6

NEW YORK STATE OF OPPORTUNITY

E

Department of Environmental Conservation DEPARTMENT USE ONLY

DEC APPLICATION NO.

ACTIVITY NUMBER(S)

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	MATER	IALS MANAGEMENT		
Please read all instruc	ctions bef	ore completing this application	Reset Form	
Please TYPE or PRINT clearly				
1. APPLICATION TYPE (CHECK ALL APPLICABLE BO)	(ES):			
✓ Initial (New) Modification Renew	al (Existin	g permit expiration date:	)	
2. APPLICANT IS:	3. IS API	PLICATION FILED BY OR ON BEHALF OF A	MUNICIPALITY?	
✓ Facility Owner Facility Operator	YES	(Name of municipality:	) 🖌 NO	
4. FACILITY NAME AND LOCATION (Attach USGS To Name: ESMI of New York LLC	оро Мар	showing exact location)		
Address: 304 Towpath Lane				
Town: Fort Edward	Cou	nty: Washington		
Coordinates: NYTM-E	NYT	M-N		
Existing solid waste management facility permit nu	mber (if a	pplicable): 5-5330-00038/00019		
Check here if facility owner, operator and/or r	eal prope	rty owner has changed since last applicat	ion was submitted.	
5. FACILITY OWNER'S INFORMATION		6. FACILITY OPERATOR'S INFORMATION Name: Same as Facility Owner		
Address: 304 Towpath Lane		Address:		
City/State/Zip: Fort Edward, New York, 12828		City/State/Zip:		
Phone number: 518.747.5500		Phone number:		
Email: rmartin@harsco.com E		Email:		
7. ENGINEER'S INFORMATION		8. REAL PROPERTY OWNER'S INFORMA	TION	
Name:		Name:		
NYS Professional Engineer License #:		Address:		
Firm Name:		City/State/Zip:		
Address:		Phone number:		
City/State/Zip:		Email:		
Phone number:		Check here if facility owner is not real property own		
Email:		See instruction page for written permission	n requirement.	
9. TYPE OF FACILITY (CHECK ALL APPLICABLE BOXI	ES)		-	
Combustion & Thermal Treatment (362-1)		Navigational Dredge Material Handling	& Recovery (361-9)	
C & D Debris Handling & Recovery (361-5)	361-5) Nonspecific Facilities (360.17)			
Composting & Other Organics Processing (36)	1-3)	Recyclables Handling & Recovery (361-	1)	
Household Hazardous Waste Collection (362-	362-4) Research, Development, and Demonstration (360.18)		ration (360.18)	
Land Application & Associated Storage (361-2	2)	Transfer (362-3)		
Landfill (363)		Waste Oil (374-2)		
Regulated Medical Waste (365)		Waste Tire Handling & Recovery (361-6	5)	
Mulch Processing (361-4)	Used Cooking Oil & Yellow Grease (361-8)			
Municipal Solid Waste Processing (362-2)	L			

10. NAME(S) OF ALL MUNICIPALITIES IN SERVICE AREA:	<b>11. SOLID WASTE ACCEPTED:</b> Identify facility capacity and throughput of each waste type, as applicable			
States: New York, Vermont, New Hampshire, Connecticut, Massachusetts, New Jersey	Up to 5000-tons of PFAS contaminated soil for treatment by thermal desorption under a 360.18 Research, Development, and Demonstration Permit.			
FOR MODIFICATION APPLICATION ONLY				
12. DOES THE MODIFICATION APPLICATION INVOLVE (CH	IECK ALL APPLICABLE BOXES):			
✓ New waste type New equipment Waste acce	ptance rate increase Facility expansion (including landfill)			
SKIP QUESTION #13 AND #14 IF APPLYING FOR RENEWAL	ONLY			
13. APPLICATION DESCRIPTION	14. FACILITY SIZE			
Include a brief description of new or modification request	a. Facility size proposed (acres)			
	b. Total site area (acres)			
The allowance for the facility to receive PFAS contaminated sol	For modification application ONLY			
deployed at the facility to treat soils contaminated with PEAS	c. Associated facility size change (acres)			
while controlling emissions.	For Landfill ONLY			
	d. Facility size ultimately planned (acres)			
	e. Existing landfill area on this site			
	and adjacent properties (acres)			
	J. Ultimate facility height above			
15. IS A VARIANCE REQUESTED FROM ANT PROVISION O	riance and site specific provision/s) here:			
Corporation Partnership Sole Proprietorship	Municipality/other government entity Other:			
I hereby attest that I am the owner of the real property on which the fair my individual capacity.	acility is located or the proposed or modified facility will be located and am signing			
Or if signing in a representative capacity: I hereby attest that I am the (indicate title or capacity) <u>Senior Vice President</u> , an authorized representative of the owner of the real property on which the facility is located or the proposed or modified facility will be located). I am duly authorized on behalf of said owner to sign make this certification on this application.				
I grant permission for the applicant to apply for the permit, and construct and operate the facility described in the application in accordance with a final DEC permit or approval. I also grant permission for the department to access the above-described real property, including any adjacent areas, during all reasonable times (including but not limited to 7:00 am to 7:00 pm Monday through Friday, and additional facility hours of operation, and as appropriate during emergencies and similar exigent circumstances) without the property owner, applicant or other representative of the property owner or facility present. If the property is posted with "keep out" signs or fenced with an unlocked gate, department staff may still enter the property. Department staff may traverse the property, inspect the facility, take measurements, analyze site physical characteristics, take soil and vegetation samples, sketch and photograph the property, and conduct other activities necessary to evaluate the permit application or assess the facility's compliance with the permit and any other applicable statutory or regulatory requirements.				
I am aware that any false statement made herein is punishable as a Class A mise	demeanor pursuant to Section 210.45 of the Penal Law.			
Signature: ////// Print Name:	Michael Goebner Date: 12/29/2023			
Title or Representation if signing in a representative capacity: <u>S</u>	enior Vice President			
17. APPLICANT CERTIFICATION	Municipality/other government entity Other			
Corporation Partnership Sole Proprietorship	eral Partner Sole Proprietor Duly Authorized Municipal Representative			
of (APPLICANT) <u>ESMI of New York LLC</u> and the leg statements and information provided on this application and all attachments	sally responsible party for this application as presented to NYSDEC. I affirm that the submitted herewith are true, accurate, and complete.			
I am aware that any false statement made herein is punishable as a Class A mis damage, direct or indirect, of whatever nature, and by whomever suffer harmless the State from any and all causes of action in law or equity, resulting f	demeanor pursuant to Section 210.45 of the Penal Law. I accept full responsibility for all ed, arising out of the project described herein and agree to indemnify and hold rom the said project.			
Signature: /////// Print Nam	e: Michael Goebner Date: 12/29/2023			





Lat: 43\* 16\* 45" N Long: 73\* 33\* 0" W DMS DD A MGR UTM Scale 1:18,056 Map Records: 29 Clouds, 32" near Fort Edward, NY.





REV'D 3 29 13

Environmental Soil Management of New York, L.L.C. Operations and Maintenance Manual

Figure 3 Site Map

3	LEGEND	
	-136	PROPERTY LINE EXISTING 2' CONTOUR EXISTING ELECTRIC EXISTING WATER EXISTING SEWER EXISTING GAS FIRE EXTINGUISHER MONITORING WELL
	ENVIRONMENTAL S OF NEW YO	SOIL MANAGEMENT DRK, L.L.C.
	SOIL RECYCLIN	IG FACILITY
	ESMI OF N	IEW YORK
OIL Streppel	304 Towpat VILLAGE OF FORT EDWARD, STATE OF 1	th Road COUNTY OF WASHINGTON NEW YORK
ZU'PT	DATE: 9/7/2010 BY:	Richard T. Trudeau P.E

December 29, 2023

New York State Department of Environmental Conservation 232 Golf Course Road Warrensburg, New York 12885 Attention: Kevin Wood; Regional Material Management Engineer, Paul Sierzenga; Regional Air Pollution Control Engineer

RE: Research Project; Per- and Polyfluoroalkyl Substances (PFAS) Soil Treatment and Emissions Testing at ESMI of New York, a Clean Earth Company

Dear Mr. Wood and Miss Patel,

ESMI of New York (ESMI), a Clean Earth Company, who operates a permitted thermal desorption facility, Solid Waste Permit 5-5330-00038/00019 (Solid Waste Permit) and Air Resources Permit 5-5330-00038/00021 (Air Permit), located at 304 Towpath Lane, Fort Edward, New York is formally requesting approval of a Research, Development, and Demonstration (RD&D) Permit under the authority of New York State Department of Environmental Conservation (NYSDEC) 6 NYCRR 360.18 and 201-1.16. The intent of the RD&D Permit is to demonstrate the ability of ESMI's thermal desorption technology to treat media contaminated with Per- and Poly-fluoroalkyl Substances (PFAS) to soil concentration acceptable for beneficial reuse in accordance with NYSDEC Guidance<sup>1</sup> and to control process effluent air emissions to a level acceptable to regulatory agencies within the State of New York<sup>2</sup>.

Thermal desorption is a robust remedial technology that has been proven to significantly reduce or eliminate contaminant concentrations within soil and media. Since ESMI's inception in 1995, approximately 4.0-million tons of soil has been recycled through the Fort Edward Facility's Thermal Desorption Unit (TDU) with most of the soil beneficially reused in accordance with the Facility's State approved beneficial use determination. Soil and media contaminants managed at the facilities include conventional fuels, chlorinated solvents, coal tar, natural oil and waxes, polychlorinated biphenyls, and PFAS through RD&D Permit 58Z10005 (2018 RD&D Project).

### Facility Process and System Components:

Thermal Desorption is a treatment process by which soil and media (solid matrix/matrices) are heated to a temperature that exceeds the boiling point of the soil contaminants. As the boiling point of the contaminant is reached, contaminants are desorbed from the soil matrix reducing or eliminating the contaminant(s) from the solid matrix. Desorbed contaminants are then thermally oxidized, a process that utilizes heat to degrade desorbed contaminants, converting the contaminants to carbon dioxide and water. Soils meeting criteria set forth in the facilities Solid Waste Permit and Beneficial Use Determination (BUD), BUD #610-5-58, may be reused as a product at either residential or non-residential properties. A Process Flow Diagram for the ESMI thermal desorption and EPA's A Citizens Guide to Thermal Desorption is within Attachment A of this document for reference.

Solid Matrices accepted at ESMI are weighed by a certified truck scale. This system allows for tracking and verification of the mass received by the facility for accounting and permit reporting

<sup>&</sup>lt;sup>1</sup> Sampling, Analysis, and Assessment of Per- and Polyfluoroalkyl Substances under NYSDEC's Part 375 Remedial Programs; April 2023

<sup>&</sup>lt;sup>2</sup> NYSDEC, DAR-1, Guidelines for the Evaluation and Control of Ambient Air Contaminants Under 6NYCRR Part 212

purposes. Trucks delivering material to the facility offload into an environmentally secure storage building. The storage building was designed to control particulate and odor emissions as well as to minimize noise resulting from the pre-processing of solid matrices prior to treatment. The control of particulate and odor emissions is accomplished using an induced draft fan paired with gas phase carbon bed absorber system. The storage building's concrete floor has been placed over a 40 mil and 60 mil high density polyethylene (HDPE) liner to prevent the migration of hydrocarbons and other contaminants to subsurface soils and water.

Solid matrices treated at ESMI by the thermal desorption unit (TDU) are heated within the Primary Treatment Unit (PTU; Rotary Kiln) to temperatures ranging between 400°F and 975°F, dependent upon soil contaminant. These treatment temperatures not only desorb contaminants but also volatilize natural organics within the soil and media matrix. Solid matrices exiting the PTU are cooled and rehydrated in the TDU's pugmill. This paddle-screw system homogenizes soil from the PTU and air pollution control (APC) system Baghouse fines while amending the matrices with water to control fugitive particulate emissions. Soils exiting this system are conveyed and placed into permitted stockpiles locations and analyzed in accordance with the ESMI Operations & Maintenance (O&M) Manual to demonstrate compliance with the facility's solid waste permit and BUD.

### Facility Assessment:

ESMI, in accordance with the facilities Solid Waste and Air Permit, continually assesses the efficiency and operating parameters of the TDU. ESMI personnel and an automated process logic control (PLC) system monitor direct reading devices. These devices capture the TDU's treatment temperatures, draft pressures, and process unit operating parameters, to ensure compliance with both State permits and the Facility's O&M Manual. These systems and monitoring processes will be used to log and demonstrate targeted operating parameters as outlines in this submittal for the RD&D Project. These processes have been demonstrated through various State required compliance tests and the ESMI PFAS thermal RD&D Permit 58Z10005.

ESMI will be measuring PFAS concentrations in various TDU system inputs to determine the potential effect on emissions testing and post treatment soil PFAS concentrations. An example of a system input would be water. Water is utilized to rehydrated treated soil (as discussed above) and to cool effluent air from the thermal oxidizer in the evaporative cooling chamber prior to entry into the baghouse. PFAS testing will include EPA Method 1633 for both totals and synthetic precipitation leachate procedure, and total oxidizable precursor assay (TOPA) analysis by either EPA Method 1633 or 537.1 depending upon analytical methods available at the time of testing. Results will be used to calculate total PFAS mass that is added to the TDU during treatment and determine potential influence on PFAS emissions and post-treatment soil concentrations. These concentrations will be reported in the completion report with analysis and identification of any or potential correlations between analysis and testing results associated with treated soil or air emissions.

### Primary Treatment Unit (PTU):

As discussed in the **Facility Process and System Components** section of this document, TDU's operate by exceeding the boiling point of the soil contaminant(s), desorbing the contaminants from the soil matrix leaving the solid matrices with minimal residual or non-detect analytical levels. The PTU associated with ESMI's Direct Fired TDU, permitted Process 001, can reach an average treatment temperature up to 975°F.

# Table 1 Demonstrates boiling points of Per- and Polyfluoroalkyl Substances (PFAS)<sup>3</sup>

Perfluoropentanoic Acid (PFPeA)	284°F
Perfluorohexanoic Acid (PFHxA)	334°F
Perfluoroheptanoic Acid (PFHpA)	347°F
Perfluorooctanoic Acid (PFOA)	399°F
Perfluorononanoic Acid (PFNA)	432°F
Perfluorodecanoic Acid (PFDA)	462°F
Perfluorooctanesulfonic Acid (PFOS)	480°F

ESMI will operate the PTU at soil treatment temperatures consistent with Facility operations and to identify a targeted PFAS desorption temperature that limits energy usage and meets NYSDEC PFAS soil guidance values. ESMI intends to treat soils at 700°F, 800°F, and 900°F during this research project. **Table 1** demonstrates that the treatment temperatures exceed the boiling points of the PFAS noted and should reduce the PFAS soil concentration to NYSDEC Guidance. During the 2018 RD&D Project, results from the post-treatment soil analysis demonstrated that a temperature at or near 915°F was successful in reducing leachable PFAS from the 2018 RD&D Project soils to less than NYSDEC drinking water maximum concentration levels (MCL's) of 10-parts per trillion (PPT) under synthetic precipitation leachate procedure (SPLP) analysis for PFOA and PFOS and reduced these compounds to non-detect levels through totals analysis.

ESMI believes that soil organic matter (SOM) plays a role in PFAS retention in soil by binding PFAS and slowing the leaching of the substances<sup>456</sup>. The 2018 RD&D Project soils were high in organics based on the composting process from which the soil was generated and ESMI summarized that the SOM may have inhibited the desorption of PFAS from the soil.

It was demonstrated that complete SOM removal was not necessary to reach the desired soil cleanup objectives (SCO's) for the 2108 RD&D Project. To further our understanding of the relationship between SOM and PFAS concentrations, ESMI will be analyzing soil to be treated

<sup>&</sup>lt;sup>3</sup> Interstate Technology Regulatory Council PFAS Regulatory Guidance Document; Section 4: Physical and Chemical Properties Table Excel File

<sup>&</sup>lt;sup>4</sup>A review of emerging technologies for remediation of PFASs; Ian Ross, Jeffrey McDonough, Jonathan Miles, Peter Storch, Parvathy Thelakkat Kochunarayanan, Erica Kalve, Jake Hurst, Soumitri S. Dasgupta Jeff Burdick

<sup>&</sup>lt;sup>5</sup> Sorption of perfluoroalkyl substances (PFASs) to an organic soil horizon e Effect of cation composition and pH; Hugo Campos Pereira, Malin Ullberg, Dan Berggren Kleja, Jon Petter Gustafsson, Lutz Ahrens

<sup>&</sup>lt;sup>6</sup> Occurrence and behavior of per- and polyfluoroalkyl substances from aqueous film-forming foam in groundwater systems; Jim Hatton, Chase Holton, Bill DiGuiseppi

in this RD&D to determine SOM levels prior to and post treatment to develop additional data that may demonstrate the effect of SOM on PFAS concentrations in soil.

### Secondary Treatment Unit (STU):

ESMI installed a new Secondary Treatment Unit (STU; thermal oxidizer), on the TDU in 2016. The intent of the installation was to increase the operating efficiency of the unit in two ways; increase energy efficiency and destruction removal efficiency (DRE). The project was a success. Testing demonstrated that the DRE of the STU increased from 99.8% to 99.9995% during a PCB Proof-of-Performance (PoP) Test, reaching this increased efficiency at a temperature nearly 200°F less than previously tested and demonstrated. Increased STU efficiency was accomplished by increasing STU retention time and the generation of turbulent system airflow.

Although the STU is permitted to operate at 1500°F for volatile and semi-volatile organic compounds and 1512°F for polychlorinated biphenyls (PCB's), the STU can operate at temperatures up to 2000°F. NYSDEC required the STU be operated at 1800°F during the 2108 RD&D Project. Based on the PoP Test results on coal tar and PCB contaminated soil, ESMI believes the TDU has the capacity and efficiency to control PFAS at a temperature lower than the 1800°F required during the 2018 RD&D Project. Therefore, within the PoP Test Protocol submitted with this document, ESMI is proposing to perform tests on the system at 1550°F, 1650°F and 1750°F.

Based on oxidation temperatures noted in the **Application of thermal desorption to PFAS Treatment** section, the temperature ranges noted for the TDU have been demonstrated to reach high destruction removal efficiencies and supports the temperature selection for the STU by ESMI. Links to the noted referenced are provided in Attachment B of this document.

Takahiro Yamada (T. Yamada) is the most widely referenced scientist when it comes to degradation of PFAS compounds in thermal environments. In 2003<sup>7</sup> and 2005<sup>8</sup> T. Yamada set out to establish 99% and 99.9% destruction removal efficiencies for PFAS. Experimentation in 2003 demonstrated a 99% DRE at 900°C (1652°F). Subsequent analysis to determine 99.9% DRE was conducted on treated articles and PFAS alone. The concluded DRE temperature was 750°C (1382°F) and 1000°C (1832°F) respectively. Further, it is noted, that properly operating systems with a retention time of 2.0-seconds will sufficiently destroy PFAS and such systems would not be a significant source of PFOA in the environment.

In recent years, several entities have engaged in the evaluation of thermal technologies to control PFAS emissions through PFAS destruction. Studies have shown that high DRE's can be achieved at temperatures near 900°C. EA Engineering, Science, and Technology, Inc., through the Department of Defense (DoD) Strategic Environmental Research and Development Program (SERDP), demonstrated "... that TO operating in the range of 900-1,000C° (1652°F to 1832°F) at a nominal residence time of 2.0 seconds can achieve a DRE of greater than 99.9997% for exhaust gas emissions…"<sup>9</sup>

<sup>&</sup>lt;sup>7</sup> Final Report – Laboratory Scale Thermal Degradation of Perfluoro-Octanyl Sulfonate and Related Precursors; Philip Taylor and Tak Yamada

<sup>&</sup>lt;sup>8</sup> Thermal degradation of fluorotelomer treated articles and related materials; Takahiro Yamada a, Philip H. Taylor, Robert C. Buck Mary A. Kaiser, Robert J. Giraud

<sup>&</sup>lt;sup>9</sup>Evaluation of Indirect Thermal Desorption Coupled with Thermal Oxidation to Treat Solid PFAS-Impacted Investigation-Derived Waste; Frank Barranco Paul Caprio George Hay EA Engineering, Science, and Technology, Inc., PBC

In the **Air Resources** section of this document additional references are provided noting similar thermal oxidation temperatures for PFAS compounds. Number List, item 2, notes that thermal degradation of PFOA and PFOS in the presence on oxygen and water were used as carrier gasses, no lighter fluorinated compounds were identified in the offgas at 1,706°F. In the article "Thermal Mineralization of Perfluorooctanesulfonic Acid (PFOS) to HF, CO2, and SO2"<sup>10</sup>, it was concluded that "Overall, combined air (O2) and excess water vapor and temperatures above 850°C as reaction conditions provide an inexpensive source of H, OH, and O that can mineralize all PFOS into HF, CO2, and SO2."

