Chemosphere 110 (2014) 17-22

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Investigation of waste incineration of fluorotelomer-based polymers as a potential source of PFOA in the environment



Chemosphere

癯

P.H. Taylor^{a,*}, T. Yamada^a, R.C. Striebich^a, J.L. Graham^a, R.J. Giraud^b

^a University of Dayton Research Institute, Environmental Engineering Group, 300 College Park, Dayton, OH 45469, United States ^b E.I. du Pont de Nemours and Company, Inc., 1007 Market Street, Wilmington, DE 19898, United States

HIGHLIGHTS

• Test composites represented all fluorotelomer-based polymers (FTBPs) in commerce.

• Test conditions were typical of full-scale solid waste incinerator operations.

• Testing did not result in detectable levels of PFOA in exhaust gas.

• Preliminary testing demonstrated that PFOA would have been detected if present.

• Waste incineration of FTBPs is not expected as a source of PFOA in the environment.

ARTICLE INFO

Article history: Received 1 November 2013 Received in revised form 31 January 2014 Accepted 6 February 2014 Available online 5 April 2014

Handling Editor: H. Fiedler

Keywords: Fluorotelomer Incineration PFOA Municipal waste End of life MSW

ABSTRACT

In light of the widespread presence of perfluorooctanoic acid (PFOA) in the environment, a comprehensive laboratory-scale study has developed data requested by the U.S. Environmental Protection Agency (EPA) to determine whether municipal and/or medical waste incineration of commercial fluorotelomer-based polymers (FTBPs) at end of life is a potential source of PFOA that may contribute to environmental and human exposures. The study was divided into two phases (I and II) and conducted in accordance with EPA Good Laboratory Practices (GLPs) as described in the quality assurance project plan (QAPP) for each phase. Phase I testing determined that the PFOA transport efficiency across the thermal reactor system to be used in Phase II was greater than 90%. Operating at 1000 °C over 2 s residence time with 3.2–6.6 mg dscm⁻¹ hydrogen fluoride (HF), corrected to 7% oxygen (O₂), and continuously monitored exhaust oxygen of 13%, Phase II testing of the FTBP composites in this thermal reactor system yielded results demonstrating that waste incineration of fluorotelomer-based polymers does not result in the formation of detectable levels of PFOA under conditions representative of typical municipal waste combustor (MWC) and medical waste incinerator (MWI) operations in the U.S. Therefore, waste incineration of these polymers is not expected to be a source of PFOA in the environment.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

The widespread detection of PFOA in the environment has spurred the need to understand the sources that contribute to its environmental presence (Lau et al., 2007; Buck et al., 2011). A global inventory of the sources of PFOA emissions to the environment has identified degradation of fluorotelomer-based polymers (FTBPs) as a potential source (Prevedouros et al., 2006). A number of studies have reported investigations of the biodegradation of FTBPs in soil (Washington et al., 2009; Russell et al., 2010). Similarly, the aerobic degradation of fluorotelomer alcohol used as a raw material in the synthesis of FTBPs has been extensively investigated (Wang et al., 2009; Liu et al., 2010). Hori and his coworkers have investigated photodegradation of a model fluorotelomer alcohol in air over TiO_2 particles (Kutsuna et al., 2006). The global inventory also identified waste incineration of FTBP products at end of life as a potential degradation pathway to PFOA in the environment. EPA and FTBP manufacturers entered into an enforceable consent agreement (ECA) for conducting a laboratory-scale incineration testing program to develop data needed by EPA to determine whether municipal and/or medical waste incineration of FTBPs at end of useful life is a potential source of PFOA that may contribute to environmental and human exposures (EPA, 2005). The ensuing study is presented in this paper.



^{*} Corresponding author. Tel.: +1 937 672 3065; fax: +1 937 229 2503. *E-mail address:* ptaylor1@udayton.edu (P.H. Taylor).

