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Environmental impact of PFAS incineration

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ABSTRACT

A first-order thermodynamic model for the incineration of poly- and per-fluorinated alkyl substances (PFAS) in aqueous film-forming foam (AFFF) in a rotary kiln incinerator (i.e., a typical hazardous waste disposal) as well as decomposition at lower temperatures used in waste-to-energy incineration processes is used to discuss the global warming potential (GWP) impact of such incineration. Approximate orders of magnitude of tons of CO_2 per ton of AFFF combusted are determined based on AFFF disposal data from a survey on the incineration of the US military's AFFF supplies for complete and incomplete combustion of the AFFF wastewater. The model suggests that incomplete combustion of fluorosurfactants at low temperature will result in the release of high GWP waste products such as CF-alkanes. The risk of incomplete PFAS combustion may be amplified with diluted AFFF streams as the net reaction will be endothermic, potentially depressing the reactor temperature and promoting the formation of high-GWP byproducts. For more complete combustion cases evaluated, the estimated emission is on the order of 2 metric tons of CO_2 per ton of AFFF combusted. In the worst-case scenario with CF-alkane release, the expected emission is between 439 and 537 metric tons of CO_2 per ton of AFFF combusted. In this scenario, the incineration impact of 10,007 metric tons of AFFF combusted is equivalent to the emissions resulting from firing an average coal-fired power plant for approximately 3.6 years or the annual emissions of approximately 1 million automobiles.

Introduction

PFAS

Per- and poly-fluorinated alkyl substances (PFAS) are a class of fluorinated hydrocarbons, comprising more than 3,000 chemical species that contain at least one fluorinated alkyl chain and optionally additional fluorinated alkyl chains and functional groups (Wang et al. 2017). This definition includes both perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl sulfonic acids (PFSAs). Chain lengths of 4–7 carbon atoms for PFCAs and 4–5 carbon atoms for PFSAs are generally considered short-chain PFAS, while chain lengths in excess of 8 carbon atoms for PFCAs and 6 carbon atoms for PFSAs are considered long-chain (Goodrow and Schlosser 2022). These varied species are grouped together in a class based on shared chemical properties, and similar environmental and toxicological impacts (Kwiatkowski et al. 2020). Originally developed in the 1930 s and 1940s, PFAS have been employed in a number of formulations for consumer and industrial goods, including non-stick coatings, stain and water-resistant coatings, corrosion-protective coatings, electrical insulation, adhesives, fire-fighting foams, architectural resins, and as components in specialized industrial and chemical processes (Mueller and Schlosser 2020).

However, because PFAS chemicals are persistent organic pollutants with negative impacts on human health even at trace levels, the regulatory agencies in the U.S. and elsewhere have been phasing out their industrial and commercial use since the early 2000s (Mueller and Schlosser 2020). These detrimental health impacts are important and well-documented in recent review articles (Fenton et al. 2021; Pelch et al. 2019; Sunderland et al. 2019). However, these health implications are only one facet of the impact that the release of PFAS chemicals have on our environment. Another issue is related to the recent incineration of PFAS chemicals with a potential global warming and climate change impact of fluorocarbon combustion, which is the subject of the present study.

Incineration

Incineration is widely used as a waste management technique for

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municipal solid waste (MSW) as well as for hazardous waste. Hazardous waste can be either processed in hazardous-waste permitted incinerators or in cement kilns which use waste blends prepared as "cement fuel" (Boateng 2016). There are 126 operating waste combustion facilities in the United States including 72 stand-alone municipal waste combustors, 27 hazardous waste incinerators, 9 medical waste incinerators, and 18 industrial combustors that accept outside wastes (Weitz et al. 2024). Each year these facilities directly treat 29,000,000 metric tons of nonhazardous MSW and 681,000 tons of hazardous waste (Weitz et al. 2024). In the rest of the world, incineration is also a very common technique even if more attention is now focusing on old technologies (i.e., pyrolysis, gasification) in the context of the energy transition (Garg et al. 2023).

