A Thermal Desorption Solution for Per- and Polyfluoroalkyl Substances (PFAS) in Soils

Clean Earth

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i. EXECUTIVE SUMMARY

Preface: Per- and polyfluoroalkyl Substances (PFAS) comprise a family of chemicals that were manufactured from the 1940s to 2002 and have found their way into soils and groundwater around the world. The toxicology of some of the dominant members of this group such as perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) has been studied extensively and linked to a variety of human health effects including low birth weights, immunological and hormonal disruptions, and cancer[1]. PFAS chemicals have been identified in wells which supply drinking water to one in seven Americans[2]. Based on their demonstrated health effects and wide distribution in the environment, this family of chemicals is now considered an emerging contaminant in need of remedial action by the U.S. EPA[3].

In response to the growing need to address this environmental contaminant, Clean Earth has taken its first step to evaluate the use of thermal desorption as a viable technology to remove PFAS from soils. This technology has been used effectively and safely by Clean Earth since 1992 to recycle a variety of organic contaminants. An initial test, under the direction of the New York State Department of Environmental Conservation (NYSDEC), was performed on 22.6 tons of contaminated soil at Clean Earth's Fort Edward, New York facility in December 2018 and February 2019. Based on measurements of specific compounds before and after treatments, the thermal desorption approach successfully eliminated greater than 99% of PFOS and PFOA from the soil when measured by both total mass concentration and synthetic precipitation leaching procedure (SPLP) analysis. The other PFAS compounds analyzed for and detected were removed to below detectable limits from the soil samples analyzed. Based on the encouraging results of this preliminary thermal desorption treatment of PFAS contaminated soil, Clean Earth is continuing work with state agencies to establish criteria to demonstrate the efficiency of the process and to optimize the treatment process.

[1] "Basic Information on PFAS." *EPA*, Environmental Protection Agency, 6 Dec. 2018, www.epa.gov/pfas/basic-information-pfas.

[2] "Basic Information on PFAS." *EPA*, Environmental Protection Agency, 6 Dec. 2018, www.epa.gov/pfas/basic-information-pfas#exposed.

[3] *EPA's Per- and Polyfluoroalkyl Substances (PFAS) Action Plan*. USEPA, Feb. 2019, EPA's Per- and Polyfluoroalkyl Substances (PFAS) Action Plan.

I. Background

This white paper summarizes the results of a research, development, and demonstration (RD&D) test under the direction of the NYSDEC using thermal desorption as the treatment technology for PFAS contaminated soil at Clean Earth's Fort Edward facility. The original soil sample underwent two subsequent thermal desorption treatments, once in December 2018 and again in February 2019. Thermal desorption is a robust remedial technology that has been proven to significantly reduce or eliminate organic contaminant levels within soil and other solid matrices. To our knowledge, thermal desorption had not been applied to the treatment of PFAS contaminated soil at the time of the test, which prompted this demonstration of the efficacy of thermal treatment for this emerging environmental contaminant group.

In a thermal desorption process, contaminants are separated from soil by heating the material to near or above the contaminant's boiling point. This results in a process air stream containing the desorbed contaminants that are thermally reduced in a secondary treatment unit to their elemental oxidized state. Treated soil is rehydrated before it is stockpiled to await confirmatory sample collection and analysis.

The thermal treatment process is reproducible and predictable due to its direct dependence on the boiling point of the contaminant. PFAS are good candidates for this approach because their boiling points are generally below 500˚F, far lower than many of the recalcitrant contaminants in matrixes such as coal tar, for example.

II. Demonstration Details and Results

Clean Earth Fort Edward received approximately 22 tons of PFAS contaminated soil from a NYSDEC remediation project with PFOA and PFOS as the predominant PFAS compounds. Based on the limited soil volume associated with this sample, the treatment capability of the thermal oxidizer was not assessed leaving the investigation to concentrate on the efficacy for thermal desorption of PFAS compounds from the soil.