Aqueous dispersions of FTBPs are topically applied to textiles and paper to provide unique surface properties to them such as oil and water repellency for textiles and oil and grease penetration prevention for paper used in packaging food (Rao and Baker, 1994; Kissa, 2001). At the time of this study, fluorotelomer-based acrylate polymeric products were prepared by aqueous emulsion polymerization of fluorotelomer acrylate monomer, $F(CF_2)_nCH_2CH_2OC(O)CH=CH_2$ (n = 6, 8, 10, 12) with other monomers (Rao and Baker, 1994; Kissa, 2001; Telomer Research Program, 2002). A typical FTBP structure is shown in Fig. S-1 in the Supplementary Material. Textile applications include nonwoven medical garments (Washburn et al., 2005). At the end of the product life-cycle, fluorotelomer-treated textile and paper articles are disposed of as municipal waste or in some cases as medical waste. Paper accounted for 37% of municipal solid waste (MSW) generated in the U.S. in 2000, and textiles accounted for 4% of MSW (EPA, 2002). Incineration, typically with energy recovery, is used for over 10% of MSW in the U.S., approximately 20% of MSW in Western Europe, and over 70% of MSW in Japan (Sipila, 2003). Consequently, a significant fraction of fluorotelomer-treated textiles and paper is subject to degradation in MWCs, and a lesser fraction of fluorotelomer-treated textiles is expected to be subject to degradation in MWIs. In a prior study, the thermal degradation of an article composed of a blend of polyester and cellulose fibers and treated with an FTBP under laboratory conditions representative of the time and temperature typical for MWCs indicated that the FTBP in the treated article was destroyed and that no detectable amount of PFOA was formed (Yamada et al., 2005).

FTBPs are also used to impart soil and stain resistance to carpeting (Washburn et al., 2005). Recent tracking of carpet landfill diversion in the U.S. documents that 2% of carpet discards were managed via waste-to-energy MWCs in 2011 and 1% of carpet discards was managed in cement kilns during the same time period (Carpet America Recovery Effort, 2012). EPA's study of the fate of FTBPtreated carpet in a pilot-scale rotary kiln incinerator simulator indicated no statistical difference between PFOA levels while burning natural gas (869 °C kiln temperature) and while burning FTBP-treated carpet (952 °C to 998 °C kiln temperature), suggesting effective destruction of FTBPs used in carpet applications and that trace PFOA emission levels (where detected) were due to use of fluoropolymers in sampling or analysis (Lemieux et al., 2007).

The study described in this paper was comprehensive in scope, evaluating the waste incineration fate of two composites comprised of the FTBP solids from nine individual proprietary fluorotelomer formulations (across all FTBP manufacturers) that EPA concluded were "representative of the individual fluorotelomer components and the remaining non-component FTBPs, for all FTBPs used in commerce" (EPA, 2005). Under the ECA, these composites included the F—(CF₂)_x— and —(CF₂—CF₂)_x moieties of FTBPs that have the potential to form PFOA when incinerated (EPA, 2005). A rigorous framework for the study was maintained through conformance with EPA-approved QAPPs, adherence to GLPs as described in the QAPPs, and oversight monitoring by the project quality assurance unit in the form of inspections and third-party data validation.

The purpose of this study was to assess the potential for waste incineration of each FTBP composite to emit PFOA based on quantitative determination of potential exhaust gas levels of PFOA from laboratory-scale combustion testing under conditions representative of typical MWC and MWI operations in the U.S.

2. Materials and methods

The ECA incineration testing program was divided into two phases (I and II). Phase I testing evaluated the efficiency of PFOA transport across the reactor system at the University of Dayton Research Institute (UDRI) to be used in Phase II testing of the two FTBP composites. Each composite was comprised of the FTBP solids dewatered from individual (one with three, the other with six) FTBP product aqueous dispersions at ambient conditions.

2.1. Thermal reactor system

The thermal reactor system used in this study is a non-flame, batch-charged, continuous flow reactor system. Based on the design of reactor systems widely used for thermal degradation studies at UDRI (Graham et al., 1986; Taylor et al., 1990; Yamada et al., 2005), this system was configured to represent gas-phase behavior in a full-scale waste incinerator prior to air pollution controls.