The work completed by those referenced in items 5 and 6 of the Number List, tested using aqueous film forming foam (AFFF). A 3% AFFF concentrate has a minimum PFAS concentration of 30,000-parts per million (PPM). These levels far exceed anticipated soil contamination values within soil and those modeled by ESMI.

A study completed by EPA ORD, Combustion of C1 and C2 PFAS: Kinetic modeling and experiments<sup>11</sup> (C1/C2 Document), utilized the Rainbow Furnace to evaluate products of incomplete combustion (PIC's) generation when thermally oxidizing CF4, CHF3, and C2F6. This document has been used as a reference to discuss the thermal oxidation temperatures required to degrade CF4. Clean Earth notes that the facility is not intending to treat CF4 (a gas) and does not utilize CF4 in any processes at the facility.

EPA ORD notes "We believe that C2F6 may be an important potential surrogate PFAS compound for combustion studies because its single C-C bond is analogous to the multiple C-C bonds in larger PFAS." Review of Table 3 in the C1/C2 Document demonstrates the PIC's generated during the 45kW (burner heat input) experiment. The lowest CF4 concentration remaining post thermal oxidation of CF4 was when CF4 was injected with natural gas directly into the burner. The resultant emission was  $3.57 \pm 0.06$  (ppbv). Compare this value to CF4 generated through C2F6 degradation at Ports 6, 8, and 10 respectively ( $5.95 \pm 0.02$ ,  $0.93 \pm 0.02$ ,  $0.21 \pm 0.004$ ) and note the temperatures at Ports 6, 8, and 10 were ( $2210^{\circ}F^{12}$ ,  $2070^{\circ}F$ ,  $1706^{\circ}F$ ). This data demonstrates that less CF4 is generated when thermally oxidizing C2F6 than when injecting CF4 directly into the burner which is where the highest DRE for CF4 was measured. It may also be concluded that at higher thermal degradation temperatures of CHF3 and C2F6 that greater concentrations of CF4 are generated.

### **Regulatory Review:**

### **Research and Development Project Authorization:**

Title 6, Chapter IV, Subchapter B, Part 360, Subpart 360.18 and Title 6, Chapter III, Subchapter A, Part 201, Subpart 201-1.16 allows for and outlines the criteria necessary for the State to authorize Research Development and Demonstration Registrations and Permits for the management of solid waste and emissions on a defined time basis. The conditions set forth in

<sup>&</sup>lt;sup>10</sup> Thermal Mineralization of Perfluorooctanesulfonic Acid (PFOS) to HF, CO2, and SO2; Nathan H. Weber, Cameron S. Delva, Sebastian P. Stockenhuber, Charles C. Grimison, John A. Lucas, John C. Mackie,\* Michael Stockenhuber, and Eric M. Kennedy\*

<sup>&</sup>lt;sup>11</sup> Combustion of C1 and C2 PFAS: Kinetic modeling and experiments; Jonathan D. Krug, Paul M. Lemieux, Chun-Wai Lee, Jeffrey

V. Ryan, Peter H. Kariher, Erin P. Shields, Lindsay C. Wickersham, Martin K. Denison, Kevin A. Davis, David A. Swensen, R. Preston Burnette, Jost O.L. Wendt & William P. Linak

<sup>&</sup>lt;sup>12</sup>Temperature derived from CHF3 results on Page 265 of the document as a Port 6 temperature is not provide in the data for the C2F6 test

these Subparts were the development basis of this submission and the information contained herein.

### Solid Waste:

ESMI's Solid Waste Permit 5-5330-00038/00019 does not allow for the acceptance of PFAS at the facility and is the reason for this RD&D Project submittal. Currently, Sampling, Analysis, and Assessment of Per- and Polyfluoroalkyl Substances under NYSDEC's Part 375 Remedial Programs; April 2023 is the State's guidance document outlining Guidance Values for Anticipated Site Use (Page 3; Soil Sample Results). ESMI will be comparing treated soil PFAS concentrations to the Guidance Values for Anticipated Site Use values to determine beneficial reuse applications for the soil post-treatment analytical review in accordance with the Facility's O&M Manual.

PFAS soil concentrations are discussed in the Air Resources section below and are demonstrated on Page 23 of the Summary of Emission Point Modeling Using AERMOD Software.

### Air Resources:

ESMI's review of NYSDEC air resources regulations identified an ambient air concentration for PFOA<sup>13</sup>. ESMI did not identify any specific regulations for PFOS emissions standards in NYSDEC regulations. The State of Michigan has been on the forefront of regulating PFAS in environmental media. Michigan Air Quality Division has generated screening levels for PFOA, PFOS, and 6:2 FTS<sup>14</sup>. ESMI will utilize these guidance values in addition to the PFOA value associated with NYSDEC regulations in determining successful completion of the RD&D Project.

PFAS emissions, as discussed in the **Secondary Treatment Unit** section of this document, have been calculated utilizing soil data obtained by ESMI from various Clean Earth clients, the 2018 RD&D Project, and soil analytical discussions with various engineering firms who have engaged in PFAS contaminated soil investigations. PFAS compounds identified in this evaluation were utilized to develop potential-to-emit (PTE) calculations and AERMOD emissions modeling.

In accordance with NYSDEC Policy DAR-10: NYSDEC Guidelines on Dispersion Modeling Procedures for Air Quality Impact Analysis, this RD&D Project followed the Division of Air Resources' recommended dispersion modeling procedures for conducting ambient impact analyses. By following these procedures, the protocol also followed the USEPA approved methodologies, as incorporated in Appendix W of 40 CFR Part 51 regulations. In performing such assessments, a set of recommended and acceptable procedures has been defined by USEPA and NYSDEC to assist source applicants to assure the proper application of the modeling analysis. As detailed within DAR-10, source analyses at major sources should adhere strictly to the requirements and preferred modeling procedures described in the USEPA Guidelines, with the added requirements of NYSDEC on the application of AERMOD.

<sup>&</sup>lt;sup>13</sup> NYSDEC, DAR-1, Guidelines for the Evaluation and Control of Ambient Air Contaminants Under 6NYCRR Part 212

<sup>&</sup>lt;sup>14</sup> Table 1. Michigan Department of Environment, Great Lakes, and Energy - Air Quality Division List of Screening Levels (ITSL, IRSL & SRSL) in Alphabetical Order

ESMI utilized two DRE's in the model; 99.9% and 99.99%. Summary results for the 99.9% DRE are noted in **Table 2.** 

Contaminant	Max Hourly Dispersion Concentration	SGC	% of SGC	Max Annual Hourly Dispersion	AGC	% of AGC
	All values in ug	/m3				
Total Sampled PFAS (99.9% DRE, full receptor grid)	2.75E-05	N/A	N/A	2.72E-07	0.00531	0.005%
Total Sampled PFAS (99.9% DRE, 1.5 mile endpoint)	5.39E-06	N/A	N/A	7.08E-08	0.00531	0.001%
Hydrogen Fluoride (HF)	1.26	5.6	23%	0.0124	0.071	17%
Carbon Tetrafluoride (CF4)	5.28E-03	N/A	N/A	5.21E-05	0.332	0.02%

Table 2AERMOD Modelling Summary

1 – Individual AGC for PFOA

2 – NYSDOH recommended AGC, not formally accepted by the NYSDEC

Fluorine is noted in NYSDEC DAR-1, Guidelines for the Evaluation and Control of Ambient Air Contaminants Under Part 212 and was modelled as noted in **Table 2**. Based on soil PFAS concentrations, and emissions calculations contained within Attachment C of this document, Fluorine emissions, including hydrogen fluoride emissions, are demonstrated to be below both State and Federal air emissions pollutant criteria.

PoP Testing will be completed during each different secondary treatment unit operating temperature to demonstrate and determine system emissions. During each PoP Test, ESMI intends to complete the following testing parameters at the thermal desorption unit emission stack:

- EPA Method 1,2,3/3A, and 4 (Gas Flow)
- EPA Method 3A (O2 and CO2)
- Other Test Method (OTM); OTM-45
- OTM-50
- EPA Method 26A (HF/F)

The testing methods noted will demonstrate PFAS mass emissions, whether products of incomplete combustion are generated, and whether fluorine emissions are generated. Results from the testing will be compared to feed soil samples (discussed below) to determine DRE's for PFAS, compared to AERMOD results to validate PTE calculations and air dispersion potentials, and demonstrate compliance with applicable State and Federal air emission guidelines.

During each PoP Test, ESMI will also be analyzing the soil feed into the system. Grab samples, approximately 8 to 12-ounces each, will be collected from the feed belt to the TDU approximately every 10 to 12-minutes during the duration of each PoP Test. These grab samples will be composited, and from the composite three (3) separate samples will be

collected and analyzed utilizing EPA Method 1633 for total PFAS and SPLP, total oxidizable precursor analysis via EPA Method 537.1 or EPA Method 1633 (dependent upon laboratory offerings available at the time of testing). These analyses are intended to identify measurable PFAS mass in the soil, including potential precursor mass that is not detected through totals and SPLP analysis.

PFAS results will be utilized to calculate PFAS mass placed into the TDU and, when compared to PoP Test results, calculate destruction removal efficiencies (DRE's) for PFAS. Actual emissions and calculated DRE's will be compared to the potential to emit (PTE) calculations and DRE's utilized in the facility Modeling to determine if the model should be re-run based on the measured data or whether the projected emissions were representative of the actual emissions. Measured emissions will then be compared to State and Federal guidelines (should Federal guidelines exist) to determine compliance.

ESMI is providing notice that one or more PoP Test may include the addition of a lime product to the effluent process airstream from the PTU prior to the STU. EPA ORD concluded "Removal of FTOH vapors and subsequent products of incomplete destruction through CaO (calcium oxide) thermal treatment requires moderately low temperatures (<800°C), thus reducing the energy needed to achieve thermal destruction."<sup>15</sup> ESMI would replicate the operating parameters of a PoP Test STU temperature without the hydrated lime injection to allow the test results to be compared to one another and determine if benefits were demonstrated for DRE, PFAS mass emissions, and PIC generation.

### Application of thermal desorption to PFAS Treatment:

As noted in the **Primary Treatment Unit** and **Secondary Treatment Unit** sections of this document, ESMI's TDU components have the capacity to not only exceed the boiling points of the PFAS compounds but to also meet the scientifically demonstrated thermal decomposition temperatures necessary to control PFAS at high DRE level. Since the 2018 RD&D Project, several entities and the Environmental Protection Agency Office of Research and Development (EPA ORD) have completed projects demonstrating that PFAS can be desorbed from soil (including the ESMI 2018 RD&D Project) and PFAS emissions can be controlled by thermal oxidation to meet State identified emissions criteria. The State of Alaska has permitted two (2) companies to utilize thermal desorption units for the treatment of PFAS contaminated soil<sup>16</sup>.

Several field and full-scale studies have been completed to evaluate the desorption of PFAS from soil in thermal desorption systems but also the control and destruction of PFAS from emission sources. A list of references is provided:

- Frank Barranco, Paul Caprio, and George Hay, "Final Report Evaluation of Indirect Desorption Coupled with Thermal Oxidation Technology to Treat PFAS-Impacted Investigation-Derived Waste, SERDP Project ER18-1572", February 2020. (Documents PFAS removal from soil processed through a thermal desorber and subsequent destruction with a thermal oxidizer.)
- 2. Nathan H. Weber, Sebastian P. Stockenhuber, Ammar Abu Fara, Charles C. Grimison, John A. Lucas, John C. Mackie, Michael Stockenhuber and Eric M. Kennedy,

<sup>&</sup>lt;sup>15</sup> Low temperature thermal treatment of gas-phase fluorotelomer alcohols by calcium oxide Theran P. Riedel, M. Ariel Geer Wallace, Erin P. Shields, Jeffrey V. Ryan, Chun Wai Lee, William P. Linak\*

<sup>&</sup>lt;sup>16</sup> Alaska DEC Website: <u>https://dec.alaska.gov/spar/csp/offsite-remediation/</u>

"Experimental Thermal Decomposition of PFOS and PFOA", proceedings of the IT3 Conference, January 27-28, 2021. (Study evaluated the products formed at temperatures of 1,706 and 1,994°F and under various types of atmospheres - argon, nitrogen, air, water. When air plus water vapor were used as the carrier gas, no lighter fluorinated compounds were identified in the offgas at 1,706°F. PFOS data was also presented at 1,994°F with similar trends evident.)

- 3. Benjamin Hanley, John Lucas, and Annette Nolan, "Remediation of PFAS-impacted Soil Using Innovative Treatment Technologies", presentation at Ecoforum Conference and Exhibition, 2016 (Study of removal of PFOS and PFOA from soil using thermal desorption)
- J. Ryan, B Gullett, Analysis of Fate of PFAS During Incineration PFAS Emissions Measurement Methods Development and Emissions Characterization Study at National Response Corporation Alaska, LLC AFFF Contaminated Soil Thermal Treatment Facility SERDP Project ER19-1408, Nov. 2020. (Treated PFAS contaminated soil in an incinerator followed by a thermal oxidizer.)
- EA Engineering, Science and Technology and Montrose Environmental, Report on PFAS Destruction Testing Results at Clean Harbors' Aragonite, Utah Hazardous Waste Incinerator, November 2021 (as cited in "Interim Guidance on Destruction or Disposal of Materials Containing Per- and Polyfluoroalkyl Substances in the United States", DOD, July 2023). (Full PFAS mass balance and shows DRE >99.9999% for spiked PFAS compounds in a hazardous waste incinerator).
- 6. E. Shields, et al, "Pilot Scale Thermal Destruction of PFAS in a Lagacy AFFF", May 2023. (Study measured PIC in the offgas from direct destruction of AFFF liquid at different residence times and temperatures in a pilot scale furnace.)

### PFAS Soil Sources, Anticipated Tonnage, and Treatment Timeframes:

ESMI is proposing to treat 3,000 to 5,000-tons of PFAS contaminated soil during the project. Based on a 30-ton/hour treatment rate, ESMI anticipates that the TDU will be treating PFAS contaminated soil for approximately 167-hours over a two (2) week period. The range in tonnage is based upon the various testing parameters ESMI intends to evaluate during this RD&D Project. A single PFAS emission test, which includes 3-separate sampling events, is anticipated to require 16-hours to complete; or one emissions test per day. The noted tonnage will allow ESMI to generate full-scale operating data, at various process temperatures, allowing both ESMI and NYSDEC to make informed decisions on future RD&D Projects and permit conditions associated with thermal desorption treatment activities.

ESMI anticipates that multiple soil sources will be leveraged to generate the total soil required for the RD&D Project. All soils received for the RD&D Project will be blended to generate a feed stock of consistent PFAS mass to be treated by the TDU. ESMI has not engaged in identifying soil sources for the RD&D Project and will not actively seek soil for the project until NYSDEC had provided authorization for the RD&D Project. Estimated soil PFAS concentrations are contained in Appendix XXX, AERMOD Modelling.

### **PFAS Soil Acceptance:**

PFAS Soil will be managed in accordance with ESMI's Operations & Maintenance (O&M) Manual. Inbound Soil will be stored within the Soil Storage Building (building). Acceptance of the soil associated with this RD&D will not increase the annual number of trucks received at the facility or increase the number of hours the facility operates on average annually. Additional discussion on this point is contained below. Once received and placed into the building, the soil will be segregated from other soils by noting the boundaries of the pile with cones, a cover, or other similar measures. In addition, a sign will be placed adjacent to the soil pile noting the contaminant as PFAS. Communications with site personnel will be managed to ensure the soil is not commingled with other soils in the building and maintains segregation until treated by the TDU.

If multiple projects are received to meet the desired tonnage for the RD&D Project, ESMI will blend the received soils together to generate a material that has a consistent PFAS mass. Soil blending will occur utilizing equipment currently operating within the building and consistent with normal facility operations. Once blended and stockpiled, the PFAS Soil will be composite sampled in accordance with ESMI's O&M Manual Section 2.5.2. Samples will be collected and analyzed utilizing EPA Method 1633 in accordance with Sampling, Analysis, and Assessment of Per- and Polyfluoroalkyl Substances under NYSDEC's Part 375 Remedial Programs; April 2023 guidance.

ESMI will also complete pH, total organic carbon (TOC), proximate/ultimate, Btu, and Loss on Ignition analysis. Proximate/ultimate analysis will help identify the amount of Ash and Carbon in the sample which will assist in demonstrating the soil organic matter (SOM) content. Btu and Loss on Ignition analysis will further support the proximate/ultimate analysis if the only contaminant and fuel source within the soil is PFAS and SOM. If other organic contaminants are contained within the soil, ESMI will utilize current acceptance practices outlined in the O&M Manual to determine the organic contaminant mass and determine the effect on the SOM (Ex. VOC and SVOC analysis via Methods 8260 and 8270 respectively.).

Since the soil will be stockpiled in the building for a period to allow for soil analysis and evaluation, the floorspace taken by the RD&D Project will limit the material than can be accepted by the facility. This floorspace would normally be utilized to store and manage inbound soil projects. Limiting available floor space to accept contaminated soils limits the facilities ability to operate at full-scale, reducing material acceptance, and limiting truck traffic to the facility during the RD&D Project.

### Soil Post Treatment Confirmation Analysis:

RD&D Project treated soil will be segregated from other soils in the ESMI approved soil storage areas and sampled in accordance with Section 2.5.2 of the ESMI Facility O&M Manual. A minimum of three (3) composite samples will be collected and analyzed using the same test methods identified in the **PFAS Soil Acceptance** section of this document.

Post treatment sample results will be compared to the soil acceptance analytical to demonstrate PFAS removal efficiency, evaluate SOM influence on PFAS concentrations in the soil, and evaluate soil reuse in accordance with the **Beneficial Use Determination** section of this document.

#### **Beneficial Use Determination and Disposition of Treated Soil:**

NYSDEC guidance document, Sampling, Analysis, and Assessment of Per- and Polyfluoroalkyl Substances under NYSDEC's Part 375 Remedial Programs; April 2023, identifies Guidance Values for PFAS soil concentrations for various Anticipated Site Use. ESMI is requesting that the guidance values be utilized to allow soil treated during the RD&D Project to be beneficially reused in accordance with the Facility's BUD. Treated soils meeting the Unrestricted criteria

could be utilized in residential applications and soils meeting the Restricted Residential could be utilized in Commercial/Industrial applications as identified within the BUD.

If the RD&D Soil does not meet the PFAS criteria, soil will be moved back to the soil storage building for subsequent thermal treatment or disposed of in accordance with regulatory guidelines at permitted disposal facilities with whom ESMI and Clean Earth have existing business relationships.

### Summary Report:

Within 90-days after the completion of the Project, ESMI will submit a report outlining the Project findings and conclusions. The 90-day clock will not start until such time as ESMI has received analytical results from the laboratories utilized. This point is being brought forth as several laboratories at present have turn-around-time exceeding 30-days upon sample receipt.

The completion report will include the total amount of PFAS Soil received for the Project; tabulation of all pre- and post-treatment analytical results; demonstrate PFAS mass reduction through the treatment process; the analytical, calculations, and reporting to be completed in accordance with the PoP Test Protocol; demonstrated compliance with the beneficial use criteria for PFAS Soil; issues identified with the management and treatment of the PFAS Soil; and an initial determination as to whether ESMI will pursue a permit modification for the acceptance of PFAS contaminated soils at the facility.

