60.3025.

[55] DEIS at 3.1-14 to 3.1-15.

[56] Thabet Tolaymat et al, *A Critical Review of Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS) Landfill Disposal in the United States*, 905 Sci. of the Total Env't 167185 at *1 (2023) DOI: 10.1016/j.scitotenv.2023.167185 (a copy of this study is attached as **Exhibit D**).

[57] *Id.*

While Ecology has considered solidifying AFFF before sending it to a hazardous waste landfill, evidence suggests that PFAS solidification doesn't fully immobilize the chemicals. One study reports that the "[o]verall immobilization of PFAS analytes that were detectable in the leachate from two PFAS contaminated soils ranged from 87.1% to 99.9%"[58] Ecology must evaluate the possibility that some PFAS escape from the solidified AFFF and enter the air, soil, or groundwater.

### A. PFAS Leach from Landfills, Creating the Need for Perpetual Management of Liquid Waste and the Likelihood of Uncontained PFAS Releases

Ecology glosses over concerns about PFAS washing out of landfills in the liquid waste or "leachate," stating that "leaching of PFAS compounds would be detected by leak detection system and PFAS compounds would be captured by the leachate collection and recovery system."[59] Ecology further states "the consequences [of landfilling] would be insignificant because, as described above, the partial pressure of PFAS in AFFF in the groundwater would be very low and the resulting ambient PFAS concentrations would be much less than the significance criteria."[60] But studies have estimated a significant amount of uncaptured PFAS leachate, and landfills often fail to destroy or permanently contain the PFAS in the leachate that they do capture.

PFAS are commonly detected in landfill leachate, across many different geographic locations and landfill types. One paper in particular measured PFAS in leachate from a landfill housing only municipal solid waste incinerator ash. The ash was residues of materials that were burned at 950º C, yet the landfill leachate contained more than 2000 ng/L of PFAS.[61] This indicates both that notable amounts of PFAS remained after incineration and were soluble in landfill liquids.

PFAS also leach from hazardous waste landfills. An analysis of 29 leachate samples from two California hazardous waste landfills measured average PFAS concentrations of 68,000 ng/L, with a maximum measured value of 377,000 ng/L.[62] Given this evidence that PFAS will leach from even solidified AFFF waste, Washington must more carefully consider the management and fate of leachate generated from any landfill accepting PFAS waste.

The options for perpetual leachate collection and safe disposal are far more complex than the disposal of a single containerized shipment of AFFF waste. Some landfills send leachate to wastewater treatment plants that are ill-equipped to remove PFAS compounds.[63] Others return

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[58] E. Barth et al., *Investigation of an Immobilization Process for PFAS Contaminated Soils*, 296 J. Env't Mgmt., 113069 (2021), DOI: 10.1016/j.jenvman.2021.113069.
[59] DEIS at 3.1-14.
[60] *Id.*
[61] Tolaymat, *supra* note 60, at *7 (citing S Liu et al, *Perfluoroalkyl Substances (PFASs) in Leachate, Fly Ash, and Bottom Ash from Waste Incineration Plants: Implications for the Environmental Release Oof PFAS*, 795 Sci. of the Total Env't 148468 (2021)).
[62] *Id.* at *8 (citing California Water Boards's GeoTracker PFAS Map).
[63] *Id.* at *11 ("In the US, most landfill leachate generated from RCRA-permitted landfills is managed off-site … represent[ing] a significant flux of PFAS leaving the landfill.")

leachate into the landfill for perpetual circulation, increasing the likelihood that the PFAS will eventually leach into the environment. We are only aware of one instance in which a landfill is exploring the use of on-site advanced destruction technology to destroy PFAS in leachate liquids.[64] Ecology did not consider that leachate treatment option in the DEIS.

### B. PFAS Volatilize From Landfills and are not Destroyed by Methane Gas Flares

The DEIS also failed to adequately account for landfills' potential releases of PFAS to the air. The DEIS describes the possibility of PFAS volatilizing from solidified AFFF as "very low."[65] However, data on the failure rate for PFAS solidification should be also considered in context of new information about PFAS volatilization from landfills. The recent Tolaymat landfill review paper estimated that about 470 kg of PFAS per year up volatilizes into air annually from U.S. landfills.[66] The amount of landfill gas generation depends on the amount of moisture and microbial activity in the landfill. Injecting landfill leachate back into the landfill for circulation would increase both the PFAS and the moisture content of the landfill.

About three quarters of the landfill gas is captured or collected each year, with approximately 25% released to the air as fugitive emissions.[67] For the gas that is captured, even when landfills are equipped with flares to burn landfill gas the flare temperatures of 650-850º C are lower than the temperatures that would be expected to destroy gaseous PFAS. Instead of assuming "low" releases from the volatilization of PFAS from landfills, Ecology must consider the latest research and estimate the potential for air releases over the centuries that landfilled AFFF would remain on site. Moreover, since EPA is still years away from regulating any PFAS as hazardous waste, Ecology cannot assume that existing landfill permits and federal regulations will be sufficient to prevent significant adverse impacts from PFAS in leachate or landfill gas.

## V. Ecology Understates the Environmental Justice Impacts Associated with PFAS Landfilling and Disposal

The DEIS also understates the environmental justice impacts associated with PFAS incineration and landfilling, asserting that the risks associated with those disposal options are "low to insignificant."[68] But Ecology underestimates both the likelihood of PFAS releases from those disposal options and the impacts of such releases on environmental justice communities who already bear a disproportionate burden of existing PFAS contamination.

As Ecology acknowledges, "[t]he first step in an EJ assessment is to identify the study area."[69] The DEIS defines the study area too narrowly, focusing solely on effects within a 10-mile radius of AFFF storage locations or potential disposal sites.[70] While that approach may be appropriate for pollutants with primarily localized impacts, it fails to capture the sweep of highly

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[64] EPA, Town of Conway Landfill Leachate Treatment Emerging Contaminants Project (2002), https://www.epa.gov/system/files/documents/2022-11/Conway-CWSRF-Emerging-Contaminants.pdf
[65] DEIS at 3.1-13
[66] Tolaymat, *supra* note 60, at 1.
[67] *Id.* at 13.
[68] DEIS at 3.11-20 to 3.11-22.
[69] *Id.* at 3.11-2.
[70] *Id.* at 3.11-20 to 3.11-22.

mobile and persistent chemicals like PFAS. PFAS that are emitted by an incinerator, that volatize from a landfill, or that leach into groundwater do not remain within a 10-mile radius of their release point. They spread long distances through the air, water, and soil, leaving a trail of contamination that extends from the peaks of Mount Everest to the depths of the ocean floor.[71] The communities that face the greatest risks from PFAS releases are not merely those nearest to the release site, but also those who are already exposed to PFAS contamination and are more susceptible to harm from further exposures.

As with many toxic pollutants, PFAS disproportionately harm lower income communities and communities of color. Low income households are 15 percent more likely to live around PFAS-contaminated sites than would be expected based on their share of the population, and African American households are 48 percent more likely to live around PFAS-contaminated sites than would be expected.[72] Another study found that "watersheds serving higher proportions of Hispanic/Latino and non-Hispanic Black populations had significantly greater odds of containing PFAS sources."[73] These inequities must be considered in Ecology's environmental justice analysis, since people who already have elevated levels of PFAS in their bodies are more likely be harmed by any additional releases from Ecology's AFFF disposal. Ecology's finding that there are no "communities of concern" within a 10-mile radius of its proposed landfills or incinerators does not mean that the proposed PFAS disposal will have no significant environmental justice impacts.[74] It just means that Ecology has drawn its study radius too narrowly.

## VI. Ecology Prematurely Dismisses Available Alternatives With Lower Environmental Impacts

Washington Ecology's EIS rigidly focused on three traditional methods of hazardous waste disposal, ignoring promising innovations that could be much safer and more effective than incineration, landfilling and deep well injection. Notably both EPA and the Department of Defense have invested time, staff power and research money in honing options for advanced destruction techniques. DOD recently announced a PFAS treatment hub to pilot test PFAS destruction technologies.[75] EPA's PFAS Innovative Treatment Team research project was a limited-duration effort to review alternative destruction tools. It determined that four techniques held promise for achieving high levels of PFAS destruction.[76]

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[71] Murray Carpenter, *'Forever Chemicals,' Other Pollutants Found Around the Summit of Everest*, Wash. Post (Apr. 17, 2021), https://www.washingtonpost.com/science/mt-everest-pollution/2021/04/16/7b341ff0-909f-11eb-bb49-5cb2a95f4cec_story.html;

[72] Genna Reed, Union of Concerned Scientists, *PFAS Contamination Is an Equity Issue, and President Trump's EPA Is Failing to Fix It* (Oct. 30, 2019), https://blog.ucsusa.org/genna-reed/pfas-contamination-is-an-equity-issue-president-trumps-epa-is-failing-to-fix-it/.

[73] Jahred M. Liddie et al., *Sociodemographic Factors Are Associated with the Abundance of PFAS Sources and Detection in U.S. Community Water Systems*, 57 Env't Sci. & Tech. 7902-7912 (2023), https://pubs.acs.org/doi/pdf/10.1021/acs.est.2c07255.

[74] DEIS at 3.11-20 to 3.11-22.

[75] Megan Quinn, *DOD Taps PFAS Remediation Companies, Including Clean Earth, for Mitigation Research Project*, Waste Dive (Jan. 23, 2024), https://www.wastedive.com/news/pfas-remediation-department-of-defense-clean-earth-arcadis-aquagga/705285/.

[76] EPA, *PFAS Innovative Treatment Team* (2021), https://www.epa.gov/chemical-research/pfas-innovative-treatment-team-pitt

Advocates have long called for more equitable practices for hazardous waste disposal, to ensure the PFAS pollution crisis isn't simply shifted from one community to another.[77] Several key principles are:

(1) The need for tools that can be used onsite, obviating the need to transport waste long distances and keeping the hazardous waste impacts from being concentrated in historically burdened communities;
(2) The need to treat waste in contained systems, which can ensure destruction is complete before wastes are released to the environment.
(3) The need for a very high level of waste destruction efficiency with minimal formation of harmful byproducts.

As described below, significant progress is being made to pilot alternative technologies that live up to these principles. Washington State should be at the forefront of this process.

Two particular destruction technologies hold promise for achieving the key principles for equitable waste destruction. EPA scientists published a test of three commercial services using Super Critical Water Oxidation for AFFF destruction in 2022. It concluded, "as a destructive technology, SCWO may be an alternative to incineration."[78] SCWO is currently being used to treat PFAS in Michigan,[79] and it has been used to destroy other persistent wastes, including chemical weapons, for decades. A second treatment option, Hydrothermal Alkaline Treatment or HALT, has also been used to destroy PFAS in AFFF, with notable reduction of measurable PFAS compounds.[80]

The DEIS acknowledges several emerging PFAS destruction technologies, but states that "[g]iven the uncertainty of when these technologies could be available for commercial use, and the uncertainty of acquiring the receiving state's approval to ship the AFFF, they were eliminated from further consideration as well."[81] That alleged "uncertainty" is not a valid reason for rejecting those alternatives, particularly if they are capable of destroying PFAS with lower environmental and health impacts than traditional disposal options. First, as explained above, technologies like SCWO are readily "available" and have shown promise in treating AFFF. In one place, the DEIS references the potential use of a SCWO treatment facility in Grand Rapids, MI, but Ecology fails to explain why that option was not further pursued.[82]

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[77] *See* Letter from 65 Community Leaders to Brenda Mallory, White House Council on Environmental Quality (Dec. 6, 2022), https://www.sierraclub.org/sites/www.sierraclub.org/files/2022-12/Biden_CEQ%20Letter-%20PFAS%20clean%20up%20and%20disposal%202022.pdf.
[78] Max J Krause et al., *Supercritical Water Oxidation as an Innovative Technology for PFAS Destruction*, J Env't Eng'g 05021006 (2021), https://www.ncbi.nlm.nih.gov/pmc/articles/PMC10428202/pdf/nihms-1786112.pdf; *see also* EPA, Industrial SCWO for the Treatment of PFAS/AFFF Within a Water Matrix (Sept. 2022), https://cfpub.epa.gov/si/si_public_file_download.cfm?p_download_id=546712&Lab=CESER (reporting >99.99% PFAS destruction from SCWO treatment of AFFF).
[79] *See* Isiah Holmes, *System to 'Annihilate' PFAS Chemicals Deployed in Michigan*, Wisc. Examine (June 27, 2023), https://wisconsinexaminer.com/2023/06/27/system-to-annihilate-pfas-chemicals-deployed-in-michigan/.
[80] Aquagga, *Case Studies, AFFF Stockpiles*, https://www.aquagga.com/case-studies.
[81] DEIS at 2-24.
[82] *Id.* at 3.9-9.

Nor does the alleged "uncertainty of acquiring the receiving state's approval" justify Ecology's failure to consider advanced treatment technologies.[83] First, under state law, receiving state approval is not required if dangerous waste is sent to treatment facility that "is operating either: [u]nder a permit issued pursuant to the requirements of this chapter; or, if the TSD facility is located outside of this state, under interim status or a permit issued by United States EPA under 40 C.F.R. Part 270, or under interim status or a permit issued by another state which has been authorized by United States EPA pursuant to 40 C.F.R. Part 271."[84] The DEIS fails to examine whether any advanced treatment technologies could be employed at any facilities that would not require out-of-state authorization. The DEIS also does not state whether Ecology has affirmatively sought authorization from all states with advanced treatment capacity, and what those states' responses have been. If Ecology has done so, it must describe those efforts in greater detail in the final EIS. If Ecology has not, it cannot reject treatment technologies based on its speculation over how other states may respond.[85]

Finally, during a public webinar on the DEIS, Ecology referenced questions over whether other Washington state regulations governing the storage and disposal of "dangerous wastes," including PFAS, may preclude the use of SCWO and other emerging treatment technologies. The DEIS does not specify the nature of those concerns, leaving the public unable to evaluate and respond to them. However, we note that Ecology's dangerous waste regulations permit "treatability studies" to determine "whether the waste is amenable to the treatment process; what pretreatment (if any) is required; the optimal process conditions needed to achieve the desired treatment; the efficiency of a treatment process for a specific waste or wastes; or the characteristics and volumes of residuals from a particular treatment process."[86] At a minimum, we urge Ecology to consider the use of some or all of the collected AFFF in a treatability study to evaluate advanced PFAS treatment technologies and inform future disposal decisions.

Finally, we urge Ecology to consider temporary, off-site storage at a permitted hazardous waste storage facility as a disposal option. The U.S. Environmental Protection Agency and other agencies are currently pursuing a series of short-term and medium term research and development initiatives related to PFAS disposal, which are intended to enable decision-makers "to make informed decisions about the tradeoffs between different risk management solutions, leading to better environmental outcomes."[87] Interim off-site storage would enable Ecology to consider the results of this pending research and to make a more informed choice among disposal options. Moreover, the hazardous waste incinerator that Ecology identified as a potential recipient of the state's AFFF (Clean Harbors' Aragonite facility) is also permitted to store PFAS and hazardous waste. By Clean Harbors' own account, that facility has "ample on-site storage capacity," including "a bulk liquid tank farm (sixteen ~30,000 gallon tanks); container storage areas (~12,000 55-gallon drum capacity); direct burn tanker storage areas (~30,000 gallons total capacity); sludge storage tanks (~38,000 gallon total capacity); and bulk solids storage tanks

[83] *Id.* at 2-24.
[84] Wash. Admin. Code § 173-303-141.
[85] *See King County v. Cent. Puget Sound Bd.*, 979 P.2d 374 (1999) ("An alternative considered for purposes of an EIS need not be certain or uncontested, it must only be reasonable.")
[86] Wash. Admin. Code §§ 173-303-040, 173-303-071(3)(r).
[87] EPA, *Interim Guidance on the Destruction and Disposal of Perfluoroalkyl and Polyfluoroalkyl Substances and Materials Containing Perfluoroalkyl and Polyfluoroalkyl Substances* at 93–97.

(~1100 yd3 total capacity)."[88] Moreover, while state regulations require hazardous waste generators to ship dangerous waste off-site within 90 days, they do not foreclose the use of safe off-state (and out-of-state) disposal pending the results of testing that may identify a safer permanent disposal option.

## VII. Conclusion

We recognize the time and effort that went into the preparation of the DEIS, and we appreciate Ecology's efforts to ensure the safe and efficient disposal of its AFFF. To inform that decision, however, Ecology must do more to evaluate the adverse impacts of PFAS incineration and landfill disposal, as well as modern disposal technologies that can eliminate or reduce those impacts.

Respectfully submitted,

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[88] Clean Harbors, *Aragonite Incineration Facility*, https://fr.cleanharbors.com/node/1156 (last visited Feb. 4, 2024); Utah Dep't of Env't Quality, *Aragonite Permit: Clean Harbors, LLC*, https://deq.utah.gov/waste-management-and-radiation-control/aragonite-permit-clean-harbors-llc (last updated December 21, 2023).