A schematic of the thermal reactor system is presented in Fig. 1. The solid sample was placed into a 12.7 mm long capillary tube quartz cartridge (CDS Analytical Inc.) designed to be inserted into the coil of a 6.35 mm o.d. temperature-programmable pyroprobe (CDS-2000) following weighing on a microbalance (AX26, Mettler Toledo). Upon insertion into the inlet end of the tubular fused silica quartz reactor (14 mm i.d. \times 18 mm o.d. \times 997 mm length, H.S. Martin), the pyroprobe was used to introduce the gasified solid test substance into the system. The reactor tube was housed in a three-zone temperature controlled split tube furnace (SST-3.00-0-30-3C-D2155-BE, Thermcraft). An Ultra-Torr fitting (Swagelok) with a silicone O-ring was used to connect the tapered inlet end of the reactor tube to the stainless steel inlet tubing that supplied gas premixed with vaporized liquid (water during Phase I testing, methanol during Phase II testing) using a Kenics laminar flow gas mixer (6.35 mm tube with 27 elements, Chemineer). The liquid feed to the vaporizer was supplied by a high-pressure syringe pump (Model 100DX, Teledyne ISCO). Gases were metered and controlled with electronic mass flow controllers (Model 5850S, Brooks Instrument Division, Emerson Electric Co.). An Ultra-Torr fitting with an O-ring was used to connect the tapered outlet end of the reactor to Silcosteel tubing (Restek) that discharged the reactor exhaust (>600 scc min⁻¹) into a set of three glass 30 mL midget impingers (Part 737550-0000, Kimble-Kontes) (two with HPLC water and the third empty to contain potential carry-over) in an ice bath. In addition, a nominal 1 scc min⁻¹ side stream discharged to a fused silica capillary transfer line heated with a GC oven en route to a mass selective detector (MSD) (Model 5970B, Hewlett-Packard, Inc.) to track O₂, carbon dioxide (CO₂), nitrogen, and water vapor in the exhaust gas. A continuous gas analyzer (CGA) (EL3020, ABB) connected to the exit of the impingers quantitatively monitored the reactor exhaust for O_2 , CO_2 , and carbon monoxide (CO) in real time. The silicone O-ring in the exit Ultra-Torr fitting was replaced with use of perfluoroelastomer O-rings (Kalrez[®] 7075, DuPont) during Phase II testing due to the higher temperature rating of the perfluoroelastomer O-ring (Coughlin et al., 2001). In order to provide steady methanol vapor flow at the very low liquid flows employed in combustion testing, the syringe pump was retrofitted with temperature control and capillary tubing, and the vaporizing section of the feed system was configured to co-feed air and liquid through custom narrow-bore tubing to atomize the liquid feed.

Reactor tube outside wall temperatures, transfer line wall temperatures, gas flow rates, pump injection rates, CGA concentrations, ambient pressure, and other system parameters were continuously monitored using computer data acquisition. Prior to each phase, a calibrated NIST-traceable reference thermocouple (Omega Engineering) inserted into the reactor with gas flowing was used with a calibrated NIST-traceable thermocouple reader (Omega Engineering) to relate the gas temperature inside the reactor to the outside wall temperatures to be monitored during the experiments. This was done to profile the length of the reactor to



Fig. 1. Thermal reactor system schematic. Major system components are shown including major thermocouple locations. The mass flow controller for MSD and CGA cal gas, initially calibrated for CO₂, was recalibrated for N₂ to be compatible with CO₂ in N₂ cal gas prior to Phase II testing.

establish the effective reactor length at target temperature and to define required furnace setpoints.

2.2. PFOA transport testing

Phase I transport testing was performed using the thermal reactor system at the same general conditions planned for Phase II combustion testing with two exceptions - a reactor gas temperature of 250 °C, below PFOA's 307 °C 2-s half-life (Krusic et al., 2005), was used to minimize PFOA degradation and PFOA was gasified as the test substance - in order to allow quantitative determination of PFOA transport efficiency. The PFOA concentration was 99.8% (branched PFOA + linear PFOA) as supplied by Oakwood Products. A blend of synthetic air (20.96% oxygen, 1.045% argon, balance nitrogen; Airgas) and CEM-Cal Zero nitrogen (99.9995%, Airgas) was used to maintain an O₂ concentration of approximately 13% as monitored by the CGA. A reactor system exhaust gas water concentration of approximately 10% (calculated) was maintained through HPLC water injection via the syringe pump. The target oxygen and water concentrations as well as the 16 min duration for experimental runs were based on stoichiometric calculations for complete combustion of 100 µg polytetrafluoroethene (PTFE), as a highly fluorinated polymer of known molecular composition, in the presence of methanol fuel at approximately 150% excess air and an HF concentration of 10 mg dscm⁻¹. This was done in order to facilitate consistency of experimental conditions with those for later combustion testing; see Stoichiometric Calculations in Supplementary Material. Pyroprobe cartridge weighings demonstrated complete gasification of the nominal 100 µg PFOA loaded. The outlet transfer line was maintained above 200 °C to minimize PFOA condensation, and post-run steam cleaning assured collection of any PFOA that may have condensed. The experimental sequence is shown in Table 1 with the results of impinger analysis via liquid chromatography with tandem mass spectrometry (LC/ MS/MS) at MPI Research and calculation of PFOA transport efficiency. With over 90% transport efficiency (well above the 70% threshold required in the ECA), Phase I testing demonstrated that if PFOA were to be present in the exhaust gas during Phase II combustion testing, it would be captured in the impingers.