Disposal of PFAS

The disposal of PFAS compounds is a technical challenge that is the subject of numerous ongoing research efforts. Efforts on the part of academia and industry are focused not only on describing impacts on soil, water and air from disposing sequestered PFAS residual wastes but also on understanding the completeness of incineration practices for PFAS and characterizing incineration byproducts (Weitz et al. 2024). While other emerging disposal techniques, such as advanced oxidation, which is still not fully implemented (Ross et al. 2018; Hori et al. 2004; Cui, Gao, and Deng 2020), and pyrolysis, with a capacity of 400,000 tons/year, show promise, incineration remains the primary disposal method for PFAS and other hazardous waste, with a global capacity of 200 to 300 million tons (Garg et al. 2023). Electrochemical oxidation, while selective at the laboratory scale, requires the extraction of PFAS to an appropriate electrolyte (such as a boron-doped diamond) and has not yet been scaled up for industrial use to compete with incineration (Sharma et al. 2022). Adsorption and desorption onto metal–organic nanocomposite materials can selectively target PFAS (Van Thang et al. 2024), but they do not address the destruction of PFAS. The challenge remains: how to mineralize the collected PFAS at scale.

Incineration is a standard technique employed to decompose hazardous chemical waste, and previous literature reviews have attempted to characterize methods to mitigate toxic and carbon emissions from several waste streams as well as the sustainability of incineration practices and conditions (Block et al. 2015). PFAS may be present in various incineration residues, including flue gases, fly ash, slag, and condensates. Studies have shown that PFAS, particularly short-chain variants, are often found in fly ash and bottom ash due to incomplete destruction during incineration at conditions used in waste-to-energy plants (Strandberg et al. 2021). This indicates a secondary pathway for PFAS emissions to the environment, through which water sources may become contaminated with fly and bottom ash, such as in landfill leachates.

In the case of PFAS, long-chain PFAS molecules may be broken down at typical municipal incineration temperatures, as low as 600 °C (Yamada et al. 2005). However, for small-molecule fluorinated alkanes (i.e., C_nF_{2n+2}), higher temperatures are required (Tsang, Burgess Jr, and Babushok 1998). Recent research has also explored the impact of water vapor on the thermal decomposition of PFAS compounds, demonstrating that effective PFAS destruction occurs at conditions with the primary byproducts being HF and CO (Weber et al. 2022). The EPA recognizes that incineration at temperatures greater than 1,000 °C will break down long-chain fluorotelomer-based PFAS molecules, but holds there are insufficient studies on the emissions of fluorinated and mixed halogenated organic compounds to draw a clear conclusion (Gullett and Gillespie 2020; Weitz et al. 2024; Shields et al. 2023). In addition to temperature threshold, adequate turbulence and sufficient residence time in the reactor are required to fully decompose PFAS compounds (Winchell et al. 2021).

Given that ordinary commercial incineration may occur at temperatures as low as 600 °C, the temperature setpoint is the key variable in the estimation of environmental impact of PFAS incineration. Additionally, Winchell's review notes studies that observe low temperature incineration may produce shorter-chain PFAS instead of proportionally destroying all PFAS compounds present (Winchell et al. 2021). Complicating the analysis is the fact that C-F bonds are incredibly stable, and for incomplete combustion of perfluorooctanoic acid (PFOA) and perfluorosulfonic acid (PFOS) where oxygen and hydrogen are not present in excess, the most common combustion product is a CF-alkene (i.e., C_nF_{2n}) where some quantity of F is released in the form of HF, leaving a partially fluorinated carbon backbone (Tsang, Burgess Jr, and Babushok 1998).

Aqueous Film-Forming foam

Historically, a sub-class of approximately 15 PFAS chemicals were used as fluorosurfactants in AFFF for outdoor fire-fighting since the 1960s, comprising perfluorooctanoic acid PFOA, perfluorooctanoic sulfonic acid PFOS, and several 6:2 fluorotelomer PFAS species (Barzen-Hanson et al. 2017). AFFF was typically produced and stored in a concentrated form, comprising water, organic solvents, surfactants including the fluorosurfactants, and a remainder of additives, stabilizers, and other modifiers (Kempisty, Xing, and Racz 2019). Manufacturers under current U.S. federal regulations have not been required to disclose the specific composition of AFFF foam products (Gold and Wagner 2020). Different formulations of AFFF have been used for fighting wildfires and oil fires, particularly at transportation hubs like airports, seaports, and military bases. The use of AFFF results in an appreciable quantity of PFAS and potentially its thermal decomposition products being directly released to the environment, which causes drinking water contamination and contributes to human health issues (Domingo and Nadal 2019). Release of PFAS in outdoor fire-fighting and leakage from military bases are noted and studied in the scientific literature (Maga, Aryan, and Bruzzano 2021; East, Anderson, and Salice 2021; Filipovic et al. 2015; Houtz et al. 2013).