# Exhibit A

# Final Report: Assessment of a Report on PFAS Destruction Testing Results at Clean Harbors' Aragonite, Utah Hazardous Waste Incinerator

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January 26, 2022

## Outline of Assessment

This assessment is divided into two sections. The first section gives an overall assessment of the PFAS Destruction Testing Results. The focus is the attainment of the primary and secondary objectives of the testing program. As stated in the PFAS Destruction Testing Results report, the primary objective was to demonstrate high DRE for the four spiked chemicals PFOA, PFOS, PFHxS, and HFPO-DA. The secondary objectives were to develop a mass balance for incidental PFAS in the waste infeed and to demonstrate high HF removal efficiency coincident with the high PFAS DRE. Some additional comments are provided at the end of this section. The second section is a detailed review of the PFAS Destruction Testing Results report and Appendices with specific questions, answers from Clean Harbors or its representatives, and in some instances, follow-up questions and answers. This approach laid the foundation for the overall assessment of the testing program.

## Overall Assessment

The primary objective of demonstrating high DRE for spiked PFAS compounds was clearly achieved. Although there were serious issues with the transfer of the stack gas samples to the analytical laboratories, the analytical data are not in question given the extremely high thermal stability of PFAS at ambient or near-ambient conditions. Calculations are provided in Attachment A demonstrating the extreme thermal stability of PFOA and PFOS, corroborating the assertions of the report that the stack gas sample transfers to the analytical laboratory did not affect the accuracy of the measurements.

Greater than 99.9999% DRE was achieved for the spiked PFAS (PFOA, PFOS, PFHxS, and HFPO-DA) for average temperatures of greater than 1000 C in both the RK and the AB and residence times of greater than 3.0 sec (AB). While the testing stands on its own merit, there are recent bench-scale experimental (PFOS) and theoretical (*ab initio* modeling) published studies (PFOS, PFBA, and PFPA) that provide scientific support for these measurements. I have taken the kinetics reported in the published studies and calculated DREs and the data is shown in Attachment B. The calculations suggest temperatures of 800 C is sufficient to achieve > 99.9999 DRE of these compounds for afterburner residence times of 2.0 sec. (Note that the highlighted cells point to the lowest energy pathways for each substance.) It is interesting to note that the dominant breakdown pathway for PFOS, PFBA, and PFPA is not C-C scission along the $C_8$ carbon chain, but instead HF elimination from the polar end of the molecules. The $C_8$ chain is left intact and requires higher temperatures for the C-C bonds to be ruptured. This is the likely source of the $C_1$ and $C_2$ perfluorocarbon (PFC) PICs that are of concern.

The secondary objectives were considered the most difficult to achieve as they involve more complex sampling issues.

The PFAS mass balance is credible and the resulting assertions regarding a conservative DRE are also credible. It is possible that some of the PFAS that was not sampled in the infeed may have been more difficult to gasify and burn, contrary to the assertions in the report. However, studies have shown that PFOA is very reactive on surfaces at low temperatures. And once in the gas-phase, PFOA and other PFAS appear to be of modest thermal stability. Based on current understanding, I believe that the PFAS DRE is conservative as stated in the report.

The HF removal efficiency assertion is not quite as clearcut. The data collected in Attachment C, the revised fluorine mass balance calculations provided by Focus Environmental, point to serious issues with respect to the fluoride measurements. While a HF removal efficiency of >99.6% is reported, the sinks for the HF were not accurately quantitated leading to some question about the validity of the reported HF removal efficiency. A confounding issue is the claim that all fluorine in the waste is converted to HF upon combustion. For this assumption to be scientifically valid, a large excess of hydrogen to fluorine is needed. This data is not provided in the report. Likely sources of hydrogen beyond what is in the waste feed would be an auxiliary fuel, e.g., natural gas, burned during the testing and/or the presence of moisture in the waste feed. Proof of complete conversion of the organic fluorine to HF can also be shown with the analytical data. However, this was not the case. There was a demonstrated lack of accuracy of the analytical methods for measuring inorganic fluorine in the residual streams. The data in the revised fluorine mass balance (Attachment C) indicate mass balances of only 2-10%. An assessment of the reasons for this low recovery of fluorine suggests there were likely analytical issues associated with the slag and spray dryer solids samples. Development of better analysis methods (for complex matrices) for inorganic fluorine are needed before high HF removal efficiencies can be reported with confidence at the full-scale.

In a related matter, it is also likely from the analysis of the ratio of fluorine in the brine relative to the waste infeed that the accuracy of the organic fluorine measurements is also questionable. This ratio varied over a very wide range (52 to 457%) in this testing program.

In summary, development of better analysis methods for both organic and inorganic fluorine are needed to support PFAS performance testing at the full-scale.

## Additional Comments

PIC Formation – Full-scale testing is not generally a good source of data to examine PIC formation. In this testing, the low DRE of PFBA in runs 1, 3 and 7 (< 99%) is suggestive of PIC formation as there were many longer chain perfluoroalkyl acids in the waste infeed that could yield PFBA by a simple mechanism, C-C bond rupture. However, the higher DREs for PFBA in runs 4-6 where PFOA was spiked at higher concentrations is inconsistent with this hypothesis. In addition, the low PFBA DREs may simply be due to very low waste infeed concentrations.

PFBA has also been seen in high relative concentrations in the stack gases for other PFAS testing programs, e.g., MacGregor et al., 38th IT3 Conference, January 27, 2021. From Attachment B, it is shown that PFBA is not predicted to be thermally stable relative to other PFAS such as PFOS and PFPA. It is therefore unclear what mechanism is responsible for its relatively high emission rate compared to other PFAS. Perhaps it is not related to PIC formation but some other phenomena or a sampling and analysis artifact.

Final Comments – It is my opinion that the high PFAS DREs observed in this testing program are consistent with the state of the science of PFAS combustion. This science suggests that many PFAS compounds including the ones spiked in the waste infeed in this program are of modest thermal stability. The larger question from an environmental viewpoint is the complete mineralization of these substances and the prevention of emission of highly stable $C_1$- $C_2$ PFCs. The extensive fluoride measurements performed in this study are commendable although they did not provide accurate data in support of the mineralization of these substances. It should also be noted that demonstration of PFAS mineralization was not a goal of this testing program.

## References to the Literature used for Calculations in Attachment 1 and 2

M. Altarawneh, “A Theoretical Study on the Pyrolysis of Perfluorobutanoic Acid as a Model Compound for Perfluoroalkyl Acids,” Tetrahedron Letters, 53, 2012, pp. 4070.

M. Altarawneh, “A Chemical Kinetic Model for the Decomposition of Perfluorinated Sulfonic Acids,” Chemosphere, 263, 2021, pp. 128256.

M. Altarawneh, M. H. Almatarneh, and B. Z. Dlugogorski, “Thermal Decomposition of Perfluorinated Carboxylic Acids: Kinetic Model and Theoretical Requirements for PFAS Incineration,” Chemosphere, 286, 2022, pp. 131685.

S. W. Benson, “Thermochemistry and Kinetics of Sulfur-Containing Molecules and Radicals,” Chemical Reviews, 78, 1978, pp. 23.

S. J. Blanksby and G. B. Ellison, “Bond Dissociation Energies of Organic Molecules,” Acc. Chem. Res., 36, 2003, pp. 255.

P. J., Krusic, Alexander A. Marchione, and D. Christopher Roe, “Gas-phase NMR studies of the thermolysis of perfluorooctanoic acid,” J. Fluorine Chemistry, 126, 2005, pp. 1510.

M. Y. Khan and G. da Silva, “Decomposition Kinetics of Perfluorinated Sulfonic Acids,” ChemRxiv, doi.org/10.26434/chemrxiv.8306414.v1. 2019.

W. Tsang, D. R. Burgess, Jr., and V. Babushok, "On the Incinerability of Highly Fluorinated Organic Compounds, Combustion Science and Technology 139, 1998, pp. 385.

N. H. Weber, S. P. Stockenhuber, C. S. Delva, A. A. Fara, C. C. Grimison, J. A. Lucas, J. C. Mackie, M. Stockenhuber, and E. M. Kennedy, “Kinetics of Decomposition of PFOS Relevant to Thermal Decomposition Remediation of Soils, Ind. Eng. Chem. Res. 60, 2021, pp. 9080.

# Specific Observations from Review of Report on PFAS Destruction Testing Results at Clean Harbors' Aragonite, Utah Hazardous Waste Incinerator

Executive Summary:

1. From report: It should also be noted that high temperature treatment processes such as incineration probably have an effect on hidden PFAS mass in a waste stream similar to the laboratory chemical/thermal oxidation in the TOPA.

Question: Please provide further context and justification for this assertion.

Response: The TOPA process is a chemical oxidation process at mildly elevated temperatures. The chemical oxidation cleaves some bonds in the PFAS molecules, resulting in lower molecular weight compounds that are more likely to be target analytes. For example, AFFF may contain a variety of PFAS compounds, including 4:2 FTS, 6:2 FTS, 8:2 FTS, 10:2 FTS, 12:2 FTS. The first four compound are target analytes by EPA Method 537, whereas 12:2 FTS is not. The TOPA analysis revealed increases in the concentrations of the first four compounds, which were likely the result of the oxidation of higher molecular weight compounds, including 12:2 FTS or possibly other compounds. It is likely that a similar process could occur in high temperature thermal treatment processes, but at a much higher conversion efficiency.

Follow-up response: No additional questions.

2. From report: Due to the high efficiency of the dual dry scrubber/wet scrubber system, low HF emissions were measured throughout the testing. Measured values of fluorine ion in the stack gas samples were all J flagged values (values falling between the method detection limit and the limit of quantitation). The associated HF stack emission rate averaged 8.13E-03 lb/hr during the testing and the HF gas stack concentrations ranged from 0.07 to 0.14 parts per million dry volume basis, corrected to 7% oxygen. There are currently no HF emission limits under either the RCRA Hazardous Waste Incinerator Standards or the HWC Maximum Achievable Control Technology Standard. However, as points of comparison, the RCRA hydrogen chloride emission limit is 4.0 lb/hr and the Maximum Achievable Control Technology hydrogen chloride limit for existing HWC is 32 parts per million dry volume basis, corrected to 7% oxygen. HF is a Hazardous Air Pollutant (HAP) under the Clean Air Act, with a major source threshold of 10 tons/year. At the average HF emission rate measured during testing, annual emissions would be less than 100 pounds/year.

3. Question: Is there any evidence to suggest complete destruction of the spiked PFAS compounds occurred?

Response: There is a significant difference between "destruction" and "mineralization". Per

the RCRA definition of destruction, a molecule is destroyed if it is chemically altered. This test program conclusively showed that >99.9999% destruction and removal efficiency could be obtained for a number of PFAS compounds if there was sufficient material in the feed to perform this demonstration, based on the analytical detection limit in the stack gas.

"Mineralization" requires showing that feed compounds are converted to stable end products including $CO_2$ and HF. Demonstrating complete PFAS mineralization would require performing a fluorine balance and verifying that all organic fluorine was converted to HF. This was not a goal of this program for the following reasons:

1) The plant was run under "normal" operating conditions, which included feeding solid waste (containers and shredded materials). Due to heterogeneity of these materials, there was no way to collect representative samples and analyze them for fluorine. Therefore, the total fluorine input to the system is not quantifiable for the solid waste materials. Hence, a complete fluorine balance is impossible for this type of system when feeding normal waste feed materials.
2) There may be multiple sources of fluorine in the feed material in addition to PFAS compounds. Examples include pesticides, pharmaceuticals, etc. There is no practical way to distinguish between the sources of fluorine in the feed materials that contribute to the HF produced in the offgas.

Follow-up response: No additional questions.

Section 1:

4. From report: PFAS are particularly challenging to degrade, both environmentally and thermally, due to the strength of the multiple carbon-fluorine (C-F) chemical bonds in these compounds.

Question / Response: There is growing evidence that the destruction of the C-4 through C-10 perfluorocarboxylates and C4-C10 perfluorosulfonates can be achieved at temperatures well below 1000 C. The destruction of lighter C1-C4 fluorocarbons derived as PICs from these parent compounds are likely to require higher temperatures, perhaps above 1000 C for CHxFy where x = 0 or 1 and y = 3 or 4, for complete destruction to CO2 and HF.

Response: No question asked, Clean Harbors agrees with the observation.

Follow-up response: None

5. From report: During the testing, the operating temperature of the RK ranged from 1,893 to 2,008 degrees Fahrenheit (F) and the operating temperature of the ABC ranged from 2,052 to 2,110 F.

Question: In Appendix B, minimum temperatures ranging from 1731 F (Test Condition 1) to

1773 F (Test Condition 3) were recorded for the RK. Are you reporting average temperatures in the statement from the report?

Response: The values cited in the text are the range of average temperatures for the nine test runs. They are not the absolute minimum and maximum values recorded in Appendix B.

Follow-up response: It is suggested that the text be modified as described in the response.

Response 2: Clean Harbors agrees that if the report is revised this statistical basis for the temperatures should be clarified.

6. From report: Combustion gas residence time in the ABC is estimated at 2 to 3 seconds.

Question: Are there calculations to back up this statement? I did not see any calculations in the report or the Appendices.

Response: Afterburner residence time cannot be measured directly; it can only be calculated from mass and energy balance calculations. Residence time is also not a regulatory parameter, therefore, there are no calculations of afterburner residence time in the report. However, based on mass and energy balance calculations that were performed for other purposes using the PFAS test data, the estimated average gas residence time in the afterburner during the PFAS tests was 3.1 seconds.

Follow-up response: No additional questions.

Section 2:

7. From report: This secondary test program goal was to demonstrate, to the extent practicable, an overall mass balance for the process and to calculate DREs for as many of the 49 target PFAS analytes as possible, based on PFAS feed rates and stack gas analytical detection limits.

Question: What mass balance are you referring to? The mass of PFAS compounds being fed? It is unclear on what is met by mass balance here. Mass balance can have several different meanings based on the context used.

Response: "Mass Balance" in the context of this report refers to calculating the mass of each individual PFAS compound in each process stream, including waste feed streams, reagent input streams, and process residual streams to the extent possible. The response to Question #3 explained the limitations on sampling and analysis of solid material, hence, PFAS materials in the solid waste feeds could not be included in the mass balance. Figures 6-1, 6-2, and 6-3 present a summary of the total PFAS mass balance data for each type of stream that was sampled and analyzed.

Please note that there are caveats that should be applied to these data because of how analytical detection limits were handled in calculations. For waste feed, reagent, and process residual streams, non-detects were assigned a value of zero in all calculations. For stack gas samples, all non-detects were assigned the detection limit in all calculations. This was done so that DRE calculations were done on the most conservative basis possible (i.e., likely omitting some PFAS mass in the feed and likely overestimating PFAS stack gas emission rates). Therefore, reported DRE values are likely underestimated.

Follow-up response: The wording here describing mass balance within the context of this report should be considered in a future revision of the report.

Response 2: Clean Harbors agrees that if the report is revised the use of the term "mass balance" should be clarified.

8. From report: Due to the high molar proportion of fluorine in PFAS chemicals, thermal treatment of these materials breaks the C-F bonds and generates byproduct HF, a HAP regulated under the Clean Air Act. Maximizing thermal breakdown of PFAS into products of complete combustion also maximizes the production of HF. Hence, current U.S. Environmental Protection Agency (EPA) guidance on PFAS thermal treatment emphasizes the importance of not only high PFAS DRE but also achieving low stack gas concentrations of HF. Stack gas samples for quantifying the presence of HF were withdrawn using an EPA Method 26A sampling train during each of the nine test runs to measure HF emission rates.

Question: Was PFAS destruction to HF measured directly in this study? This would be a direct and clear way to demonstrate a F mass balance and complete destruction of the PFAS in the feed.

Response: See response to Question #3.

Follow-up response: No additional questions.

Section 3:

9. From report: A detailed work plan was developed before conducting the tests to facilitate systematic execution of the field activities, including sampling, analysis, and quality control, to ensure that the project objectives would be met. Tests were run under each of three different process conditions typical of normal waste processing operations. Test Condition 1 (Test Runs 1-3) was intended to establish a baseline for results without adding additional PFAS spiking compounds to the waste feed. During Test Condition 2 (Test Runs 4-6), the feed rates of PFOA, PFOS, PFHxS, and HFPO-DA were augmented by spiking to facilitate calculation of DRE values for these compounds. During Test Condition 3 (Test Runs 7-9), AFFF concentrate was also fed to the incinerator.

Question: What was the purpose of test condition 3, how does it relate to test condition 1 and 2, and how was the data used to demonstrate PFAS DRE?

Response: The purpose of Test Condition #1 was to feed normal waste feed materials that were not known to specifically contain PFAS compounds (baseline conditions). The purpose of Test Condition #2 was to feed normal waste feed materials (similar to Test Condition #1) but to also spike four PFAS compounds at feed rates that had been calculated for each compound to be sufficient to demonstrate >99.9999% DRE based on the estimated analytical detection limit in the stack gas for each specific spiking compound. The purpose of Test Condition #3 was to feed a waste material (AFFF) that was believed to contain a significant concentration of PFAS and is also a commercial product that is likely to be processed though the incinerator on a routine basis.

DRE values were calculated for every target analyte for every run for each test condition. However, it should be noted that feed concentrations of many of the PFAS target analytes were too low to demonstrate the 99.99% DRE value required by RCRA regulations at the analytical detection limits that were achievable in the stack gas.