2.3. FTBP combustion testing

Phase II combustion testing investigated the fate of gasified FTBPs under conditions representative of the high-temperature zone of a full-scale waste incinerator prior to air pollution controls. The overall Phase II experimental program is outlined in Fig. 2. Elemental analysis of the FTBP composites resulting from dewatering of the fluorotelomer aqueous dispersion products is summarized in Table S-1. Thermogravimetric analysis (TGA) was performed on each composite at three heating rates (10 °C min⁻¹, 17.5 °C min⁻¹, and 25 °C min⁻¹) to provide the basis for setting gasification conditions for combustion testing. A TGA display plot showing the mass loss versus temperature for both composites at 25 °C min⁻¹ is presented in Fig. S-2. The pyroprobe was programmed to gasify the FTBP across the experimental run. Temperature profiling of the reactor at combustion test gas flow prior to testing (see Section 2.1) defined the effective reactor length and gas residence time: see Fig. S-3.

Stoichiometric calculations were used to finalize combustion test experimental setpoints (e.g., air flow) consistent with QAPP targets as described in Supplementary Material.

Target and actual operating conditions for combustion testing are summarized in Table 2 along with typical values for MWCs and MWIs in the U.S. (upon which the target conditions were based). Synthetic air (21.1% oxygen, balance nitrogen; Airgas)

Table 1
PFOA transport efficiency.

Sample identification	Impinger PFOA concentration (ng L^{-1})	Sample volume collected (mL)	Mass _{PFOA} out	Mass _{PFOA} in	
			PFOA mass in sampleª (μg)	PFOA mass in feed to reactor (μg)	PFOA transport efficiency (%)
Pre test steam clean Run 1 thermal blank	NQ ^b ND ^c				
Run 1 experimental run	1.16E+06	64.32	74.61	105	
Run 1 steam clean	3.15E+05	47.41	14.93		
Subtotal			89.55	105	85.3
Run 2 thermal blank	5.16E+02	62.04			
Run 2 experimental run	1.40E+06	64.29	90.01	110	
Run 2 steam clean	3.89E+05	47.58	18.51		
Subtotal			108.51	110	98.6
Run 3 thermal blank	6.35E+02	61.5			
Run 3 experimental run	1.09E+06	62.84	68.50	99	
Run 3 steam clean	3.82E+05	47.76	18.24		
Subtotal			86.74	99	87.6
Post test steam clean	2.44E+04	49.2	1.20		
Post test thermal blank	4.77E + 02	62.37			
		Overall	286.00	314	91.1

ND < LOD < NQ < LOQ.

^a Sample volume based on weight measurements at UDRI using density of $H_2O = 1.0 \text{ g mL}^{-1}$.

^b NQ – Compound detected at a level between the LOD and LOQ. Result is not quantifiable. Limit of Quantitation (LOQ) for this matrix is 25 ng L^{-1} .

^c ND – Compound not detected. Limit of Detection (LOD) for this matrix is 5 ng L⁻¹.



Fig. 2. Overall phase II experimental program.

was used, and continuous monitoring during FTBP combustion testing assured representative operation throughout the test.

Pyroprobe cartridge weighings demonstrated complete gasification of the 100 μ g (nominal) FTBP composite fed to the system during each experimental run. For each composite tested, each combustion test run consisted of a pre-run thermal blank, an experimental run, a steam cleaning, and a post-run thermal blank, resulting in 4 impinger samples per run for a total of 12 impinger samples per combustion test set.