### **Closing:**

ESMI would like to thank the State for their time, assistance, and consideration of this submittal. We look forward to working with the State to develop a treatment method that will assist in the management of emerging contaminants such as PFAS. Should you have any questions on the document or require additional information please do not hesitate to contact us.

Sincerely,

**Robert Martin** 

Technical Director P: 518.747.5500 E: rmartin@harsco.com

### Attachment A

ESMI Process Flow Diagram and EPA's A Citizens Guide to Thermal Desorption



# Secondary Treatment Unit

# Community Guide to Thermal Desorption



# What Is Thermal Desorption?

Thermal desorption removes contaminants by heating them so that they un-stick (desorb) from soil, sludge or sediment. This heating is done in a machine called a thermal desorber, and causes the contaminants to evaporate. Evaporation changes the contaminants into vapors (gases) and separates them from the solid material. Thermal desorption can remove many organic contaminants. These include volatile organic compounds, or "VOCs," and some semi-volatile organic compounds (SVOCs). VOCs such as solvents and gasoline evaporate easily when heated. SVOCs such as diesel fuel, creosote (a wood preservative), coal tar and some pesticides require higher temperatures to evaporate. Thermal desorption generally is not used to treat metals but can partially remove metals like mercury and arsenic, which may evaporate at the temperatures used in thermal desorption.

A thermal desorber is not the same as an incinerator, which heats contaminated materials to temperatures high enough to destroy the contaminants. (See <u>Community Guide to Incineration</u>.)



Thermal desorber heats contaminated material to evaporate contaminants.

# How Does It Work?

Thermal desorption involves excavating soil or other contaminated material for treatment in a thermal desorber. The desorber may be assembled at the site for onsite treatment, or the material may be loaded into trucks and transported to an offsite thermal desorption facility. To prepare soil for treatment, large rocks or debris are first removed or crushed. The smaller particle size allows heat to more easily and evenly separate contaminants from the solid material. If the material is very wet, water may need to be removed to improve treatment. The water may require treatment using other methods.

The prepared soil is placed in the thermal desorber to be heated. Low-temperature thermal desorption is used to heat the solid material to 200-600°F to treat VOCs. If SVOCs are present, then the soil is heated to 600-1000°F.

Gas collection equipment captures the vapors, which may require further treatment, such as removal of dust particles. Organic vapors are usually destroyed using a thermal oxidizer, which heats the vapors to temperatures high enough to convert them to carbon dioxide and water vapor. At sites with high concentrations of organic vapors, the vapors may be cooled and condensed to change them back to a liquid form. The liquid chemicals may be recycled for reuse or treated by incineration. If the concentrations of contaminants are low enough and dust is not a problem, the vapors may be released without treatment to the atmosphere.

Treated soil often can be used to backfill the excavation at the site.

# How Long Will It Take?

Thermal desorption may take a few weeks to a few years. The cleanup time will depend on several factors that vary from site to site. For example, thermal desorption will take longer where:

- The contaminated area is large or deep.
- Contaminant concentrations are high.
- The soil contains a lot of clay or organic material, which causes contaminants to stick to the soil and not evaporate easily.
- A lot of debris must be crushed or removed.
- The capacity of the desorber is small. (Most thermal desorbers can clean over 25 tons of contaminated material per hour.)

# Is Thermal Desorption Safe?

A well-designed and operated desorber will safely remove harmful chemicals from contaminated materials. Workers take measures, such as covering loose soil during excavation, to control dust and vapors. Proper temperatures are maintained in the desorber to ensure complete removal of contaminants. If necessary, gases will be collected for treatment.

# How Might It Affect Me?

You may notice increased truck traffic when excavation equipment and thermal desorption systems come to the site. You also might hear heavy machinery, such as backhoes and bulldozers, during construction and treatment. If an offsite desorber is used, truckloads of soil must be transported from the site to the desorber.

# Why Use Thermal Desorption?

Thermal desorption can be used to clean up soil that has been contaminated with VOCs and SVOCs shallow enough to reach through excavation.

Thermal desorption may be faster and provide better cleanup than other methods, particularly at sites that have high concentrations of contaminants. A faster cleanup may be important if a contaminated site poses a threat to the community or needs to be cleaned up quickly so that it can be reused. Thermal desorption has been selected for use at dozens of Superfund sites and other cleanup sites across the country.



Onsite thermal desorber.

### Example

Thermal desorption was used to clean up contaminated soil at the Industrial Latex Superfund site in New Jersey. From 1951 to 1983, Industrial Latex manufactured rubber and adhesives, contaminating soil with PCBs and SVOCs.

From April 1999 to June 2000, about 53,600 cubic yards of contaminated material were excavated to depths of up to 14 feet. Materials greater than 2 inches in diameter were removed before placing the soil in the desorber and heating it to 900°F. About 225 tons of contaminated soil were treated each day. A small amount of treated soil had to be placed back in the desorber a second time to meet cleanup goals for PCBs and SVOCs. The cleaned soil was used to backfill the excavated areas.

Vapors from the desorber passed through scrubbers and filters that removed dust particles and contaminant vapors. Air quality was monitored daily to make sure the air released from the desorber met permitted levels. The site was removed from the National Priorities List in 2003.

### For More Information

- About this and other technologies in the Community Guide Series, visit: <u>https://clu-in.org/cguides</u> or <u>https://clu-in.org/</u> remediation/About use of
- cleanup technologies at a Superfund site in your community, contact the site's community involvement coordinator or remedial project manager. Select the site name from the list or map at <u>http://</u> www.epa.gov/superfund/ <u>sites</u> to view their contact information.

NOTE: This fact sheet is intended solely as general information to the public. It is not intended, nor can it be relied upon, to create any rights enforceable by any party in litigation with the United States, or to endorse the use of products or services provided by specific vendors.

### Attachment B Reference Documents

Sampling, Analysis, and Assessment of Per- and Polyfluoroalkyl Substances under NYSDEC's Part 375 Remedial Programs; April 2023

https://extapps.dec.ny.gov/docs/remediation hudson pdf/pfassampanaly.pdf

NYSDEC, DAR-1, Guidelines for the Evaluation and Control of Ambient Air Contaminants Under 6NYCRR Part 212

- https://extapps.dec.ny.gov/docs/air\_pdf/dar1.pdf

Interstate Technology Regulatory Council PFAS Regulatory Guidance Document; Section 4: Physical and Chemical Properties Table Excel File

- <u>https://pfas-1.itrcweb.org/wp-content/uploads/2022/01/PhysChemProp\_Table\_July2023-</u> <u>FINAL.xlsx</u>

Sorption of perfluoroalkyl substances (PFASs) to an organic soil horizon e Effect of cation composition and pH; Hugo Campos Pereira, Malin Ullberg, Dan Berggren Kleja, Jon Petter Gustafsson, Lutz Ahrens

- https://www.sciencedirect.com/science/article/pii/S0045653518308543

Final Report – Laboratory Scale Thermal Degradation of Perfluoro-Octanyl Sulfonate and Related Precursors; Philip Taylor and Tak Yamada

- https://clu-in.org/download/contaminantfocus/pfas/UDR-TR-03-00044.pdf

Thermal degradation of fluorotelomer treated articles and related materials; Takahiro Yamada a, Philip H. Taylor, Robert C. Buck Mary A. Kaiser, Robert J. Giraud

https://pubmed.ncbi.nlm.nih.gov/16257319

Occurrence and behavior of per- and polyfluoroalkyl substances from aqueous film-forming foam in groundwater systems; Jim Hatton, Chase Holton, Bill DiGuiseppi

- https://onlinelibrary.wiley.com/doi/abs/10.1002/rem.21552

Evaluation of Indirect Thermal Desorption Coupled with Thermal Oxidation to Treat Solid PFAS-Impacted Investigation-Derived Waste; Frank Barranco Paul Caprio George Hay EA Engineering, Science, and Technology, Inc., PBC

- https://apps.dtic.mil/sti/trecms/pdf/AD1134384.pdf

Thermal Mineralization of Perfluorooctanesulfonic Acid (PFOS) to HF, CO2, and SO2; Nathan H. Weber, Cameron S. Delva, Sebastian P. Stockenhuber, Charles C. Grimison, John A. Lucas, John C. Mackie,\* Michael Stockenhuber, and Eric M. Kennedy\*

<u>https://pubs.acs.org/doi/abs/10.1021/acs.iecr.2c03197</u>

Combustion of C1 and C2 PFAS: Kinetic modeling and experiments; Jonathan D. Krug, Paul M. Lemieux, Chun-Wai Lee, Jeffrey V. Ryan, Peter H. Kariher, Erin P. Shields, Lindsay C. Wickersham, Martin K. Denison, Kevin A. Davis, David A. Swensen, R. Preston Burnette, Jost O.L. Wendt & William P. Linak

- https://pubmed.ncbi.nlm.nih.gov/34994684/

Low temperature thermal treatment of gas-phase fluorotelomer alcohols by calcium oxide Theran P. Riedel, M. Ariel Geer Wallace, Erin P. Shields, Jeffrey V. Ryan, Chun Wai Lee, William P. Linak\*

- https://www.sciencedirect.com/science/article/pii/S0045653521003283

## Attachment C Summary of Emission Point Modeling Using AERMOD Software Model and Potential to Emit Calculations

December 2023



# Summary of Emission Point Modeling Using AERMOD Software

Clean Earth LLC 304 Towpath Lane Village of Fort Edward, Washington County, New York

Prepared for:

CLEAN EARTH LLC 304 Towpath Lane Fort Edward, New York 12828

Prepared by:

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C.T. Male Project No.: 22.2756

Unauthorized alteration or addition to this document is a violation of New York State Education Law.

# SUMMARY OF EMISSION POINT MODELING USING AERMOD SOFTWARE CLEAN EARTH LLC, 304 TOWPATH LANE VILLAGE OF FORT EDWARD, WASHINGTON COUNTY, NEW YORK

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# SUMMARY OF EMISSION POINT MODELING USING AERMOD SOFTWARE CLEAN EARTH LLC, 304 TOWPATH LANE VILLAGE OF FORT EDWARD, WASHINGTON COUNTY, NEW YORK

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Attachment A:	Summary of Dispersion and Deposition Modeling Results and Graphical Representations of Output at 99.90% Destruction Efficiency
Attachment B:	Summary of Dispersion and Deposition Modeling Results and Graphical Representations of Output at 99.99% Destruction Efficiency
Attachment C:	NYSDOH Prepared "Summary of Toxicological Assessment for Carbon Tetrafluoride in Support of the Development of an AGC and SGC for the NYSDEC"

# 1.0 **PROJECT OVERVIEW**

Clean Earth LLC (Clean Earth) owns and operates an existing facility permitted under an Air State Facility Permit issued by the New York State Department of Environmental Conservation (NYSDEC), Permit ID 5-5330-00038/00021. The permit is listed as being issued under the facility name of "Environmental Soil Management of New York LLC dba ESMI A Clean Earth Company". The facility is in the process of preparing for requesting authorization to treat Per- and polyfluoroalkyl substances (PFAS) contaminated media. The work is being completed for the Clean Earth facility located at 304 Towpath Lane in the Village of Fort Edward, Washington County, New York. This project conducted air dispersion/deposition modeling of the facility's proposed operations in order to estimate the level of impact associated with PFAS emissions from the facility.

In accordance with the previously prepared protocol, the air dispersion/deposition modeling was completed in accordance with generally accepted modeling practices and utilized software which runs the current version of the United States Environmental Protection Agency's (USEPA) AERMOD software as detailed in Section 2. Estimated contaminant-specific maximum deposition was derived from the model based on the estimated PFAS control efficiency for the soil treated at the facility and anticipated PFAS levels in incoming soil.

The modeling described within this report does not include an attempt to predict groundwater or surface water concentrations that may result from air deposition because there is currently no accepted method for such an evaluation.

The contaminants evaluated relative to dispersion and deposition include the following USEPA regulated Per- and polyfluoroalkyl substances (PFAS) compounds; perfluorooctanoic acid (PFOA), perfluorooctane sulfonate (PFOS), perfluorononanoic acid (PFNA), perfluorohexane sulfonate (PFHxS), and perfluorobutane sulfonate (PFBS). This analysis also includes dispersion modeling of Hydrogen Fluoride (HF) and Carbon Tetrafluoride (CF<sub>4</sub>) per the request of the NYSDEC. As HF and CF<sub>4</sub> are not particulates, only dispersion modeling was completed for these compounds.

# 2.0 MODELING SOFTWARE

### 2.1 Selection of AERMOD Software

In accordance with NYSDEC Policy DAR-10: NYSDEC Guidelines on Dispersion Modeling Procedures for Air Quality Impact Analysis, this project followed the Division of Air Resources' recommended dispersion modeling procedures for conducting ambient impact analyses. By following these procedures, the protocol also followed the USEPA approved methodologies, as incorporated in Appendix W of 40 CFR Part 51 regulations. In performing such assessments, a set of recommended and acceptable procedures has been defined by USEPA and NYSDEC to assist source applicants to assure the proper application of the modeling analysis. As detailed within DAR-10, source analyses at major sources should adhere strictly to the requirements and preferred modeling procedures described in the USEPA Guidelines, with the added requirements of NYSDEC on the application of AERMOD.

### 2.2 Description of AERMOD Software

AERMOD is a regulatory steady-state plume modeling system with three separate components: AERMOD (Dispersion Model), AERMAP (Terrain Preprocessor), and AERMET (Meteorological Preprocessor). AERMAP characterizes the terrain, and generates receptor grids for the AERMOD dispersion model, while AERMET provides AERMOD with the meteorological information it needs to characterize the planetary boundary layer.

AERMET uses meteorological data and surface characteristics to calculate boundary layer parameters (e.g., mixing height, friction velocity, etc.) needed by AERMOD. This data is representative of the meteorology in the modeling domain.

AERMAP uses gridded terrain data for the modeling area to calculate a representative terrain-influence height associated with each receptor location. The gridded data is supplied to AERMAP in the format of the Digital Elevation Model (DEM) data from the United States Geological Survey (USGS). The terrain preprocessor can also be used to compute elevations for both discrete receptors and receptor grids.

In developing AERMOD, AERMIC adopted design criteria to yield a model with desirable regulatory attributes. It was felt that the model should: 1) provide reasonable concentration estimates under a wide variety of conditions with minimal discontinuities; 2) be user friendly and require reasonable input data and computer resources as is the case with the ISCST3 model; 3) capture the essential physical processes while remaining fundamentally simple; and, 4) accommodate modifications with ease as the science evolves.

In order to provide consideration to downwash, cavity impacts, and building wakes and eddies, the software incorporates a feature known as the Building Profile Input Program (BPIP). The BPIP incorporates a program that calculates building heights (BH) and projected building widths (PBW), and is designed to determine whether or not a stack is being subjected to wake effects from a structure or structures, and may lead to different BH and PBW values than those calculated for GEP. These calculations are performed only if a stack is being influenced by structure wake effects.

The current version of AERMOD, version 23132 was used to complete the Air Dispersion/Deposition Modeling.

# 3.0 SUMMARY OF MODEL INPUTS

# 3.1 Facility Modeling Parameters

Design data for the facility was used as the basis for running the model in conjunction with the anticipated maximum operations which would involve thermal treatment of PFAS containing soil through thermal desorption. The model input data includes emission point parameters (stack location, stack base elevation, emission rate, stack height, stack exit temperature, stack gas velocity and stack diameter), as well as existing building footprints and heights. The model is capable of being run using specific area settings (i.e., urban or rural settings), and utilized the rural setting based on the layout of the facility and surrounding area.

In order to estimate anticipated facility emissions, destruction efficiencies of 99.90% and 99.99% were used for PFAS in soil to be treated. A summary of deposition (for PFAS) and dispersion (for PFAS, HF and CF<sub>4</sub>) modeling results with graphical representations of outputs are included in Attachment A and Attachment B for destruction efficiencies of 99.90% and 99.99%, respectively.

# 3.2 Receptor Area Modeled

The modeling was conducted for the area in the vicinity of the site, with the receptors oriented in a Cartesian grid pattern set up following the initial receptor grid spacing suggested in DAR-10: NYSDEC Guidelines on Dispersion Modeling Procedures for Air Quality Impact Analysis:

- Receptor spacing of 25m along the facility property line;
- 25m receptor spacing from the center of the facility to the facility property line;
- 70m receptor spacing from the facility property line to 1km;
- 100m spacing from 1km to 2km; and
- 250m spacing from 2km to 5km.

A total of 4,001 receptors (including sensitive receptors) were modeled under this scenario, covering an area of approximately 100,000,000 square meters (±24,700 acres), and includes areas mapped as Potential Environmental Justice Area (PEJA) Community

15000US361150801001 in the Village of Hudson Falls, and a small portion of PEJA Community 15000US361130705002 on the eastern edge of the City of Glens Falls.

As recommended in DAR-10, a 25m receptor spacing within the property boundaries was included as public access is not precluded by means of a fence or other physical barrier. All receptor data corresponds to the interpolated ground level elevation as assigned by AERMAP.

Online resources were consulted to identify the location of additional, discrete sensitive receptors such as schools, hospitals, parks, nursing homes and daycares within the modeling area. A summary of the sensitive receptors within 2 km of the site are summarized in Table 1. Figure 3 provides a depiction of the receptor grid including the sensitive receptors.

Facility Name	Location (UTM Coordinates)	Approximate Distance from Facility (km)
Fort Edward Jr. Sr. High	614811.26m, 4792114.38m	0.97
School		
School on Burgoyne	615068.06m, 4793260.20m	0.83
Fort Edward Village	615168.68m, 4791200.98m	0.86
Recreation		
Learning Express Family	614061.73m, 4792415.84m	1.75
Daycare		
A Mother's Dream Daycare	614550.77m, 4794149.78m	1.80
Fort Edward-Kingsbury	614987.73m, 4791610.57m	1.38
Health Center		
Fort Edward Village	615155.76m, 4792128.53m	0.85
Recreation		
Wedgewood Golf Club	616233.14m, 4792572.79m	0.85
Mullen Park	615253.85m, 4792023.77m	0.85

Table 1 - List of Sensitive Receptors Within Modeling Area

# 3.3 AERMAP Data Input

The current version of AERMAP, version 18081 was used to complete the proposed Air Dispersion Modeling. The AERMAP terrain preprocessor will utilize USGS 7.5 Minute Native Format DEM topographical data for the Hudson Falls, Fort Miller, Gansevoort, and Glens Falls, New York quadrangles, data which provides a resolution of 10 meters.

# 3.4 AERMET Data Input

The AERMET meteorological preprocessor utilized surface and upper air data for the most recently available five year period from the NYSDEC, which includes the years 2017-2021. The National Weather Service (NWS) website indicates that climate data for the region of the project site is available from five regional climatology reporting locations: Albany, NY; Bennington, VT; Glens Falls, NY; Pittsfield, MA; and Poughkeepsie, NY. The Glens Falls location is closest to the site, and as such, was chosen as the most representative climate data for the facility. The meteorological data provided by the NYSDEC includes surface data for Glens Falls, and upper air data from Albany.

# 3.5 AERMOD Data Input

PFAS emissions estimates for on-site activities were generated based on maximum material processing capacity for equipment on-site and estimated destruction efficiencies of PFAS of the treatment system at 99.90% and 99.99%. As the feed material will vary from project to project, data was evaluated from existing PFAS containing soils as part of the input data.

Using the emission point data, the layout of the site buildings, the model calculated the concentration of PFAS from the emissions from the emission point. The model considered complex terrain through incorporating the AERMAP program into the modeling scenario. USGS topographical data was imported into the modeling software to account for the complex terrain (i.e., those areas where the terrain exceeds the stack base elevation). For deposition calculations from AERMOD, particle size information is needed and data to be used is described in Section 3.5.1.

# 3.5.1 Particle Deposition Parameters

Ambient air measurements for the PFAS compounds of interest (Barton et al., 2006; Dreyer et al., 2015; Shin et al., 2012; Paustenbach et al., 2007) have shown that these compounds are primarily present in particulate form (and not in the vapor phase), therefore, conducting particulate deposition modeling is appropriate.