However, one drawback of these studies is they do not address the GWP of the intentional incineration as a means of final destruction of AFFF concentrate and stored wastewater. In parallel with societal efforts to reduce greenhouse emissions through, for example, reductions in the use of fossil fuel energy sources, it is vital to assess the risk of new increased GWP sources – outside of the energy and transportation segments, especially those that may be large and created paradoxically by new environmental regulations or well-intended legislation. In addition, Björklund et al. reported that some PFASs are not fully degraded by the high temperatures during waste-to-energy conversion and can be emitted from the plant via ash, gypsum, treated process water, and flue gas (Björklund, Weidemann, and Jansson 2023).

The authors do note that regulations around PFAS in AFFF have shifted in recent years: multiple states in the U.S. have passed local restrictions on PFAS-containing AFFF usage, and the 2019 National Defense Authorization Act (NDAA) instructed the Department of Defense to phase out purchase and usage of PFAS-containing AFFF by October 2024 (Glicksman and Adashek 2024). However, extant stocks of PFAS-containing AFFF must be disposed and areas near airports and other AFFF use sites may contain groundwater contaminated with PFAS.

Environmental AFFF release

Reported in *The Guardian* (Bond 2021), a survey by an academic team at Bennington College showed the U.S. military disposed of approximately 20 million pounds of AFFF and wastewater by burning at seven or more incineration sites between the years of 2016 and 2020. Samples taken from a nearby site (i.e., the Norlite facility in Cohoes, NY), where the incineration was conducted, indicated the presence of PFAS compounds, typically found in AFFF, in the soil. This suggests that the combustion process did not completely decompose the PFAS component.

PFAS present in the residuals (i.e., ash, slag) from an incinerator have not been intensively studied so far. These residuals are stabilized to reach land disposal restriction (LDR) program standards under the EPA. However, as of 2023, there is no PFAS regulation imposed on these residuals. If PFAS are present in these residuals, they may be found afterwards in the landfill leachates. While the Bennington College survey was not peer-reviewed for scientific rigor, it highlights the potential risk that a PFAS incineration event, intended for the final destruction of the PFAS, could instead release these substances to the environment. The incomplete incineration at a hazardous waste disposal site poses the question on how effective incineration can be as a tool to safely dispose of these chemicals.

According to the Environmental Working Group, a non-profit environmental watchdog group, there are at least 704 PFAS-polluted military sites, and numerous other contaminated industrial sites and municipal water sites that bring the total to 2,337 across the U.S. as of January of 2021 (Parkman et al. 2021). Other studies, including those published by Environmental Business Journal in a 2019 report, include landfills and sewage treatment plants, and estimate that a total of over 41,000 sites have been contaminated with PFAS-type fluorosurfactants with concentration ranging from the parts per trillion to parts per million (EBJ 2019). The authors note that the landfill and water treatment sites are ultimately downstream of both industrial sources of PFAS emission and waste discarded by the public.

The objective of the present study was to investigate the global warming potential (GWP) impact of the incineration of PFAS in AFFF by developing a thermodynamic model, including incineration such as in a rotary kiln as well as those at lower temperatures in waste-to-energy incineration processes.

Methods

The present study estimated the GWP of the combustion of two synthetic AFFF mixtures, each comprising one PFAS fluorosurfactant and associated components. The study proposed a range in equivalent metric tons of CO_2 released based on the quantity of AFFF combusted, decomposition products, and incineration process conditions. Net heats of reaction were calculated through the bond enthalpy method (Atkins, De Paula, and Keeler 2023; Sonntag and Borgnakke 2001) (see Appendix 1). Sensible and latent heats of the reactants were considered for common incineration temperatures. From these figures, an electrical power requirement for each combustion case was calculated, and that data was used with EPA-developed Avoided Emissions and Generation Tool (AVERT) software to estimate the carbon emissions required to incinerate the AFFF mixture (https://www.epa.gov/avert/avert-web-edition). GWP was calculated algebraically for each case by multiplying the post-incineration waste products by the respective GWP over a standard 100-year impact window.

AFFF composition

Under current federal regulations, the specific compositions of PFAS-containing AFFF used in the field may be protected as trade secrets by industry, and thus the exact compositions are often unknown (Gold and Wagner 2020). However, based on publicly available safety data sheet (SDS) documents, white papers, and published university research, it is straightforward to build a model for a "synthetic" AFFF concentrate (Table 1) (Kempisty, Xing, and Racz 2019). The primary components of AFFF concentrate are diluent water, organic solvents and surfactants, the fluorosurfactant, and finally a small percentage (generally less than 5 %) of additives, stabilizers, and other modifiers, including salts. The components for the synthetic AFFF concentrate were selected based on the following rationale: 1) compounds that appear in multiple PFAS-containing AFFF SDSs and thus are representative of the class of AFFF chemicals being burned, and 2) compounds with detailed chemical properties available in publicly available chemical property databases such as NIST and Chemeo. These synthetic mixtures are meant to simulate average properties of PFAS-containing AFFF for the purposes of enthalpy calculations and do not reflect other additives present in small quantities that do not significantly affect the thermodynamic properties of the mixture.