In accordance with the ECA, the impinger samples were analyzed for PFOA and fluoride. MPI Research analyzed for PFOA via LC/MS/MS as described in Table S-2 and for fluoride via ion chromatography using EPA Method 300.0 (EPA, 1993) with an AS14 column (Dionex). During PFOA analysis, each sample was spiked with isotopically labeled ¹³C-PFOA as the surrogate prior to extraction. All analytical results were verified through third-party data validation by Environmental Standards, Inc. Samples from initial FTBP Composite 1 testing were mistakenly spiked by the laboratory at 1000 times the expected surrogate spike level. This resulted in peaks for PFOA observed in the samples at concentrations below the limit of quantitation (LOQ) of 50 ng L⁻¹. A separate evaluation of the labeled standard showed these peaks were attributable to presence of native PFOA as an impurity in the labeled ¹³C-PFOA rather than PFOA present in the impinger samples. Therefore, Composite 1 combustion testing was repeated, and the repeat testing is described here.

3. Results and discussion

The experimental run impinger analysis results for PFOA and fluoride as HF on an exhaust gas concentration basis corrected to 7% oxygen are presented in Table 3. The underlying impinger analytical results for all runs are listed in Table S-3. Calculations converting these results into exhaust gas concentrations for the experimental runs are presented in Tables S-4 and S-5.

Testing results demonstrate that no detectable levels of PFOA were produced from the combustion of the FTBP composites. Similarly, the analytical results for all thermal blanks and post-run steam cleaning samples showed that PFOA also was not detected at an LOD (limit of detection) of $5 \text{ ng } \text{L}^{-1}$, equivalent to \leq 54 ng dscm⁻¹ corrected to 7% O₂ (see Table S-5). Labeled ¹³C-PFOA surrogate spike recoveries for combustion test impinger samples ranged from 94% to 119%; see Table S-6. Due to the scale of the system, there was not sufficient sample volume to permit duplicate analysis; hence, precision was not assessed for each analytical measurement. However, combustion testing for each composite was performed in triplicate. Third-party validation determined the impinger PFOA results met QAPP requirements and were valid as reported by the laboratory without any gualification. The data validators noted that the instrument calibration showed the instrument was capable of producing a reproducible response with acceptable sensitivity throughout the analytical sequence, recoveries for calibration verification standards demonstrated instrument stability, and laboratory control standard (LCS) and ¹³C-labeled PFOA surrogate recoveries within 70-130% confirmed analytical accuracy. Had PFOA been present in the reactor system exhaust gas, prior transport testing clearly shows that it would have been detected. (As indicated in Table 1, over 90% of the PFOA input to the reactor system during prior transport testing was captured in the impingers.) Transport testing also showed that any PFOA potentially condensed in the reactor system outlet transfer line or otherwise lost to the system would have been quantitatively recovered through the use of post-run steam cleaning.

The fluoride results demonstrate hydrogen fluoride (HF) was formed during combustion of the FTBP composites. Fluoride was detected in Composite 1 experimental run samples at approximately 3-10 times the associated thermal blanks and in Composite 2 experimental run samples at approximately 2-5 times the associated thermal blanks. Comparison of the experimental results to levels predicted from the fluorine content of the polymers in Table S-2 provides an overall check on the experimental results. Although theoretical recoveries tabulated in Table S-4 range from 43% to 89% of the predicted fluoride concentration implying a low bias in the analytical results, reported analytical results for two out of three test runs for each composite yielded recoveries between 70% and 130% supporting that both composites were completely combusted. Fluoride loss to silicon tetrafluoride via surface reaction is doubtful due to the dilute fluoride concentration and excess of water (c.a. 10%) in the reaction gas. Third-party validation of the impinger fluoride results pointed out that instrument calibration and stability did not meet QAPP requirements and consequently qualified these results as quantitative estimates. Insufficient time was available between completion of data validation and expiration of the 28-d hold time in EPA Method 300.0 to reanalyze fluoride samples at a GLP-compliant laboratory. Further examination of the raw data indicates that the apparent low bias is in part due to a negative y-intercept in the instrument calibration curve, perhaps due to contamination of the calibration standards. Hence, the fluoride recoveries strongly suggest mineralization of the starting polymers.