For estimating particulate deposition, the AERMOD model allows the user to input particle information in one of two ways. Since AERMOD version 19191, Method 2 deposition modeling has been reclassified from a non-default option to an alpha option as the Method 2 deposition algorithms undergo further evaluation. Therefore, C.T. Male completed deposition modeling using Method 1 as it is the default option in AERMOD.

# Method 1

For Method 1 deposition, the particle size distribution in Barton et al., 2006 was used. This particle size distribution reflects ambient air measurements downwind of a manufacturing facility. As noted above, because Method 1 deposition is typically used for particulates greater than 10 microns in diameter, the applicability of this method for estimating deposition is uncertain. A particle density of  $1.8 \text{ g/cm}^3$  was used in the modeling analyses as it is representative of the contaminants to be modeled, PFOA, PFOS, PFHxS, PFNA, and PFBS, which range from 1.780 to  $1.841 \text{ g/cm}^3$ .

# Model Output

For PFOA, PFOS, PFHxS, PFNA, and PFBS compounds, the model was used to calculate annual deposition (total, wet, and dry) in  $g/m^2/year$ .

## 3.5.2 Stack and Deposition Parameters

Stack and deposition parameters utilized in the dispersion/deposition modeling include:

Stack Height	55 feet
Stack Diameter	3.67 feet
Flow Rate	56,181 ACFM (average from stack test)
Exit Velocity	88.68 feet/second (average from stack test)
Exit Temperature	398°F

Table 1 –	Stack Parame	eters (from	2014 Stack	Testing)
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Table 2 - Deposition Parameters	(Method 1 Parameters <sup>1</sup> )
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Particle Diameter (µm)	Mass Fraction %
>4.0	5.6
1.7	12.9
0.8	9.2
0.5	7.2
0.3	5.3
<0.28	59.8

<sup>1</sup> - Method 1 deposition parameters from Barton et al., 2006, Table 4

The calculations accounted for the annual total deposition (dry + wet) using the maximum annual deposition at each receptor and results are presented from Method 1 modeling.

### 4.0 SUMMARY OF MODELING RESULTS

The AERMOD modeling analysis accounts for the operations currently contemplated for the facility, including operation of the facility's thermal desorption system for the treatment of PFAS containing soil. Modeling data included the dimensions and footprints of the facility's buildings, as well as specific information relative to the emission point. The model incorporates topographical data from the USGS, and meteorological data from Glens Falls and Albany Airports. A summary of the model results is presented within the summary report in Attachments A and B, which also include graphical representations of the model output at 99.90% and 99.99%, respectively.

The results of the modeling software specific to air dispersion modeling were subsequently compared to the AGC and SGC values for individual contaminants as determined by the NYSDEC, and as listed within the NYSDEC document titled "DAR-1 AGC/SGC Tables". A summary of the modeled maximum hourly concentration and annual hourly concentrations, and a comparison of those values to the established SGC and AGC values are presented below. As a conservative approach, the sum of the five (5) modeled PFAS compounds was compared to the individual AGC for PFOA. CF4 does not have an established AGC, and the value presented herein is based on the recommendation of the New York State Department of Health (NYSDOH) in their October 2023 assessment, included as Attachment C. The summary table shows that the modeled concentrations will not result in exceeding concentrations established by the NYSDEC or NYSDOH, which were developed to be protective of human health and the environment.

	Max Hourly			Max Annual				
	Dispersion		% of	Hourly		% <b>of</b>		
	Concentration	SGC	SGC	Dispersion	AGC	AGC		
Contaminant	All values in ug/m <sup>3</sup>							
Total Sampled PFAS								
(99.9% DRE, full receptor								
grid)	2.75E-05	N/A	N/A	2.72E-07	0.00531	0.005%		
Total Sampled PFAS								
(99.9% DRE, 1.5 mile								
endpoint)	5.39E-06	N/A	N/A	7.08E-08	0.00531	0.001%		
Hydrogen Fluoride (HF)	1.26	5.6	23%	0.0124	0.071	17%		
Carbon Tetrafluoride								
(CF <sub>4</sub> )	5.28E-03	N/A	N/A	5.21E-05	0.33 <sup>2</sup>	0.02%		

Table 3 –	Summary	of Conc	entration	Data	from	Modeling
						· · · · · · · · · · · · · · · · · · ·

<sup>1</sup> – Individual AGC for PFOA

<sup>2</sup> – NYSDOH recommended AGC, not formally accepted by the NYSDEC

### 4.1 Locations of Maximum Concentration Receptors

The location of the receptor for the maximum concentration is provided within the summary report. Isopleths indicating the results of the modeling demonstrating the concentrations of PFAS are also included within the summary report. None of the maximum concentration receptors was located in close proximity to any of the sensitive receptors. The maximum receptor for all model runs was located on-site, approximately 18 meters southwest of the emission point.

### 5.0 REFERENCES

Barton, C.A., Butler, L.E., Zarzecki, C.J., Flaherty, J., and Kaiser, M., 2006. Characterizing Perfluorooctanoate in Ambient Air near the Fence Line of a Manufacturing Facility: Comparing Modeled and Monitored Values. Journal of the Air & Waste Management Association, 56:48-55.

Barton, C.A., Zarzecki, C.J., and Russell, M.H., 2010. A Site-Specific Screening Comparison of Modeled and Monitored Air Dispersion and Deposition for Perfluorooctanoate. Journal of the Air & Waste Management Association, 60:4, 402-411, DOI:10.3155/1047-3289.60.4.402

Dreyer, A., Kirchgeorg, T., Weinberg, I., and Matthias, V. 2015. Particle-size Distribution of Airborne Poly- and Perfluorinated Alkyl Substances. Chemosphere, 129 (2015), 142-149, dx.doi.org/10.1016/j.chemosphere.2014.06.069

Paustenbach, D.J., Panko, J.M., Scott, P.K., and Unice, K.M., 2007. A Methodology for Estimating Human Exposure to Perflurooctanoic Acid (PFOA): A Retrospective Exposure Assessment of a Community (1951e2003). Journal of Toxicology and Environmental Health 70, 28-57

Shin, H.-M., Vieira, V.M., Ryan, P.B., Detwiler, R., Sanders, B., Steenland, K., and Bartell, S.M., 2011. Environmental Fate and Transport Modeling for Perfluorooctanoic Acid Emitted from the Washington Works Facility in West Virginia. Environmental Science and Technology, 2011, 45, 14351442, dx.doi.org/10.1021/es102769t

Shin, H.-M., Ryan, P.B., Vieira, V.M., and Bartell, S.M., 2012. Modeling the Air-Soil Pathway of Perfluorooctanoic Acid in the Mid-Ohio Valley Using Linked Air Dispersion and Vadose Zone Models. Atmospheric Environment, 51 (2012), 67-74, doi:10.1016/j.atmosenv.2012.01.049
United States Environmental Protection Agency (ongoing) – American Meteorological Society / EPA Regulatory Model - AERMOD Modeling System currently located and documented at EPA Home>> Air & Radiation>> Technology Transfer Network>> Support Center for Regulatory Atmospheric Modeling>> Preferred/Recommended Models

# <u>Figure 1</u>

Site Location Map



## Figure 2

### Facility Buildings, Emission Points, Elevation and Property Line Map



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Figure 3

**Receptor Grid Depiction Map** 



AERMOD View - Lakes Environmental Software

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#### Attachment A

Summary of Dispersion and Deposition Modeling Results and Graphical Representations of Output at 99.90% Destruction Efficiency Clean Earth Fort Edward, NY Site Air Deposition Modeling Results C.T. Male Project No.: 22.2756

Compound	CAS#	Soil Concentration (in ppb)	Emission Rate based on 99.90% DRE (in g/s)	Deposition Results (in g/m^2) <sup>1</sup>				Dispersion Results (in ug/m^3)		
				Low Year	Low Year	High Year	High	Maximum	Maximum	File Name
				Maximum		Maximum	Year	Hourly	Annual Hourly	
Perfluorobutane Sulfonate (PFBS)	375-73-5	0.085	6.42589E-10	2.17166E-11	4 of 5	2.83866E-11	5 of 5	2.61465E-08	2.58227E-10	PFBS9990
Perfluorooctanoic acid (PFOA)	335-67-1	4.482	3.38833E-08	1.14510E-09	4 of 5	1.49681E-09	5 of 5	1.37869E-06	1.36161E-08	PFOA9990
Perfluorononanoic acid (PFNA)	375-95-1	2.061	1.55809E-08	5.26564E-10	4 of 5	6.88292E-10	5 of 5	6.33975E-07	6.26124E-09	PFNA9990
Perfluorohexanesulfonic acid (PFHxS)	335-46-4	0.220	1.66317E-09	5.62077E-11	4 of 5	7.34712E-11	5 of 5	6.76733E-08	6.68352E-10	PFHS9990
Perfluorooctanesulfonic acid (PFOS)	1763-23-1	58.793	4.44467E-07	1.50210E-08	4 of 5	1.96345E-08	5 of 5	1.80851E-05	1.78611E-07	PFOS9990
Sum of all PFAS Compounds <sup>2</sup>	N/A	89.485	6.76495E-07	2.28625E-08	4 of 5	2.98844E-08	5 of 5	2.75261E-05	2.71852E-07	PFAS9990
Sum of all PFAS Compounds (1.5 mile endpoint) <sup>2</sup>	N/A	89.485	6.76495E-07	1.01361E-09	4 of 5	9.09221E-10	5 of 5	5.39259E-06	7.08090E-08	PFASENDP
Hydrogen Fluoride (HF) <sup>3</sup>	7664-39-3	N/A	3.08737E-02	N/A <sup>5</sup>				1.25623	1.24067E-02	HF
Carbon Tetrafluoride (CF <sub>4</sub> ) <sup>4</sup>	75-73-0	N/A	1.29685E-04					5.27681E-03	5.21146E-05	CF4
"Representative" PFAS at 0.1 g/s	N/A	N/A	0.1	3.37955E-03	4 of 5	4.41754E-03	5 of 5	4.06893	4.01854E-02	CEFE2023

<sup>1</sup> - Results based on 5 years of climate data with AERMOD generating annual depostion. Results show the highest and lowest individual year per model run.

<sup>2</sup> - Sum of all sampled PFAS compounds.

<sup>3</sup> - Calculated emission rate based on conversion of all fluorine within PFAS compounds to hydrofluoric acid.

<sup>4</sup> - Calculated emission rate based on the following article: Jonathan D. Krug, Paul M. Lemieux, Chun-Wai Lee, Jeffrey V. Ryan, Peter H. Kariher, Erin P. Shields, Lindsay C. Wickersham, Martin K. Denison, Kevin A. Davis, David A. Swensen, R. Preston Burnette, Jost O.L. Wendt & William P. Linak (2022) Combustion of C1 and C2 PFAS: Kinetic modeling and experiments, Journal of the Air & Waste Management Association, 72:3, 256-270, DOI: 10.1080/10962247.2021.2021317

<sup>5</sup> - Compound does not behave as a particulate therefore deposition modeling is not applicable.

#### Summary of Modeling Results at 99.90% Destruction Efficiency



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#### Air Dispersion and Deposition Modeling - Clean Earth Fort Edward, NY Site Year 4 of 5 - Average Annual Deposition Based on 99.90% PFAS DRE



AERMOD View - Lakes Environmental Software

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#### PROJECT TITLE:

# Air Dispersion and Deposition Modeling - Clean Earth Fort Edward, NY Site Maximum Hourly Dispersion Concentration



AERMOD View - Lakes Environmental Software

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#### PROJECT TITLE:

# Air Dispersion and Deposition Modeling - Clean Earth Fort Edward, NY Site Maximum Hourly Dispersion Concentration



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## **Attachment B**

Summary of Dispersion and Deposition Modeling Results and Graphical Representations of Output at 99.99% Destruction Efficiency Clean Earth Fort Edward, NY Site Air Deposition Modeling Results C.T. Male Project No.: 22.2756

Compound	CAS#	Soil Concentration (in ppb)	Emission Rate based on 99.99% DRE (in g/s)	Deposition Results (in g/m^2) <sup>1</sup>				Dispersion Results (in ug/m^3)		
				Low Year	Low Year	High Year	High	Maximum	Maximum	File Name
				Maximum		Maximum	Year	Hourly	Annual Hourly	
Perfluorobutane Sulfonate (PFBS)	375-73-5	0.085	6.42589E-11	2.17166E-12	4 of 5	2.83866E-12	5 of 5	2.61465E-09	2.58227E-11	PFBS9999
Perfluorooctanoic acid (PFOA)	335-67-1	4.482	3.38833E-09	1.14510E-10	4 of 5	1.49681E-10	5 of 5	1.37869E-07	1.36161E-09	PFOA9999
Perfluorononanoic acid (PFNA)	375-95-1	2.061	1.55809E-09	5.26564E-11	4 of 5	6.88292E-11	5 of 5	6.33975E-08	6.26124E-10	PFNA9999
Perfluorohexanesulfonic acid (PFHxS)	335-46-4	0.220	1.66E-10	5.62077E-12	4 of 5	7.34712E-12	5 of 5	6.76733E-09	6.68352E-11	PFHS9999
Perfluorooctanesulfonic acid (PFOS)	1763-23-1	58.793	4.44E-08	1.50210E-09	4 of 5	1.96345E-09	5 of 5	1.80851E-06	1.78611E-08	PFOS9999
Sum of all PFAS Compounds <sup>2</sup>	N/A	89.485	6.76495E-08	2.28625E-09	4 of 5	2.98844E-09	5 of 5	2.75261E-06	2.71852E-08	PFAS9999
Hydrogen Fluoride (HF) <sup>3</sup>	7664-39-3	N/A	3.08737E-02	N/A <sup>5</sup>				1.25623	1.24067E-02	HF
Carbon Tetrafluoride $(CF_4)^4$	75-73-0	N/A	1.29685E-04					5.27681E-03	5.21146E-05	CF4
"Representative" PFAS at 0.1 g/s	N/A	N/A	0.1	3.37955E-03	4 of 5	4.41754E-03	5 of 5	4.06893	4.01854E-02	CEFE2023

<sup>1</sup> - Results based on 5 years of climate data with AERMOD generating annual depostion. Results show the highest and lowest individual year per model run.

<sup>2</sup> - Sum of all sampled PFAS compounds.

<sup>3</sup> - Calculated emission rate based on conversion of all fluorine within PFAS compounds to hydrofluoric acid.

<sup>4</sup> - Calculated emission rate based on the following article:

Jonathan D. Krug, Paul M. Lemieux, Chun-Wai Lee, Jeffrey V. Ryan, Peter H. Kariher, Erin P. Shields, Lindsay C. Wickersham, Martin K. Denison, Kevin A. Davis, David A. Swensen, R. Preston Burnette, Jost O.L.

Wendt & William P. Linak (2022) Combustion of C1 and C2 PFAS: Kinetic modeling and experiments, Journal of the Air & Waste Management Association, 72:3, 256-270, DOI:

<sup>5</sup> - Compound does not behave as a particulate therefore deposition modeling is not applicable.

### Summary of Modeling Results at 99.99% Destruction Efficiency



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### Attachment C

NYSDOH Prepared "Summary of Toxicological Assessment for Carbon Tetrafluoride in Support of the Development of an AGC and SGC for the NYSDEC"
Bureau of Toxic Substance Assessment Division of Environmental Health Assessment Center for Environmental Health October 2023

> Summary of the Toxicological Assessment of Carbon Tetrafluoride in Support of the Development of an Annual Guideline Concentration (AGC) and Short-term Guideline Concentration (SGC) for the NYS Department of Environmental Conservation (NYS DEC)

#### 1. Executive Summary of Recommended Annual Guideline Concentration

At the request of the NYS DEC's Division of Air Resources, the New York State Department of Health's (NYS DOH) Bureau of Toxic Substance Assessment (BTSA) evaluated the toxicity of carbon tetrafluoride in support of the development of an AGC. As described in the bulleted summaries below, the NYS DOH searched for acute, subchronic and chronic toxicity information from authoritative bodies and the scientific literature. The toxicological database for carbon tetrafluoride was found to be very limited and inadequate to derive an AGC. Chemical-specific toxicity data sufficient to evaluate the potential for portal-of-entry effects (including irritation at the site of contact) and/or systemic effects from acute, subchronic or chronic exposures (via oral and inhalation routes of exposure) were not available for carbon tetrafluoride. Thus, NYS DOH evaluated the toxicity of structurally similar chemicals to derive an AGC for carbon tetrafluoride by inference to structurally similar chemicals for which toxicity information is available. This approach is permitted under the NYS DEC (2021) guidelines for the derivation of AGCs, which states: "if information about a chemical is limited, structure activity relationships for chemicals of close or similar structure will be used to calculate an interim AGC." Therefore, the NYS DOH recommends an AGC for carbon tetrafluoride of 0.33 milligrams per cubic meter (mg/m<sup>3</sup>) based upon the toxicity of two structurally similar analogues (i.e., trichlorofluoromethane and dichlorodifluoromethane). Since chemical-specific toxicity information on carbon tetrafluoride was found to be insufficient to inform whether the health effects of carbon tetrafluoride are likely to be portal-of-entry, systemic or both, carbon tetrafluoride is being treated as a Category 3 gas based on toxicity studies for the two selected analogues (trichlorofluoromethane and dichlorodifluoromethane), which demonstrate that the predominant toxicological effects from inhalation exposure to these two chemicals are systemic effects. Inhalation toxicity values from authoritative bodies are available for these two chemicals and are based on noncancer health effects from inhalation exposures in animals and humans. The NYS DOH used these inhalation toxicity values, along with the application of uncertainty factors to account for less than lifetime exposures in the critical studies to derive the recommended AGC for carbon tetrafluoride. Based on the uncertainties and limitations presented by the absence of chemical-specific toxicity information for carbon tetrafluoride, the NYS DOH supports the adoption of 0.33 mg/m<sup>3</sup> as an interim AGC value, which could change if new and adequate chemical-specific toxicity data become available.

# 2. Search Criteria Used to Evaluate the Toxicity of Carbon Tetrafluoride

To evaluate whether an AGC and/or SGC could be derived based on chemical-specific toxicity information on carbon tetrafluoride, internet searches were performed for the following six key areas of information:

- 1) Physical-chemical properties
- 2) Basic information on chemical use and manufacturing

- 3) Chronic and subchronic toxicity values (including oral and inhalation cancer and noncancer toxicity values)
- 4) Toxicity studies from the scientific literature (acute, subchronic and chronic studies for oral and inhalation routes of exposure)
- 5) Other toxicity information (e.g., pharmacokinetics and mode-of-action (MOA) for toxicity)
- 6) Occupational exposure limits

# 3. <u>Physical-Chemical Properties and Chemical Use of Carbon Tetrafluoride</u>

Carbon tetrafluoride is a colorless, odorless, nonflammable gas that is used as a refrigerant (PubChem, 2023). Carbon tetrafluoride is also a stable combustion byproduct that can be emitted into air via the incineration of fluorine-containing waste (Lohmann et al., 2020). Carbon tetrafluoride can also be emitted into air through industrial activities, such as aluminum production (US EPA and IAI, 2008). Additional information on the physical-chemical properties of carbon tetrafluoride is provided in Appendix B (Table B – 1).

# 4. Toxicity Information on Carbon Tetrafluoride

The available information on the toxicity of carbon tetrafluoride is very limited. Chronic and subchronic toxicity values from authoritative bodies are not available. In addition, chronic or subchronic carbon tetrafluoride toxicity studies by the inhalation or oral routes of exposure were not found. The toxicological database on carbon tetrafluoride is inadequate to derive toxicity values<sup>1</sup> based on cancer or noncancer long term health effects, and thus, is inadequate to derive an AGC using chemical-specific information.

NYS DEC (2021) uses acute toxicity data (e.g., lethality data) for toxicity classification of air contaminants and uses occupational exposure limits to derive AGC/SGC values in the absence of chronic toxicity values. While BTSA has not derived health-based guidance values for evaluating acute occupational exposures in the past, in order to assess the overall completeness of the toxicological database for carbon tetrafluoride, acute toxicity studies (inhalation and oral routes of exposure) and occupational exposure limits were included in the search criteria.

