PFAS Remediation – Mass Balance and Vapor Treatment

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Having completed two field demonstration studies and currently implementing a third, TRS Group (TRS) has extracted virtually all per- and polyfluoroalkyl substances (PFAS) mass (typical remaining concentrations approach non-detect levels) from soil by applying thermal conduction heating (TCH) and capturing the produced vapors with an integral vapor recovery system. This document discusses TRS's approach to treatment, sustainable vapor handling and mass balance issues.

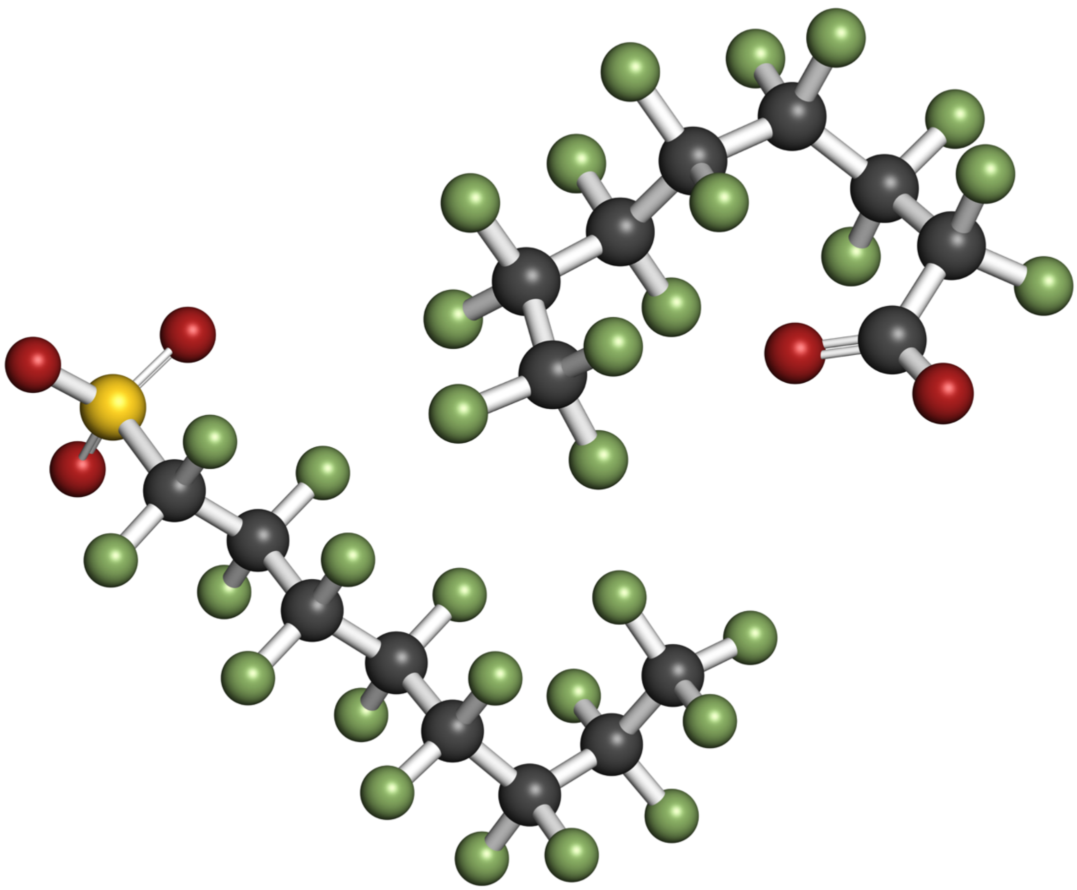

FIGURE 1: PFOA and PFOS molecules

More than 13,000 individual compounds

As analytical capabilities become more sensitive and precise, the list of known PFAS compounds and precursors grows. PFAS molecules can be long chain, short chain, carboxylic acids, sulfonic acids, non-polar, cationic, anionic and zwitterionic. Precursors can transform into PFAS compounds over time. The result is a complex group of compounds that vary in terms of chemical and physical properties. Finding a solution that works for the suite of compounds is challenging. Searching for the best available technology (BAT), we should select a robust solution that works not only for most compounds, but also for the ones found in high concentrations in soil.

Boiling points, vapor pressure and phase behavior

As PFAS compounds have a carbon backbone, in terms of volatility they behave similarly to other organic molecules, with vapor pressures that increase with temperature. Thus, raising the temperature to near the boiling point of these compounds will lead to vaporization and the ability to remove them via vapor extraction.