Prior to the demonstration, a representative sample was collected and analyzed providing the baseline concentrations of PFAS compounds. For this demonstration, Clean Earth chose two laboratories, TestAmerica Laboratories of Sacramento, CA and Con-Test Analytical Laboratories of East Longmeadow, MA, to run split samples. The total mass concentration of all 20 PFAS compounds measured in the pre-treatment soil was 122.91 ug/kg (ppb). The results are presented in Table 1 of the Appendix. NYSDEC has set a targeted soil cleanup objective of 72 ppb for the total of PFOA and PFOS.

Since there is significant concern for the leachability of these compounds to ground water, SPLP analysis was also performed on the representative sample to determine the effectiveness for reducing the concentrations and the leachability of the compounds from the treated soil. The analysis of the representative sample identified leachable PFAS concentrations totaling 807.37 ng/L (ppt). PFOA and PFOS comprised 79% of the leachable compounds combined, PFOS comprising 65% of the total on its own. The results are presented in Table 2 of the Appendix.

a. December 2018 Demonstration Test

In December 2018, the sample was treated in the thermal desorption unit. The primary treatment unit (PTU) temperature range for the one-hour test was operated between 910 and 940°F and the thermal oxidizer was operated at 1800°F.

An analysis of the confirmatory sample, which was collected and analyzed after the first treatment, identified that PFAS total concentrations had decreased by 93.7% to 7.76 ppb. The results are presented in Table 1 of the Appendix. This total concentration was well below the targeted soil cleanup objective of 72 ppb. The dominant PFAS compound in the mixture was PFOS which comprised almost 72% of the total for all 20 PFAS compounds before treatment. After treatment, this compound was reduced by 91.3% in the soil. PFOA decreased from 4.50 ppb to non-detect levels, a 100% reduction. A summary of the results and removal efficiency from the first treatment run are noted in Figure 1 contained in the Appendix of this document.

SPLP results were also collected on the soil sample after the initial thermal treatment in December 2018. After the first treatment, the summation of SPLP results was reduced to 22.45 ppt; a 97.2% reduction. PFOA was reduced by 99.6% while PFOS was reduced by 96.1%. The NY State targeted SPLP result for PFOA and PFOS was 10 ppt individually. 10 ppt is the current Maximum Concentration Level (MCL) for drinking water within the state. Summary results of the SPLP analysis are in Table 2 of the Appendix of this document. Some of the minor PFAS compounds (i.e. those whose initial concentrations were below 0.6 ppt) showed less than 100% reduction or even an increase in concentration after treatment. We attribute these results to the fact that the concentrations of these minor PFAS approached the limit of analytical detection, a situation that made it difficult to detect changes with confidence.

b. February 2019 Demonstration Test

In February 2019, the treated sample from December 2018 was treated again in the thermal desorption unit to investigate whether complete removal of all PFAS compounds could be achieved. The PTU temperature and thermal oxidizer temperature ranges were consistent with those in the first test.

The analysis of the confirmatory sample collected after the second treatment confirmed that any remaining PFAS concentrations had been reduced below the detectable concentrations for both the total mass concentration and the SPLP analyses. The results for samples collected after the second treatment for the total mass concentration and the SPLP analyses are presented in Table 1 and Table 2 of the Appendix, respectively.

III. Analysis of the Results

Analyses completed after the second treatment run demonstrated that thermal desorption technology has the ability to render soils with PFAS levels well below the standards set for the NYSDEC RD&D targeted goals for leachate. Both PFOA and PFOS were demonstrated to be well below the 10 ppt target level.

In comparison to adjacent states that have set standards for soil, the analytical results from the first treatment run would have rendered the soil acceptable for residential reuse in Vermont and New Hampshire. Further, the leachate from the same treatment run would have met the drinking water standards for Connecticut, Maine, Massachusetts, New Hampshire, and Pennsylvania. The leachate from the second treatment run would meet the drinking water standards for Vermont and New Jersey.