Combustion testing was performed at the target operating conditions for reactor gas temperature, gas residence time, exhaust gas oxygen concentration, and exhaust gas water concentration in Table 2. Experiments were performed with a gas-phase residence time of 2 s at a mean gas temperature of 1000 °C over the effective length of the reactor; see Fig. S-3. Observed average O_2 and CO_2 concentrations across the experimental runs were within ±0.1% of combustion stoichiometry calculated values (13.1% and 5.7% on dry basis, respectively). Steady state conditions were maintained during the experimental runs. The only CO spikes observed were during thermal blanks and are attributed to methanol flow disturbances associated with pump valving. Maintaining O₂ levels at an average of 13% and preventing dips below 10% assured steady oxidation of gasified polymer as would occur in the high-temperature zone of a full-scale waste incinerator. Experimental HF exhaust concentrations calculated from the observed fluoride levels range from 3.2 to 6.6 mg dscm⁻¹ (corrected to 7% O₂) which are comparable to the 2.3-7.9 mg dscm⁻¹ uncontrolled HF levels typical for MWCs; see Table 2. Conformance with target operating conditions (temperature, time, exhaust gas O₂ concentration, and exhaust gas water concentration) along with the observed HF levels confirm that this testing was conducted under conditions representative of typical MWC and MWI operating conditions.

There are only two prior studies investigating potential PFOA emissions from the thermal decomposition of FTBPs - one in the authors' laboratory at UDRI (Yamada et al., 2005) and one by EPA's Office of Research & Development (Lemieux et al., 2007). The present study evaluated FTBP composites representative of all FTBPs in commerce and was therefore much broader in scope than either of the prior studies, each of which examined the fate of individual FTBPs. EPA conducted pilot-scale combustion testing of fluorotelomer-treated carpet and untreated carpet in its 0.73 W rotary kiln with an unfired afterburner (Lemieux et al., 2007). The PFOA emission results across six runs (1 natural gas only combustion blank, 2 untreated carpet, 2 fluorotelomer-treated carpet with reported fluorine level of 0.3% by mass, 1 fluorotelomer-doped carpet) were either non-quantifiable or at trace (<600 ng dscm⁻¹) levels. Based on these results, EPA concluded that there was no statistically significant difference between PFOA emission levels while burning only natural gas (869 °C, 14% oxygen) and while burning treated or doped carpet (952 °C-998 °C, 11.7%-12.6% oxygen), suggesting

Table 2	2
---------	---

Combustion test operation conditions.

	Municipal waste combustor ^a	Medical waste incinerator ^a	Test target ^b	Test actual
Exhaust O ₂ (%)	10	13	>10	13
Mean temperature (°C)	>1000	1000	1000 ± 10 (T3)	1000 ^c
Residence time (sec)	2	2	1.8-2.2	2 ^c
Exhaust H ₂ O (%)	15	>10	8-20	10
HF prior to control (mg dscm ^{-1} at 7% O ₂)	2.3-7.9	Not available	5.4-7.5	3.2-6.6

^a Municipal waste combustor (MWC) and medical waste incinerator (MWI) exhaust O₂ values are based on Table S-7 in the Supplementary Material. Typical values for temperature of high temperature zone, gas residence time, and exhaust gas H₂O for MWCs and MWIs in the U.S. are from Giraud and Taylor, in preparation. Municipal waste combustor levels for HF prior to air pollution control are from the first table in the Stoichiometric Calculations section of Supplementary Material (Table A-1).

^b Test targets for exhaust O₂, gas temperature, residence time, and exhaust H₂O are from the Quality Assurance Project Plan, and test target levels for HF are the predicted reactor system exhaust HF concentrations in Table S-4.

^c Supplemental calculations after the completion of the testing program indicate that oxidation of the methanol fuel feed to the reactor could have resulted in temperature overshoot as high as 1283 °C (adiabatic reaction temperature) at the inlet end of the reactor followed by approximately 0.15 s cool down. Such overshoot would result in the actual mean temperature of the reactor increasing from 1000 °C to 1003 °C, and the actual total residence time at or above1000 °C increasing from 1.98 s to 2.13 s.

Table 3	
FTBP combustion	test results.