Fluorine-based occupational exposure limits for carbon tetrafluoride from European countries (NIOSH, 2023) were found (Appendix B, Table B - 2). However, occupational exposure limits for carbon tetrafluoride are not available from the authoritative bodies that are preferred by NYS DEC (2021) for AGC/SGC development (e.g., American Conference of Governmental Industrial Hygienists (ACGIH)).

Information on the acute toxicity of carbon tetrafluoride is very limited. An acute exposure study is available in the scientific literature (Makowski et al., 2022). However, this study does not use a traditional study design for acute toxicity testing (US EPA, 1998). Rats were exposed via inhalation to normobaric air, hyperbaric air, or a hyperbaric mixture containing a high concentration of carbon tetrafluoride (i.e., 79% carbon tetrafluoride, 21% oxygen) for 30 minutes per day for 5 days. Statistically significant effects on bodyweight were reported in females exposed to hyperbaric carbon tetrafluoride, but the authors reported that these bodyweights were within the normal range reported in the scientific literature. The lowest published lethal concentration is 895,000 parts per million per 15 minutes in rats via inhalation exposure (NIOSH, 2023). The available

<sup>&</sup>lt;sup>1</sup> Both inhalation and oral toxicity values were considered based on the potential use of route-to-route extrapolation for health effects that are systemic (i.e., not point-of-contact).

information, while limited, suggests low acute toxicity.<sup>2</sup> However, the available information on the acute toxicity of carbon tetrafluoride is limited and insufficient to derive a chemical-specific SGC.

# 5. Identification of Structurally Similar Carbon Tetrafluoride Analogues

Given that the available chemical-specific information on carbon tetrafluoride was insufficient to derive an AGC (which was the focus of this assessment), the next phase of the assessment was to identify possible carbon tetrafluoride analogues to evaluate the chronic and subchronic toxicity of structurally similar compounds. Use of toxicity data on structurally similar compounds for inference to the potential toxicity of carbon tetrafluoride, in the absence of chemical-specific information, is permitted under NYS DEC (2021) guidelines for the derivation of AGCs.

Online tools, including ChemIDPlus<sup>3</sup> (NLM, 2022), Integrated Chemical Environment (NTP, 2022) and the Comptox Dashboard (US EPA, 2022)<sup>4</sup>, were used to identify structurally similar analogues to carbon tetrafluoride. Structurally similar analogues meeting criteria of greater than or equal to 80% similarity, 0.8 similarity threshold or 0.8 Tanimoto score are included in Appendix B (Table B – 3). While disparate similarity metrics cannot be directly compared, higher values (on scales of 0 to 100% or 0 to 1) generally indicate higher levels of structural similarity to carbon tetrafluoride. Table 1 includes structural similarity scores from Appendix B (Table B – 3) for a subset of structurally similar carbon tetrafluoride analogues for which inhalation toxicity values are available.

# 6. Method for Obtaining Toxicity Information on Structurally Similar Carbon Tetrafluoride Analogues

The online tools for quantitatively assessing structural similarity to carbon tetrafluoride provided approximately 20 structurally similar analogues for consideration (Appendix B, Table B - 3). For these chemicals, online searches were performed for the six key areas of information listed in Section 2 (e.g., physical chemical properties, acute, subchronic and chronic toxicity values, scientific literature on acute, subchronic and chronic toxicity).

To streamline the process for obtaining toxicity information on structurally similar analogues, initial searches were performed using the Comptox Dashboard (US EPA, 2022), which provided available toxicity values. Moreover, consistent with NYS DEC (2021) guidance, toxicity values derived by US EPA were prioritized in this

<sup>&</sup>lt;sup>2</sup> Two additional studies were found that evaluate the health effects of exposure in mice to different pressures of gases and gas mixtures (Clarke et al, 1978; Daniels et al., 1979). However, these studies could not be used to assess acute inhalation toxicity as they do not utilize a traditional acute toxicity study design (US EPA, 1998), there were co-exposures to gas mixtures, and air concentrations of carbon tetrafluoride were not reported. Exposure metrics were reported as measures of pressure in these studies (i.e., in atmosphere (ATM) or pounds per square inch (PSI)).

<sup>&</sup>lt;sup>3</sup> The ChemIDPlus (NLM, 2022) is no longer active as of 2023. The ChemIDPlus database is now part of PubChem. However, the chemical similarity tool in PubChem (NLM, 2023) differs from and provides a different suite of chemicals than ChemIDPlus. The PubChem tool provides less useful analogues than the original ChemIDPlus similarity results and were not considered in this assessment.

<sup>&</sup>lt;sup>4</sup> Structurally similar compounds were retrieved from the Comptox Dashboard using the "Chemical Details" tab in the carbon tetrafluoride chemical profile. The Comptox Dashboard GenRA tool was also used to determine whether the ToxRef (*in vivo* data) and ToxCast (*in vitro* data) databases could provide suitable analogues for assessment using the automated read-across feature in the Comptox Dashboard GenRA tool. However, the chemicals retrieved via GenRA using *in vivo* data filters (i.e., ToxRef) generally had lower structural similarity based on toxprint and morgan fingerprints (e.g., < 0.5 jaccard similarity for most analogues). Thus, while GenRA was performed as part of this assessment, it ultimately was not used for surrogate selection given the emphasis on identifying chemicals with a high level of structural similarity to carbon tetrafluoride as a means of inferring and predicting toxicity.

assessment for screening of carbon tetrafluoride analogues. The Comptox Dashboard was also used to screen and identify toxicity studies on carbon tetrafluoride analogues via the PubMed Abstract Sifter (US EPA, 2022).

ChemIDPlus (NLM, 2022) and PubChem (NLM, 2023) chemical databases were used to obtain general information on chemical structure, use, physical chemical properties, and acute toxicity information on structurally similar analogues. While additional internet searches were performed, as needed, this hierarchal approach to sourcing and prioritizing toxicity information was implemented given the large number of chemicals that were screened and evaluated in this assessment.

# 7. Toxicity Information on Structurally Similar Carbon Tetrafluoride Analogues

There was limited toxicity information available on most of the identified surrogates. Only three of the approximately 20 structurally similar chemicals (i.e., trichlorofluoromethane, dichlorodifluoromethane and carbon tetrachloride) had available toxicity values that could be used to derive an AGC. Table 1 shows the available cancer and noncancer inhalation toxicity that were found on the three surrogates. However, as described in previous sections, chemical-specific toxicity information on carbon tetrafluoride is insufficient to evaluate carcinogenicity or to support a biological rationale for assessing carbon tetrafluoride carcinogenicity using chemical correlation. Therefore, while searches were performed for information on both cancer and noncancer toxicity of carbon tetrafluoride analogues, noncancer toxicity was prioritized for consideration in the development of a potential AGC.

Of the three analogues, carbon tetrachloride had the most extensive toxicity database. For example, US EPA Integrated Risk Information System (IRIS) derived cancer and noncancer toxicity values for carbon tetrachloride based on oral and inhalation exposure (US EPA IRIS, 2010). Additional inhalation toxicity values were also identified via the Comptox Dashboard (US EPA, 2022) from authoritative bodies such as the Agency for Toxic Substances and Disease Registry (ATSDR, 2005, 2023) and California Office of Environmental Health Hazard Assessment (CA OEHHA, 2008, 2023). By comparison, the toxicity databases were limited for trichlorofluoromethane and dichlorodifluoromethane. For example, oral reference doses for each chemical were derived by US EPA IRIS. However, inhalation toxicity and the potential for carcinogenicity were not assessed under the IRIS program. US EPA derived subchronic reference concentrations (RfCs) under US EPA's Superfund program (i.e., provisional peer-reviewed toxicity values (PPRTV)). However, US EPA did not derive chronic RfCs for trichlorofluoromethane and dichlorodifluoromethane, and determined that there was "inadequate information to assess the carcinogenic potential" of these chemicals.

Table 1 below includes summaries of available inhalation toxicity values for trichlorofluoromethane, dichlorodifluoromethane and carbon tetrachloride from US EPA and other authoritative bodies (e.g., CA OEHHA, Danish Ministry of the Environment (DME), ATSDR and the Michigan Department of Environmental Quality (DEQ)). The toxicity values derived by US EPA, CA OEHHA, ATSDR and the Michigan DEQ are based on extra-respiratory (systemic) effects in animals or humans, and involve application of physiologically based pharmacokinetic (PBPK) modeling or dosimetric adjustment factors for Category 3 gases to calculate human equivalent concentrations (HECs). These methods are consistent with currently accepted risk assessment practices for deriving RfCs.<sup>5</sup> However, the DME did not calculate HECs to derive RfCs and instead used

<sup>&</sup>lt;sup>5</sup>US EPA guidance for deriving RfCs (US EPA, 1994, 2012) recommends inhalation dosimetry to extrapolate from inhalation exposure levels in animals to inhalation exposures in humans. In the absence of physiologically based pharmacokinetic (PBPK) models for

uncertainty factors to account for pharmacokinetic and pharmacodynamic differences between animals and humans.

extrapolating between animals and humans, the default recommended approach for application of inhalation dosimetry considers physical-chemical properties as determinants of chemical uptake into the respiratory system (US EPA, 1994, 2012). Category 1 gas characteristics include high solubility in water and/or rapid irreversible reactivity. Category 1 gases do not accumulate in blood and elicit site of contact effects at the portal of entry. Category 2 gases have moderate solubility in water, may be rapidly reversibly reactive or moderately to slowly irreversibly metabolized in the respiratory tract. Category 2 gases have the potential for accumulation in blood and effects may be systemic or at the portal of entry. Category 3 gases have low water solubility, are relatively unreactive in surface liquid and tissue, can accumulate in blood, and have systemic toxicity.

Chemical Name/ CAS	Toxicity	ogues luci				Uncertainty
Number	Value	Source	Study Details	POD/DAF	<b>Toxicity Endpoint</b>	Factors
Analogues (listed in the or	der of most t	o least struc	turally similar to carbon tetraflu	ioride)		
Trichlorofluoromethane (Freon 11)	1 mg/m <sup>3</sup> Subchronic p-RfC	US EPA, 2009; provisional peer- reviewed toxicity Value (PPRTV)	Single exposure concentration study; 5620 mg/m <sup>3</sup> in humans exposed via inhalation 8 hour/day, 5 days/week, for 2 to 4 weeks	LOEL <sub>ADJ</sub> = 1338 mg/m <sup>3</sup>	Small decrements in cognitive performance in humans	1000 UFL = 10 UF <sub>H</sub> = 10 UF <sub>D</sub> = 10
75-69-4 *95% structural similarity to carbon tetrafluoride	570 mg/m <sup>3</sup> Health- based quality criterion in air	DME, 2014	Single exposure concentration study; Guinea pigs, rats and dogs exposed continuously to 57,000 mg/m <sup>3</sup> for 90 days.	NOEL = 57,000 mg/m <sup>3</sup> An HEC was not calculated; Applied UF approach <sup>c</sup>	No adverse effects reported	100 UF <sub>A</sub> = 10 UF <sub>H</sub> = 10
	0.13 mg/m <sup>3</sup> Initial Threshold Screening Level (ITSL)	Michigan DEQ, 2019a	Adopted US EPA (2009) PPRT additional u	V (See above) w ncertainty factor	ith application of	10,000 UFL = 10 UFH = 10 UFD = 10 UFS = 10
Dichlorodifluoromethane	1 mg/m <sup>3</sup> Subchronic p-RfC; Chronic screening level <sup>p</sup>	US EPA, 2010; PPRTV	Single exposure concentration study; 0 or 4,136 mg/m <sup>3</sup> for 8 hours/day, 5 days/week for 6 weeks in guinea pigs, rabbits, dogs, and monkeys	LOEL <sub>ADJ[HEC]</sub> = 985 mg/m <sup>3</sup> DAF = 1 (Category 3 Gas)	Decreased bodyweight gain in guinea pigs, rabbits, dogs, and monkeys	1000 UF <sub>A</sub> = 3 UF <sub>H</sub> = 10 UF <sub>L</sub> = 10 UF <sub>D</sub> = 3
(Freon 12) 75-71-8 *95% structural similarity to carbon tetrafluoride	14 mg/m <sup>3</sup> Health- based quality criterion in air	DME, 2014	90 day continuous exposure in guinea-pigs showed to single concentration of 4,100 mg/m <sup>3</sup>	LOEL = 4,100 mg/m <sup>3</sup> An HEC was not calculated; Applied UF approach <sup>c</sup>	Fatty infiltration and necrosis in the liver	100 UF <sub>A</sub> = 10 UF <sub>H</sub> = 10
	0.33 mg/m <sup>3</sup> ITSL	Michigan DEQ, 2019b	Adopted US EPA (2010) PPRT additional ur	V (See above) w ncertainty factor	ith application of E	3000 UF <sub>A</sub> = 3 UF <sub>H</sub> = 10 UF <sub>L</sub> = 10 UF <sub>S</sub> = 10
Carbon tetrachloride (Freon 10) 56-23-5 *88% structural similarity to carbon tetrafluoride	0.1 mg/m <sup>3</sup> RfC	US EPA IRIS, 2010	Whole body exposure in rats to 0, 31.5, 157, or 786 mg/m <sup>3</sup> (99.8% pure) vapor for 6 hours/day, 5 days/ week for 104 weeks	BMCL <sub>10[HEC]</sub> = 14.3 mg/m <sup>3</sup> *A human PBPK model was used to obtain HEC (Category 3 gas)	Fatty changes in the liver	100 UF <sub>A</sub> = 3 UF <sub>H</sub> = 10 UF <sub>D</sub> = 3

# Table 1. Available Inhalation Toxicity Values for Structurally Similar Carbon Tetrafluoride Analogues Identified via Quantitative Structural Similarity Assessment Tools<sup>A,B</sup>

Chemical Name/ CAS Number	Toxicity Value	Source	Study Details	POD/DAF	Toxicity Endpoint	Uncertainty Factors
	6 × 10⁻⁵ per mcg/m³ Unit Risk <sup>F</sup>		BDF1 mice exposed to carbon tetrachloride vapor for 104 weeks (6 hours/ day, 5 days/week)	LEC <sub>10</sub> , lower 95% bound on exposure at 10% extra risk - 1.78 × 10 <sup>4</sup> mcg/m <sup>3</sup>	Increased incidence in adrenal gland tumors	Not applicable
	0.04 mg/m <sup>3</sup> Chronic Reference Exposure Level	CA OEHHA (2008, 2023)	Guinea pigs exposed to 0, 5, 10, 25, 50, 100, 200 and 400 ppm (0, 37, 74, 186, 372, 744, 1487, 2974 mg/m <sup>3</sup> ) carbon tetrachloride for varying duration. At the LOEL (37 p mg/m <sup>3</sup> ) exposure was for 7 hours/day, 5 days/week for 7.3 months.	LOEL <sub>ADJ[HEC]</sub> = 10.7 mg/m <sup>3</sup> RGDR = 1.7 (Category 3 gas)	Increase in liver weight and liver lipid content	300 UF <sub>A</sub> = 3 UF <sub>H</sub> = 10 UF <sub>L</sub> = 3 UF <sub>S</sub> = 3
	4.2 x 10 <sup>-5</sup> per mcg/m <sup>3</sup> Unit Risk	CA OEHHA (2011, 2023)	Based on cross-route extrapola oral cancer potency factor deriv in 1984.	ation from an ved by US EPA	Increased incidence in liver tumors in mice	Not applicable
	0.19 mg/m <sup>3</sup> (0.03 ppm) Inhalation Minimal Risk Level	ATSDR, 2005	Whole body exposure to e (>99% pure) to 0, 5, 25, or 125 ppm (0, 37, 186, 930 mg/m <sup>3</sup> ) carbon tetrachloride for 6 hours/day, 5 days/week for 104 weeks. LOEL = 186 mg/m <sup>3</sup>	NOEL <sub>ADJ[HEC]</sub> = 0.9 ppm (6.7 mg/m <sup>3</sup> ) DAF = 1 (Category 3 gas)	increased liver weight, serum enzymes, and liver histopathology (fatty change, granulation, foci, deposition of ceroid, fibrosis, and cirrhosis)	30 UF <sub>A</sub> = 3 UF <sub>H</sub> = 10

<sup>A</sup>Table Definitions: ADJ (adjusted for continuous exposure), BMCL (benchmark concentration lower bound), DAF (dosimetric adjustment factor), HEC (human equivalent concentration), LOEL (lowest-observed-effect-level), NOEL (no-observed-effect-level), POD (point-of-departure), p-RfC (provisional reference concentrations), RfC (reference concentration), RGDR (Regional Gas Dose Ratio), UF<sub>A</sub> (interspecies uncertainty factor), UF<sub>D</sub> (database uncertainty factor), UF<sub>H</sub> (intraspecies uncertainty factor) UF<sub>L</sub> (LOEL-to-NOEL uncertainty factor), UF<sub>S</sub> (uncertainty factor for less than lifetime exposure).

- <sup>B</sup> As described in Section 5, structural similarity scores for carbon tetrafluoride analogues come from online tools, including ChemIDPlus<sup>6</sup> (NLM, 2022), Integrated Chemical Environment (NTP, 2022) and the Comptox Dashboard (US EPA, 2022). Higher structural similarity scores (on scales of 0 to 100% or 0 to 1) generally indicate higher levels of structural similarity to carbon tetrafluoride. Table 1 includes the subset of carbon tetrafluoride analogues for which inhalation toxicity values were found. The full list of structurally similar analogues meeting criteria of greater than or equal to 80% similarity, 0.8 similarity threshold or 0.8 Tanimoto score can be found in Appendix B (Table B – 3).
- <sup>C</sup>Current US EPA guidance for deriving RfCs (US EPA, 1994) recommends the use of mathematical models (i.e., physiologically based pharmacokinetic modeling (PBPK)) or dosimetric adjustment factors (DAFs) to extrapolate from inhalation exposure levels in animals to inhalation exposures to humans. In the absence of available PBPK models for extrapolating between animals and humans, the default recommended approach for application of DAFs considers the physical-chemical properties of chemicals (i.e., whether chemicals are particles or gases) and pharmacokinetics (i.e., whether chemicals are reactive at the site of contact (Category 1 gases), absorbed and distributed systemically and elicit systemic effects (Category 3 gases), or both (Category 2 gases)) in order to calculate human equivalent concentrations (HECs) from inhalation exposure levels in animals. US EPA used a DAF to calculate an HEC for dichlorodifluoromethane from animal inhalation exposure levels and did not use a DAF for trichlorofluoromethane as the POD was based on human health effects. However, DME (2014) used the uncertainty factor approach to account for both pharmacokinetic and pharmacodynamic differences between animals and humans (i.e., applied a total uncertainty factor of 10 for interspecies extrapolation) in toxicity value derivations.

<sup>&</sup>lt;sup>6</sup> The ChemIDPlus (NLM, 2022) is no longer active as of 2023. The ChemIDPlus database is now part of PubChem. However, the chemical similarity tool in PubChem (NLM, 2023) differs from and provides a different suite of chemicals than ChemIDPlus. The PubChem tool provides less useful analogues than the original ChemIDPlus similarity results and were not considered in this assessment.

<sup>D</sup>US EPA (2010) did not derive a chronic RfC for dichlorodifluoromethane. However, US EPA indicated that a "screening level" chronic RfC of 0.1 mg/m<sup>3</sup> could be derived by using an additional UF of 10 for chronic-to-subchronic extrapolation, which would result in a total UF 10,000. According to current risk assessment practices for deriving an RfC, total uncertainty factors (i.e., for extrapolation from a LOEL to a NOEL, from a subchronic to lifetime study, and for intra- and interspecies extrapolation) are typically limited to a maximum of 3000, even when there are four areas of uncertainty being addressed through application of uncertainty factors. <sup>E</sup>Michigan DEQ (2019b) also calculated a screening chronic provisional value of 0.1 mg/m<sup>3</sup> using a total UF of 10,000.