The intent and purpose of operating the PTU at a temperature range significantly above the PFAS boiling points during the second test was due to the high soil organic matter (SOM) in the soil. PFAS compounds have a demonstrated affinity for SOM. Through laboratory experimentation, it has been found that PFAS retention in soil is altered by the organic content in the soil matrix[4]. Initial SOM of the soil was 7.15% prior to treatment. Post the first and second treatment runs the SOM was reduced to 1.54% and 1.03% respectively. Though PFAS concentrations did decrease along with SOM, it was not determined whether PFAS removal during the second treatment run was due to the increase in average treatment temperature in the PTU or a decrease in SOM. Additional analysis and testing will be required to develop such a correlation.

Summarizing the results of the demonstration;

1. Thermal desorption technology applied to PFAS contaminated soils at Clean Earth's Fort Edward treatment facility reduced the total mass concentration of 20 measured PFAS compounds during the first treatment run by 93.7% and SPLP concentrations by 97.2%. PFOA total mass concentration and SPLP were reduced by 100% and 99.6% respectively. PFOS total mass concentration and SPLP were reduced by 91.3% and 96.1% respectively.
2. The second treatment run rendered the soil leachate concentrations to lower than drinking water standards for federal and various state regulations or proposed regulations
3. Thermal Desorption Technology is robust enough to manage PFAS concentrations in soil to lower than presently identified regulatory required cleanup objectives.

[4] Sun, Y., Ji, R., Gao, B., & Wu, J. (n.d.). *Transport and retention of perfluorooctanoic acid (PFOA) in natural soils: Importance of soil organic matter and mineral contents, and solution ionic strength* (Journal of Contaminant Hydrology). Retrieved from https://www.researchgate.net/publication/332150535_Transport_and_retention_of_perfluorooctanoic_acid_PFOA_in_natural_soils_Importance_of_soil_organic_matter_and_mineral_contents_and_solution_ionic_strength

IV. Next Steps

Clean Earth intends to continue to explore the utilization of thermal desorption as an option to treat soil contaminated with PFAS. A secondary RD&D Permit request will be submitted to the State of New York to increase Clean Earth's knowledge of how PFAS reacts within the thermal desorption process and whether other soil characteristics can be used to determine the efficacy of PFAS desorption. Clean Earth also intends to demonstrate the ability of the thermal desorption process to control PFAS emissions during this second RD&D with NYSDEC.

Clean Earth is continuing to pursue additional opportunities to further the application of their technology and will publish additional reports at their discretion.

For more information, please contact Averil Rance, the Senior Vice President of Environmental Health and Safety at Clean Earth. His contact information has been provided on the cover page.