Test substance	Sample identification	Exhaust Gas Concentration, corrected to 7% Oxygen	
		Hydrogen fluoride (mg dscm ⁻¹)	PFOA (ng dscm ⁻¹)
Composite 1	Experimental Run #1	6.6	ND
	Experimental Run #2	5.5	ND
	Experimental Run #3	3.2	ND
Composite 2	Experimental Run #4	5.1	ND
	Experimental Run #5	5.3	ND
	Experimental Run #6	3.3	ND

ND – Compound not detected. Limit of Detection (LOD) for the analytical procedure is 5 ng L^{-1} , which for this reactor system is equivalent to an exhaust gas PFOA concentration of $\leq 54 \text{ ng dscm}^{-1}$ corrected to 7% oxygen.

effective destruction via combustion of FTBPs used in carpet applications. EPA also noted that trace PFOA emission levels were likely due to the historical use of fluoropolymers in pilot combustor duct sampling or to the use of fluoropolymers in analytical laboratories. EPA's pilot-scale testing for carpet was performed at temperature and oxygen levels similar to those in the present study. In contrast to the historic use of fluoropolymers in the EPA pilot combustor system, the thermal reactor system in the present study was designed to be free of fluoropolymers except for the perfluoroelastomer O-ring used on the reactor exit seal. With the apparent absence of background PFOA levels, the present study more definitively supports EPA's tentative conclusion that fluorotelomer polymers are effectively destroyed in combustors. Similarly, the present study confirms and extends the findings of Yamada et al. (2005) that under laboratory conditions representative of the time and temperature typical for MWCs FTBP in treated articles was destroyed and that no detectable amount of PFOA was formed.

4. Conclusions

Phase II combustion testing of both FTBP Composite 1 and FTBP Composite 2 in the laboratory-scale thermal reactor system determined that waste incineration of fluorotelomer-based polymers does not emit detectable levels of PFOA under conditions representative of typical MWC and MWI operations in the U.S. Based on this testing, waste incineration of fluorotelomer-based polymers is not expected to be a source of PFOA in the environment.

Acknowledgements

This research was funded by the Telomer Research Program (AGC Chemicals, Clariant, Daikin, and DuPont). The authors gratefully acknowledge David Blye, Phil Ourisson, Eric Lahr, Meg Michell, Bob Buck, Mary Galaska, Gary Foggin, Mike Peo, Art Tressler, Rich McKay, Mary Kaiser, Bob Clements, Maria Zannes, Jim Grant, Ed Gaffney, Concetta LaMarca, Ray Mendelsohn, Larry Bonam, Troy Francisco, Roger Blaine, John Blouin, Rich Leukroth, Greg Fritz, Majd El-Zoobi, David Menotti, Seiji Shinya, and Steve Korzeniowski for their insights, assistance, review, and support at various stages of this program.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere. 2014.02.037.

References

Buck, R.C., Franklin, J., Berger, U., Conder, J.M., Cousins, I.T., de Voogt, P., Jensen, A.A., Kannan, K., Mabury, S.A., van Leewen, S.P.J., 2011. Perfluoroalkyl and polyfluoroalkyl substances in the environment: terminology, classification, and orgins. Integr. Environ. Assess Manage. 7, 513-541.