Transformation expected

PFAS compounds are surface-active and can interact with each other, solid surfaces and soil minerals. During heating, longer chain compounds may transform into shorter chains with some recombination of smaller compounds into larger ones. We often observe compounds in the extracted gases that are not the dominant ones in the soil, indicating that these transformations can be significant. Thus, designing the vapor treatment system based on soil analyses may lead to suboptimal outcomes. Therefore, it is important to design the vapor treatment system to cope with unexpected compounds.

Total fluorine, organic fluorine, extractable organic fluorine, TOP assay

Fluorine is present in soils in non-PFAS organic compounds and in inorganic species such as calcium difluoride (CaF_2). PFAS compounds typically make up a small fraction of the total fluorine in soils (in some studies, less than 10%), making fluorine-based mass balance approaches impractical. Comparison of untreated and treated soils shows small differences on Total Organic Fluorine (TOF) but sometimes strong reductions in Extractable Total Organic Fluorine (ETOF). Total Oxidizable Precursors (TOP) include compounds that may transform into targeted PFAS compounds over time. These analytical options shed light on the distribution of fluorine compounds in soils and the difficulty to close the PFAS mass balance during thermal treatment.

TCH and vapor extraction strategies

Applying TCH, TRS places the PFAS-impacted soil under vacuum, volatilizes the compounds, pulls the generated vapors through the soil and extracts them. Initially, we produce steam by boiling soil pore water. As the soil dries, the gases in the soil consist of atmospheric air entering via vadose zone migration, inlet wells or leaks in the system. These gases carry vaporized PFAS compounds to extraction wells and above-grade to the vapor treatment system.

Vapor treatment options

There are many vapor and liquid treatment systems under development. Currently, the most applied options for the vapor phase are thermal oxidation with acid gas scrubbing, and condensation, separation and treatment at near ambient temperatures. TRS prefers the latter method, as it is simpler and more economical than thermal oxidation, where the parameters are ill-defined, typically leading to the selection of high treatment temperatures and long residence times to ensure destruction of all relevant compounds. Further, the systems are large, consuming lots of fossil fuel, with attendant sustainability issues. Table 1 below compares the technologies.

Operations	Thermal oxidation with acid gas scrubbing	Quenching, condensation and ambient temperature treatment
System construction cost (1,000 scfm example)	$1-2 million – large system due to high temperature and long residence time	$200-400,000
Fossil fuel demand	Natural gas or propane, 1-2 MM BTU/hr per 1,000 scfm	None
Electricity demand	Moderate (blowers and burners)	Moderate (blowers, pumps)
Waste generated	Alkaline scrubber blow-down	Spent filter bags and GAC
Sustainability evaluation	Poor score due to fossil fuel usage and materials used to construct system	Good score due to small scale of system and energy usage

TABLE 1: Comparison of commonly applied technologies for PFAS vapor treatment

TRS uses conventional, low-temperature equipment to quench the vapors and separate water and liquids, then treats the effluent streams by filtration and granular activated carbon (GAC) or ion exchange resins. While we expect continued development of treatment options, TRS will focus its efforts on efficacious, low cost, sustainable methods.

Fluorine mass balance issues and impact on vapor treatment

A large pile of soil may contain just a few grams of PFAS. As discussed above, attempts to establish a PFAS or fluorine mass balance will be challenging:

- Fluorine compounds present in soils will mask the small mass of PFAS-related fluorine.
- PFAS transformation and break-down during heating is poorly understood.
- Targeted PFAS compounds may be removed or destroyed in the soil, while fluorinated by-products can remain or be extracted.
- PFAS can adhere to inner surfaces in and wetted portions of the vapor treatment system, reducing the mass of PFAS that makes it to the final treatment step, such as GAC filtration.

TRS collects data to inform mass balance discussions; however, as mentioned above, we consider attempts to close the mass balance futile. Key performance metrics should include:

- The treated soil meets regulatory standards and is safe to handle and reuse.
- Vapor emissions are minimal and acceptable.
- Water discharge criteria are met with no adverse impacts.
- Generated wastes are safe and economical to handle.

TRS continues to refine and improve our low-impact, sustainable PFAS vapor treatment systems based on quenching, condensation and ambient temperature treatment. TRS focuses its PFAS thermal remediation efforts to ensure optimal treatment and minimal discharges. Further, we collaborate with firms that offer promising solutions for destroying PFAS in vapors and liquids on site.