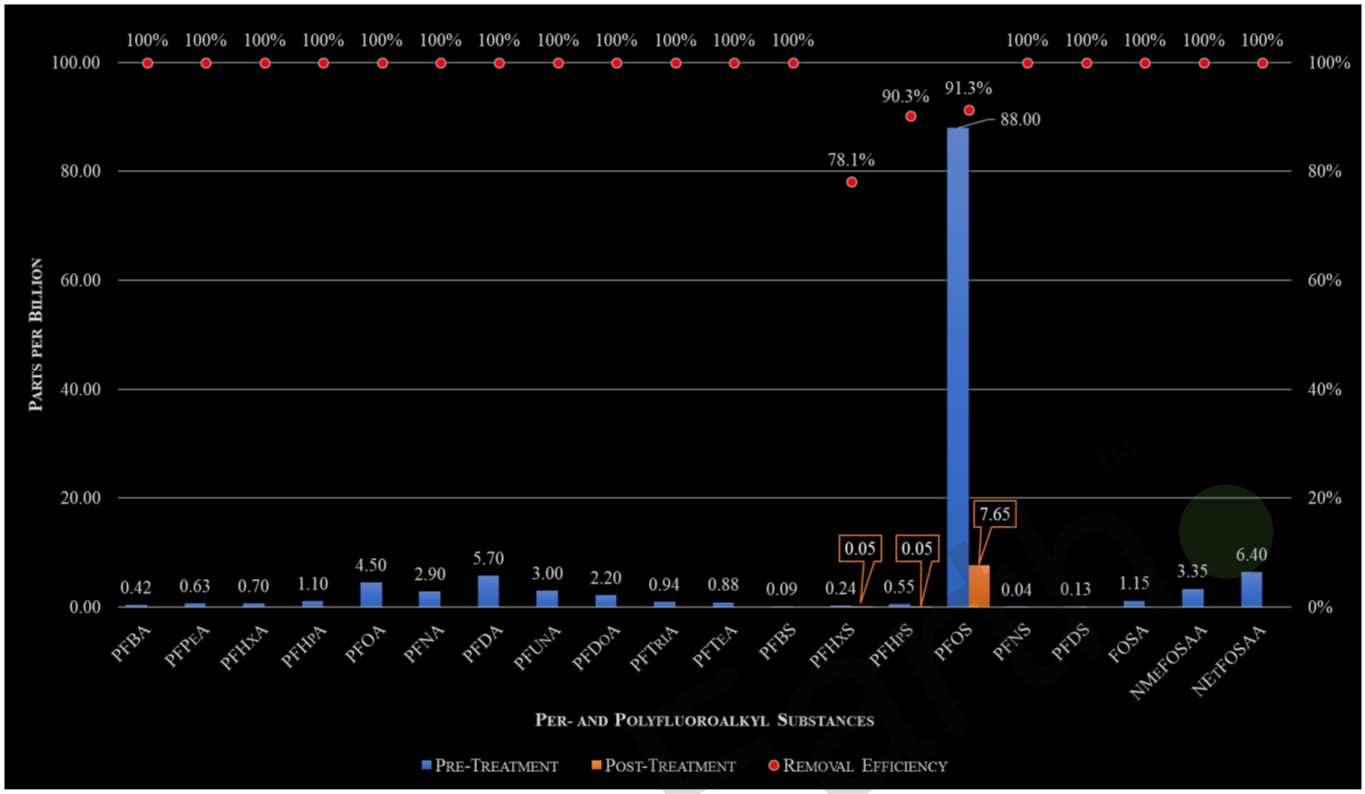
Appendix

Table 1. Pre-Primary, Post-Primary, and Post-Secondary Treatment measurements for total mass concentration of 20 PFAS compounds in soil

Substance	Pre-Primary Treatment (ppb)	Post-Primary Treatment (ppb)	Post-Primary Removal Efficiency	Post-Secondary Treatment (ppb)	Post-Secondary Removal Efficiency
Perfluorobutanoic acid (PFBA)	0.42	ND	100%	ND	100%
Perfluoropentanoic acid (PFPeA)	0.63	ND	100%	ND	100%
Perfluorohexanoic acid (PFHxA)	0.70	ND	100%	ND	100%
Perfluoroheptanoic acid (PFHpA)	1.10	ND	100%	ND	100%
Perfluorooctanoic acid (PFOA)	4.50	ND	100%	ND	100%
Perfluorononanoic acid (PFNA)	2.90	ND	100%	ND	100%
Perfluorodecanoic acid (PFDA)	5.70	ND	100%	ND	100%
Perfluoroundecanoic acid (PFUnA)	3.00	ND	100%	ND	100%
Perfluorododecanoic acid (PFDoA)	2.20	ND	100%	ND	100%
Perfluorotridecanoic acid (PFTriA)	0.94	ND	100%	ND	100%
Perfluorotetradecanoic acid (PFTeA)	0.88	ND	100%	ND	100%
Perfluorobutanesulfonic acid (PFBS)	0.09	ND	100%	ND	100%
Perfluorohexanesulfonic acid (PFHxS)	0.24	0.05	78.1%	ND	100%
Perfluoroheptanesulfonic acid (PFHpS)	0.55	0.05	90.3%	ND	100%
Perfluorooctanesulfonic acid (PFOS)	88.00	7.65	91.3%	ND	100%
Perfluorononanesulfonic acid (PFNS)	0.04	ND	100%	ND	100%
Perfluorodecanesulfonic acid (PFDS)	0.13	ND	100%	ND	100%
Perfluorooctanesulfonamide (FOSA)	1.15	ND	100%	ND	100%
(NMeFOSAA)	3.35	ND	100%	ND	100%
(NEtFOSAA)	6.40	ND	100%	ND	100%
Total PFAS	**122.91**	**7.76**	**93.7%**	**ND**	**100%**