Follow-up response: No additional questions.

10. From report: The mass balance for the four spiked PFAS also included the spiked amounts.

Question: What is meant by this statement?

Response: For the overall mass balances as shown in Figures 6-1, 6-2, and 6-2 the amounts of PFAS spiked during Test Condition #2 make up a significant fraction of the overall PFAS mass fed to the system. Please see Appendix A, page 5, table titled "Total PFAS Input – Contribution from Waste Feeds and Spiked Materials". For Runs 4, 5 and 6, the spiked materials make up 83, 76, and 92% respectively of the total mass of PFAS in the feed materials. This must be considered in comparing mass balance results between Test Conditions #1, #2 and #3.

Follow-up response: No additional questions.

11. From report: Table 3-1 presents the approach for calculating spiking rates for the four PFAS compounds to demonstrate a DRE > 99.9999% for each of the four spiked PFAS compounds. Demonstrating DRE > 99.9999% is equivalent to demonstrating that for every million mass units of a POHC introduced into an incinerator, only one mass unit is detected at the stack. Hence, it is necessary to work backwards from the achievable detection limit for the specific analyte in the stack gas. A sample calculation demonstrating the contribution of the spiking component inputs to the DRE calculation are presented in Table 3-1. Note that the example calculation presented below is actually based on achieving > 99.99995% DRE. This contingency factor is necessary to

account for uncertainty in the PFAS method detection limit (MDL) and stack gas flow rate.

Question: What is the accuracy of the PFAS feed rates and stack emission rates? To how many significant digits?

Response:
One key factor that affects the accuracy of the calculations of PFAS feed rates and stack emissions is how non-detect analytical values were handled in calculations. Please see response to Comment #7 for a discussion of this issue. As explained in that comment, the most conservative approach was taken to handling non-detects in performing DRE calculations.

Mass feed rates of waste materials are reported in units of lb/hr to five or six significant figures (i.e., XXX.XX or X,XXX.XX). Concentrations of PFAS in liquid feed materials are reported in concentrations of ng/l to three significant figures (X.XX). Stack gas sampling train fractions (4) are reported in units of ng/sample to four significant figures (X.XXX). Stack gas sample volumes are reported in units of dscf to five significant figures (XXX.XX). Stack gas flow volumes rates are reported in units of dscfm to five significant figures (XX,XXX).

Follow-up response: Given the accuracy stated above, are the DRE numbers stated in the report still correct? In other words, the report states the spiked PFAS was destroyed to a DRE greater than 99.9999%. Is this still correct given the low feed rates and the accuracy of the measurements?

Response 2: The calculations were performed following the protocol described in RCRA for hazardous waste incineration (40 CFR 264.343) and are believed to be correct. An error propagation test based on number of significant figures has not been performed nor is such a test required by RCRA.

It should be noted that part of the test planning included calculating the mass of each PFAS compound that was required to be spiked to demonstrate >99.9999% DRE based on the analytical detection limit in the stack gas. As noted in Table 6-2, the mass of PFAS in the waste feed materials was insufficient to demonstrate >99.9999% DRE for many of the PFAS target analytes.

12. From report: All of the temperatures recorded for samples on receipt at the laboratory were higher than 4 degrees Celsius (C). Interviews with EAL employees revealed that proper temperature measurement procedures were not observed. Further, it was confirmed through analysis of XAD media blank samples retained at the lab and the fact that PFAS are very thermally, chemically, and biologically stable, that XAD sample integrity was likely not compromised by temperatures that were above the target value. Other Test Method 45 (OTM-45) does not require refrigeration of the sample filter, which indicates there is a low level of concern with sample loss at ambient temperatures. Details of this reconciliation are summarized in a Technical Memorandum

provided in Appendix E.

Question: What is the basis for this statement (highlighted text)? I will provide calculations to test this assertion.

Response: Comment acknowledged, and Clean Harbors concurs that PFAS compounds do not have unusual thermal stability at typical combustion temperatures. However, the statement is made in the context of the temperatures that were recorded for various samples, which ranged from ~8 to ~24°C. The statement is believed to be true in that PFAS compounds would be thermally stable within this temperature range, but no data have been found to confirm this.

Follow-up response: Calculations are provided that give support for this assertion based on the prior work of Krusic et al, 2005.

Response 2: Based on telecon with Dr. Taylor, I understand that these calculations will be provided in a separate report that he is preparing and were not intended to be part of this document.

13. From report: The Test Plan was based on a comprehensive approach to sampling that included as many process inputs and outputs as practicable. The purpose of this was to develop as complete a PFAS mass balance as possible and to identify potential sources of PFAS entering the process and PFAS sinks for materials leaving the process. Sampling included waste feed streams, process treatment chemical inputs, process residue streams, and stack gas. The principal exclusions from sampling were the containerized, shredded and bulk solids waste feed streams. Due to their complexity and heterogeneity, it was considered infeasible to sample and perform PFAS analyses on these materials. Hence, any PFAS compounds contained in these waste streams were not included in the mass balance or DRE calculations.

Question / Comment: Once again, not sure what is meant by mass balance here.

Response: See response to Question No. 7.

Follow-up response: No additional questions.

14. From report: Field QC for PFAS in process samples included rinsate/equipment blanks and field blanks collected per the master sample matrix (Appendix G), and field duplicates collected at a rate of 10% of the total process samples. At the laboratory, for every extraction batch (≤ 20 samples), a method blank and a matrix spike were performed. Surrogates were spiked into the samples to verify extraction efficiency and internal standards were spiked into extracts to verify instrument drift. The Gas Chromatography-Liquid Chromatography instrument was calibrated using a minimum of five concentration levels. All assays were bracketed by passing continuing calibration verification standards. A maximum of 10 samples were assayed between continuing

calibration verifications. All laboratory QC procedures and results are documented in the EAL Report.

Question: Is this correct (highlighted text)? My understanding is that LC/MS/MS was used to analyze for PFAS.

Response: The analytical instrument was described incorrectly in the text, it was in fact LC/MS/MS.

Follow-up response: No additional questions.

15. From report: EPA Method 3A is an instrumental test method that was used to measure the concentration of O2 and CO2 in the stack gas, and nitrogen by difference. Three effluent gas samples were collected in Tedlar bags during each run. Following the completion of the test run, the contents of the bags were conveyed to continuous emissions analyzers that measured the concentration of O2 and CO2. The average of the three bags for each run was used for the O2 and CO2 concentration. The performance requirements of the method were met to validate data.

Question: Was CO measured in any of the test runs? PFAS are within a class of known flame inhibitors and may result in CO formation, depending on the concentrations fed. It would be good to verify that the PFAS had no effect on the combustion process.

Response: CO is continuously monitored and recorded as a condition of the plant's RCRA permit. The permit limit is 100 ppmv, dry basis, 1 hour rolling average. CO emissions were well within permit limits during all test runs. However, the CO emission concentrations are not reported within the PFAS report.

As reported in Appendix A, page 2, PFAS Mass Flow rate, the average total PFAS feed rate in all feed streams was 0.0132 lb/hr (excluding PFAS spiking chemicals). The average total PFAS spiking rate during Runs 4-6 was 0.348 lb/hr. Data in Appendix B shows that the average total waste feed rate during all runs was 12,818 lb/hr. Therefore, PFAS (without spiking) make up only 0.00001% of the total waste feed material. Including the spiking compounds, PFAS made up only 0.003% of the total waste feed. Clean Harbors believes it is unlikely that PFAS at these concentrations would have a significant effect as a flame inhibitor. However, Clean Harbors is not aware of any qualitative studies to support this assumption.

Follow-up response: No additional questions.

16. From report: Figure 3-1 and Table 3-2.

Question: Was the tubing within the OTM-45 sampling train rinsed and analyzed for PFAS? This includes all tubing from the particulate filter to the 5th impinger as shown in Fig. 3.1.

Response: Stack testing was conducted according to the procedures in OTM-45, which requires rinsing all sampling train glassware, including the sampling probe, impingers, and all connecting glassware.

Follow-up response: No additional questions.

Section 4:

17. From report: The laboratory performed data validation by comparing the final data deliverable/report to the project objectives, summarizing QC outliers in the final deliverable, and applying data validation qualifiers to associated results. The data were evaluated against project data quality objectives and measurement performance criteria, such as precision, accuracy, and completeness, as shown in Table 4-1.

Question: Was third-party data validation conducted?

Response: Third party data validation was conducted for all analytical data. This Data Validation Report is presented as Appendix J of the test program report.

Follow-up response: No additional questions.

Section 5:

No questions

Section 6:

18. From report: The secondary objectives of developing a mass balance for incidental PFAS in waste infeed and demonstrating high HF removal efficiency coincident with high PFAS DRE were also achieved.

Question / Comment: It is unclear that successful demonstration of the secondary objective was achieved. Specifically, high HF removal efficiency.

Response: HF removal efficiency was calculated using a procedure that is analogous to the procedure required by the RCRA Incineration Regulations to demonstrate HCl removal efficiency. This procedure is based on measuring the amount of organic chlorine in the waste feed materials and converting it to an HCl using a stoichiometric conversion factor (assuming 100% conversion efficiency). The amount of HCl in the stack gas is measured by capturing the chloride ion in impingers and converting it to HCl using a stoichiometric conversion factor. The formula for HCl removal efficiency is:

((HCl feed – HCl stack gas)/HCl feed) *100.

Calculated HF removal removal efficiency values for each test run are presented in Table 6 in the test report. Measured HF removal efficiencies were >99.6% in all cases.

Follow-up response: Is Clean Harbors still confident that the HF was removed to >99.6% given the large variance in the fluoride measurements in the residual streams (Attachment B)?

19. From report: Depending on the Test Condition, between 24 and 26 of the 49 target PFAS analytes were not detectable in the waste infeed and DREs for these could not be calculated. However, stack gas concentrations for all 49 target PFAS analytes were either not detectable, or if detectable, the mass emission rates from the stack were extremely low, generally ranging from 10-9 to 10-7 lb/hr. PFBA, PFHxA, perfluoropentanesulfonic acid (PFPeS), perfluoro-2-methoxyacetic acid (PFMOAA), N-EtFOSE, N-MeFOSE, and perfluoro(3,5,7,9,11-pentaoxadodecanoic) acid (PFO5DA) had reported emission rates between 10-7 and 10-6. PFBA, the compound with the highest calculated emission rate, was present in the method blank (XAD resin media blank). Therefore, the reported PFBA emission rate is likely biased high, and the DRE is biased low for at least some of the test runs by this blank contamination. Calculated stack emission rates for all 49 target PFAS analytes are presented in Table 6-3 and stack emission concentrations are presented in Table 6-4.

Question: What are the blank-corrected emission rates for PFBS in Table 6-3?

Response: See blank corrected emission rates in Attachment D.

Follow-up question: The DRE for PFBA is less than 99% for runs 1, 3, and 7 (Table 6-2). Did the blank-corrected data make a measurement improvement (order of magnitude) in the DRE numbers for runs 1, 5, and 7? Can you offer any explanation for the low DRE besides a low initial concentration in the waste feed?

Response 2: See revised Attachment D which shows blank corrected DRE calculations for PFBA. Blank correction generally results in a small increase in DRE, but far less than an order of magnitude for each run that was blank corrected.

Table 6-2 shows that there are several PFAS target analytes with DRE values <99.99%, even though the analyte was non-detect in the stack gas. This result is clearly caused by low concentrations of the PFAS target analyte in the feed material.

PFBA may also be a PIC. It is the lowest molecular weight (C4) carboxylic acid and would be expected to be a breakdown product of higher molecular weight carboxylic acids. Data presented by MacGregor (attached) also shows PFBA as residual product in multiple residual stream matrices (ash, water, stack gas) which may corroborate the PIC theory.

20. From report: The HF removal efficiency, based on the HF potential to emit and the and

measured HF in the stack gas, averaged 99.7% for the nine test runs.

Question: This statement assumes that you measured all the fluorine in the infeed. I don't think this is true. It also assumes that all fluorine fed into the incinerator was converted to HF. What basis do you have for this second assertion?

Response: Table 6-4 in the project report presents HF removal efficiency data and all values are reported as ">" values partially for the reason noted (fluorine was not sampled and analyzed in the waste feed). There were several reasons for reporting HF removal as a ">" value as explained in footnotes a, b, and c of Table 6-4. The statement in the text should also be qualified as a ">"value.

As described in the response to Question 18, HF removal efficiency was calculated is procedures analogous to those described in the RCRA incineration regulations for calculating HCl removal efficiency, which assumes that all chlorine in the feed material is converted to HCl. The point is acknowledged that there is a possibility that some fluorine could be converted to compounds other than HF. However, fluorinated products of incomplete combustion were not measured during this test program.

Follow-up response: I agree with the response. It is possible if not likely that some of the input F was converted to stable PICs such as CF4 and C2F6 in this testing. The report should reflect this current status of the science with respect to complete F mineralization.

Response 2: See initial response to Question #3.

21. From report: Table 6-5.

Question: How is Intermediate HF defined? A footnote should be added to this table providing that calculation. HF removal rate is calculated by subtracting HF stack emission rate from fluorine from waste feed with the difference divided by the fluorine from waste, correct? If so, what is the purpose of adding the Intermediate HF column? What does this data signify?

Response: HF removal percentage is calculated by converting all fluorine in the feed to HF and converting all fluorine in the stack gas to HF and then performing the calculation as describe above. "Intermediate HF" is the potential HF calculated by converting all of the fluorine in the waste feeds and spiking chemical to HF by using a stoichiometric equation (as shown in the table heading below the term "Intermediate HF". Clean Harbors agrees that the use of the term "Intermediate HF" is potentially confusing, and the term should be removed from the table.

Follow-up response: No additional questions.

22. From report: The technical memorandum also addresses the recorded temperatures of

the sample coolers upon receipt at the laboratory, which ranged from 6 °C to 13.3 °C except for one measurement of 19.4 °C recorded for three coolers containing non-hazardous stack gas samples. However, it is believed that this measurement was not made in accordance with standard procedures, as documented in the memorandum (Appendix E). The measured temperatures for the three coolers containing non-hazardous stack gas samples were noted as an exceedance relative to standard requirements, and associated sample data were qualified as estimated (J or UJ) per standard validation procedures. Additionally, the hazardous stack gas samples required shipment in specialized hazardous materials compliant fiberboard boxes, which precluded cooling during shipping; the temperatures of these samples upon delivery were greater than 23 °C.

Question: This data (highlighted text) is missing from Appendix J. Data for the non-hazardous waste samples is provided twice.

Response: Please confirm that the question references the proper Appendix. Temperature data for hazardous gas constituents is provided in Appendix E, Reconciliation of Sample Handling Deviations, pages 41-42 (Fed Ex documents).

Follow-up Response: In the current version of Appendix E, Attachment 2 (COCs for hazardous stack gas samples) is a duplicate of Attachment 3 (COCs for non-hazardous stack gas samples). Appendix E should be corrected with the appropriate COCs for Attachment 2.

Response: The term "Hazardous" refers to the DOT shipping classification of the samples, not the toxicological properties of the samples. The COCs in question refer to the OTM-45 samples. The "front-half rinse", "back-half rinse", and "impinger rinse" fractions are a 95% methanol/5% NH4OH solvent mixture that are defined as hazardous materials for DOT shipping purposes. These remaining four samples (front half filter, 1st XAD trap, Condensate, Breakthrough XAD) are considered non-hazardous per DOT regulations. These groups of samples should have been listed on separate COC forms and shipped separately. However, they were erroneously combined on a single COC form. This form is included in the referenced Attachment 2 (Hazardous Stack Gas Samples COCs) and Attachment 3 (non-hazardous Stack Gas Samples COCs) because the form contains information for samples in both hazardous and non-hazardous categories.

23. From report: Although the impact of temperature on the stability of PFAS in samples similar to those collected for this project has not been specifically documented, PFAS compounds are generally highly stable and resistant to degradation under normal environmental conditions. The stability of these compounds is reflected in Method OTM-45, which does not require refrigeration of sample filters. Therefore, although the data were qualified based on the temperature exceedances, the exceedances do not affect data usability.

Question: A calculation will be provided to test this assertion (highlighted text) using kinetic

data from the literature.

Response: See response to Question #12.

Follow-up response: Calculations are provided that give support for this assertion based on the prior work of Krusic et al, 2005.

Response 2: See response to Question 12.

24. From report: The media blanks associated with the OTM-45 train were prepared and analyzed as method blanks. These blanks were collected in association with the XAD resin, the impinger solution, and the filter. The two blanks associated with the impinger solution were non-detect for all analytes. Analytical results for the filter blank were non-detect except for PFTeDA, which had a concentration of 0.061 ng/sample. Analytical results for the two XAD resin blanks were non- detect for all analytes except PFBA, PFHxA, and PFMOAA. The detected result for PFBA was 5.53 ng/sample, the detected results for PFHxA were 0.247 ng/sample and 0.234 ng/sample, and the detected results for PFMOAA were 1.35 ng/sample and 1.39 ng/sample.

Question: Is this consistent with footnote (d) in Table 6-4? The footnote seems to suggest that PFBA was detected in different components of the OTM-45 sampling train for different runs. It's confusing.