<sup>F</sup>10<sup>-6</sup> Cancer Risk Level = 0.17 mcg/m<sup>3</sup> (0.00017 mg/m<sup>3</sup>)

#### 8. Comparison of Carbon Tetrafluoride Analogues

#### 8.1. Comparison of Toxicity Values

Of the three structurally similar analogues for which toxicity values were found (Table 1), trichlorofluoromethane and dichlorodifluoromethane had the highest structural similarity to carbon tetrafluoride (both with about 95% structural similarity). The structural similarity between carbon tetrachloride and carbon tetrafluoride was lower (about 88%). However, the toxicity of carbon tetrachloride is well characterized compared to the other two analogues, and carbon tetrachloride has the lowest inhalation toxicity value from US EPA<sup>7</sup> (Table 1) of the three analogues. In addition, the US EPA IRIS (2010) RfC derivation for carbon tetrachloride (0.1 mg/m<sup>3</sup>) includes several favorable attributes, such as use of a lifetime-exposure toxicity study in rodents, benchmark dose modeling to estimate a point-of-departure (POD), and pharmacokinetic modeling to obtain a human equivalent concentration (instead of use of default dosimetry calculations). US EPA IRIS (2010) assigned a medium overall confidence in their RfC assessment, high confidence in the selected key study, and medium confidence in the toxicity database for carbon tetrachloride.

By contrast, the US EPA derivations for trichlorofluoromethane and dichlorodifluoromethane (subchronic provisional RfCs of 1 mg/m<sup>3</sup> for each chemical) are limited in that they are both subchronic toxicity values and are based on lowest-observed-effect levels (LOELs) from short-term, single exposure studies (Table 1). The RfC for trichlorofluoromethane is based on health effects in humans (i.e., cognitive effects in humans exposed via inhalation to 5620 mg/m<sup>3</sup> trichlorofluoromethane for 8 hours per day, 5 days per week, for up to 4 weeks (Stewart et al., 1975, 1978, reviewed in US EPA, 2009)). PODs based on health effects in humans are generally preferred to use of health effects in animals for derivation of inhalation toxicity values. However, US EPA (2009) also applied a database uncertainty factor of 10 due to the limited availability of inhalation toxicity studies). US EPA (2009) assigned a low overall confidence in the provisional subchronic RfC for trichlorofluoromethane, medium-to-low confidence in the selected key study, and low confidence in the toxicity database.

The provisional RfC for dichlorodifluoromethane is based on short-term health effects in laboratory animals. The LOEL selected as the POD based on toxicity in animals is lower than the no-observed-effect level (NOEL) of 1,179 mg/m<sup>3</sup>) reported in a study of humans exposed via inhalation to a single concentration for 8 hours per day, 5 days per week for up to 4 weeks (Stewart et al., 1978, reviewed in US EPA, 2010). The US EPA provisional RfC for dichlorodifluoromethane includes a database uncertainty factor of 3 for lack of reproductive and developmental toxicity. US EPA did not apply a full database uncertainty factor of 10, in part, due to the presence of one chronic duration inhalation study of dichlorodifluoromethane in rodents (Maltoni et al., 1988). This study examined the carcinogenicity of dichlorodifluoromethane and reported no treatment related differences in tumor incidence in the organs and systems of rats and mice examined in the study (e.g., brain, mammary glands, blood). However, this study reported limited information on noncancer toxicity (US EPA, 2010). The OS PPA (2010). The OS PPA (2010) considered the highest exposure concentration tested in this study to be a NOEL (2,976 mg/m<sup>3</sup>). It should be noted that the NOEL from the Maltoni et al. (1988) study is

<sup>&</sup>lt;sup>7</sup> Consistent with NYS DEC (2021) guidance, toxicity values derived by US EPA were prioritized in this assessment for screening of carbon tetrafluoride analogues.

much higher than the POD of 985 mg/m<sup>3</sup> selected as the basis of US EPA's subchronic provisional RfC for dichlorodifluoromethane. US EPA (2010) assigned a low overall confidence in the provisional subchronic RfC, low confidence in the selected key study, and low-to-medium confidence in the toxicity database.

With respect to the two fluorinated structurally similar analogues, the US EPA provisional RfC derivations for trichlorofluoromethane and dichlorofluoromethane are of similar quality, with similar strengths and weaknesses. Thus, for trichlorofluoromethane and dichlorofluoromethane a strong rationale for choosing one chemical and corresponding toxicity value over the other as a potential basis of an AGC for carbon tetrafluoride was not apparent. Therefore, it was concluded at this stage in the assessment that additional information was needed on the three analogues (carbon tetrachloride, trichlorofluoromethane and dichloroffluoromethane) in order to determine whether a biological rationale could be formulated to inform surrogate selection based on factors such as pharmacokinetics and modes-of-action for toxicity. Surrogate selection for use in deriving an AGC for carbon tetrafluoride is covered in subsequent sections of this document (Sections 8.2, 9.1, 9.2, 10, 11.1 and 11.2). These sections consider additional supporting information and provide a scientific rationale for recommending an approach to deriving an AGC for carbon tetrafluoride.

# 8.2. Chemical Property Considerations

In comparing the toxicity of carbon tetrachloride, trichlorofluoromethane and dichlorodifluoromethane, physical-chemical properties (Appendix B, Table B - 1), including chemical makeup, were also considered. For example, the low boiling points of the three analogues (Appendix B, Table B - 1) indicate that they are volatile organic chemicals. In terms of chemical makeup, while the analogues are all fully halogenated methanes, carbon tetrachloride and carbon tetrafluoride differ in chemical composition given that the former is fully chlorinated and the latter is a fully fluorinated. Toxicity comparisons between groups of chemicals with similar halogen makeup is a common practice in human health risk assessment (e.g., per- and polyfluoroalkyl substances (PFAS), polychlorinated dibenzo-p-dioxins, polybrominated diphenyl ethers, polychlorinated biphenyls). However, evidence to support a rationale for assuming similar toxicity between chemicals with dissimilar halogen makeup, such as fully chlorinated and fully fluorinated chemicals, was not found. The presence or absence of fluorine could also play an important role in chemical attributes. For example, the carbon-fluorine covalent bond is considered the strongest in organic chemistry, and has a low reactivity due to factors such as the electronegativity of fluorine, the polarity of the bond, and poor accessibility to the bonded fluorine atom's valence electrons (Chan et al., 2011). In addition, information on fully fluorinated chemicals, such as PFAS, indicates that some fluorinated chemicals have high thermal and chemical stability, are persistent in the environment, and do not readily undergo biological transformation (Langenbach and Wilson, 2021). Thus, the dissimilarities in halogen makeup between carbon tetrachloride and carbon tetrafluoride reduced the confidence in the use of a precautionary principal approach at this stage of the assessment (i.e., selection of carbon tetrachloride, the chemical with the lowest RfC and most robust toxicity database, as the basis of an AGC for carbon tetrafluoride).

# 9. Structurally Related Fluorinated Chemicals

# 9.1. Identification of Related Fluorinated Chemicals

Since there was limited toxicity information on the approximately 20 chemical analogues initially identified by the structural similarity tools, the assessment of potential carbon tetrafluoride analogues was widened to include additional fluorinated compounds (e.g., partially halogenated methanes and haloalkanes identified in

authoritative body documents on chlorofluorocarbons, chemicals identified in other online structural assessment tools (e.g., the free ChemMine tool (Backman et al., 2022) and through professional judgement). This additional screening was performed to address important limitations in the assessment due to compounding uncertainties presented by both the absence of chemical-specific toxicity data on carbon tetrafluoride and the limited toxicity databases on the inhalation toxicity of structurally similar compounds as a whole and for trichlorofluoromethane and dichlorodifluoromethane, specifically. While the additional screening of fluorinated chemicals was not exhaustive, it provided additional related chemicals for consideration (e.g., 20 to 30 additional chemicals).

Any chemicals that had carbon chains of greater than 2 carbons or that had carbon-to-carbon double bonds were excluded from screening as the focus of this part of the assessment was to find chemicals with potential structural and functional similarities to carbon tetrafluoride. The remaining related fluorinated chemicals were screened for chronic or subchronic toxicity values, with an emphasis on inhalation toxicity values (Section 9.2). If other relevant toxicity information were readily available (e.g., pharmacokinetics or MOA), the information was captured in the assessment.

#### 9.2. Toxicity Screening of Related Fluorinated Chemicals

The same search method for obtaining toxicity information described in Section 6 was used to identify toxicity values for screening of related chemicals. These searches of more than 20 related chemicals yielded 10 additional chronic and subchronic inhalation toxicity values for eight fluorinated chemicals (halomethanes and haloalkanes) for consideration. The available toxicity values for these additional compounds (Table 2) were generally higher than the ones found for the three structurally similar analogues evaluated in this assessment (Table 1). While the toxicity databases for the additional chemicals were limited, the additional data on fluorinated halomethanes and haloalkanes were not suggestive of high noncancer toxicity. Had the available toxicity data for these compounds demonstrated higher toxicity than the initial three analogues identified by structural similarity, application of the precautionary principal to select carbon tetrachloride as the surrogate chemical for use in deriving an AGC could have been reconsidered at this stage in the assessment. However, since this was not the case, the two fluorinated analogues from the initial structural similarity assessment (i.e., trichlorofluoromethane and dichlorodifluoromethane) remained options for deriving an AGC for carbon tetrafluoride. Thus, the screening of these additional related fluorinated compounds served to increase the confidence in the selection of the two partially fluorinated structurally similar carbon tetrafluoride analogues.

Chemical Name/ CAS Number	Toxicity Value	Source	Study Details	POD/DAF	Toxicity Endpoint	Uncertainty Factors
Dichlorofluoromethane (Freon 21) 75-43-4	0.13 mg/m <sup>3</sup> Health- based quality criterion in air	DME, 2014	Rats exposed via inhalation to 213, 640 or 2130 mg/m <sup>3</sup> (6 hours/day, 5 days/week, for 90 days). LOEL = 213 mg/m <sup>3</sup>	LOEL <sub>ADJ</sub> = 38 mg/m <sup>3</sup> An HEC was not calculated; Applied UF approach <sup>C</sup>	Histopathological changes in the liver	300 UF <sub>A</sub> = 10 UF <sub>H</sub> = 10 UF <sub>L</sub> = 3
Chlorodifluoromethane (Freon 22) 75-45-6	50 mg/m <sup>3</sup> RfC	US EPA IRIS, 1993	Whole-body exposure to 0, 3540, 35,370, or 176,800 mg/m <sup>3</sup> for 5 hours/day, 5 days/week, for up to 118 weeks (females) or 131 weeks (males). LOEL = 176,800 mg/m <sup>3</sup>	NOEL <sub>ADJ[HEC]</sub> = 5260 mg/m <sup>3</sup> DAF = 1	Increased kidney, adrenal and pituitary weights in rats.	100 UF <sub>A</sub> = 3 UF <sub>H</sub> = 10 UF <sub>D</sub> = 3
2-Chloro-1,1,1- trifluoroethane (Freon 133a) 75-88-7	2.1 mg/m <sup>3</sup> Health- based quality criterion in air	DME, 2014	Inhalation exposure to rat dams (2,500 mg/m <sup>3</sup> for 6 hours/day on gestation days 6 to 15), which corresponds to 625 mg/m <sup>3</sup> after adjusting for continuous exposure. Documentation of study details is limited.	LOEL <sub>ADJ</sub> = 625 mg/m <sup>3</sup> An HEC was not calculated; Applied UF approach <sup>C</sup> .	Developmental toxicity at concentrations that did not cause maternal toxicity	300 UF <sub>A</sub> = 10 UF <sub>H</sub> = 10 UF <sub>L</sub> = 3
1,1,1,2- Tetrafluoroethane (Freon 134a) 811-97-2	80 mg/m <sup>3</sup> RfC	US EPA IRIS, 1995a	Rats whole-body exposed 0, 10,400, 41,700, and 208,600 mg/m <sup>3</sup> for 6 hours/day, 5 days/week. Duration adjusted concentrations = 1860, 7450, or 37,250 mg/m <sup>3</sup> LOEL = 37,250 mg/m <sup>3</sup>	BMC <sub>10[ADJ]</sub> = 8200 mg/m <sup>3</sup> DAF = 1 (Category 3 Gas)	Leydig cell hyperplasia	100 UF <sub>A</sub> = 3 UF <sub>H</sub> = 10 UF <sub>D</sub> = 3
1,1,2-Trichloro-1,2,2-	5 mg/m <sup>3</sup> Chronic p-RfC 50 mg/m <sup>3</sup> Subchronic p-RfC	US EPA, 2016; PPRTV	cross-sectional study of workers exposed via inhalation for an average of 2.77 years. LOEL = 19,160 mg/m <sup>3</sup>	NOEL <sub>ADJ</sub> = 1440 mg/m <sup>3</sup>	Slight impairment of psychomotor performance reported in two male volunteers for 1.5 hours	$\begin{array}{c} 300 \\ UF_{H} = 10 \\ UF_{S} = 10 \\ UF_{D} = 3 \\ \hline 30 \\ UF_{H} = 10 \\ UF_{D} = 3 \end{array}$
(Freon 113) 76-13-1	109 mg/m <sup>3</sup> Health- based quality criterion in air	DME, 2014	2-year inhalation study in rats exposed 5 days/week to 15,300 mg/m <sup>3</sup> and 76,600 mg/ <sup>3</sup> . LOEL = 76,600 mg/m <sup>3</sup>	NOEL <sub>ADJ</sub> = 10,900 mg/m <sup>3</sup> An HEC was not calculated; Applied UF approach <sup>C</sup>	Decreased body weight	100 UF <sub>A</sub> = 10 UF <sub>H</sub> = 10
1,1,1-Trifluoroethane (Freon 143a) 420-46-2	20 mg/m <sup>3</sup> Chronic p-RfC	US EPA 2015; PPRTV	3–8-weeks-old rats exposed via inhalation (whole-body) to 0, 2,000, 10,000, or 40,000 ppm (0, 6,874, 34,370, and 137,500 mg/m <sup>3</sup> ) 6 hours/day, 5 days/week, for 90 days.	NOELADJ[HEC] = 24,550 mg/m <sup>3</sup> DAF = 1 (Category 3 Gas) NOELADJ[HEC] =	No effects reported at highest concentration	1000 UF <sub>A</sub> = 3 UF <sub>H</sub> = 10 UF <sub>D</sub> = 3 UF <sub>S</sub> = 10
	200 mg/m*	ĺ		24,550 mg/m <sup>3</sup>		UF <sub>A</sub> = 3

# Table 2. Available Inhalation Toxicity Values for Chemicals that are Structurally Related to Carbon Tetrafluoride<sup>A,B</sup>

Chemical Name/	Toxicity Value	Source	Study Details		Toxicity Endpoint	Uncertainty Factors
	Subchronic p-RfC	Jource	Study Details	DAF = 1		$UF_{H} = 10$ $UF_{D} = 3$
				(Category 3 Gas)		
1-Chloro-1,1- difluoroethane (Freon 142b) 75-68-3	50 mg/m <sup>3</sup> RfC	US EPA IRIS, 1995b	Rats were exposed via whole- body inhalation exposure for 6 hours/day, 5 days/week for 104 weeks to 0, 1000, 10,000, or 20,000 ppm (4110, 41,100, or 82,200 mg/m <sup>3</sup> ). NOEL corresponds to the highest concentration tested.	NOEL <sub>ADJ[HEC]</sub> = 14,710 mg/m <sup>3</sup> DAF = 1 (Category 3 Gas)	No effects reported at the highest concentration	300 UFA = 3 UF <sub>H</sub> = 10 UF <sub>D</sub> = 10

<sup>A</sup>Per the search methodology of this assessment, this Table provides inhalation toxicity values derived by US EPA, if available, or toxicity values from other authoritative bodies when toxicity values from US EPA were not found.

<sup>B</sup>Table Definitions: ADJ (adjusted), BMC (benchmark concentration), DAF (dosimetric adjustment factor), HEC (human equivalent concentration), LOEL (lowest-observed-effect-level), NOEL (no-observed-effect-level), POD (point-of-departure), p-RfC (provisional reference concentrations), RfC (reference concentration), UF<sub>A</sub> (interspecies uncertainty factor), UF<sub>D</sub> (database uncertainty factor), UF<sub>H</sub> (intraspecies uncertainty factor) UF<sub>L</sub> (LOEL-to-NOEL uncertainty factor), UF<sub>S</sub> (uncertainty factor for less than lifetime exposure) <sup>C</sup>Current US EPA guidance for deriving RfCs (US EPA, 1994) recommends the use of mathematical models (i.e., physiologically based pharmacokinetic modeling (PBPK) or dosimetric adjustment factors (DAFs) to extrapolate from inhalation exposure levels in animals to inhalation exposures to humans. In the absence of available PBPK models for extrapolating between animals and humans, the default recommended approach for application of DAFs considers the physical-chemical properties of chemicals (i.e., whether chemicals are particles or gases) and pharmacokinetics (i.e., whether chemicals are reactive at the site of contact (Category 1 gases), absorbed and distributed systemically and elicit systemic effects (Category 3 gases), or both (Category 2 gases)). in order to calculate human equivalent concentrations (HECs) from inhalation exposure levels in animals. US EPA used a DAF to calculate an HEC for dichlorodifluoromethane from animal inhalation exposure levels and did not use a DAF for trichlorofluoromethane as the POD was based on human health effects. However, DME (2014) used the uncertainty factor approach to account for both pharmacokinetic and pharmacodynamic differences between animals and humans (i.e., applied a total uncertainty factor of 10 for interspecies extrapolation) in toxicity value derivations.

<sup>D</sup>ECETOC (2008) summarized a gestational study with a lower LOEL in rats (1,400 mg/m<sup>3</sup>). Female Sprague-Dawley rats were exposed to 280, 1,400, 2,800 mg/m<sup>3</sup> for 6 hours/day, 5 days/week on gestation days 6 through 15. Slight increases in extra ribs were reported at 1,400 and 2,800 mg/m<sup>3</sup> (Coate, 1977). ECETOC (2008) also summarized additional findings from Coate et al. (1977), which reported an even lower LOEL for effects in male Sprague-Dawley rats exposed for 6 hours/day 5 days/week to 0, 280, 1,400 or 2,800 mg/m<sup>3</sup> chlorofluoromethane for 13 weeks. Relative spleen weights were significantly lower than the control in all exposed groups (i.e., LOEL of 280 mg/m<sup>3</sup>) and reproductive effects (i.e., decreased relative testis weight and hypospermatogenesis) occurred at the highest level of exposure.

#### 10. Summary of Information on MOA for Noncancer Toxicity of Carbon Tetrafluoride and Analogues

Since chemical correlation analyses can be informed by both structural and functional similarities, the final phase of the assessment included consideration of available information on the MOA for noncancer toxicity as well as pharmacokinetics (i.e., absorption, distribution, metabolism, excretion) of carbon tetrafluoride and the three structurally similar analogues (trichlorofluoromethane, dichlorodifluoromethane and carbon tetrachloride). The assessment was also informed by any relevant information found for the related fluorinated compounds identified for screening. The purpose of this was to explore potential biological rationales for structurally similar analogue selection. The following bullets summarize the key findings of this phase of the assessment.