Table 1
Synthetic AFFF concentrate composition for use in the present modeling.

Component	Percentage (%)
Water	60
Polypropylene Glycol	20
Dodecanol	9
PFOA/PFOS	6
Magnesium sulfate	5

Combustion cases

Multiple cases for the combustion of AFFF were examined: full combustion of the organic components of the AFFF, and then two cases where the fluorosurfactant component of the AFFF is partially combusted into CF-alkene and CF-alkane products. Instead of proposing mechanisms or reaction schema for each of these cases, the present study focuses on these sample reactions to illustrate the variability in GWP impact resulting from full and partial combustions of both PFOA and PFOS, which produce CO_2 and fluorinated carbon products, respectively.

Since the GWPs of various CF-alkanes are several orders of magnitude greater than those of various CF-alkenes, we believe these sample reactions provide a reasonable estimate of the potential risks associated with incomplete combustion. Furthermore, this model is expected to capture the maximum GWP impact resulting from CF-alkane formation. The three cases for each PFAS component, along with minor AFFF components, are summarized in Table 2.

Results and Discussion

PFAS and combustion cases

The primary difference between PFOA and PFOS is an additional fluorinated carbon along the backbone and the replacement of the carboxylic acid head with a sulfonic acid group, resulting in an additional two fluorocarbon bonds per molecule in PFOS as compared to PFOA, which results in a different balance of fluorinated reaction products. This results in different combustion reactions and waste products, as described in Table 2. Thermodynamically, this results in more carbon products, including CO_2, directly produced when PFOA is the primary PFAS component, but more SO_2 emissions when PFOS is the primary PFAS component.

It is assumed the organic solvents and non-fluorinated surfactants combust completely to CO_2 and H_2O, and the PFOA and PFOS react according to the reactions presented in Table 2. Since both the propylene glycol and dodecanol combustion reactions are exothermic, these reactions are assumed to progress to completion in all cases even at low incineration temperatures.

The authors calculate the reaction enthalpies for the PFAS reaction Cases 1 and 3 at Table 2 are exothermic, while for Case 2 the reaction enthalpy is endothermic (see a sample calculation in Appendix 1). One takeaway from comparing the reaction enthalpies is that for the synthetic mixtures, the heat produced by reacting non-PFAS organic components is sufficient to offset the PFAS decomposition reaction whether it is endothermic or exothermic. The introduction of water enables the formation of HF as a waste product, which carries its own safety concerns but has the advantage of being fully mineralizable and thus will reduce the GHG impact.

Table 2
Combustion cases with AFFF component reactions studied. (See Appendix 1 for enthalpy calculations).

	Combustion Temperature	PFOA, $C_8HF_{15}O_2$	kJ/mol	PFOS, $C_8HF_{17}O_3S$	kJ/mol
Case 1	1,500 °C (Full Comb.)	$C_7F_{15}COOH + 3.5O_2 + 7H_2O \longrightarrow 8CO_2 + 15HF$	−1,649	$C_8F_{17}SO_3H + 3.5O_2 + 8H_2O \longrightarrow 8CO_2 + SO_2 + 17HF$	−1,417
Case 2	1,250 °C (Partial to CF-Alkene)	$C_7F_{15}COOH \longrightarrow 2C_2F_4 + C_3F_6 + CO_2 + HF$	450	$C_8F_{17}SO_3H + H_2O \longrightarrow 2C_2F_4 + C_3F_6 + CO_2 + SO_2 + 3HF$	682
Case 3	800 °C (Partial to CF-Alkane)	$C_7F_{15}COOH + 3O_2 \longrightarrow 2CF_4 + C_2F_6 + 4CO_2 + HF$	−1,278	$C_8F_{17}SO_3H + 2.5O_2 \longrightarrow CF_4 + 2C_2F_6 + 3CO_2 + SO_2 + HF$	−819

OTHERS	Reactions	kJ/mol
Poly-propylene glycol	$C_3H_8O_2 + 4O_{2(g)} \rightarrow 3CO_{2(g)} + 4H_2O_{(v)}$	−1,744
Dodecanol	$C_{12}H_{26}O + 18O_{2(g)} \rightarrow 12CO_{2(g)} + 13H_2O_{(v)}$	−7,456
Magnesium sulfate	$MgSO_4 \rightarrow MgO + SO_{2(g)} + 0.5O_{2(g)}$	−1,285

SO_2 emissions

Sulfur oxide emissions expected from the combustion of PFAS-containing AFFF originate from two sources: sulfate-containing PFAS species such as PFOS, and the small fraction of additives that include sulfate-containing salts such as magnesium sulfate.