Response: See data in Attachment A. Footnote (d) refers to the concentration of PFBA in the Method Blank. The XAD-resin reagent blank was used as a method blank. Footnote (d) should be reworded as follows:

(d) Detected as a contaminant (5.53 ng/sample) in method blank No. MB-12020-PFAS. The XAD-2 resin reagent blank was used as the method blank. The PFBA mass in the following stack gas sample fractions exceeded the mass in the method blank:

Run 1 – Back-half
Run 5 – Back-half
Run 5 – Breakthrough XAD Resin
Run 7 – Back-half

Follow-up response: No additional questions.

Section 7:

25. From report: The results of testing conducted at Clean Harbors' Aragonite Incineration Facility from 17 to 19 June 2021 successfully demonstrate that the process can effectively destroy legacy terminal PFAAs such as PFOA, PFOS, and PFHxS, and the Gen-X

PFAS HFPO-DA, at DREs exceeding 99.9999%, when the feed rate of these materials is augmented and DREs are calculated using very conservative assumptions. It is worth noting that this is the required performance level for thermal destruction of polychlorinated biphenyls and dioxins/furans, which are demonstrably more hazardous and generally less thermally stable than currently (federally) unregulated PFAS.

Comment: The current, evolving scientific understanding does not support this statement. PFAS parent compounds are almost certainly less thermally stable that PCBs.

Response: Comment acknowledged. Clean Harbors is not aware of any published studies comparing the thermal stability of PFAS compounds with PCBs that were conducting using identical or similar test procedures. Therefore, this statement in the original report is unsubstantiated by any published data that is known to Clean Harbors and should be removed.

Follow-up response: No additional questions.

26. From Report: Section 7.2 Title: Incidental PFAS DRE and Mass Balance

Comment: Title is misleading. PFAS mass balance (as fluorine) was not reported. No evidence for the complete destruction of the spiked PFAS was provided.

Response: See responses to Question #3 and Question #7. Demonstrating a PFAS mass balance as fluorine was not a goal of the testing program and was technically impracticable for the reasons noted in the previously referenced responses.

Follow-up response: No additional questions.

27. From report: Mass balance results indicate that total PFAS input into the system in the treatment chemicals and process water are extremely low, with non-detect or close to non-detect concentrations of all analytes in the process water, TMT, and powdered activated carbon. The soda ash solution has a PFAS input into the system in the range of 10-6 to 10-5 lb/hr. This mass was comprised exclusively of FBSA, which was detected in all nine runs.

    Mass balance results indicate the total PFAS emitted from the system in the slag, spray dryer solids, baghouse dust, and stack gas are extremely low (10-8 to 10-4 lb/hr for each stream). Mass emission rates in the slag and stack gas are approximately equal and the mass emission rates in the spray dryer solids and baghouse dust are both about one order of magnitude less than the flow rates in the slag or stack gas.

Comment: The significance of these paragraphs is unclear to me. Are you saying there was little background PFAS in the incoming streams and unit operations (except for AFFF and the spiked PFAS in test condition 2) and little PFAS in the stack gas and air pollution control

systems? I agree with the latter assertion but not so sure about the first; the report states that not all of the incoming streams were analyzed for PFAS or total organic fluorine.

Response: Comment is correct in that PFAS could not be analyzed in solids streams as described in response to Comment #3. The text should be qualified to clarify that it is based only on those streams that were sampled and analyzed and does not address any PFAS that may be in solid waste streams which were not sampled and analyzed.

Follow-up response: No additional questions.

28. From report: Given that laboratory standards enabling targeted analysis exist for only about 50 of the thousands of extant PFAS, other analytical tools such as non-targeted PFAS analysis and Total Organic Fluorine, combined with TOPA, could be employed in the future to more completely characterize the PFAS profiles in the waste and other process streams, as well as in the stack gas.

Comment: This statement (highlighted text) relates to both determination of complete PFAS destruction and the ability to perform a meaningful F balance. The need for this analytical capability could be further emphasized as such outcomes would be beneficial for both your industry and the general public.

Response: Not a question, comment acknowledged about analytical capability. However, as explained in the response to Comment #3, Clean Harbors does not believe it is possible to perform a meaningful fluorine balance on a commercial hazardous waste incinerator feeding a normal mixture of solid materials for the reasons previously noted.

Follow-up response: None.

29. From Report: Performing a fluorine balance, considering all fluorine inputs, could provide insights into how and where fluorine is removed from the system. Most (probably nearly all) of the organic fluorine is expected to be oxidized to form HF within the RK or ABC. This HF may then reactwith inorganic components of the slag, be neutralized and collected in the spray dryer solids, collected in the baghouse as an inorganic solid, or neutralized in the scrubber.

Question: What is the basis for this assertion (highlighted text)?

Response: The assertion is based on the typical operating temperatures in the rotary kiln and afterburner (~2,000°F) as described in Comment # 5, the gas phase residence time of 3.1 seconds as described in the response to Comment #6, and the oxygen content of the stack gas (~11%) as described in Appendix H of the test report. These operating conditions are believed to be sufficient to convert F to HF at a high efficiency. However, there is no publicly available data that is known to Clean Harbors to quantify the efficiency of the fluorine to HF conversion.

Follow-up response: No additional questions.

## Appendices

Appendix A:

Fluorine Mass Balance Spreadsheet – The two tables entitled: Fluorine Feed Rate and Fluorine Mass Flow Rate in Residual Streams. Mass Balance Closure (%).

Comment: The mass balance closure for fluorine should be >100% if fluorine input in waste streams to incinerator is not fully characterized as repeatedly asserted in the final report. The data here do not provide strong support or corroboration for that claim as 6 of 9 test runs give only ~ 100% recovery (+/- 10%) and only one test run is well above 100% (130%). I suggest that the assertion in the final report that PFAS DREs are conservative be reconsidered in light of this data.

Response: The data in the Fluorine Mass Balance spreadsheet in Appendix A is incorrect, it is an obsolete version that uses assumed fluorine concentrations in Residual Streams rather than actual measured values. Actual measured values were not available when the spreadsheet was originally developed.

The corrected fluorine mass balance is attached (Attachment C, Fluorine Balance). The calculated fluorine mass balance closures ranged from approximately 2-10%. However, it is believed that the analytical method used to analyze fluorine in the spray dryer ash and baghouse dust was not appropriate for these matrices and therefore returned ND values for most of the samples. There is empirical evidence to support this, in that the mass flow rates of fluorine in the brine ranged from ~1.5 to 9.8 lb/hr. The brine is evaporated in the spray dryer, and this mass of fluorine should have been detected as fluorine in the spray dryer solids or the baghouse dust. It should be noted that there could be additional fluorine in these two streams if fluorine was initially removed from the flue gas as it passed through these two devices (which is highly likely).

A better indication of the fluorine mass balance closure is provided by the ratio of fluorine in the brine to the total fluorine in the feed. These values ranged from 105% to 457% for Runs 1-3 and from 52-65% for Runs 4-9. Ratios exceeding 100% may indicate that there was a significant amount of fluorine in the solid feed materials that could not be sampled and analyzed. This could have resulted in more fluorine being recovered in the brine than could be accounted for in the feed materials that were analyzed.

For Runs 4-9, the ratio of fluorine in the brine to fluorine measured in the feed materials was <100%. This could be the result of fluorine initially being removed from the flue gas as it passed through these spray dryer and baghouse, but not being detected because of analytical issues.

As noted in the response to Comment #3, PFAS DRE values and mineralization efficiency to HF are two totally different parameters. Clean Harbors believes assertions that calculated DRE values are reported on a conservative basis is correct because of how non-detects were used in DRE calculations for waste feed (ND assumed 0.0) and stack gas samples (ND assumed to be present at the ND).

Follow-up response: The large variance in the fluoride measurements in the residual streams suggest some significant analytical issues. This should be reflected in the report and additional testing and/or R&D is recommended to further investigate this issue.

Response: Clean Harbors agrees with this conclusion and acknowledges that there were likely analytical issues associated with the slag and spray dryer solids samples that need to be investigated in future test programs.

Appendix E:

Question: The 2nd page, last paragraph, states that "The sample temperature issues involved at the recording of 19.4 C of non-hazardous stack gas samples, and temperatures ranging from 23.4 to 24.1 C for hazardous stack gas samples . . ." The COC documents providing the temperatures for the hazardous stack gas samples is not provided in this Appendix.

Response: Temperature data for hazardous gas constituents is provided in Appendix E, Reconciliation of Sample Handling Deviations, pages 41-42 (Fed Ex documents). The shipment of the hazardous gas samples was not properly documented on a COC document.

Follow-up Response: In the current version of Appendix E, Attachment 2 (COCs for hazardous stack gas samples) is a duplicate of Attachment 3 (COCs for non-hazardous stack gas samples). Appendix E should be corrected with the appropriate COCs for Attachment 2.

Response 2: See response to Question 22.

# Exhibit B

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Article

# Pilot-Scale Thermal Destruction of Per- and Polyfluoroalkyl Substances in a Legacy Aqueous Film Forming Foam

Erin P. Shields,* Jonathan D. Krug, William R. Roberson, Stephen R. Jackson, Marci G. Smeltz, Matthew R. Allen, R. Preston Burnette, John T. Nash, Larry Virtaranta, William Preston, Hannah K. Liberatore, M. Ariel Geer Wallace, Jeffrey V. Ryan, Peter H. Kariher, Paul M. Lemieux, and William P. Linak

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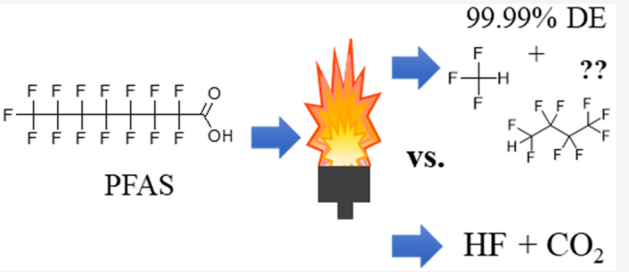
**ABSTRACT:** The destruction of per- and polyfluoroalkyl substances (PFAS) is critical to ensure effective remediation of PFAS contaminated matrices. The destruction of hazardous chemicals within incinerators and other thermal treatment processes has historically been determined by calculating the destruction efficiency (DE) or the destruction and removal efficiency (DRE). While high DEs, >99.99%, are deemed acceptable for most hazardous compounds, many PFAS can be converted to other PFAS at low temperatures resulting in high DEs without full mineralization and the potential release of the remaining fluorocarbon portions to the environment. Many of these products of incomplete combustion (PICs) are greenhouse gases, most have unknown toxicity, and some can react to create new perfluorocarboxylic acids. Experiments using aqueous film forming foam (AFFF) and a pilot-scale research combustor varied the combustion environment to determine if DEs indicate PFAS mineralization. Several operating conditions above 1090 °C resulted in high DEs and few detectable fluorinated PIC emissions. However, several conditions below 1000 °C produced DEs > 99.99% for the quantifiable PFAS and mg/m$^3$ emission concentrations of several nonpolar PFAS PICs. These results suggest that DE alone may not be the best indication of total PFAS destruction, and additional PIC characterization may be warranted.




**KEYWORDS:** *PFAS, AFFF, incineration, products of incomplete combustion, destruction efficiency*

## INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) are a class of synthetic chemicals that possess strong carbon−fluorine bonds that give PFAS high stability and low surface energies.[1] These unique properties have made PFAS useful in heat resistant products, hydrophobic and oleophobic coatings, firefighting foams, and many other products and manufacturing processes.[1−3] The widespread use and stability of PFAS have led to the ubiquitous presence of PFAS in the environment and waste streams.[4−7] Even low levels of PFAS exposure can lead to bioaccumulation and has been associated with adverse health effects,[8−11] leading to low parts per trillion drinking water health advisory levels for several PFAS.[12] The current concentrations of PFAS in the environment have been determined to be near or over recent exposure guidelines,[13,14] indicating the need for PFAS emission reductions.[14]

Hazardous organic chemicals are often incinerated to destroy the compounds and prevent their release to the environment.[15,16] To ensure harmful emissions are not released into the atmosphere, the destruction efficiency (DE) or destruction and removal efficiency (DRE) of the parent organic molecule, or principle organic hazardous constituent (POHC), has been used to determine the destruction of the molecule.[15,17−19] Typically, a DE or DRE determined for a highly stable POHC (based on an incinerability index[20]) is used to ensure adequate destruction for all waste species.[15,18,20] The DE or DRE can be calculated using eq 1,

$$DE\ or\ DRE = [1 - (W_{out}/W_{in})] \times 100\% \quad (1)$$

where $W_{in}$ is the mass feed rate of the molecule in and $W_{out}$ is the mass emission rate of the POHC coming out of the incinerator for DE or out of the stack and into the atmosphere for DRE. The distinction between DE and DRE is that DRE includes credit for POHC removal in facility air pollution control devices (e.g., particulate control, acid gas scrubbers,

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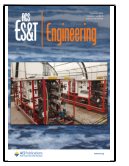

activated carbon beds) where DE does not. Although this results in some transference of the POHC to the liquid and solid discharges from air pollution control devices, these discharges are themselves treated as hazardous wastes. The regulation, 40 CFR Part 63.1203, states that a DRE of 99.99% indicates complete destruction of most chemicals.[19] For perspective, a requirement of 99.99% DRE indicates that for every 1 kg of POHC introduced, 100 mg of the POHC could be released in the air emissions. When applied to an aqueous film forming foam (AFFF) containing ∼2% PFAS, ∼200 mg of PFAS could be emitted for every 100 kg of the AFFF incinerated.

Many PFAS of industrial importance are composed of a fluoroalkyl chain and a polar functional group. PFAS can easily be altered from their original form by the removal of the functional group thermally at temperatures as low as 100 to 300 °C[21−23] and by other mechanisms at ambient temperatures.[24,25] The removal of the functional group creates volatile PFAS, from the carbon−fluorine backbone, that are greenhouse gases;[26,27] most have unknown toxicity, and some can transform to perfluorocarboxylic acids in the atmosphere.[28] The complete destruction of PFAS, the breaking of all the carbon−fluorine bonds and mineralization to form hydrofluoric acid (HF) and carbon dioxide ($CO_2$), is necessary to ensure PFAS are not released into the environment during the thermal treatment of PFAS contaminated media.

The primary objective of this study was to evaluate whether DEs indicate complete destruction of PFAS during thermal treatment. As an indicator of incomplete destruction, volatile products of incomplete combustion (PICs) were quantified along with the DEs of the quantifiable PFAS. The study was performed using a pilot-scale natural gas-fired refractory-lined combustor. The PFAS mixture used was an AFFF predominantly containing legacy perfluorooctanesulfonic acid (PFOS).

AFFF was injected into the combustor at various locations experiencing different peak temperatures. The AFFF was atomized through the flame, with exposure to flame generated radicals and near adiabatic flame temperatures, and at postflame locations with peak temperatures ranging from 1180 to 810 °C. These temperatures span realistic high temperatures achieved in hazardous waste incinerators (HWIs), as well as lower temperatures that may be more typical of other thermal destruction systems such as sewage sludge or municipal waste incinerators.[29] To our knowledge, this study is the first to use a pilot-scale incinerator to examine AFFF destruction over a wide range of temperatures and include PIC measurements as an indicator of performance.

## MATERIALS AND METHODS

**Experimental Furnace.** Experiments were performed using a small pilot-scale U.S. Environmental Protection Agency (EPA) research combustor named the Rainbow furnace that has been described in previous studies.[30−32] Here the furnace load and flame stoichiometric ratio (SR) were varied between 30 and 45 kW and 1.3 and 2.0, respectively. To provide similar mass flows and thorough mixing of the effluent, high amounts of excess air were used to reduce and vary furnace temperatures to those more typical of HWIs and other incineration systems. Figure 1 presents a cutaway drawing of the Rainbow furnace with AFFF injection locations (burner, port 4, port 8) and stack sampling locations identified. In this configuration, the combustor most closely resembles a hazardous waste incinerator injecting a low heating value

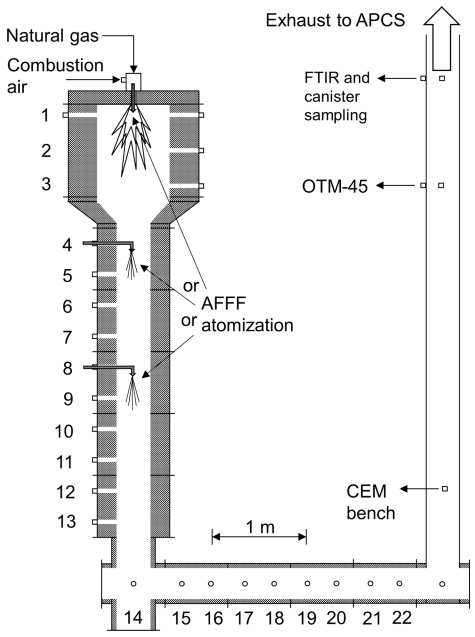


**Figure 1.** EPA refractory-lined natural gas-fired furnace showing the AFFF injection locations, through the flame with the natural gas and at ports 4 and 8 and the stack sampling locations indicated. Measurements are made prior to the facility air pollution control system (APCS).

liquid waste. Hazardous waste incinerators often introduce aqueous waste through lances downstream of the flame.