- There are no studies available on the pharmacokinetics or chronic and subchronic toxicity of carbon tetrafluoride. While it is unknown whether carbon tetrafluoride is metabolized following inhalation exposure, a study of energetic parameters associated with carbon tetrafluoride molecular bonds and information on other related chemicals, suggests that carbon-fluorine bonds may be less prone to biological transformation than carbon bonds with other halogens (Koski et al., 1997; Yin et al., 1995).
- The hypothesized MOA for the noncancer liver effects of carbon tetrachloride involves the production of highly reactive chlorinated metabolites, which occurs through reductive dehalogenation via cytochrome P-450.<sup>8</sup> However, since carbon tetrafluoride is fully fluorinated, even if metabolized by reductive dehalogenation via cytochrome P-450, it would be unlikely for the metabolites to be chlorinated free radicals like those produced during the metabolism of carbon tetrachloride. As noted in the bullet above, studies on carbon tetrafluoride metabolism were not found. However, a study of chemical properties (energetic parameters such as bond strength and vertical electron affinity) suggests that metabolism of carbon tetrafluoride and free radical production may be unlikely (Koski et al., 1997).
- According to US EPA (2009), available data suggest little or no metabolism of inhaled trichlorofluoromethane. Most of the compound is rapidly eliminated unchanged via exhaled air and only traces of radioactivity are recovered in the urine or feces (from exposure to radiolabeled trichlorofluoromethane). An *in vitro* study suggests that rat liver microsomes could dechlorinate trichlorofluoromethane to a fluorinated metabolite (dichlorofluoromethane). However, there are currently no *in vivo* data to support this finding. Studies on dichlorodifluoromethane also suggest little to no metabolism following inhalation exposures (WHO, 1990).

<sup>&</sup>lt;sup>8</sup> Carbon tetrachloride is metabolized via a cytochrome P-450 pathway, which includes reductive dehalogenation (reductive cleavage of one carbon-chloride bond) and formation of the trichloromethyl radical. The trichloromethyl radical can undergo anaerobic or aerobic transformation to other chlorine containing intermediates. Regarding the potential MOA for noncancer effects, US EPA IRIS<sup>11</sup> stated the following: "liver metabolism rate was selected as the primary dose metric for liver effects, based on evidence that metabolism of carbon tetrachloride via CYP2E1 to highly reactive free radical metabolites plays a crucial role in its MOA in producing liver toxicity (described in Section 4.5). The primary reactive metabolites that are thought to participate in carbon tetrachloride toxicity are the trichloromethyl radical (·CCl<sub>3</sub>) and the trichloromethyl peroxy radical (O-OCCl<sub>3</sub>), although other reactive species may also contribute to a lesser extent (e.g., dichlorocarbene, :CCl<sub>2</sub>)."

#### 11. Derivation of an AGC for Carbon Tetrafluoride

#### 11.1. Uncertainties and Limitations of the Assessment

Traditional toxicological assessments rely heavily on chemical-specific toxicity studies on the chemical of interest. However, when such data are not available, a risk assessment can be performed using structural activity relationships and read-across to infer the toxicity of a chemical lacking toxicity data by drawing comparisons to a structurally similar chemical with a more robust toxicological database (Health Canada, 2022; OECD, 2023). While this approach fulfills data needs when chemical-specific toxicity data are lacking, assessing and outlining of uncertainties is a key step in the selection of analogues and the implementation of a weight-of-evidence approach (Health Canada, 2022; Schultz et al., 2015).

The assessment of the toxicity of carbon tetrafluoride and structurally similar analogues has three main areas of uncertainty.

- As described in Section 4, there was no information available on the chronic or subchronic toxicity of carbon tetrafluoride in an online search of the toxicological literature. Given that toxicity data were lacking, there was insufficient information to evaluate MOA or to assess whether the effects of carbon tetrafluoride are likely to be systemic or point-of-contact based on chemical specific information. Appendix A provides additional information on the potential for carbon tetrafluoride to elicit point-ofcontact and/or systemic effects based on toxicity information for structurally similar analogues.
- 2) Carbon tetrachloride and its toxicologically active metabolites do not contain any fluorines. Thus, while the toxicity database for carbon tetrachloride is more robust than other analogues considered in this assessment, there is no strong biological rationale to suggest similar toxicity or similar toxicity pathways for carbon tetrafluoride and carbon tetrachloride, despite the chemicals having similar structures, since they don't share similar chemical makeup (i.e., the chemicals do not contain any common halogens). Therefore, carbon tetrachloride was not selected as the basis of an AGC due to uncertainties related to chemical properties and considerations related to MOA.
- 3) With respect to the two fluorinated structurally similar analogues (trichlorofluoromethane and dichlorodifluoromethane), the overall databases on inhalation toxicity as well as the critical studies used to derive provisional RfCs are limited. The provisional RfC derivation corresponding to the lowest LOEL for dichlorodifluoromethane (i.e., the US EPA (2010) subchronic RfC of 1 mg/m<sup>3</sup>) is based on short-term exposure in animals (6 weeks) and a total uncertainty factor of 1000 across four areas of uncertainty (Table 1). The provisional RfC derivation corresponding to the lowest LOEL for trichlorofluoromethane (i.e., the US EPA (2009) subchronic RfC of 1 mg/m<sup>3</sup>) is based on a short-term exposure in humans (2 to 4 weeks) and has a total uncertainty factor of 1000 based on three areas of uncertainty (Table 1).

With respect to the third point, some of the uncertainties associated with the limited inhalation toxicity databases on trichlorofluoromethane and dichlorodifluoromethane were reduced through the additional screening of structurally related fluorinated chemicals (e.g., partially fluorinated halomethanes and haloalkanes). These structurally related fluorinated chemicals were not captured in the structural similarity assessment. However, some of these chemicals, in addition to being structurally related to carbon tetrafluoride, have similar industrial use as refrigerants. As a whole, the available inhalation toxicity values for

these chemicals did not demonstrate a high level of toxicity. With the exception of dichlorofluoromethane, all seven of the other structurally related chemicals had inhalation toxicity values that are higher than the RfCs derived by US EPA for trichlorofluoromethane and dichlorodifluoromethane. The DME (2014) derived an inhalation toxicity value of 0.13 mg/m<sup>3</sup> for dichlorofluoromethane based on histopathological effects in the liver of rats following repeated inhalation exposure (i.e., 213, 640 or 2130 mg/m<sup>3</sup> dichlorofluoromethane for 6 hours per day, 5 days per week, for 90 days). Effects were reported at the lowest level of exposure, which corresponds to 38 mg/m<sup>3</sup> when adjusted for continuous exposure. The DME applied a total uncertainty factor of 300 (i.e., 10 for interspecies extrapolation, 10 for intraspecies extrapolation and 3 for use of a LOEL). The LOEL in the DME derivation for dichlorofluoromethane is lower than the LOELs selected as the POD for trichlorofluoromethane and dichlorodifluoromethane in the US EPA derivations of provisional subchronic RfCs (i.e., LOELs of 1338 and 985 mg/m<sup>3</sup>, respectively). However, US EPA applied total uncertainty factors of 1000 in the derivations for both trichlorofluoromethane and dichlorodifluoromethane (Table 1). Therefore, the provisional subchronic RfCs for trichlorofluoromethane and dichlorodifluoromethane (1 mg/m<sup>3</sup> for both chemicals) are 38-fold lower than the LOEL of 38 mg/m<sup>3</sup> for dichlorofluoromethane. Therefore, screening of additional fluorinated chemicals (described in Section 9 and Table 2), increased overall confidence in the assessment of structurally similar carbon tetrafluoride analogues and the potential selection of trichlorofluoromethane and/or dichlorodifluoromethane as the basis of an AGC for carbon tetrafluoride.

#### 11.2. Surrogate Selection and AGC Recommendations

Both trichlorofluoromethane and dichlorodifluoromethane are selected as surrogates for evaluating the toxicity of carbon tetrafluoride given that a biological rationale for selecting one analogue over the other was not apparent based on an assessment of the toxicity and pharmacokinetics of the chemicals (See Sections 7, 8 and 10). In addition, the strengths and weaknesses of the respective US EPA provisional subchronic RfC derivations for trichlorofluoromethane and dichlorodifluoromethane were similar. Therefore, the approach for derivation of an AGC based on structural activity relationships is to use the subchronic RfCs for the two fluorinated analogues (1 mg/m<sup>3</sup> each for trichlorofluoromethane and dichlorodifluoromethane, Table 1) and increase the total uncertainty factor from 1000 to 3000, which is typically the maximum total uncertainty factor that can be applied to a derivation of an RfC across 4 areas of uncertainty.<sup>9</sup> The increase in total uncertainty factors addresses the use of subchronic toxicity endpoints in the derivation and would yield an AGC of 0.33 mg/m<sup>3</sup> for carbon tetrafluoride. Given the selection of trichlorofluoromethane and dichlorodifluoromethane as surrogates, carbon tetrafluoride is being treated as a Category 3 gas based on the systemic effects of the surrogates in the absence of chemical-specific toxicity data on carbon tetrafluoride (see Appendix A for additional details). The PODs used in the US EPA provisional RfC derivations for trichlorofluoromethane and dichlorodifluoromethane are based on extrarespiratory effects (e.g., cognitive effects in humans and effects on bodyweight gain in laboratory animals, respectively). In addition, for both analogues, the most reliable evidence of toxicity from inhalation exposure correspond to systemic effects.

Evidence to support the derivation of an AGC of 0.33 mg/m<sup>3</sup> for carbon tetrafluoride also comes from the screening of several structurally related fluorinated chemicals. The results of the screening collectively suggest that an AGC of 0.33 mg/m<sup>3</sup> for carbon tetrafluoride would be adequately protective of noncancer health effects if the toxicity of carbon tetrafluoride is similar to that of other fluorinated halomethanes or fluorinated

<sup>&</sup>lt;sup>9</sup>According to current risk assessment practices for deriving an RfC, total uncertainty factors are typically limited to a maximum of 3000, even when there are four areas of uncertainty being addressed through application of uncertainty factors.

haloethanes (Tables 1 and 2). Of the inhalation toxicity value derivations for structurally related chemicals (Table 2), the POD corresponding to the lowest LOEL is 38 mg/m<sup>3</sup> for dichlorofluoromethane. The AGC of 0.33 mg/m<sup>3</sup> is about 115-fold lower than this effect level.

The recommended approach for deriving an AGC for carbon tetrafluoride of 0.33 mg/m<sup>3</sup> is also supported by mechanistic information, which suggests that trichlorofluoromethane and dichlorodifluoromethane are not metabolized or metabolized to a small degree. While the MOAs for these chemicals are not known, it seems possible that toxicity could be resulting from the parent compounds, which both contain fluorine atoms. However, given the technical limitations of the assessment presented by data gaps in the available toxicity information on carbon tetrafluoride and the selected surrogates, the AGC should be reconsidered by NYS DEC if studies on the toxicity of carbon tetrafluoride become available in the future and suggest a different degree of toxicity that is not addressed by the current assessment.

# 12. <u>References</u>

- ACGIH (American Conference of Governmental Industrial Hygienists). 2023. Carbon Tetrafluoride. Available online at: <u>https://www.acgih.org/carbon-tetrachloride/</u>
- ATSDR (Agency for Toxic Substances and Disease Registry). 2005. Toxicological Profile for Carbon Tetrachloride. Available online at: <u>https://www.atsdr.cdc.gov/toxprofiles/tp30.pdf</u>
- ATSDR (Agency for Toxic Substances and Disease Registry). 2023. Minimal Risk Levels (MRLs) for Hazardous Substances. Available online at: <u>https://wwwn.cdc.gov/tsp/MRLS/mrlslisting.aspx</u>
- Backman TW, Cao Y, Girke T. 2022. ChemMine Tools. Available online at: <u>https://chemminetools.ucr.edu/about/</u>
- CA OEHHA (California Office of Environmental Health Hazard Assessment). 2008. Technical Supporting Document for Noncancer RELs, Appendix D3. Available online at: https://oehha.ca.gov/media/downloads/crnr/appendixd3final.pdf
- CA OEHHA (California Office of Environmental Health Hazard Assessment). 2011. Appendix B: Chemical-Specific Summaries of the Information Used to Derive Unit Risk and Cancer Potency Values. Available online at: <u>https://oehha.ca.gov/air/crnr/technical-support-document-cancer-potency-factors-2009</u>
- CA OEHHA (California Office of Environmental Health Hazard Assessment). 2023. Carbon Tetrachloride. Available online at: <u>https://oehha.ca.gov/chemicals/carbon-tetrachloride</u>
- Chan PWY, Yakunin AF, Edwards EA, Pai EF. 2011. Mapping the Reaction Coordinates of Enzymatic Defluorination. J Am Chem Soc. 133(19):7461-7468.
- Clarke RF, Daniels S, Harrison CB, Jordan MJ, Paton WD, Smith EB, Smith RA. 1978. Potency of mixtures of general anaesthetic agents. Br J Anaesth. 50(10):979-83.
- Clayton, JW. 1966. The mammalian toxicology of organic compounds containing fluorine. Hand Exp Pharmakol. 20:459–500.Coate WB. 1977. 90-day inhalation toxicity study in albino rats, Genetron 31. Unpublished final report No. 165-178. Hazleton Laboratories America, Vienna, Virginia, USA. Allied Chemical, Morristown, New Jersey, USA.
- Daniels S, Paton WD, Smith EB. 1979. The effects of some hydrophobic gases on the pulmonary surfactant system.Br J Pharmacol. 65(2):229-235.
- DME (Danish Ministry of the Environment). 2014. Chlorofluorocarbons: CFC-11, CFC-12, CFC-113, HCFC-21, HCFC-31, HCFC-133a. Available online at: <u>https://www2.mst.dk/Udgiv/publications/2014/04/978-87-93178-40-3.pdf</u>

- ECETOC (European Centre for Ecotoxicology and Toxicology of Chemicals). 2008. Toxicity of Possible Impurities and By-products in Fluorocarbon Products. Available online at: <u>https://www.ecetoc.org/wp-content/uploads/2021/10/ECETOC-TR-103.pdf</u>
- Health Canada. 2022. Use of analogues and read-across in risk assessment. Available online at: <u>https://www.canada.ca/en/health-canada/services/chemical-substances/fact-sheets/analogues-read-across-risk-assessment.html</u>
- Jenkins LJ, Jones RA, Coon RA, Siegel J. 1970. Repeated and continuous exposures of laboratory animals to trichlorofluoromethane. Toxicol Appl Pharmacol. 16:133–142.
- Koski et al. 1997. Potential Toxicity of CF(3)X Halocarbons. In Vitro Toxicology. 10(4):455-457.
- Langenbach B and Wilson M. 2021. Per- and Polyfluoroalkyl Substances (PFAS): Significance and Considerations within the Regulatory Framework of the USA. Int J Environ Res Public Health. 18: 11142.
- Leuschner F, Neumann RW, Hubscher F. 1983. Report on subacute toxicological studies with several fluorocarbons in rats and dogs by inhalation. Arzneim. Forsch. 33(10):1475–1476.
- Lohmann R, Cousins IT, DeWitt JC, Glüge J, et al. 2020. Are Fluoropolymers Really of Low Concern for Human and Environmental Health and Separate from Other PFAS? Environ Sci Technol. 20: 12820-12828.
- Makowski MS, Sproul C, Swartz C, Everitt JI, Knaus DA, Wilbur JC, Moon RE. 2022. Safety evaluation of carbon tetrafluoride as an inert hyperbaric breathing gas in Sprague-Dawley rats. Toxicol Appl Pharmacol. 444:116023.
- Maltoni C, Lefemine G, Tovoli D, Perino G. 1988. Long-term carcinogenicity bioassays on three chlorofluorocarbons (trichlorofluoromethane, FC11; dichlorodifluoromethane, FC12; chlorodifluoromethane, FC22) administered by inhalation to Sprague-Dawley rats and Swiss mice. Ann NY Acad Sci. 534:261-82.
- Michigan DEQ (Michigan Department of Environmental Quality). 2019a. Screening Level Update for Trichlorofluoromethane [Interoffice Communication] . Available online at: https://www.egle.state.mi.us/aps/downloads/ATSL/75-69-4/75-69-4 1hr annual ITSL.pdf
- Michigan DEQ (Michigan Department of Environmental Quality). 2019b. Screening Level Update for Dichlorodifluoromethane [Interoffice Communication] . Available online at: https://www.egle.state.mi.us/aps/downloads/ATSL/75-71-8/75-71-8 8hr annual ITSL.pdf
- NIOSH (National Institute for Occupational Safety and Health). 2022. Registry of Toxic Effects of Chemical Substances (RTECS). Carbon tetrafluoride. Available online at: <u>https://www.cdc.gov/niosh-rtecs/FG4B12C0.html.</u>
- NIOSH (National Institute of Occupational Safety and Health). 1994a. Immediately Dangerous to Life or Health Concentrations (IDLH). Dichlorodifluoromethane. Available online at: <u>https://www.cdc.gov/niosh/index.htm</u>
- NIOSH (National Institute of Occupational Safety and Health). 1994b. Immediately Dangerous to Life or Health Concentrations (IDLH). Fluorotrichloromethane. Available online at: <u>https://www.cdc.gov/niosh/index.htm</u>
- NIOSH (National Institute of Occupational Safety and Health). 1994c. Immediately Dangerous to Life or Health Concentrations (IDLH). Fluorotrichloromethane. Available online at: <u>https://www.cdc.gov/niosh/index.htm</u>
- NIOSH (National Institute of Occupational Safety and Health). 2023. Carbon Tetrafluoride. Available online at: <u>https://www.cdc.gov/niosh-rtecs/FG4B12C0.html</u>
- NLM (National Library of Medicine). 2022. ChemIDPlus (searchable chemical database). Available online at: <u>https://pubchem.ncbi.nlm.nih.gov/source/ChemIDplus</u>
- NLM (National Library of Medicine). 2023. PubChem (open chemistry database). Available online at: <u>https://pubchem.ncbi.nlm.nih.gov/</u>

- NTP (National Toxicology Program). 2022. Integrated Chemical Environment (chemical database). Available online at: <u>https://ice.ntp.niehs.nih.gov/</u>
- NYS DEC (New York State Department of Environmental Conservation). 2021. DAR-1 Guidelines for the Evaluation and Control of Ambient Air Contaminants Under 6NYCRR Part 212. <u>https://www.dec.ny.gov/docs/air\_pdf/dar1.pdf</u>
- OECD (Organisation for Economic Co-operation and Development). 2023. Grouping of Chemicals: Chemical Categories and Read-Across. Available online at: <u>https://www.oecd.org/chemicalsafety/risk-assessment/groupingofchemicalschemicalcategoriesandread-across.htm</u>
- OSHA (Occupational Health and Safety Administration). 2015. Shipyard Employment Hazards during the Repair and Maintenance of Refrigeration Systems on Vessels. Available online at: <u>https://www.osha.gov/sites/default/files/publications/OSHA3836.pdf</u>
- Prendergast JA, Jones RA, Jenkins LJ Jr, Siegel J. 1967. Effects on experimental animals of long-term inhalation of trichloroethylene, carbon tetrachloride, 1,1,1-trichloroethane, dichlorodifluoromethane, and 1,1-dichloroethylene. Toxicol Appl Pharmacol. 10(2):270-89.