Magnesium sulfate decomposes into waste products including magnesium oxide and sulfur dioxide at a temperature of 1,080 °C in the absence of reducing agents, and with partially oxidized carbon such as CO present to catalyze the reaction, at temperatures as low as 600 °C (Scheidema and Taskinen 2011). Therefore, at common waste incineration temperatures, it is possible the $MgSO_4$ survives an incineration process with a residence time of less than one minute. At hazardous waste incineration temperatures, typically above 1,200 °C, $MgSO_4$ decomposes.

Additional SO_2 can be produced on a 1:1 stoichiometric basis with PFOS as the active PFAS component over PFOA, or approximately 0.128 tons of SO_2 per ton of PFOS reacted. While the presence of SO_2 emissions may mitigate the GWP of the other reaction products, it is assumed the quantity is small enough and commercial incinerators have adequate scrubbing installed as to eliminate this from consideration.

Enthalpy and dilution

The exercise of calculating the latent and sensible heats of bringing the AFFF up to incineration temperature offers some insights on the process. Of the heat capacity calculations for the synthetic AFFF, the largest individual component, by approximately one order of magnitude, is the heat of vaporization of the aqueous component at 100 °C. The second greatest component is the vaporization of the organic solvents and surfactants at approximately 180–190 °C. The third greatest component is the expected heat of vaporization of the PFAS component, followed by the sensible heats. Therefore, the net enthalpy of this process is a function of **how diluted the AFFF concentrate is**.

One important observation is that the evaporation temperature for PFOA is approximately 189 °C, while according to a theoretical modeling study of the decomposition of fluorinated polymers, four-nines destruction (i.e., 99.99 %) of carbon–fluorine alkane bonds may only be guaranteed at temperatures greater than 1,400 °C (Tsang, Burgess Jr, and Babushok 1998). The only individual component that may not undergo a phase change is the magnesium sulfate, which decomposes at approximately 1,080 °C to MgO and SO_2 products (Scheidema and Taskinen 2011).

Whether the net process of combusting the AFFF is exothermic or endothermic depends on the concentration of the AFFF, and the ratio of the water to the full slate of organic components, additives, and modifiers. This may be estimated algebraically by multiplying the enthalpy of reaction by molar fraction of each component being combusted per the reactions in Table 2. For a concentrate at 60 % water to 40 % AFFF concentrate, the overall incineration process is solidly in the exothermic range. However, if the waste stream is diluted with additional water by more than 20 %, bringing the approximate ratio to 79–80 % water to 20–21 % other components, the quantity of heat released by the organic components is not sufficient to boil off the water in the fresh inlet feed. The specific breakeven point varies by less than a percentage point, based on assumptions around the PFAS species and combustion case. The net enthalpy as a function of water fraction in the incineration feedstock, and thus indirectly the degree to which the AFFF is diluted, is depicted graphically in Fig. 1.

This insight is notable for two reasons. First, combustion of highly diluted waste streams, wherein water comprises more than approximately 80 % of the AFFF waste stream, is **more likely to be endothermic than exothermic**, which necessitates fine control over the reactor temperature to maintain the setpoint required to break the C-F bonds. Failure to do so may result in increased emissions of fluorinated gas byproducts such as those described in Cases 2 and 3 in Table 2, particularly if the endothermic effect of water evaporation is reinforced by the incomplete, endothermic reaction of the PFAS component of the AFFF (Tsang, Burgess Jr, and Babushok 1998).

Second, this observation may suggest that a facility incinerating both concentrated AFFF and its wastewater may experience process control problems when sequencing dilute AFFF wastewater after reaching a steady state for AFFF concentrate. Facilities which incinerate continuously and have slower control schemes, may experience a drop in reaction temperature, causing high-GHG-potential products to form.