- Carpet America Recovery Effort, 2012. Carpet America Recovery Effort 2011 Annual Report. <www.carpetrecovery.org/reading.php>. 16 April 2013.
- Coughlin, M., Schnell, R., Wang, S., 2001. Perfluoroelastomers in Severe Environments: Properties, Chemistry, and Applications. Paper No. 24. Presented at a Meeting of the Rubber Division of the American Chemical Society, Providence, RI, April 24–27, 2001.
- EPA, 1993. Method 300.0: Determination of Inorganic Anions by Ion Chromatography, Revision 2.1.
- EPA, 2002. Muncipal Solid Waste in the United States: 2000 Facts and Figures. EPA530-R-02-001.
- EPA, 2005. Final Consent Agreement and Testing Consent Order for Two Formulated Composites of Fluorotelomer-based Polymer Chemicals; Export Notification, Federal Register, vol. 70(130), pp. 39624–39630, July 8, 2005.
- Giraud, R.J., Taylor, P.H., in preparation. Combustion Operating Conditions for Municipal and Medical Waste Incinerators in the U.S.
- Graham, J., Hall, D., Dellinger, B., 1986. Laboratory investigation of thermal degradation of a mixture of hazardous organic compounds. Environ. Sci. Technol. 20, 703–710.
- Kissa, E., 2001. Fluorinated surfactants and repellents. Surf. Sci. Series, Marcel Dekker, New York, NY 97, 1–615.
- Krusic, P.J., Marchione, A.A., Roe, D.C., 2005. Gas-phase NMR studies of the thermolysis of perfluorooctanoic acid. J. Fluor. Chem. 126, 1510–1516.
- Kutsuna, S., Nagaoka, Y., Takeuchi, K., Hori, H., 2006. TiO₂-induced heterogeneous photodegradation of a fluorotelomer alcohol in air. Environ. Sci. Technol. 40, 6824–6829.
- Lau, C., Anitole, K., Hodes, C., Lai, D., Pfahles-Hutchens, A., Seed, J., 2007. Perfluoroalkyl acids: a review of monitoring and toxicological findings. Toxicol. Sci. 99, 366–394.
- Lemieux, P., Strynar, M., Tabor, D., Wood, J., Cooke, M., Rayfield, B., Kariher, P., 2007. Emissions of fluorinated compounds from the combustion of carpeting. In: International Conference on Incineration and Thermal Treatment Technologies (IT3) Conference, May 14–18, 2007.
- Liu, J., Wang, N., Szostek, B., Buck, R.C., Panciroli, P.K., Folsom, P.W., Sulecki, L.M., Bellin, C.A., 2010. 6–2 Fluorotelomer alcohol aerobic biodegradation in soil and mixed bacterial culture. Chemosphere 78, 437–444.
- Prevedouros, K., Cousins, I.T., Buck, R.C., Korzeniowski, S.H., 2006. Sources, fate and transport of perfluorocarboxylates. Environ. Sci. Technol. 40, 32–44.
- Rao, N.S., Baker, B.E., 1994. Textile finishes & fluorosurfactants. In: Smart, B.E., Tatlow, J.C. (Eds.), Organofluorine Chemistry. Principles and Commercial Applications. Plenum Press, New York, pp. 321–336.
- Russell, M.H., Berti, W.R., Szostek, B., Wang, N., Buck, R.C., 2010. Evaluation of PFO formation from the biodegradation of a fluorotelomer-based urethane polymer product in aerobic soils. Polym. Degrad. Stab. 95, 79–85.
- Sipila, K., 2003. Waste to energy: new integrated concepts. In: Ludwig, C., Hellweg, S., Stucki, S. (Eds.), Municipal Solid Waste Management: Strategies and Technologies for Sustainable Solutions. Springer-Verlag, Berlin, pp. 167– 184.
- Taylor, P.H., Dellinger, B., Lee, C.C., 1990. Development of a thermal stability based ranking of hazardous organic compound incinerability. Environ. Sci. Technol. 24, 316–328.
- Telomer Research Program, 2002. Telomer Research Program (TRP) Update; 25 November 2002. US EPA Administrative Record AR226-1141. Publicly available at <www.regulations.gov>.
- Wang, N., Szostek, B., Buck, R.C., Folsom, P.W., Sulecki, L.M., Gannon, J.T., 2009. 8–2 Fluorotelomer alcohol aerobic soil biodegradation: pathways, metabolites, and metabolite yields. Chemosphere 75, 1089–1096.
- Washburn, S.T., Bingman, T.S., Braithwaite, S.K., Buck, R.C., Buxton, L.W., Clewell, H.J., Haroun, L.A., Kester, J.E., Rickard, R.W., Shipp, A.M., 2005. Exposure assessment and risk characterization for perfluorooctanoate in selected consumer articles. Environ. Sci. Technol. 39, 3904–3910.
- Washington, J.W., Ellington, J.J., Jenkins, T.M., Evans, J.J., Yoo, H., Hafner, S.C., 2009. Degradability of an acrylate-linked, fluorotelomer polymer in soil. Environ. Sci. Technol. 43, 6617–6623.
- Yamada, T., Taylor, P.H., Buck, R.C., Kaiser, M.A., Giraud, R.J., 2005. Thermal degradation of fluorotelomer treated articles and related materials. Chemosphere 61, 974–984.