PubChem. 2023. Carbon Tetrafluoride. Available online at: <u>https://pubchem.ncbi.nlm.nih.gov/compound/6393</u>

- Schultz TW, Amcoff P, Berggren E, et al. 2015. A strategy for structuring and reporting a read-across prediction of toxicity. Regul Toxicol Pharmacol. 72(3):586-601. doi:10.1016/j.yrtph.2015.05.016.
- Stewart RD, Baretta ED, Herrmann AA et al. 1975. Acute and repetitive human exposure to fluorotrichloromethane. The Medical College of Wisconsin, Department of Environmental Medicine.
- Stewart RD, Newton PE, Baretta ED et al. 1978. Physiological response to aerosol propellants. Environ. Health Perspect. 26:275–285.
- US APHC (U.S. Army Public Health Command). 2013. Technical Guide 230 Environmental Health Risk Assessment and Chemical Exposure Guidelines for Deployed Military Personnel. Available online at: <u>https://phc.amedd.army.mil/PHC%20Resource%20Library/TG230-DeploymentEHRA-and-MEGs-2013-Revision.pdf</u>
- US DOE (United States Department of Energy). 2022. PAC Database Revision 29. https://edms3.energy.gov/pac/Search/Reports/573
- US DOE (United States Department of Energy). 2022. Protection Action Criteria Tables. Available online at: <u>https://edms3.energy.gov/pac/docs/Revision\_29A\_Table3.pdf</u>
- US EPA (United States Environmental Protection Agency). 1994. Methods for Derivation of Inhalation Reference Concentrations and Application of Inhalation Dosimetry. Available online at: <u>https://www.epa.gov/risk/methods-derivation-inhalation-reference-concentrations-and-application-inhalation-dosimetry</u>
- US EPA (United States Environmental Protection Agency). 1998. Health Effects Test Guidelines OPPTS 870.1300 Acute Inhalation Toxicity. Available online at: <u>https://www.epa.gov/test-guidelines-pesticides-and-toxic-substances/series-870-health-effects-test-guidelines</u>
- US EPA (United States Environmental Protection Agency). 2009. Provisional Peer-Reviewed Toxicity Values for Trichlorofluoromethane (CASRN 75-69-4). Available online at: <u>https://cfpub.epa.gov/ncea/pprtv/documents/Trichlorofluoromethane.pdf</u>
- US EPA (United States Environmental Protection Agency). 2010. Provisional Peer-Reviewed Toxicity Values for Dichlorodifluoromethane (CASRN 75-71-8). Available online at: https://cfpub.epa.gov/ncea/pprtv/documents/Dichlorodifluoromethane.pdf
- US EPA (United States Environmental Protection Agency). 2012. Advances in Inhalation Gas Dosimetry for Derivation of a Reference Concentration (RfC) and Use in Risk Assessment. Available online at: <u>https://cfpub.epa.gov/ncea/iris\_drafts/recordisplay.cfm?deid=244650#tab-3</u>

- US EPA (United States Environmental Protection Agency). 2016. Provisional Peer-Reviewed Toxicity Values for 1,1,2-Trichloro-1,2,2-trifluoroethane (CASRN 76-13-1). Available online at: https://cfpub.epa.gov/ncea/pprtv/documents/Trichloro122trifluoroethane112.pdf
- US EPA (United States Environmental Protection Agency). 2022. Comptox Dashboard. Available online at: https://comptox.epa.gov/dashboard/
- US EPA (United States Environmental Protection Agency).2015. Provisional Peer-Reviewed Toxicity Values for 1,1,1-Trifluoroethane (CASRN 420-46-2). Available online at: https://hhpprtv.ornl.gov/issue\_papers/Trifluoroethane111.pdf
- US EPA and IAI (United States Environmental Protection Agency and International Aluminum Institute. 2008. Protocol for Measurement of Tetrafluoromethane (CF<sub>4</sub>) and Hexafluoroethane (C<sub>2</sub>F<sub>6</sub>) Emissions from Primary Aluminum Production. Available online at:<u>https://www.epa.gov/sites/default/files/2016-02/documents/measureprotocol.pdf</u>
- US EPA IRIS (United States Environmental Protection Agency Integrated Risk Information System). 2010. Carbon tetrachloride. CASRN 56-23-5. DTXSID8020250. Available online at: <u>https://iris.epa.gov/ChemicalLanding/&substance\_nmbr=20</u>
- US EPA IRIS (United States Environmental Protection Agency Integrated Risk Information System). 1987a. Trichlorofluoromethane. CASRN 75-69-4. DTXSID5021384 Available online at: <u>https://iris.epa.gov/ChemicalLanding/&substance\_nmbr=120</u>
- US EPA IRIS (United States Environmental Protection Agency Integrated Risk Information System). 1987b. Dichlorodifluoromethane. CASRN 75-71-8. DTXSID6020436Available online at: <u>https://iris.epa.gov/ChemicalLanding/&substance\_nmbr=40</u>
- US EPA IRIS (United States Environmental Protection Agency Integrated Risk Information System). 1993. Chlorodifluoromethane. CASRN 75-45-6. DTXSID6020301. Available online at: <u>https://cfpub.epa.gov/ncea/iris2/chemicalLanding.cfm?substance\_nmbr=657</u>
- US EPA IRIS (United States Environmental Protection Agency Integrated Risk Information System). 1995a. 1,1,1,2-Tetrafluoroethane. CASRN 811-97-2. DTXSID1021324. Available online at: <u>https://iris.epa.gov/ChemicalLanding/&substance\_nmbr=656</u>
- US EPA IRIS (United States Environmental Protection Agency Integrated Risk Information System). 1995b. 1-Chloro-1,1-difluoroethane. CASRN 75-68-3. DTXSID9023960. Available online at: <u>https://iris.epa.gov/ChemicalLanding/&substance\_nmbr=661#:~:text=1%2DChloro%2D1%2C1%2Ddi</u> <u>fluoroethane</u>
- WHO (World Health Organization). 1990. Environmental Health Criteria 113. Fully halogenated chlorofluorocarbons. Available online at:

https://apps.who.int/iris/bitstream/handle/10665/39345/9241571136-eng.pdf?sequence=1

Yin H, Anders MW, Korzekwa KR, et al. 1995. Designing safer chemicals: predicting the rates of metabolism of halogenated alkanes. Proc Natl Acad Sci. 92 (24): 11076-11080.

# A.1. <u>Summary of Toxicity Information Relevant to the Assessment of Portal-of-Entry versus Systemic Effects</u> of Carbon Tetrafluoride

The literature review on carbon tetrafluoride included a search for both oral and inhalation toxicity studies (acute, subchronic and chronic). However, chemical-specific toxicity data to evaluate the potential for portalof-entry effects (including irritation at the site of contact), first pass liver effects, and systemic effects from acute oral or inhalation studies are not available for carbon tetrafluoride.

In the absence of chemical specific toxicity studies that provide evidence as to whether the toxicological effects of carbon tetrafluoride are portal-of-entry and/or systemic, carbon tetrafluoride is being treated as a Category 3 gas based on the available toxicity information on carbon tetrafluoride analogues (i.e., trichlorofluoromethane and dichlorodifluoromethane). The points-of-departure (PODs) used by US EPA (2009, 2010) to derive subchronic reference concentrations (RfCs) for trichlorofluoromethane and dichlorodifluoromethane (e.g., cognitive effects in humans and effects on bodyweight gain in laboratory animals, respectively). In addition, for both compounds, the most reliable evidence of toxicity from inhalation exposure correspond to systemic effects (see Section A.3 below for more information).

# A.2. Odor Thresholds for Carbon Tetrafluoride and Selected Surrogates

Carbon tetrafluoride is a colorless, odorless gas. An odor threshold was not found in PubChem<sup>3</sup> or via online searches of authoritative body information.

Dichlorodifluoromethane, one of the selected carbon tetrafluoride surrogates, is a colorless gas with an etherlike odor at extremely high concentrations. An odor threshold was not listed for dichlorodifluoromethane in PubChem. However, a fact sheet from the Occupational Safety and Health Administration indicates that 1000 parts per million (ppm) is a "normal range of odor threshold" for halocarbons, including dichlorodifluoromethane (OSHA, 2015). Thus, for dichlorodifluoromethane, this corresponds to an air concentration of 4,950 mg/m<sup>3</sup>.

Trichlorofluoromethane, the other selected surrogate, is a colorless to water-white, nearly odorless liquid or gas. It has an odor threshold of 200,000 ppm  $(1.1 \times 10^6 \text{ mg/m}^3)$  in PubChem (NLM, 2023).

# A.3. <u>Additional Details on Respiratory and Liver Effects for Dichlorodifluoromethane and</u> <u>Trichlorofluoromethane Reported in US EPA (2009, 2010)</u>

# A.3.1 Trichlorofluoromethane

The POD selected by US EPA (2009) for use in deriving a subchronic RfC for trichlorofluoromethane corresponds to a lowest-observed-effect-level (LOEL) for cognitive effects in humans. Thus, a dosimetric adjustment factor was not needed for the derivation. However, evidence of toxicity in laboratory animals suggests that trichlorofluoromethane is also a Category 3 gas.

The only other LOEL from inhalation exposure identified in the US EPA (2009) assessment comes from a 90day study of continuous exposure (0 or 5620 mg/m<sup>3</sup>) trichlorofluoromethane in several species of laboratory

#### **Appendix A: Supplemental Information**

animals (Jenkins et al., 1970; reviewed in US EPA, 2009). Nonspecific inflammatory changes in the lungs of all tested species and mild vacuolar changes in the liver of guinea pigs were reported. However, details on severity or incidence of effects were not provided. The study authors concluded that these findings were not related to exposure. US EPA (2009) did not include these effects in the selection of a LOEL for trichlorofluoromethane. US EPA (2009) identified renal effects in dogs as the LOEL corresponding to this study and considered the same exposure level (5620 mg/m<sup>3</sup>) to be a NOEL for other animal species examined in this study.

The same authors (Jenkins et al., 1970; reviewed in US EPA, 2009) performed a subchronic study of intermittent inhalation exposure to trichlorofluoromethane (0 or 56,200 mg/m<sup>3</sup> for 8 hours/day, 5 days/week, for 6 weeks) and reported a variety of histopathological effects (e.g., mild discoloration, characterized as a darkening of the tissue, of the liver in rats and guinea pigs, and nonspecific inflammatory changes of the lungs in guinea pigs, rats, and monkeys (incidences not reported)). However, the authors did not consider any of these histopathological findings to be related to exposure. whether there were study quality issues. However, even if these histopathological changes were considered to be related to exposure, the exposure concentration is much higher than the LOEL for systemic effects in dogs.

In a 90-day study of male and female rats exposed to trichlorofluoromethane (0 or 56,200 mg/m<sup>3</sup> for 6 hours/day, 7 days/week), a variety of toxicity endpoints were evaluated, including liver and lung toxicity (Leuschner et al., 1983; reviewed in US EPA, 2009)<sup>1</sup>. However, adverse health effects were not reported in this study.

Effects that could be consistent with site of contact toxicity (e.g., edema and emphysema in the lungs) were reported in a short-term inhalation study (Clayton, 1966; reviewed in US EPA, 2009). A variety of other effects from histological examination were also reported (e.g., vacuolation of cells in the liver). However, study limitations (e.g., there was only a single exposure concentration of 67,416 mg/m<sup>3</sup> tested in the study, the sample size was three, and there were no control animals used in the study) preclude use of these findings to evaluate the toxicity of trichlorofluoromethane or carbon tetrafluoride by proxy.

The US EPA Integrated Risk Information System (US EPA IRIS, 1987a) has a reference dose for trichlorofluoromethane that is based on mortality and histopathological effects on the heart and lungs of rats exposed via gavage for 78 weeks.

# A.3.2 Dichlorodifluoromethane

Subchronic inhalation studies on dichlorodifluoromethane reported histopathological effects in the lungs of both controls and treated animals (Leuschner et al., 1983; Prendergast et al., 1967; reviewed in US EPA, 2010), and thus, do not provide conclusive evidence of effects at the site of contact.

Focal necrosis and fatty infiltration of the liver were reported in a subchronic inhalation study of dichlorodifluoromethane in guinea pigs (Predergast et al., 1967; reviewed in US EPA, 2010). However, liver effects were not observed in any of the other animal species tested. In addition, a subchronic inhalation study of rats and dogs that included a detailed examination of liver toxicity showed no effects on the liver at exposures of up to 12,375 mg/m<sup>3</sup> (Leuschner et al., 1983; reviewed in US EPA, 2010)<sup>2</sup>. Due to potential

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differences in species sensitivity to liver effects from inhalation exposure to dichlorodifluoromethane, US EPA (2010) did not consider liver toxicity to be a critical effect of inhalation exposure.

The POD used in the derivation of US EPA's (2010) subchronic RfC for dichlorodifluoromethane corresponds to reduced bodyweight gain in inhalation exposure studies in laboratory animals. The same critical effect was used as POD by US EPA (2010) and US EPA IRIS (1987b) to derive subchronic and chronic reference doses, respectively, for dichlorodifluoromethane based on oral exposure studies in laboratory animals.

# Appendix B: Supplemental Tables

Table B -	1. Physical-	Chemical Proper	ties of Carbo	n Tetrafluoride and	d Analogues	from ChemIDPlus <sup>a</sup>
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Analogue	Structure	Melting Point (°Celsius)	Boiling Point (°Celsius)	log P (octanol- water)	Water Solubility <sup>b</sup> (mg/L)	Vapor Pressure <sup>b</sup> (mm Hg)	Henry's Law Constant <sup>b</sup> (atm- m <sup>3</sup> /mole)	Atmospheric OH Rate Constant <sup>b</sup> (cm <sup>3</sup> /molecule- sec)
Carbon Tetrafluoride	F F	-184	-128.00	1.18		18.80	5.15	4.00E-16
Chlorotrifluoromethane (Freon-13)	F F F CI	-181	-81.40	1.65	90.00	21400	1.38	7.00E-16
Trichloromonofluoromethane (Freon-11)		-111	23.70	2.53	1100.00	803	0.10	5.00E-16
Dichlorodifluoromethane (Freon-12	Cl FCl F	-158	-29.80	2.16	280.00	4850	0.34	4.00E-16
Dibromodifluoromethane (Freon 12-B2)	Br F Br	-110	25.00	1.99	313.00	820	0.03	5.90E-16
Bromotrifluoromethane (Freon 13-B1)	F F F Br	-172	-57.80	1.86	320.00	12200	0.50	1.00E-16
Tribromofluoromethane	Br Br Br Br	-73.6	108	2.4				0.0
Dibromochlorofluoromethane	Br Br F		80.3	2.31				2.31
Bromochlorodifluoromethane (Freon 12B1)	Cl F Br F	-160	-3.70	1.90	277.00	2070	0.09	1.00E-15
Carbon tetrachloride (Freon 10)		-23	76.80	2.83	793.00	115	0.03	1.20E-16
Bromodichlorofluoromethane	Br Cl	-106	52					
Tetrabromomethane	Br Br Br Br	90.1	189.5	3.42	240.00		4.91E-04	0.0
Tribromochloromethane	Br Br Br	55	158.5	2.71				0.0
Bromotrichloromethane		-5.7	105	2.53	869	39	3.71E-04	0.0
Dibromodichloromethane		38.00	150.2	2.62				0.0
Trifluoroiodomethane (Freon 13T1)	F F		-22.5	2.01				5.2E-14

# Appendix B: Supplemental Tables

Analogue	Structure	Melting Point (°Celsius)	Boiling Point (°Celsius)	log P (octanol- water)	Water Solubility <sup>b</sup> (mg/L)	Vapor Pressure <sup>b</sup> (mm Hg)	Henry's Law Constant <sup>b</sup> (atm- m <sup>3</sup> /mole)	Atmospheric OH Rate Constant <sup>b</sup> (cm <sup>3</sup> /molecule- sec)
Trifluoromethylisocyanide	F NEC							
(Trifluoromethyl)silane	F SIH <sub>3</sub>							
Potassium trifluoro(trifluoromethyl)bor ate(1-)	K <sup>+</sup> B F F							
Trifluoromethane	F F	-155.18	-82.0	0.64	4.09E+03	3.53E+04		

<sup>a</sup>Analogues are listed non-alphabetically based on structural similarity (see Supplementary Table 3).

<sup>b</sup>At 25 degrees Celsius.

<sup>c</sup>Values obtained from PubChem (NLM, 2023).

#### **Appendix B: Supplemental Tables**

Chemical	Occupational Exposure Limit	Source/Reference
	time-weighted average 2.5 mg(F)/m <sup>3</sup>	Occupational Exposure Limits
Carbon tetrafluoride <sup>*</sup>	short term exposure limit 10 mg(F)/m <sup>3</sup>	listed in a fact sheet from the National Institute of Occupational Safety and Health (NIOSH, 2022) for Australia, Belgium, and Hungary
	3000 mg/m <sup>3</sup>	Short-term Occupational Exposure Limits listed in NIOSH (2022) for Russia
Trichlorofluoromethane	1,000 ppm (5,600 mg/m³)	NIOSH Recommended Exposure Limit (REL) Ceiling, Occupational Safety and Health Administration (OSHA) Permissible Exposure Limit (PEL) Time-weighted Average (TWA) and ACGIH Threshold Limit Value (TLV) Ceiling (NIOSH, 1994b)
Dichlorodifluoromethane	1,000 ppm (4,950 mg/m <sup>3</sup> )	NIOSH REL TWA, OSHA PEL TWA and ACGIH TLV TWA (NIOSH, 1994a)
Carbon tetrachloride	ACGIH TLV TWA: 5 ppm (31 mg/m <sup>3</sup> ) ACGIH Short-term Exposure Limit (STEL): 10 ppm (63 mg/m <sup>3</sup> ) NIOSH REL: 2 ppm (12.6 mg/m <sup>3</sup> ) 60-minute STEL; OSHA PEL: 10 ppm (74.4 mg/m <sup>3</sup> ) TWA, 25 ppm (ceiling) (185.9 mg/m <sup>3</sup> ), 200 ppm (1487.3 mg/m <sup>3</sup> ) 5-min maximum peak in any 4 hours	(ACGIH, 2023; NIOSH, 1994c)

Table B - 2. Available Occ	upational Exp	osure Limits for Str	ucturally Similar (	Carbon Tetrafluoride	Analogues
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<sup>\*</sup>The US Department of Energy (2022) and the US Department of Defense (US APHC, 2013) have short-term air guidelines for carbon tetrafluoride (i.e., Protective Action Criteria (PAC) and Military Exposure Guidelines (MEG), respectively). However, the derivation details for these values were not found online. In addition, NYS DEC (2021) guidance lists authoritative body sources for deriving AGCs and SGCs and does not include PACs or MEGs.

Table B - 3. Ca	arbon Tetrafluoride	Analogues and	<b>Similarity Metrics</b>
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Structural Analogues	BN	Structure	Molecular Weight	Similarity to Tetrafluoromethane (by % or Tanimoto Coefficient) <sup>a</sup>
Chemical of Interest: Carbon tetrafluoride	75-73-0	F F F	88.003	
Analogues Identified via ChemIDPlus	(NLM, 2022)			
Chlorotrifluoromethane (Freon-13)	75-72-9	F F F F	104.458	97.5309% similar
Trichlorofluoromethane (Freon-11)	75-69-4		137.368	95.1807% similar
Dichlorodifluoromethane (Freon-12)	75-71-8		120.913	95.1807% similar
Dibromodifluoromethane (Freon 12-B2)	75-61-6	Br F Br	209.815	91.8605% similar
Bromotrifluoromethane (Freon 13B1)	75-63-8	F F Br	148.909	91.8605% similar
Tribromofluoromethane-	353-54-8	Br Br Br	270.721	91.8605% similar
Dibromochlorofluoromethane	353-55-9	Br Cl	226.27	89.7727% similar
Bromochlorodifluoromethane (Freon 12B1)	353-59-3	F Br	165.364	89.7727% similar
Carbon tetrachloride (Freon 10)	56-23-5		181.819	87.7778% similar

			Molecular Weight	Similarity to Tetrafluoromethane (by % or Tanimoto
Structural Analogues	RN	Structure		Coefficient) <sup>a</sup>
Bromodichlorofluoromethane	353-58-2		181.819	87.7778% similar
Tetrabromomethane	558-13-4	Br Br Br	331.627	84.8837% similar
Tribromochloromethane	594-15-0	Br Cl	287.176	82.9545% similar
Bromotrichloromethane	75-62-7		198.274	81.1111% similar
Dibromodichloromethane	594-18-3	Br Br Cl	242.725	81.1111% similar
Analogues Identified via Integrated	Chemical Environm	ent (NTP, 2022)		
Trifluoroiodomethane (Freon 13T1)	2314-97-8	F F	195.905	0.882353 (Tanimoto coefficient)
Trifluoromethylisocyanide	105879-13-8	F NEC	95.02	0.833333 (Tanimoto coefficient)
(Trifluoromethyl)silane	10112-11-5	F SiH <sub>3</sub>	97.091	0.823529 (Tanimoto coefficient)
Potassium trifluoro(trifluoromethyl)borate(1-)	42298-15-7	K <sup>+</sup> F F	175.91	0.823529 (Tanimoto coefficient)
Analogues Identified via the Compto	x Dashboard (US E	PA, 2022)	Ι	
Trifluoromethane	75-46-7	F F	70.014	0.833333313 (similarity threshold)

<sup>a</sup>Structurally similar chemicals are characterized using online tools from ChemIDPlus, the Integrated Chemical Environment, and the Comptox Dashboard. Chemicals are grouped based on both similarity metric and online tool so that chemicals with common similarity metrics can be compared.