GHG (Greenhouse Gas) impact

The GHG impact of the possible decomposition products (Shine 2009) are compiled in Appendix 2. First, it is observed that all fluorinated alkane carbon waste products have a significantly greater global warming impact than carbon dioxide, the benchmark over a 100-year modeling window. The primary contribution to this effect is the stability of the C-F bond for alkane species, contributing to a long atmospheric lifetimes and ability to trap heat in the upper atmosphere (Weitz et al. 2024; Castro et al. 2021). The relative stability of CF-alkane group, encompassing CF_4, C_2F_6, and C_3F_8, means these species have a significantly greater global warming potential than any other potential waste products. The impact for the CF-alkene products, consisting of C_2F_4 and C_3F_6, is significantly lower largely because the alkene bond can be attacked, and the molecule more easily decomposed.

In terms of relating combustion temperature to GHG impact, the greatest driver of the GHG effect from PFAS combustion is the degree of completion of the combustion process. More fully oxidized carbon products are preferred from this perspective, as the GHG impact of 1 metric ton of CF-alkane products is at minimum 6,630 metric tons CO_2-equivalent over the 100-year modeling window. For CF-alkene products, which are far more reactive and prone to decompose, this comes down to 0.004 metric tons CO_2-equivalent over 100 years.

Energy Input for hazardous waste incineration

For hazardous waste incineration in a rotary kiln and in the secondary combustion chamber, the most common process involves firing the kiln with natural gas or another fuel, subsequently using the exhaust gases to preheat the incoming reactants, and finally running the cooled exhaust through a scrubbing system (Boateng 2016). A worst-case scenario for emissions, shown in Table 3, would remove the final two steps

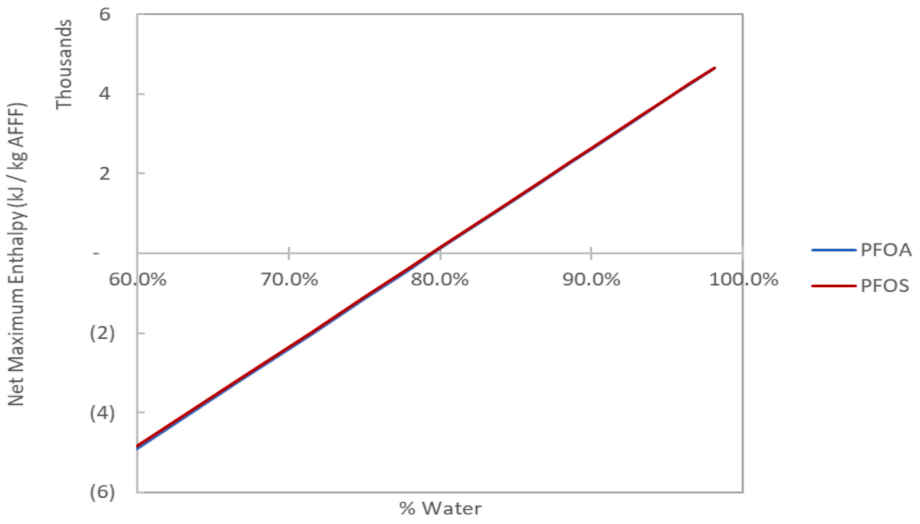

Fig. 1. Maximum enthalpy required to treat AFFF as a function of increasing dilution with water.

Table 3
Energy required and GHG impact for rotary kiln incineration.

PFAS Species	Case	Combustion Temperature	Heat Required	CH_4 Required	GHG Impact of AFFF	GHG Impact of Heating	GHG Impact of AFFF + Heating
		(°C)	(kJ/kg of AFFF)	(mol/kg of AFFF)	(tons CO_2/ton of AFFF)		
PFOA	Case 1	1,500	4,904	30.91	0.654	1.36	2.01*
	Case 2	1,250	4,602	30.9	0.611	1.36	1.97*
	Case 3	800	4,863	30.81	437	1.356	439**
PFOS	Case 1	1,500	4,837	30.89	0.644	1.36	2*
	Case 2	1,250	4,587	30.88	0.611	1.359	1.97*
	Case 3	800	4,778	30.79	536	1.355	537**

* The complete combustion of the PFAS component.
** The worst-case scenario.

and directly release the exhaust gases without pre-heating or scrubbing the outlet, thus "paying" the energy cost to bring the full volume of AFFF up to temperature. Using the lower heating value (LHV) for the combustion of methane, the present study determined for each case the quantity of methane required, and the carbon emissions associated with that reaction. The LHV was selected because it is assumed the final product stream will be wholly in the vapor phase. Table 3 contains the relevant figures and is presented below.