The Pre-Primary Treatment samples were taken from the original sample prior to the primary thermal desorption treatment in December 2018, the Post-Primary Treatment samples were taken after the initial treatment in December 2018, and the Post-Secondary Treatment samples were taken after the second treatment in February 2019. The Removal Efficiencies correspond to the difference in mass concentrations between the Pre-Primary Treatment samples and the respective Post-Treatment samples.

Figure 1. Pre- and Post-Primary Treatment results for total mass concentrations of 20 PFAS compounds.



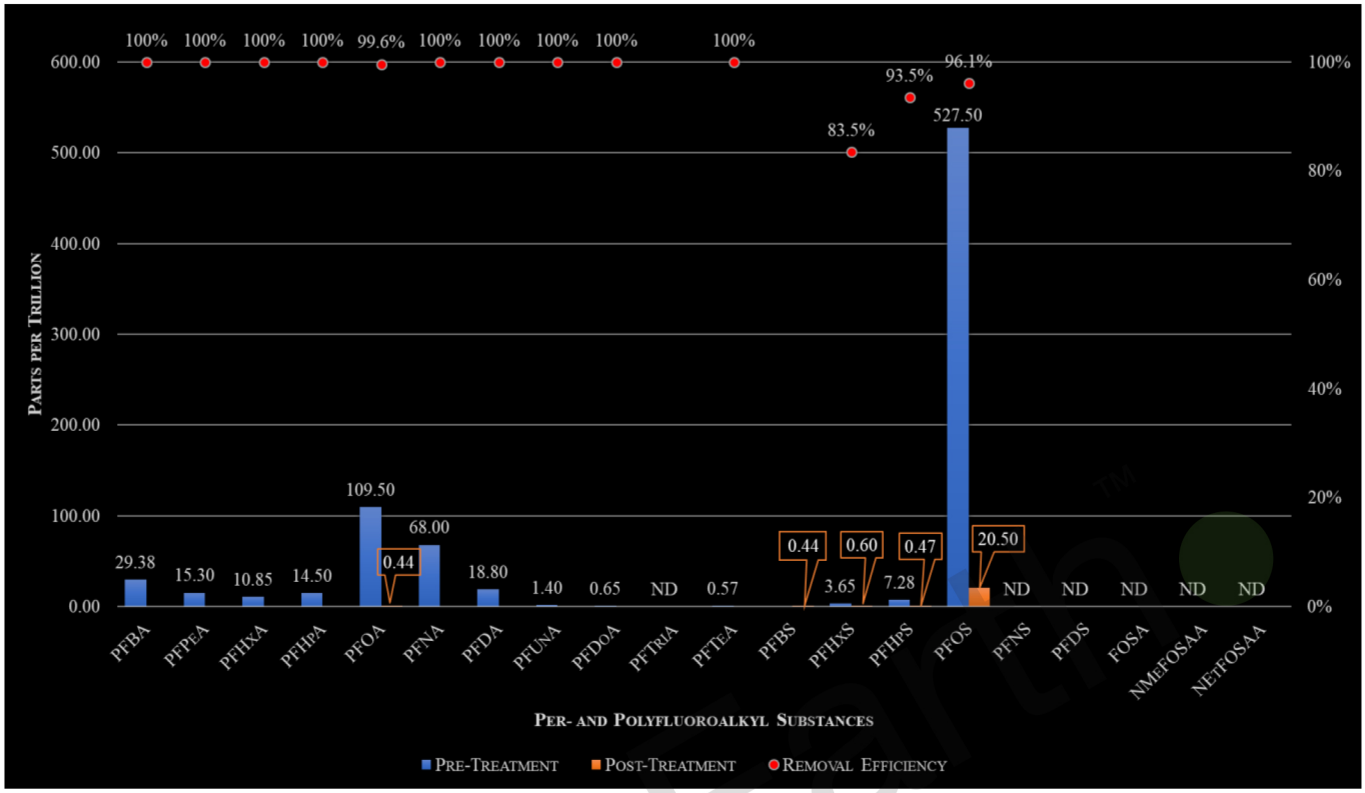
The Pre-Treatment samples were taken from the original sample prior to the primary thermal desorption treatment in December 2018 and the Post-Treatment samples were taken after the initial thermal desorption treatment in December 2018. All substances not marked with an orange text box were reduced to non-detect after the first treatment.