**AFFF Injection.** One legacy AFFF formulation composed primarily of PFOS and perfluorohexanesulfonic acid (PFHxS) was used for these experiments. The AFFF was analyzed by a commercial laboratory for PFAS according to their liquid chromatography coupled to tandem mass spectrometry (LC/MS/MS) method derived from EPA Method 533.[33] The AFFF was added to a 19 L Cornelius keg placed on a scale to monitor mass loss and feed rate. The injection technique has been used previously[34] and is described here. AFFF was atomized through the burner or through one of two axial postflame access ports along the furnace centerline using twin fluid (air/AFFF) atomizers. The Cornelius keg was air pressurized (∼584 kPa) to push the AFFF through a manually adjusted needle valve and 4−50 mL/min liquid rotameter (Brooks Instrument, Hatfield, PA) to the atomizer. Simultaneously, compressed air (584 kPa) was directed through a mass flow controller (Sierra Instruments, model Smart-Trak 50 L/min, Monterey, CA) to the atomizer. The AFFF and atomization air were combined at one end of a length of 0.1753 cm inside diameter, 0.3175 cm outside diameter stainless steel tubing. Within the tubing the atomizing air causes the liquid to form a thin film on the inner tube surface and shears the liquid film into droplets (∼50 $\mu$m diameter for water) as it leaves the other end. The injector for the two postflame axial access ports included a 90-degree bend at the atomizer tip to direct the atomized AFFF downstream cocurrent with the combustion gases along the furnace centerline. In addition, to mitigate the potential for pyrolysis, the side port atomizer included two additional concentric outer tubes through which additional "sweep" air was introduced to keep the AFFF and atomizing air cool until the atomizer tip. The volumes of these two cooling flows were minor (∼3%) compared to the combustion gas flow. The burner incorporated atomizer did not need cooling,


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and atomized AFFF into the natural gas at the center of the International Flame Research Foundation (IFRF) variable air swirl burner (using setting 4 of 0−8) where the combined natural gas AFFF mixture then burned as a diffusion flame with combustion air added annularly.

Figure S1 in the Supporting Information (SI) indicates Rainbow furnace temperature profiles, approximate residence times, and AFFF injection locations. One experiment introduced the AFFF through the flame where the AFFF would be exposed to near adiabatic flame temperatures (1963 °C for a methane−air diffusion flame at 101 kPa) and free radical chemistry characteristics of a natural gas diffusion flame. This was followed by five postflame experiments that varied the peak (injection) temperature from 1180 to 810 °C in approximate increments of 100 °C. The Rainbow furnace operating conditions for each injection experiment are listed in Table S1.

**Real-Time Measurements.** Figure 1 indicates stack locations where combustion exhaust samples were extracted for analysis. As previously described,[30] a Fourier transform infrared spectrometer (FTIR, Model 2030, MKS Instruments Inc., Andover, MA) and a continuous emission monitor (CEM, Model ZRE Analyzer, California Analytical, Orange, CA) measured furnace exhaust concentrations of oxygen ($O_2$), carbon monoxide (CO), and $CO_2$. These measurements are intended to verify combustion conditions and quantify small amounts of air in-leakage caused by the facility's induced draft blower and operation at a ∼1.27 cm $H_2O$ draft. FTIR was also used to measure moisture ($H_2O$), HF, sulfur dioxide ($SO_2$), and nitric oxide (NO). Note that CEM measurements are dry (moisture removed), and FTIR measurements are wet. Where available, the CEM and FTIR values were compared, taking into account the water, to verify the FTIR's measurements.

**Volatile Nonpolar PFAS.** The volatile PFAS and fluorochemicals (vPFAS) were sampled using evacuated 6 L Silonite coated stainless steel canisters (Entech, Simi Valley, CA). The emissions were sampled with a heated probe, filter, and perfluoroalkoxy alkane (PFA) heated sample line at 120 °C and ∼3 L/min. A 1.0 L/min slip stream of the emissions was passed through three 0.1 M sodium hydroxide (NaOH) filled mini (∼30 mL) impingers and one empty impinger in an ice bath to remove acid gases and reduce the water content in the samples. The evacuated canisters (−101 kPa) collected stack gases after the impingers and were filled to ∼−34 kPa, resulting in an ∼4 L sample volume. Subambient pressure was maintained to minimize condensation inside the canister. For analysis, the canisters were pressurized with dry nitrogen to 207 kPa, and the injections were spiked with internal standards, d5-chlorobenzene, and 1,4-difluorobenzene.

The canisters were analyzed using a Markes International Unity-xr TD system and Markes BenchTOF-Select MS system (Bridgend, U.K.) integrated with an Agilent 7890B gas chromatograph (GC, Santa Clara, CA). Tetrafluoromethane was concentrated from 15 mL of sample to avoid trap breakthrough. Aliquots of 200 mL of the samples were trapped for other PFAS. Samples were concentrated using a Markes Greenhouse Gas trap at −30 °C and desorbed at 40 °C/s to 280 °C and held for 0.5 min. Analytes were separated using an Agilent GS-GasPro column (60 m × 0.32 mm inside diameter) starting at 50 °C, held for 1 min, increased at 5 °C/min to 130 °C, and then ramped at 10 °C/min to 240 °C and held for 37 min. Quantitation of 30 vPFAS were performed using a seven-point (0.5 to 20 ppbv, 50 to 200 ppbv for $CF_4$) calibration curve for each analyte.

**Semi- and Nonvolatile Polar PFAS.** The semivolatile and nonvolatile polar PFAS were sampled and analyzed according to the U.S. EPA's Other Test Method 45 (OTM-45).[35] Briefly, ∼ 3.0 $m^3$ was sampled over 3 h at a constant rate from the furnace exhaust. Due to the low pressure drop in the ductwork, isokinetic sampling could not be performed. OTM-45 creates four fractions (probe rinsate and filter, an XAD sorbent trap, impinger water, and a breakthrough XAD sorbent trap) for analysis using LC/MS/MS with a method based on Method 533 to quantify 49 polar PFAS, see Table S2 in the SI. The PFAS mass from each fraction was summed to give the total mass for each sample. A proof blank train was created by setting up and recovering an OTM-45 train with clean glassware near the sampling location. The sample extraction and analyses were performed by a commercial environmental laboratory, Eurofins TestAmerica (Knoxville, TN), according to OTM-45 and their standard operating procedures.

**Calculation of Destruction Efficiency.** To account for variable excess combustion air and any additional dilution caused by in leakage into the furnace, the DEs for the targeted PFAS in the AFFF were calculated using Method 19[36] as done previously.[30] The DE, or percent removal, was calculated using eq 1, but $W_{out}$ was replaced with Method 19's $E_{ao}$, the mass emissions rate, and $W_{in}$ was replaced with $E_{ai}$, the mass input rate. The mass emission rates are further defined in the SI.

**Nontargeted PFAS.** Nontargeted analysis (NTA) was performed with additional mass spectrometry analysis of the OTM-45 extracts using LC coupled to a high-resolution Thermo Orbitrap Fusion mass spectrometer (Thermo Fisher Scientific, Waltham, MA, U.S.A.) described elsewhere.[37,38] Extracts were diluted 1:3 with water and then analyzed with the LC/MS using a heated electrospray ionization source operated in negative mode. Data was generated using data dependent MS/MS acquisition with a scan range of 150−1500 $m/z$ and Orbitrap resolutions of 60,000 and 15,000 for MS1 and MS2 acquisition, respectively. Instrument settings are detailed in the SI.

Raw instrument files were then processed with Thermo Compound Discoverer 3.3 to extract chemical features and tentatively matched against several databases (the USEPA's Distributed Structure-Searchable Toxicity (DSSTox), Thermo mzCloud, and Mass Bank of North America (MONA) mzvault library). The compounds' formula and potential names were generated by Compound Discoverer based on the MS1 molecular ion's mass. Some formulas and chemical names do not show fluorine, but the MS2 spectra possessed PFAS-like features. The PFAS-like features were manually identified based on a negative mass defect or predicted formula containing multiple fluorine atoms and fragmentation consistent with the fluorinated moieties listed in Table S3. Determining the presence of fluorinated molecules was the focus of this study; subsequent studies may focus on identification of unidentified compounds.

## RESULTS AND DISCUSSION

**Targeted PFAS Destruction.** The AFFF was found to contain 10 PFAS from the targeted analyte list; see Table S4 in the SI. The quantitated PFAS consisted of C4 to C8 perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl sulfonic acids (PFSAs), and concentrations of the 10 PFAS were used to calculate the DEs for the PFAS in the AFFF. The


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**Table 1. OTM-45 Results**

| Temperature (°C) | MB[a] | PBT[a] | Flame | 1180 | 1090 | 970 | 870 | 810 |
|---|---|---|---|---|---|---|---|---|
| Sample volume (dscm)[b] | - | - | 3.12 | 3.71 | 3.71 | 3.72 | 3.74 | 3.74 |
| Injection Port | - | - | burner | 4 | 4 | 8 | 4 | 8 |
| **PFAS**[a] | ng/sample | ng/sample | ng/sample | ng/sample | ng/sample | ng/sample | ng/sample | ng/sample |
| PFBA | ND | 5.57 | 22.3 | 108 | 9.10[c] | 628[c] | 3950 | 116000 |
| PFPeA | ND | 3.32 | 17.6 | 56.0 | 7.42[c] | 249[c] | 741 | 63400 |
| PFHxA | ND | 6.59 | 26.1 | 100 | 13.8 | 490 | 1240 | 151000 |
| PFHpA | 0.40 | 1.55 | 6.32 | 29.8 | 5.23 | 65.5 | 475 | 36300 |
| PFOA | ND | 2.30 | 36.8 | 156 | 144[d] | 452[d] | 1430 | 78400 |
| PFBS | 0.11 | 0.41 | 0.61 | 6.66 | 0.57 | 0.67 | 28.8 | 1860 |
| PFPeS | ND | ND | ND | 4.58 | 0.14 | 0.54 | 23.4 | 1680 |
| PFHxS | ND | 1.25 | 0.92 | 21.6 | 1.36[d] | 2.33[d] | 118 | 8520 |
| PFHpS | ND | ND | ND | 1.84 | ND | 0.34 | 17.1 | 989 |
| PFOS | ND | 9.30[d] | 3.08[d] | 116 | 42.2[d] | 18.6[d] | 819 | 62200 |

[a]MB is laboratory method blank, PBT is the proof blank train, abbreviations are in Table S2 [b]Dry standard cubic meter. [c]Pre-extraction internal standards were above of acceptance criteria, >150% [d]Pre-extraction internal standards were below acceptance criteria, <20%

**Table 2. DEs for Measured PFAS in AFFF with Gray Shading Indicating Less than Four Nines DE**

| Temperature, (°C) | Flame | 1180 | 1090 | 970 | 870 | 810 |
|---|---|---|---|---|---|---|
| **PFAS** | (%) | (%) | (%) | (%) | (%) | (%) |
| PFBA | 99.9958 | 99.9725 | 99.9978 | 99.8443[b] | 98.3336[b] | 45.7362 |
| PFPeA | 99.9993 | 99.9971 | 99.9996 | 99.9876[b] | 99.9372[b] | 94.0300 |
| PFHxA | 99.9997 | 99.9984 | 99.9998 | 99.9925 | 99.9678 | 95.6188 |
| PFHpA[a] | 99.9997 | 99.9984 | 99.9997 | 99.9965 | 99.9566 | 96.3086 |
| PFOA | 99.9996 | 99.9978 | 99.9981 | 99.9938[b] | 99.9663[b] | 97.9522 |
| PFBS[a] | >99.9999 | >99.9999 | >99.9999 | >99.9999 | 99.9996 | 99.9704 |
| PFPeS | >99.9999 | >99.9999 | >99.9999 | >99.9999 | 99.9996 | 99.9671 |
| PFHxS | >99.9999 | >99.9999 | >99.9999[b] | >99.9999[b] | 99.9997 | 99.9768 |
| PFHpS | >99.9999 | >99.9999 | >99.9999 | >99.9999 | 99.9996 | 99.9766 |
| PFOS | >99.9999[b] | >99.9999 | >99.9999[b] | >99.9999[b] | 99.9997 | 99.9751 |

[a]PFBS and PFHpA were detected in the analytical method blanks. [b]Pre-extraction internal standards were outside of acceptance criteria; DEs used estimated maximum concentrations.

PFAS found in the stack emissions from the OTM-45 sampling for all six AFFF injections are shown in Table 1, with compound abbreviations defined in Table S2. No other PFAS from the OTM-45 target list above method blank (MB) and reporting levels were detected in any of the sampling trains besides the original 10, with just perfluorononanoic acid (PFNA) being detected near blank levels in two samples and perfluorooctanesulfonamide (FOSA) being just above the detection limit in one sample. This is not surprising, as the 49 PFAS from OTM-45 are from methods for water analysis and are complex polar structures of industrial relevance that are more likely to be found in industrial discharges than to be formed via de novo synthesis during combustion processes. An exception to this may be the PFCAs which may form from fluoroalkyl fragments in the presence of water at postflame and stack conditions.

For these experiments, the train's glassware was cleaned according to OTM-45 for each test, so a field blank train was not run since the proof blank train (PBT) was the same as a field blank train. The PBT showed some near detection limit levels of contamination, mainly due to the XAD fractions of the train. The PFCAs, perfluorobutanesulfonic acid (PFBS), perfluorohexanesulfonic acid (PFHxS), and PFOS were all measured at trace levels in the proof blank train. The results are reported according to OTM-45, without any blank correction. The samples with low levels of PFAS are reported as near blank levels to indicate that the result may be biased high and the PFAS may be below the detection limit. The OTM-45 data were also impacted by the low recovery of the isotopically labeled extraction internal standard for some longer chain PFAS. This is likely due to the water that collects in the XAD decreasing the solubility of the long chain PFAS. The impacted PFAS are noted in the tables, and the values are the highest estimated value provided by the commercial laboratory.

The experimental sequence was flame, 1090, 970, 870, 810, and 1180 °C. It appears that there may have been some hysteresis due to contamination of internal furnace surfaces after the test at the lowest temperature. Experiments were performed on separate days with at least 18 h of operation at new combustion conditions without AFFF injection to achieve equilibrium. The experiment at 1180 °C was performed the



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Table 3. Volatile PFAS and Other Gases Quantified in the Emissions from AFFF Incineration

| | Temperature (°C) | | | | | |
|---|---|---|---|---|---|---|
| | Flame | 1180 | 1090 | 970 | 870 | 810 |
| **Canister Analytes ($\mu g/m^3$)** | | | | | | |
| tetrafluoromethane | ND | ND | ND | ND | ND | ND |
| hexafluoroethane | ND | ND | ND | 11.4 | 9.36 | 6.51 |
| chlorotrifluoromethane | ND | ND | ND | ND | ND | ND |
| fluoroform | ND | ND | ND | 5.47 | 601 | 7530 |
| octafluoropropane | ND | ND | ND | 267 | 903 | 795 |
| difluoromethane | ND | ND | ND | 2.87 | 8.51 | 94.4 |
| pentafluoroethane | 0.70 | 1.35 | 0.65 | 3.99 | 276 | 8950 |
| octafluorocyclobutane | ND | ND | ND | ND | ND | 14.1 |
| fluoromethane | ND | ND | ND | ND | ND | 1.30 |
| tetrafluoroethylene | ND | ND | ND | ND | 1.16 | 149 |
| hexafluoropropylene | ND | 0.19 | ND | 0.31 | 4.96 | 567 |
| 1,1,1-trifluoroethane | ND | ND | ND | ND | ND | ND |
| hexafluoropropene oxide | ND | ND | ND | ND | ND | ND |
| chlorodifluoromethane | ND | ND | ND | ND | ND | ND |
| 1,1,1,2-tetrafluoroethane | ND | ND | ND | 3.39 | 1.84 | 64.2 |
| perfluorobutane | ND | 0.30 | ND | ND | 434 | 620 |
| 1*H*-heptafluoropropane | ND | 0.99 | ND | ND | 86.8 | 2480 |
| octafluourocyclopentene | ND | ND | ND | ND | 5.15 | 235 |
| trichlorofluoromethane | 0.40 | 0.17 | 0.57 | 0.57 | 0.40 | 0.57 |
| dodecafluoro-*n*-pentane | ND | ND | ND | ND | 51.2 | 503 |
| 1*H*-nonafluorobutane | ND | 0.64 | ND | ND | 59.8 | 1230 |
| tetradecafluorohexane | ND | ND | ND | ND | 1.41 | 307 |
| 1*H*-perflluoropentane | ND | ND | ND | ND | 12.1 | 1000 |
| E1[a] | ND | ND | ND | ND | ND | ND |
| hexadecaflluroheptane | ND | ND | ND | ND | ND | 85.81 |
| 1*H*-perfluorohexane | ND | ND | ND | ND | 6.65 | 1090 |
| perfluorooctane | ND | ND | ND | ND | ND | 291 |
| 1*H*-perfluoroheptane | ND | ND | ND | ND | ND | 316 |
| 1*H*-Perfluorooctane | ND | ND | ND | ND | ND | 203 |
| E2[b] | ND | ND | ND | ND | ND | ND |
| **FTIR Analytes** | | | | | | |
| CO (ppm) | 7.2 | 3.6 | 4.5 | 5.7 | 109 | 1730 |
| $CO_2$ (%) | 6.2 | 6.3 | 5.2 | 5.0 | 4.4 | 4.0 |
| HF (ppm)[c] | 427 | 340 | 278 | 266 | 260 | 227 |
| NO (ppm)[c] | 86.7 | 91 | 63.5 | 38.1 | 4.9 | 0.4 |
| $SO_2$ (ppm)[c] | 60.9 | 41.7 | 34 | 31.4 | 35.2 | 35.4 |
| **Other Gas** | | | | | | |
| Oxygen, $O_2$ (dry, %) | 7.9 | 7.2 | 9.0 | 9.2 | 11.8 | 12.0 |

[a]Heptafluoropropyl 1,2,2,2-tetrafluoroethyl ether. [b]2*H*-Pefluoro-5-methyl-3,6-dioxanonane. [c]Values not verified with CEM data or certified transfer standard.

day after the lowest temperature injection experiment at 810 °C; Table 1 indicates slightly higher concentrations of some PFCAs than the experiment at 1090 °C, and the PFSAs had higher concentrations than the experiment at 970 °C. Even so, the concentrations were not far above the detection limits and still show very high DEs, but the potential for hysteresis is something to note. The apparent carryover could be due to the quartz probe not going through as extensive of a cleaning process as the other glassware and only being rinsed and brushed, or the furnace may not have fully desorbed PFAS deposited on refractory and ductwork surfaces during the previous 810 °C experiment. The 1180 °C experiment was not repeated due to the time to receive the analytical results and the high cost for each run. The possible contamination was relatively low, and the 1180 °C experiment measured most of the targeted compounds near the detection limit. As a result, the possible contamination did not impact the aim of these experiments to determine if DEs are an effective metric to verify treatment of PFAS. Future tests will involve more rigorous cleaning of the probe and a combustion blank to look for contamination in the system, and more time will pass between low temperature tests to allow more complete surface desorption.