In the context of the net process, the methane required to run the rotary kiln incinerator is on the order of 30 mol of gas per kg of AFFF combusted, which was supported by a recent study (Gehrmann et al. 2024). This is not particularly sensitive to the final combustion temperature because the dominant components of the heat required are the latent heats of vaporization. In terms of GHG impact, approximately 1.36 metric tons of CO_2 are emitted per metric ton of AFFF concentrate combusted if the combustion reactants are not preheated with recycled heat from the process.

Bennington survey basis

The large incineration event described in the Bennington survey (Bond 2021) allows us to scale the model developed on a per-metric ton basis to a calculated release. Applying the approximately 10,007 metric tons of concentrated AFFF and wastewater disposed of via incineration, the present study scaled the above model. In cases where complete combustion of the PFAS component occurs (i.e., Cases 1 and 2 for PFOA and PFOS in Table 3), the present study shows the releases of approximately 2 metric tons of CO_2 per ton of AFFF combusted (see Table 3 for data marked by *), which can be translated to approximately 20,000 metric tons of CO_2 per 10,007 tons of AFFF combusted. This is comparable to the amount of carbon released by firing an average coal-fired power plant for approximately 6 days (see Appendix 3 for the sample calculation for a typical 154 MW coal-fired power plant).

The worst-case scenario is far more concerning (i.e., Case 3 for PFOA and PFOS in Table 3), with the CF-alkane products pushing the expected emissions to between 439 and 537 metric tons of CO_2 per ton of AFFF combusted (see Table 3 for data marked by **), which can be translated to numbers between 4.39×10^6 and 5.37×10^6 metric tons of CO_2 per 10,007 tons of AFFF combusted. This is the equivalent of firing an average coal-fired power plant for approximately 3.6 years (see Appendix 3), or the annual emissions of approximately 1 million automobiles if one uses a typical gasoline car emission of approximately 4.6 metric tons of CO_2 per year according to EPA (EPA 2020). This calculation illustrates that **incomplete PFAS combustion has the greatest detrimental impact on the environment**. A generous safety factor on the incinerator temperature may mitigate the risk by preventing incomplete combustion that may form CF-alkanes. For example, doubling the required methane to fire the incinerator would only increase the minimum cost from 1.36 metric tons of CO_2 emissions per metric ton of AFFF to 2.7 (see Table 3), which is still orders of magnitude less emissions than what is observed in Case 3.

Conclusion

The model proposed, while simplifying some aspects of PFAS incineration, serves to explore the sensitivity of PFAS decomposition to temperature and the potential impact on GHG release. The present study indicates that if the incineration is conducted below the optimal

temperature, the possibility of producing highly fluorinated alkane and alkene products is greater, which drastically increases the GWP of the effluent gases. Additional research is needed to confirm the estimates in the study. While full combustion of the AFFF yields approximately 2 metric tons of CO_2 per ton of AFFF combusted, with approximately two-thirds of this total coming from the natural gas used to bring the mixture to temperature and no preheating with recycled heat, improper combustion may yield the equivalent impact of the release of 439–537 metric tons of CO_2 per ton of AFFF combusted, depending on the identity of the PFAS compound, and in this case the vast majority of the GHG impact is from the CF-alkane byproducts.

Applying the present model to a large scale PFAS incineration event, such as the one reported by Bond et al., gives an opportunity to put the figures in context. If incinerated properly at temperatures in excess of 1,200 °C, it was possible this event would have a relatively small GWP impact of approximately 20 thousand metric tons of CO_2 per 10,007 tons of AFFF combusted. Improper incineration at a low temperature that results in the formation of high GWP fluorocarbon byproducts may result in **two orders of magnitude greater emissions**, on par with the annual emissions of a large coal-fired power plant or the annual emissions of a million automobiles. This long-term climate impact is in addition to the more immediate toxicological effects of releasing a large quantity of fluorocarbons to the environment.

A primary conclusion is the key factor in determining whether the combustion process for AFFF concentrate or wastewater is exothermic or endothermic is the degree to which the waste stream is diluted. **Incinerating more dilute AFFF may be riskier than AFFF concentrates**, as the evaporation of water requires more heat and increases the chance of an incomplete combustion feedback loop. Based on the synthetic AFFF concentration built for this model, water content in excess of 80 % is likely to result in net endothermic combustion, with this varying by a few percentage points based on the specific composition of the AFFF. This corresponds to a 6 % AFFF diluted by a factor of 2x. The authors note this is a theoretical study of potential impact of incinerating PFAS-containing AFFF. Further study is required to evaluate the byproducts of incineration to verify the conclusions drawn from this model.