Table 2. Pre-Primary, Post-Primary, and Post-Secondary SPLP Treatment for PFAS concentrations of 20 PFAS compounds

Substance	Pre-Primary Treatment (ppt)	Post-Primary Treatment (ppt)	Post-Primary Removal Efficiency	Post-Secondary Treatment (ppt)	Post-Secondary Removal Efficiency
Perfluorobutanoic acid (PFBA)	29.38	ND	100%	ND	100%
Perfluoropentanoic acid (PFPeA)	15.30	ND	100%	ND	100%
Perfluorohexanoic acid (PFHxA)	10.85	ND	100%	ND	100%
Perfluoroheptanoic acid (PFHpA)	14.50	ND	100%	ND	100%
Perfluorooctanoic acid (PFOA)	109.50	0.44	99.6%	ND	100%
Perfluorononanoic acid (PFNA)	68.00	ND	100%	ND	100%
Perfluorodecanoic acid (PFDA)	18.80	ND	100%	ND	100%
Perfluoroundecanoic acid (PFUnA)	1.40	ND	100%	ND	100%
Perfluorododecanoic acid (PFDoA)	0.65	ND	100%	ND	100%
Perfluorotridecanoic acid (PFTriA)	ND	ND	N/A	ND	N/A
Perfluorotetradecanoic acid (PFTeA)	0.57	ND	100%	ND	100%
Perfluorobutanesulfonic acid (PFBS)	ND	0.44	N/A	ND	N/A
Perfluorohexanesulfonic acid (PFHxS)	3.65	0.60	83.5%	ND	100%
Perfluoroheptanesulfonic acid (PFHpS)	7.28	0.47	93.5%	ND	100%
Perfluorooctanesulfonic acid (PFOS)	527.50	20.50	96.1%	ND	100%
Perfluorononanesulfonic acid (PFNS)	ND	ND	N/A	ND	N/A
Perfluorodecanesulfonic acid (PFDS)	ND	ND	N/A	ND	N/A
Perfluorooctanesulfonamide (FOSA)	ND	ND	N/A	ND	N/A
(NMeFOSAA)	ND	ND	N/A	ND	N/A
(NEtFOSAA)	ND	ND	N/A	ND	N/A
Total PFAS	**807.37**	**22.45**	**97.2%**	**ND**	**100%**

The Pre-Primary Treatment samples were taken from the original sample prior to the primary thermal desorption treatment in December 2018, the Post-Primary Treatment samples were taken after the initial treatment in December 2018, and the Post-Secondary Treatment samples were taken after the second treatment in February 2019. The Removal Efficiencies correspond to the difference in mass concentrations between the Pre-Primary Treatment samples and the respective Post-Treatment samples.

Figure 2. Pre- and Post-Primary Treatment for SPLP PFAS concentrations of 20 PFAS compounds.



The Pre-Treatment samples were taken from the original sample prior to the primary thermal desorption treatment in December 2018 and the Post-Treatment samples were taken after the initial thermal desorption treatment in December 2018. All substances not marked with an orange text box were reduced to non-detect after the first treatment.