The DEs for the 10 PFAS quantified in the AFFF as determined using Method 19 are shown in Table 2, with the values below four nines, <99.99%, emphasized using gray shading. The original PFAS concentrations (Table S4), AFFF feed rates and combustion parameters (Table S1), and AFFF stack emissions (Table 1) were used in the calculations. When reported PFAS emissions were not detected (ND), the detection limit was used as a conservative value for DE calculation. The lack of corrections for blank contamination as well as corrections for recoveries (including low recoveries)



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also serve to reduce DE values and provide more conservative values.

The DEs for all five PFSAs are >99.9999% for the four PFAS injection locations >970 °C. Even at 870 and 810 °C, DEs for all five PFSAs were >99.999% and >99.9%, respectively. DEs for the five PFCAs were also high (mostly >99.99%) for injection temperatures >1090 °C and mostly >99.9% for injection temperatures >870 °C. Even at the lowest AFFF injection temperature, 810 °C, DEs > 94% were measured for four PFCAs, except for perfluorobutanoic acid (PFBA). PFBA exhibited the lowest DEs, both with respect to AFFF injection temperatures and PFCA chain length. Lower than expected DEs for PFBA and PFCAs have been reported previously with various destruction technologies[25,39,40] and may suggest either that shorter PFCAs are relatively more stable species or shorter chained PFCAs are formed via hydrolysis of fluoroalkyl fragments in the postflame. Note that PFSAs do not indicate this same trend with calculated DEs for PFBS and PFOS approximately similar at corresponding temperatures. This trend for PFCAs might also suggest a pathway or intermediate through which PFAS transition during thermal destruction. PFAS might be affected by high concentrations of hydroxyl radicals (OH), $H_2O$, and $CO_2$ in the combustion gases that promote reformation of PFCAs from fluoroalkyl fragments. This has been reported to occur in the atmosphere[28] and experimentally,[41,42] and the formation of aldehydes and acyl fluorides that can react to create carboxylic acids has been predicted by several computational mechanisms.[43−46] If true, the conversion of PFSAs to PFCAs would reduce apparent DEs for PFCAs while the PFSAs would have higher DEs. These experiments, using a complex mixture of PFAS and other unknown components in the AFFF, do not represent the best approach for addressing mechanistic questions. Further experiments using neat solutions of specific PFAS in coordination with ongoing kinetic modeling efforts are needed to better address mechanisms.

**Volatile Emissions.** The generally high DEs (>99.99%) presented in Table 2 suggest PFAS are relatively fragile, at least with respect to losing their molecular identity even at temperatures <900 °C. High DEs, however, do not necessarily ensure the absence of emissions of fluoroorganic PICs. Evacuated canisters were used to look for some known[21−23] and suspected PICs. The current method under development at the EPA can measure the 30 vPFAS listed in Table 3. The reporting limits for 29 of these compounds is 0.5 ppbv, while tetrafluoromethane ($CF_4$) is limited to 50 ppbv. These are high values with respect to OTM-45 (∼pptv concentrations), and current efforts are focused on lowering these limits of quantitation. This method was used during the AFFF incineration experiments, and the results, presented in $\mu g/m^3$, are shown in Table 3. At AFFF injection locations >1090 °C, the PIC data show very little vPFAS at the current detection limits, but as the AFFF injection temperatures fall below 1000 °C, the vPFAS increase considerably to $mg/m^3$ levels. The increase in vPFAS also coincides with elevated CO concentrations rising from single digit levels up to ∼1700 ppmv (see Table 3). Increases in CO were the result of incomplete PFAS oxidation and not associated with the natural gas combustion, as the AFFF experiments with high CO were injected postflame long after natural gas combustion was complete.

An important finding from Table 3 is the notable emissions of relatively high concentrations (∼$mg/m^3$) of all eight 1*H*-perfluoroalkanes (C1−C8) during the 810 °C injection experiment. These vPFAS are expected to be formed during the thermolysis of the PFCAs or PFSAs under both pyrolytic and oxidative conditions.[21−23,43,45,47] The fluorocarbon concentrations increase with decreasing fluoroalkyl chain length, with fluoroform ($CHF_3$) and pentafluoroethane ($C_2HF_5$) present at 810 °C, at concentrations of 7.5 and 9.0 $mg/m^3$, respectively. 1*H*-Perfluorooctane ($C_8HF_{17}$) and 1*H*-perfluoroheptane ($C_7HF_{15}$) concentrations were significantly lower (0.2 and 0.3 $mg/m^3$, respectively), possibly indicating a mechanistic pathway of incremental $\alpha$ or $\beta$ carbon removal. Tetrafluoroethylene ($C_2F_4$) concentrations are relatively low (∼0.15 $mg/m^3$), perhaps suggesting that a mechanism where $C_2F_4$ is formed[48,49] by $\beta$ carbon scission is less important under oxidative conditions.

Note that similar results have been both experimentally and computationally derived under pyrolytic and oxidative conditions. Thermolysis often yields 1*H*-perfluorocarbons and 1-perfluoroalkenes with PFCAs,[21−23,47,50,51] with PFSAs forming the same compounds[52] as well as perfluorocarbons.[47,53] Computational studies predict similar products[43−46,48] using various computational methods. All the referenced models have a lactone or sulfone intermediate with HF elimination as the first step to the loss of the functional group. After the removal of the functional group, the steps to formations of nonpolar intermediates, including the breaking of carbon−carbon and carbon−fluorine bonds, are all relatively low energy steps. These steps involve unimolecular decomposition, hydrofluorination, hydrolysis, and fragmentation of the alkyl chain. A prominent and potentially important intermediate are acyl fluorides since these can readily be hydrolyzed to carboxylic acids, as suspected in this study. Altarawneh[43] examined the temperature sensitivity of PFBS destruction from 500 to 2000 K and indicated that PFBS is destroyed at low temperatures but can create fluorinated PICs at temperatures up to 1127 °C. These studies examined different conditions than the present study, but still the similarities are remarkable and provide further support that high DEs are not necessarily indicative of the absence of PICs.

HF concentrations presented in Table 3 were not validated because no accompanying CEM measurement was available. Subsequent attempts at Method 320 validation were unsuccessful due to poor HF transport efficiencies and subsequent poor calibration gas recoveries. Additionally, the measured HF concentrations were typically observed to rise throughout the duration of an experiment indicating the HF was not yet at equilibrium with the reactive surfaces of the furnace. The HF values are included for perspective to indicate approximate HF concentrations based on the amounts of AFFF introduced. Note that NO values decrease with decreasing AFFF injection temperatures. This behavior is not fully understood but may be related to selective noncatalytic reduction (SNCR) technologies used for the control of nitrogen oxides.[54−56] SNCR decreases NO concentrations in combustion effluents by reactions with added ammonia, ammonia derivatives, or urea to the combustion gases at temperatures between 700 and 1000 °C. AFFF is known to contain percent levels of amines, sulfonamides, and amides, and these may be acting to reduce the NO concentrations as the AFFF injection temperatures fall below 1000 °C. Efforts to improve confidence in FTIR measurements including HF and NO are ongoing.



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ACS EST Engg. 2023, 3, 1308−1317

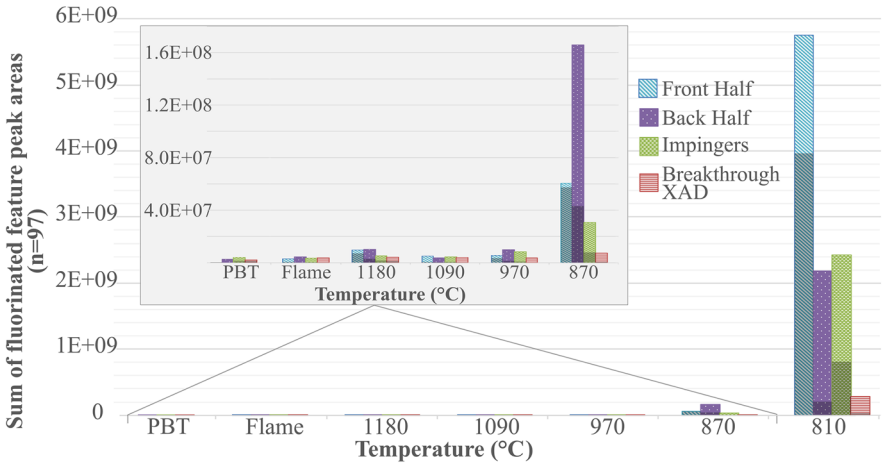


**Figure 2.** Sums of the peak areas of fluorinated features observed with nontargeted analyses of the OTM-45 extracts. Each fraction of the sampling train is shown for each temperature. The darkened portion of each bar is the sum of the targeted compounds' peak areas, included to show how well the targeted list covers the observed PFAS.

**Nontargeted PFAS Emissions.** Additional mass spectra analysis of the OTM-45 extracts revealed there were up to 92 features that indicated the presence of different semivolatile polar PFAS. Figure 2 presents the sum of the peak areas for these 92 fluorinated species for the six combustion experiments and the PBT. Where the peak area of a feature was very low, an arbitrary value was given to the peak to allow for statistical analysis by the software. This artificially makes the peak areas for fluorinated features in the blanks and some low detection samples higher than what they may actually be. Figure 2 does not correct for this, and again near blank levels may indicate the nontargeted peak areas are below detection limits. Figure 2 presents separate analysis for four OTM-45 sample fractions: front half (filter and probe rinse), back half (XAD-2 sorbent), impinger solutions, and a second volume of XAD-2 sorbent to quantify the potential for sample breakthrough. The NTA peak areas in Figure 2 are separated between those corresponding to 36 targeted PFAS (lightly shaded) and 56 nontargeted (unidentified) PFAS found. The tentative formulas and chemical names for the nontargeted PFAS are listed in Table S5. These formulas and names are based on the MS1 molecular ion; the software occasionally picked compounds that do not contain fluorine. The MS2 spectra did show PFAS-like features and are included in Table S5. The 36 targeted PFAS are part of the other OTM-45 targeted list of PFAS shown in Table S2, and Figure 2 shows how much the total PFAS present are made up of these targeted compounds. It is apparent many of the compounds sampled during these experiments are not found in the OTM-45 list. As the temperature decreases the peak area of the OTM-45 fractions shift from the back half XAD having the most area to the front half, or filter, fraction having the most area at 810 °C. This is due to the large increase of sulfonates in the emissions, see Table 1, that preferentially adsorbed on the filter, and to a lesser extent an increase of PFCAs on the filter too.

Figure 2 presents these data on two linear scales. The larger plot includes the 810 °C experiment, and the inset excludes these data to allow better comparison of the other experimental results. NTA indicates additional unidentified semivolatile polar PFAS mass in addition to the 36 targeted PFAS in all sample fractions. However, like the volatile nonpolar PIC measurements, injection temperatures > 1000 °C do not result in NTA PFAS mass significantly above blank levels. Note that the NTA also shows the suspected hysteresis effect of performing the 1180 °C experiment after the 810 °C experiment. The NTA indicates increasing PFAS emissions at AFFF injection temperatures < 1000 °C and that unidentified PFAS comprise a portion of these emissions.

## CONCLUSIONS

The functional groups of many PFAS, and perhaps many PFAS of industrial importance, can be removed at temperatures which do not fully mineralize the fluorinated chain. This would classify many industrial PFAS as Class 3 to Class 5 compounds on the U.S. EPA's Thermal Stability Index, where Class 1 is the most stable and Class 7 compounds are the least stable.[45] Despite the ranking of parent PFAS, subsequent fluorinated PICs formed are stable,[57] and the simple use of DEs as the sole indicator of complete PFAS destruction may be misleading. For some PFAS, relatively low energies are needed to remove the polar functional group, with the first step being the loss of the terminal C or S likely through a lactone or sulfone intermediate, leaving a nonpolar fluoroalkyl chain. If conditions prevent continuation of the destruction mechanisms, this may result in high DEs, >99.99%, but not necessarily the mineralization of the PFAS molecule. Here, complete destruction is defined as mineralization, which for a C, F, O, H system results in $CO_2$, HF, and $H_2O$. In these experiments, combustion conditions were examined that produced high DEs and measurable PICs. However, when AFFF was exposed to temperatures ≥1090 °C (including exposure to flames and near adiabatic flame temperatures), high DEs and near detection limit concentrations of relatively few vPFAS PICs were observed. Based on these experiments, high destruction of PFAS can be shown only by considering both high DEs and the absence of PICs.

Finally, note that these experiments focused on steady-state combustor operations. This was done to simplify the fluid dynamics and mixing behavior and allow a focus on the kinetic aspects. However, except for thermal oxidizers and some other steady-state liquid injection applications, HWIs (often rotary kilns) introduce wastes in multiple ways, including batch solids and contained liquids. These cause transient release of organics to the vapor phase that may temporarily overwhelm available


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ACS EST Engg. 2023, 3, 1308−1317

oxygen and depress temperatures. For most HWIs, the afterburner is intended to dampen and smooth this transient behavior, but it is likely that the time dependent behavior of PFAS in HWIs and other batch fed systems will depend on the system's ability to smooth these transients and maintain high temperatures. More research into rotary kiln systems and full-scale incinerators is needed.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsestengg.3c00098.

Additional combustor conditions, sampling setup, method information, analytical data, destruction efficiency calculation method, and analytical methods for nontargeted analysis (PDF)

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### Notes

The research described in this article has been reviewed by the U.S. EPA Center for Environmental Measurement and Modeling and approved for publication. The contents of this article should not be construed to represent Agency policy nor does mention of trade names or commercial products constitute endorsement or recommendation for use.
The authors declare no competing financial interest.