The authors conclude that the combustion of AFFF residues with unknown or varying dilution levels is a risky method for large-scale implementation, primarily due to the significant environmental consequences of incomplete combustion. Regulators and policymakers focusing on incineration as a method to destroy PFAS and reduce CO_2 emissions must be careful to ensure proper incentives for minimizing net global warming potential. Incomplete combustion of PFAS can have severe health and environmental consequences, especially if the focus is solely on reducing CO_2 emissions. Additionally, further research is needed on alternative methods for PFAS capture and destruction, such as adsorption, advanced oxidation processes including electrochemical-oxidation, pyrolysis, and other techniques. These alternatives may become more favorable than incineration in addressing health and global warming concerns related to PFAS release into environment.

CRediT authorship contribution statement

Jason Kovacs: Writing – original draft, Software, Investigation, Formal analysis, Data curation, Conceptualization. **Richard Higgins:** Validation, Project administration, Investigation, Formal analysis, Conceptualization. **Nathalie Ionesco:** Writing – review & editing, Investigation, Formal analysis, Conceptualization. **Young Cho:** Writing – review & editing, Investigation, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix 1:. Sample calculation of enthalpy changes in Table 2

	Bond	Energy (kJ/mol)
A	B	C
3	N-N	161
4	O-O	139
5	O–H	470
6	H-H	435
7	H-F	567
8	C–H	414
9	N–H	389
10	S-H	339
11	C-F	485
12	C-O	352
13	C–C	348
14	P-O	419
15	N-O	222
16	S-H	339
17	C-N	293
18	C-S	260
19	S-S	214
20	Si-O	369
21	C=S	477
22	O=O	498
23	C=O	800
24	C=C	615
25	N=N	418
26	C=N	615
27	N=O	607
28	F-F	155
29	S-O	348
30	S=O	522

	Name	Enthalpy (kJ/mol)	Enthalpy calculation
D		E	
3	PFOA	11,333	7*C13 + 15*C11 + C23 + C12 + C5
4	O2	498	C22
5	CF4	1940	4*C11
6	C2F4	2555	C24 + 4*C11
7	C2F6	3258	C13 + 6*C11
8	C3F6	3606	2*C13 + 6*C11
9	CO2	1600	2*C23
10	HF	567	C7
11	H2O	940	2*C5
12	F2	155	C28
13	PFOS	12,803	7*C13 + 17*C11 + C18 + 2*C30 + C29 + C5
14	C3H8O2	4824	2*C13 + 6*C8 + 2*C12 + 2*C5
15	C12H26O2	15,000	F1511*C13 + 25*C8 + C12 + C5
16	SO2	1044	2*C30
17	SO3	1218	C30 + 2*C29

$$C_7F_{15}COOH + 3.5O_2 + 7H_2O \rightarrow 8CO_2 + 15HF$$

$$\Delta H = \sum \Delta H_{(bonds\ broken)} - \sum \Delta H_{(bonds\ formed)}$$

$$= (E3 + 3.5{*}E4 + 7{*}E11) - (8{*}E9 + 15{*}E10))$$

$$= (19,656) - (21,305) = -1,417\,kJ/mol$$

Appendix 2. . GHG potentials in a standard 100-year impact window for byproducts of AFFF combustion (Shine 2009) (https://ghgprotocol.org/sites/default/files/2024–08/Global-Warming-Potential-Values%20 %28August%202024 %29.pdf).

Species	GHG Potential (tons CO_2 Eq.)
CO_2	1
CF_4 *	7,380
C_2F_4 **	0.004
C_2F_6 *	12,400
C_3F_6 **	0.09
C_3F_8 *	9,290
HF	0
H_2O	0 †

* Alkane species.

** Alkene species.

† GWP for H_2O is limited by vapor pressure.

Appendix 3. . Sample calculation for coal-fired power plant equivalent emission

For a 154 MW coal-fired power plant operating at full capacity 24/7:

Daily energy production = 154 MW × 24 h = 3,696 MWh/day

$$CO_2\ \text{emissions} = \frac{3,696\,\text{MWh/day} \times 2,180\,\text{lb}\,CO_2/\text{MWh}}{2,204.62\,\text{lb/metric ton}} = \frac{3.65x10^3 metrictonCO_2}{day} = \frac{1.33x10^6 metrictonCO_2}{year}$$

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