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## REFERENCES

(1) Lemal, D. M. Perspective on fluorocarbon chemistry. *J. Org. Chem.* **2004**, *69* (1), 1−11.
(2) Okazoe, T. Overview on the history of organofluorine chemistry from the viewpoint of material industry. *Proc. Jpn. Acad. Ser. B Phys. Biol. Sci.* **2009**, *85* (8), 276−89.
(3) Goldwhite, H. The Manhattan Project. *J. Fluor. Chem.* **1986**, *33* (1−4), 109−132.
(4) Zhu, W.; Khan, K.; Roakes, H.; Maker, E.; Underwood, K. L.; Zemba, S.; Badireddy, A. R. Vermont-wide assessment of anthropogenic background concentrations of perfluoroalkyl substances in surface soils. *J. Hazard Mater.* **2022**, *438*, 129479.
(5) Thompson, K. A.; Mortazavian, S.; Gonzalez, D. J.; Bott, C.; Hooper, J.; Schaefer, C. E.; Dickenson, E. R. V. Poly- and perfluoroalkyl substances in municipal wastewater treatment plants in the United States: seasonal patterns and meta-analysis of long-term trends and average concentrations. *ACS ES&T Water* **2022**, *2*, 690.
(6) Li, J.; Sun, J.; Li, P. Exposure routes, bioaccumulation and toxic effects of per- and polyfluoroalkyl substances (PFASs) on plants: A critical review. *Environ. Int.* **2022**, *158*, 106891.
(7) Nakayama, S. F.; Yoshikane, M.; Onoda, Y.; Nishihama, Y.; Iwai-Shimada, M.; Takagi, M.; Kobayashi, Y.; Isobe, T. Worldwide trends in tracing poly- and perfluoroalkyl substances (PFAS) in the environment. *TrAC, Trends Anal. Chem.* **2019**, *121*, 115410.
(8) Chang, C. J.; Barr, D. B.; Ryan, P. B.; Panuwet, P.; Smarr, M. M.; Liu, K.; Kannan, K.; Yakimavets, V.; Tan, Y.; Ly, V.; Marsit, C. J.; Jones, D. P.; Corwin, E. J.; Dunlop, A. L.; Liang, D. Per- and polyfluoroalkyl substance (PFAS) exposure, maternal metabolomic perturbation, and fetal growth in African American women: A meet-in-the-middle approach. *Environ. Int.* **2022**, *158*, 106964.
(9) Fenton, S. E.; Ducatman, A.; Boobis, A.; DeWitt, J. C.; Lau, C.; Ng, C.; Smith, J. S.; Roberts, S. M. Per- and polyfluoroalkyl substance toxicity and human health review: current state of knowledge and strategies for informing future research. *Environ. Toxicol. Chem.* **2021**, *40* (3), 606−630.
(10) Grandjean, P.; Andersen, E. W.; Budtz-Jorgensen, E.; Nielsen, F.; Molbak, K.; Weihe, P.; Heilmann, C. Serum vaccine antibody concentrations in children exposed to perfluorinated compounds. *JAMA* **2012**, *307* (4), 391−7.
(11) Zhang, Y.; Pan, C.; Ren, Y.; Wang, Z.; Luo, J.; Ding, G.; Vinturache, A.; Wang, X.; Shi, R.; Ouyang, F.; Zhang, J.; Li, J.; Gao, Y.; Tian, Y. Association of maternal exposure to perfluoroalkyl and polyfluroalkyl substances with infant growth from birth to 12 months: A prospective cohort study. *Sci. Total Environ.* **2022**, *806*, 151303.
(12) U.S. EPA. Lifetime Drinking Water Health Advisories for Four Perfluoroalkyl Substances. *Federal Register* June 21, 2022, *87*, 36848−36849.
(13) U.S. EPA. *Drinking Water Health Advisories for PFOA and PFOS*. 2022. https://www.epa.gov/sdwa/drinking-water-health-advisories-pfoa-and-pfos (accessed February 21, 2023).
(14) Cousins, I. T.; Johansson, J. H.; Salter, M. E.; Sha, B.; Scheringer, M. Outside the safe operating space of a new planetary boundary for per- and polyfluoroalkyl substances (PFAS). *Environ. Sci. Technol.* **2022**, *56*, 11172.
(15) Oppelt, E. T. Incineration of hazardous waste. A critical review. *J. Air Pollut. Control Assoc.* **1987**, *37* (5), 558−86.
(16) U.S. EPA. *A Citizen's Guide to Incineration*. 2012. https://www.epa.gov/sites/default/files/2015-04/documents/a_citizens_guide_to_incineration.pdf (accessed September 12, 2022).
(17) Dellinger, B.; Lamb, C. W.; Kumar, P.; Lanza, R.; Wagner, M. Theoretical estimation of incinerability of halons and hydrochlorofluorocarbons. *Environ. Eng. Sci.* **2010**, *27* (7), 587−591.
(18) Dellinger, B.; Taylor, P. H.; Lee, C. C. Full-scale evaluation of the thermal stability-based hazardous organic waste incinerability ranking. *J. Air Waste Manag. Assoc.* **1993**, *43* (2), 203−7.
(19) U.S. EPA. *What are the standards for hazardous waste incinerators that are effective until compliance with the standards under § 63.1219?* 2022. https://www.ecfr.gov/current/title-40/chapter-I/subchapter-C/part-63/subpart-EEE/subject-group-ECFRd3294690f47e3c6/section-63.1203 (accessed September 13, 2022).
(20) Taylor, P. H.; Dellinger, B.; Lee, C. C. Development of a thermal stability-based ranking of hazardous organic compound incinerability. *Environ. Sci. Technol.* **1990**, *24* (3), 316−328.
(21) LaZerte, J. D.; Hals, L. J.; Reid, T. S.; Smith, G. H. Pyrolyses of the Salts of the Perfluoro Carboxylic Acids1. *J. Am. Chem. Soc.* **1953**, *75* (18), 4525−4528.
(22) Krusic, P. J.; Marchione, A. A.; Roe, D. C. Gas-phase NMR studies of the thermolysis of perfluorooctanoic acid. *J. Fluor. Chem.* **2005**, *126* (11−12), 1510−1516.
(23) Krusic, P. J.; Roe, D. C. Gas-phase NMR technique for studying the thermolysis of materials: thermal decomposition of ammonium perfluorooctanoate. *Anal. Chem.* **2004**, *76* (13), 3800−3.
(24) Trang, B.; Li, Y.; Xue, X. S.; Ateia, M.; Houk, K. N.; Dichtel, W. R. Low-temperature mineralization of perfluorocarboxylic acids. *Science* **2022**, *377* (6608), 839−845.
(25) Wang, Y.; Pierce, R. D.; Shi, H.; Li, C.; Huang, Q. Electrochemical degradation of perfluoroalkyl acids by titanium suboxide anodes. *Environ. Sci.: Water Res. Technol.* **2020**, *6* (1), 144−152.
(26) Ivy, D. J.; Rigby, M.; Baasandorj, M.; Burkholder, J. B.; Prinn, R. G. Global emission estimates and radiative impact of C4F10, C5F12, C6F14, C7F16 and C8F18. *Atmos. Chem. Phys.* **2012**, *12* (16), 7635−7645.
(27) Mühle, J.; Ganesan, A. L.; Miller, B. R.; Salameh, P. K.; Harth, C. M.; Greally, B. R.; Rigby, M.; Porter, L. W.; Steele, L. P.; Trudinger, C. M.; Krummel, P. B.; O'Doherty, S.; Fraser, P. J.; Simmonds, P. G.; Prinn, R. G.; Weiss, R. F. Perfluorocarbons in the global atmosphere: tetrafluoromethane, hexafluoroethane, and octafluoropropane. *Atmos. Chem. Phys.* **2010**, *10* (11), 5145−5164.
(28) Ellis, D. A.; Martin, J. W.; De Silva, A. O.; Mabury, S. A.; Hurley, M. D.; Sulbaek Andersen, M. P.; Wallington, T. J. Degradation of fluorotelomer alcohols: a likely atmospheric source of perfluorinated carboxylic acids. *Environ. Sci. Technol.* **2004**, *38* (12), 3316−21.
(29) Giraud, R. J.; Taylor, P. H.; Huang, C. Combustion operating conditions for municipal Waste-to-Energy facilities in the U.S. *Waste Management* **2021**, *132*, 124−132.
(30) Krug, J. D.; Lemieux, P. M.; Lee, C. W.; Ryan, J. V.; Kariher, P. H.; Shields, E. P.; Wickersham, L. C.; Denison, M. K.; Davis, K. A.; Swensen, D. A.; Burnette, R. P.; Wendt, J. O. L.; Linak, W. P. Combustion of C1 and C2 PFAS: kinetic modeling and experiments. *J. Air Waste Manag. Assoc.* **2022**, *72* (3), 256−270.
(31) Yoo, J. I.; Shinagawa, T.; Wood, J. P.; Linak, W. P.; Santoianni, D. A.; King, C. J.; Seo, Y. C.; Wendt, J. O. High-temperature sorption of cesium and strontium on dispersed kaolinite powders. *Environ. Sci. Technol.* **2005**, *39* (13), 5087−94.
(32) Linak, W. P.; Miller, C. A.; Wood, J. P.; Shinagawa, T.; Yoo, J.-I.; Santoianni, D. A.; King, C. J.; Wendt, J. O. L.; Seo, Y.-C. High temperature interactions between residual oil ash and dispersed kaolinite powders. *Aerosol Sci. Technol.* **2004**, *38* (9), 900−913.
(33) U.S. EPA. *Method 533 - Determination of Per- and Polyfluoroalkyl Substances in Drinking Water by Isotope Dilution Anion Exchange Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry*. 2019. https://www.epa.gov/sites/default/files/2019-12/documents/method-533-815b19020.pdf (accessed September 13, 2022).
(34) Linak, W. P.; Srivastava, R. K.; Wendt, J. O. L. Metal aerosol formation in a laboratory swirl flame incinerator. *Combust. Sci. Technol.* **1994**, *101* (1−6), 7−27.


https://doi.org/10.1021/acsestengg.3c00098
*ACS EST Engg.* 2023, 3, 1308−1317

(35) U.S. EPA. *Other Test Method 45 (OTM-45) Measurement of Selected Per- and Polyfluorinated Alkyl Substances from Stationary Sources*. 2021. https://www.epa.gov/sites/default/files/2021-01/documents/otm_45_semivolatile_pfas_1-13-21.pdf (accessed September 8, 2022).
(36) U.S. EPA. *Method 19 - Determination of Sulfur Dioxide Removal Efficiency and Particulate, Sulfur Dioxide, and Nitrogen Oxide Emission Rates*. 2017. https://www.epa.gov/sites/default/files/2017-08/documents/method_19.pdf, (accessed September 13, 2022).
(37) McCord, J.; Strynar, M. Identification of per- and polyfluoroalkyl substances in the Cape Fear River by high resolution mass spectrometry and nontargeted screening. *Environ. Sci. Technol.* **2019**, *53* (9), 4717−4727.
(38) McCord, J. P.; Strynar, M. J.; Washington, J. W.; Bergman, E. L.; Goodrow, S. M. Emerging chlorinated polyfluorinated polyether compounds impacting the waters of southwestern New Jersey identified by use of nontargeted analysis. *Environ. Sci. Technol. Lett.* **2020**, *7* (12), 903−908.
(39) Wu, B.; Hao, S.; Choi, Y.; Higgins, C. P.; Deeb, R.; Strathmann, T. J. Rapid destruction and defluorination of perfluorooctanesulfonate by alkaline hydrothermal reaction. *Environ. Sci. Technol. Lett.* **2019**, *6* (10), 630−636.
(40) Sasi, P. C.; Alinezhad, A.; Yao, B.; Kubatova, A.; Golovko, S. A.; Golovko, M. Y.; Xiao, F. Effect of granular activated carbon and other porous materials on thermal decomposition of per- and polyfluoroalkyl substances: Mechanisms and implications for water purification. *Water Res.* **2021**, *200*, 117271.
(41) Singh, R. K.; Fernando, S.; Baygi, S. F.; Multari, N.; Thagard, S. M.; Holsen, T. M. Breakdown products from perfluorinated alkyl substances (PFAS) degradation in a plasma-based water treatment process. *Environ. Sci. Technol.* **2019**, *53* (5), 2731−2738.
(42) Feng, M.; Qu, R.; Wei, Z.; Wang, L.; Sun, P.; Wang, Z. Characterization of the thermolysis products of Nafion membrane: A potential source of perfluorinated compounds in the environment. *Sci. Rep* **2015**, *5*, 9859.
(43) Altarawneh, M. A chemical kinetic model for the decomposition of perfluorinated sulfonic acids. *Chemosphere* **2021**, *263*, 128256.
(44) Altarawneh, M.; Almatarneh, M. H.; Dlugogorski, B. Z. Thermal decomposition of perfluorinated carboxylic acids: Kinetic model and theoretical requirements for PFAS incineration. *Chemosphere* **2022**, *286*, 131685.
(45) Blotevogel, J.; Giraud, R. J.; Rappé, A. K. Incinerability of PFOA and HFPO-DA: mechanisms, kinetics, and thermal stability ranking. *Chem. Eng. J.* **2023**, *457*, 141235.
(46) Khan, M. Y.; So, S.; da Silva, G. Decomposition kinetics of perfluorinated sulfonic acids. *Chemosphere* **2020**, *238*, 124615.
(47) Alinezhad, A.; Challa Sasi, P.; Zhang, P.; Yao, B.; Kubátová, A.; Golovko, S. A.; Golovko, M. Y.; Xiao, F. An investigation of thermal air degradation and pyrolysis of per- and polyfluoroalkyl substances and aqueous film-forming foams in soil. *ACS ES&T Engineering* **2022**, *2*, 198.
(48) Altarawneh, M. A theoretical study on the pyrolysis of perfluorobutanoic acid as a model compound for perfluoroalkyl acids. *Tetrahedron Lett.* **2012**, *53* (32), 4070−4073.
(49) Xiao, F.; Sasi, P. C.; Alinezhad, A.; Golovko, S. A.; Golovko, M. Y.; Spoto, A. Thermal decomposition of anionic, zwitterionic, and cationic polyfluoroalkyl substances in aqueous film-forming foams. *Environ. Sci. Technol.* **2021**, *55* (14), 9885−9894.
(50) Yao, B.; Sun, R.; Alinezhad, A.; Kubátová, A.; Simcik, M. F.; Guan, X.; Xiao, F. The first quantitative investigation of compounds generated from PFAS, PFAS-containing aqueous film-forming foams and commercial fluorosurfactants in pyrolytic processes. *J. Hazard. Mater.* **2022**, *436*, 129313.
(51) Weber, N. H.; Delva, C. S.; Stockenhuber, S. P.; Grimison, C. C.; Lucas, J. A.; Mackie, J. C.; Stockenhuber, M.; Kennedy, E. M. Thermal decomposition of perfluorooctanesulfonic acid (PFOS) in the presence of water vapor. *Ind. Eng. Chem. Res.* **2022**, *61* (41), 15146−15155.
(52) Duchesne, A. L.; Brown, J. K.; Patch, D. J.; Major, D.; Weber, K. P.; Gerhard, J. I. Remediation of PFAS-contaminated soil and granular activated carbon by smoldering combustion. *Environ. Sci. Technol.* **2020**, *54* (19), 12631−12640.
(53) Weber, N. H.; Delva, C. S.; Stockenhuber, S. P.; Grimison, C. C.; Lucas, J. A.; Mackie, J. C.; Stockenhuber, M.; Kennedy, E. M. Thermal mineralization of perfluorooctanesulfonic acid (PFOS) to HF, CO2, and SO2. *Ind. Eng. Chem. Res.* **2023**, *62*, 881.
(54) Lyon, R. Method for the reduction of the concentration of NO in combustion effluents using ammonia. US3900554, Aug. 19, 1975.
(55) Arand, J. K.; Muzio, L. J.; Sotter, J. G. Urea reduction of NOx in combustion effluents. US4208386, Jun. 17, 1980.
(56) Lyon, R. K. Thermal DeNOx controlling nitrogen oxides emissions by a noncatalytic process. *Environ. Sci. Technol.* **1987**, *21* (3), 231−236.
(57) Tsang, W.; Burgess, D. R.; Babushok, V. On the incinerability of highly fluorinated organic compounds. *Combust. Sci. Technol.* **1998**, *139* (1), 385−402.

## NOTE ADDED AFTER ASAP PUBLICATION

This paper published ASAP on June 1, 2023 with errors in Table 2. The errors were corrected and the paper reposted on July 7, 2023.


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# Exhibit C

**Incineration is not a safe disposal method for PFAS**

Incineration is not proven to safely destroy per- and polyfluoroalkyl substances (PFAS). Commercial incinerators do not, and often cannot, measure their PFAS releases, and the limited laboratory testing that has been conducted does not reflect real-world incineration conditions. PFAS chemicals' carbon-fluorine bond is particularly resistant to combustion, making PFAS unusually difficult and dangerous to incinerate. Yet, despite an acknowledged lack of data, the federal government has already incinerated millions of gallons of PFAS-containing waste, placing the communities surrounding incinerators at risk.

Under the National Defense Authorization Act for Fiscal Year 2020, the Department of Defense cannot incinerate PFAS unless it first establishes that the incineration is "conducted at a temperature range adequate to break down PFAS chemicals while also ensuring the maximum degree of reduction in emission of PFAS, including elimination of such emissions where achievable" and is "conducted in accordance with the requirements of the Clean Air Act, including controlling hydrogen fluoride."[1]

The National Defense Authorization Act for Fiscal Year 2022 imposed a federal moratorium on PFAS incineration until DOD "issues guidance implementing" the foregoing requirements, as well as the recommendations in the Environmental Protection Agency's interim guidance on the destruction and disposal of PFAS and materials containing PFAS.[2] The information that would be required to inform and support that guidance does not currently exist, as there is no proof that existing incinerators are capable of breaking down PFAS chemicals without generating additional PFAS emissions or other harmful products of incomplete combustion.

We reviewed published studies related to PFAS incineration. Scientists are plagued by measurement challenges—studies have unacceptably high detection limits and/or analyze for just a limited number of potential breakdown products, or analyze the incineration of tiny amounts of PFAS compounds. Indeed, the sentinel study done for 3M on PFAS incineration used a bench scale burner and incinerated about an ounce of PFAS. As EPA itself has recognized, "the effectiveness of incineration to destroy PFAS compounds and the tendency for formation of fluorinated or mixed halogenated organic

[1] National Defense Authorization Act for Fiscal Year 2020, Pub. L. 116-92, § 330, 133 Stat. 1198 (enacted Dec. 20, 2019),
[2] National Defense Authorization Act for Fiscal Year 2022, Pub. L. No. 117–81, § 343(a), 135 Stat. 1643 (enacted Dec. 27, 2021).

byproducts is not well understood" and "[e]mission studies … have been incomplete due to lack of necessary measurement methods suitable for the comprehensive characterization of fluorinated and mixed halogenated organic compounds."[3] Instead of returning to an unproven and dangerous PFAS disposal technology, the Department of Defense should heed EPA's recommendation of "interim storage" of PFAS-containing waste "until identified uncertainties are addressed and appropriate destruction and disposal technologies can be recommended."[4]

### *1. PFAS may not be eliminated in the operating conditions of a hazardous waste incinerator*

Two original industry studies of PFOS breakdown products lack the sensitivity to ensure a high level of thermal destruction. Destruction efficiencies of 99.9999% are usually required for highly toxic, persistent wastes, like PCBs and PFAS.[5] The 3M-sponsored studies from 2003 and 2005 didn't detect PFOS and PFOA in waste gasses, but had a detection limit of 0.1%, which means concentrations of up to 1,000 parts per million of PFOS or PFOA in air would not be detected under the conditions of this study.[6],[7] Indeed, given the large stockpiles that DOD holds of PFOS-based AFFF, allowing 0.1% of the PFAS to escape unreacted from incinerators could result in a massive amount of PFAS entering the environment.

EPA is developing methods to measure individual PFAS chemicals at a higher level of sensitivity in air samples, but until these methods are perfected it will be impossible to accurately gauge how much of the PFAS in military waste passes through into the atmosphere.

### *a. Thermal breakdown of PFAS can form a range of harmful breakdown products.*

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[3] United States Environmental Protection Agency, 2020a. Per- and Polyfluoroalkyl Substances (PFAS): Incineration to Manage PFAS Waste Streams. https://www.epa.gov/sites/default/files/2019-09/documents/technical_brief_pfas_incineration_ioaa_approved_final_july_2019.pdf

[4] United States Environmental Protection Agency, 2020b. Interim Guidance on the Destruction and Disposal of Perfluoroalkyl and Polyfluoroalkyl Substances and Materials Containing Perfluoroalkyl and Polyfluoroalkyl Substances. https://www.epa.gov/system/files/documents/2021-11/epa-hq-olem-2020-0527-0002_content.pdf

[5] United States Environmental Protection Agency, 2019. Guidance for Applicants Requesting to Treat/Dispose of PCBs Using Incineration or an Alternative Method. https://www.regulations.gov/docket?D=EPA-HQ-OLEM-2018-0305

[6] Philip Taylor & Tak Yamada, Final Report – Laboratory-Scale Thermal Degradation of Perfluoro-Octanyl Sulfonate and Related Precursors (May 2003), https://clu-in.org/download/contaminantfocus/pfas/UDR-TR-03-00044.pdf.

[7] Tak Yamada et al., Thermal Degradation of Fluorotelomer Treated Articles and Related Materials , 61 Chemosphere 974–84 (Nov. 2005), https://doi.org/10.1016/j.chemosphere.2005.03.025.

Even if the carbon-fluorine bonds in PFAS could be broken by incineration, the resulting, highly reactive fluorine molecules can form a range of harmful breakdown products with varied physical and chemical qualities. Much of the published incineration research for PFAS has been done at bench scale using just milligrams of starting materials, and in optimized temperature and handling protocols. These findings are not reflective of actual incineration conditions, and they have not been replicated at an operational scale.

As many scientists have acknowledged, "There are no proven analytical technologies which have been demonstrated to detect all potential fluoro-organic by-products."[8] Of particular concern are PFAS that get volatilized or transformed into volatile organofluorine compounds and escaped detection.[9]

Independent studies detect a range of concerning breakdown products in bench scale incineration studies. They include:

**Greenhouse gasses** - The original 3M studies measured several potent greenhouse gases and other breakdown products.[4,5] In Taylor (2003) PFOS byproducts include: fluorobenzene, one- and two- carbon fluoroalkanes (tetrafluoromethane, fluoroform, and hexafluoroethane), and fluoroalkenes (1,1-difluoroethene and 1,2-difluoroethene). Yamada (2005) heated PTFE (a polytetrafluoroethylene polymer) to a maximum of 1000C with a 2 second residency time, and detected one- and two- carbon fluorochemicals (fluoroform ion and fluoropropene ion). Concentrations of these breakdown products were estimated to be less than or equal to 1,000 parts per million or 0.1%. Garcia (2007) detected one-, two- and three-chain fluorochemical formation from the thermal degradation of PTFE at temperatures between 750 to 1050C.[10]

The global warming potential of fluorine-containing byproducts is thousands of times more potent than carbon dioxide.[11]

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[8] Horst, et al. 2020. Understanding and Managing the Potential By-Products of PFAS Destruction. Groundwater Monitoring & Remediation. https://ngwa.onlinelibrary.wiley.com/doi/abs/10.1111/gwmr.12372

[9] Watanabe, et al. 2018. Thermal mineralization behavior of PFOA, PFHxA, and PFOS during reactivation of granular activated carbon (GAC) in nitrogen atmosphere. Environ. Sci. Pollut. Res. Int. 25 (8), 7200e7205. https://doi.org/10.1007/s11356-015-5353-2

[10] García, et al. 2007. Products obtained in the fuel-rich combustion of PTFE at high temperature. J. Anal. Appl. Pyrol. 80 (1), 85e91. https://doi.org/10.1016/j.jaap.2007.01.004

[11] Greenhouse Gas Protocol. 2016. Global Warming Potential Values. https://www.ghgprotocol.org/sites/default/files/ghgp/Global-Warming-Potential-Values%20%28Feb%2016%202016%29_1.pdf

**Fluorinated acetic acids** - Mono-, di-, and tri-fluoroacetic acids are common thermal breakdown products of PTFE, particularly at lower temperatures (Ellis 2001). They are toxic to aquatic ecosystems and widely detected in the atmosphere and in precipitation. Some scientists suggest they may be partially responsible for pulmonary edema seen in workers at PTFE plants.[8]

**Dioxins and furans** - Dioxins and furans can be formed in municipal solid waste incinerators when PFAS are incinerated alongside other wastes.[12] Methodological constraints hinder monitoring for dioxins and furans in other PFAS incineration studies.[13]

**Un- or partially-reacted PFAS** - EPA lists "shorter chain PFAS, partially fluorinated PFAS, and defunctionalized perfluorinated carbon chains" as other potential thermal by-products.[2] Short-chain polyfluorinated alkyl acids require higher temperatures to achieve thermal destruction than long-chain acids.[14] Wang tested for PFAS in air at two municipal solid waste incinerator facilities in China. They reporting higher concentrations of PFOA in air at the incinerator sites compared to an upwind site, while fluorotelomer concentrations were comparable across all samples.[15]

**Hydrogen fluoride** - The complete liberation of fluorine from carbon sources in the incinerator would produce hydrogen fluoride, an acutely toxic and corrosive gas. Hydrogen fluoride has to be managed to ensure it doesn't impact machinery of the incinerator itself.[16] As the ITRC reports in its PFAS destruction guidance related to incineration, "there have not been sufficient pilot studies to determine the validity of this concern. This could pose serious health and safety issues and could compromise equipment components."[17]

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[12] Merino, et al. 2016. Degradation and removal methods for perfluoroalkyl and polyfluoroalkyl substances in water. Environ. Eng. Sci. 33 (9), 615e649. https://doi.org/10.1089/ees.2016.0233

[13] Aleksandrov et al. 2019. Waste incineration of Polytetrafluoroethylene (PTFE) to evaluate potential formation of per- and Poly-Fluorinated Alkyl Substances (PFAS) in flue gas. Chemosphere. 226. 898-906.

[14] Watanabe et al. 2016. Residual organic fluorinated compounds from thermal treatment of PFOA, PFHxA and PFOS adsorbed onto granular activated carbon (GAC). Journal of Material Cycles and Waste Management. 18:625-630. https://link.springer.com/article/10.1007/s10163-016-0532-x

[15] Wang, et al. 2013. Mineralization behavior of fluorine in perfluorooctanesulfonate (PFOS) during thermal treatment of lime-conditioned sludge. Environ. Sci. Technol. 47 (6), 2621e2627. https://doi.org/10.1021/es305352p

[16] United States Environmental Protection Agency, 2020. Thermal Treatment of PFAS in Environmental Media: A review of the state-of-the-science. Mark Mills, Diana Bless Environmental Protection Agency; Kavitha Dasu, Dinsuah Siriwardena, Amy Dindal Battelle Memorial Institute.

[17] ITRC. 2020. PFAS - Per- and Polyfluoroalkyl Substances: Treatment Technologies. Interstate

Chemours, under a consent decree with the federal government and the state of North Carolina, has developed a non-target analytical method which will help map the "dark matter" of PFAS breakdown products. One recent study to develop non-target methods examined a sample of waste gasses from the thermal oxidizer at Chemours Fayetteville facility in North Carolina and found a number of unidentifiable fluorochemicals and GenX (HFPO-DA) in waste gasses. Ninety-nine percent of the waste fluorine gases were unidentified chemicals, and 1 percent was GenX.[18]

### *b. Current monitoring methods aren't able to determine exactly what is coming out of incinerator stacks*

EPA is working to develop and validate the analytical methods that will allow it and others to reliably measure PFAS and breakdown products in air and other media. Such tools are essential to allow regulators to determine whether the extremely strong carbon-fluorine bonds in PFAS can be broken in the conditions of a hazardous waste incinerator, and whether emissions controls can trap and remove byproducts. Until these methods are available there is no way to substantiate the degree of breakdown and removal of PFAS and other organic-fluorine compounds from incinerator stacks. These methods are listed as "coming soon" on the EPA website.[19]

### *2. Hazardous waste incinerators and other kilns and thermal oxidizers do not operate in compliance with existing permits*

There is no evidence that any incinerator operating in the United States can safely destroy concentrated PFAS waste such as AFFF. In part this is because neither EPA nor any other agency has established the temperatures and other operating conditions required to destroy PFAS without the formation of harmful products of incomplete combustion, and it is in part because incinerators do not conduct the monitoring required to determine the effects of their PFAS incineration. But even if minimum temperatures and operating conditions could be established, several of the hazardous waste incinerators on the Defense Logistics Agency's Qualified Facilities List have a long track record of environmental non-compliance, raising questions about their ability to maintain those temperatures and other operational requirements.

## *HERITAGE THERMAL SERVICES, INC. – EAST LIVERPOOL, OHIO*

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Technology Regulatory Council. https://pfas-1.itrcweb.org/12-treatment-technologies/

[18] Alexandria Forester, et al. Development of Total Organic Fluorine Method for the Analysis of Progress Wastewater Streams and Air from Fayetteville Works (NC). Final report. December 31, 2021.

[19] EPA. 2022. PFAS Analytical Methods Development and Sampling Research. https://www.epa.gov/water-research/pfas-analytical-methods-development-and-sampling-research

Publicly available records indicate that, since the beginning of 2018, the facility reported at least ***25*** instances where it exceeded the emissions standard for total hydrocarbons. Of these, at least two seem to coincide with violations of the minimum temperature limits for the combustor. Several of the THC exceedances were quite severe, with records showing THC levels at over three times the MACT emission standard. The facility also documented ***2*** exceedances of its opacity limits over this span.

The facility has been under heavy scrutiny from state regulators, the EPA, and the general public. Documents filed by the U.S. Department of Justice ("DOJ") indicate that there have been "numerous" documented violations of the minimum combustion temperature OPLs for the rotary kiln and the secondary combustion chamber at the Heritage East Liverpool incinerator.[20] In comments on the facility's draft permit, Save Our County, a local community group, noted 13 violations of the minimum combustion temperature OPLs from January 2015 through March of 2016.[21] In a March 2015 Finding of Violation, EPA documented an additional 13 violations of the facility's minimum combustion temperature OPLs from January 2011 through April 2014.[22] DOJ also notes "numerous" violations of the maximum flue gas flow rate OPL,[23] which, as discussed above, reflects poor operating conditions that increase the propensity for PIC formation.

### *CLEAN HARBORS ENVIRONMENTAL SERVICES – DEER PARK, TEXAS*

Publicly available records indicate that, since the beginning of 2018, the facility reported at least ***20*** deviations from OPLs. At least ***2*** of these deviations appear to relate to exceedances of the opacity standard, indicating emissions of particulate matter from the facility that could reflect inefficient combustion.

Records maintained by the state regulatory agency – the Texas Commission on Environmental Quality ("TCEQ") indicate that the most recent Semi-Annual Excess Emissions Report was filed in April of 2017, for the reporting period from April through September 2016. That report shows that the facility's two incinerator trains reported excess emissions of opacity for 13.5 minutes and of total hydrocarbons for just over 1

[20] Complaint ¶¶ 92, 101, *USA v. Heritage Thermal Servs., Inc.*, No. 4:18-cv-2419 (E.D. Ohio Oct. 18, 2018), ECF No. 1.
[21] Save Our County, Inc., Comment on Heritage Thermal Services, Inc.'s Draft Hazardous Waste Renewal Permit and Draft Title V Permit at 7 (Aug. 18, 2017), https://static1.squarespace.com/static/52d06637e4b03daab13b67f6/t/5a2ed345ec212d1fdd6093bf/1513018190690/SOC+Comment+on+Heritage+RCRA+and+Title+V+permit+renewal.pdf
[22] Finding of Violation ¶ 59, *In re Heritage Thermal Servs., Inc.*, No. EPA-5-15-OH-12 (EPA Mar. 23, 2015).
[23] Complaint, *supra* note 20, ¶ 108.

hour. That same report documented that one of the incinerators was in an upset mode (resulting in a startup/shutdown event) for 1 hour and 39 minutes.

### *VEOLIA TECHNICAL SOLUTIONS – PORT ARTHUR, TEXAS*

Publicly available records indicate that, since the beginning of 2018, the facility reported at least ***86*** violations of emission limits or OPLs. There were **40** unique exceedances of the emissions standard for carbon monoxide, and an additional ***6*** exceedances of the facility's minimum combustion chamber temperature OPL.

TCEQ has issued notices of violation ("NOVs") and cited the facility for these and other violations related to its hazardous waste incineration. In responding to a recent NOV, the facility acknowledged that "compliance with the [CO] authorized emission limit requires precise timing and control by highly skilled [o]perators to balance the fuel to oxygen ratio to achieve optimal combustion and control of CO emissions."[24] The facility has suggested that they will be able to limit CO exceedances through additional training. But state records indicate that the facility's struggles in minimizing CO emissions are longstanding, dating back at least a decade.

### *CLEAN HARBORS ENVIRONMENTAL SERVICES – KIMBALL, NEBRASKA*

Publicly available records indicate that, since the beginning of 2019, there were at least ***105*** total violations of emission limits, OPLs, or other permit terms. The facility reported at least ***57*** instances where it exceeded the emissions standard for THC. Of these, two were expressly linked in the facility's reports to problems maintaining adequate minimum temperature for the combustor. There was ***1*** additional reported violation during this span where the facility violated its minimum temperature requirement. The facility also documented ***10*** exceedances of the particulate matter standard.

However, these reports may actually undercount the compliance problems at the facility. A separate report related to leak-detection also requires reporting of startup/shutdown events; the list presented in such reports includes incidents that are not reflected in the list of OPL and emission limit violations reported for 2019.

Summary reports filed by the facility show that, during 2019, the facility was in "upset" mode and reporting excess THC emissions for a total of 45.7 hours. Of this total, 27.25 hours were attributable to "startup/shutdown" events with the remaining being attributable to "process problems." The facility reported an additional 0.4 hours of excess emissions related to $O_2$-related upset conditions.

[24] Tex. Council on Envtl. Qual., Investigation Report: Veolia ES Technical Solutions, Investigation No. 1591996 at 9–10 (Sept. 2019).

Another permit term violation related to the incineration of prohibited waste. In issuing the facility a NOV, the state regulatory agency – the Nebraska Department of Environmental Quality ("NDEQ") – classified the violation as a "high-priority violation" of its RCRA permit. The facility also reported two other incidents in 2019 that led to fires igniting on the premises. And in September of 2019, the facility received a notice of violation from EPA related to deficiencies in its processing and storage of hazardous wastes; similar violations were noted in a May 2019 notice of violation issued earlier by NDEQ.

***Conclusion - PFAS incineration is unnecessary as new and promising destruction technologies on their way.***

While PFAS incineration is fraught with technical and operational challenges and poses a serious threat to the communities surrounding incinerators, new destruction technologies could provide a safer and more effective disposal alternative. These novel technologies use heat, pressure, enzymes or other forces to deconstruct PFAS in confined systems. This means that breakdown products can be contained and studied to ensure destruction was complete before waste products are released in the environment. Among the most promising technologies are Super Critical Water Oxidation (SCWO) which EPA has said appears to be a promising alternative to incineration for AFFF waste.[25] Instead of returning to PFAS incineration, DOD and other federal agencies should be leading the transition to safer and more effective PFAS destruction technologies.

[25] EPA. 2021. Supercritical water oxidation as an innovative technology for PFAS destruction. https://cfpub.epa.gov/si/si_public_record_Report.cfm?dirEntryId=354238&Lab=CEMM