Abstract

Per- and polyfluoroalkyl substances (PFAS) have emerged as significant environmental contaminants due to their persistence, toxicity, and widespread use in various industrial and consumer products. This dissertation investigates the fate, transport, and remediation of PFAS in landfill environments, focusing on landfill leachate and gas emissions.

The first objective of this research was to develop and evaluate a thin-water-film nonthermal plasma reactor for the degradation of PFAS in landfill leachate. This study assessed the degradation efficiencies of various PFAS, including perfluorinated carboxylic acids (PFCAs) and perfluorosulfonic acids (PFSAs), in leachates collected from multiple municipal solid waste landfills in Florida. The findings demonstrated significant degradation efficiencies for long-chain PFAS, while short-chain PFAS exhibited limited removal, with some showing increased concentrations due to the breakdown of longer-chain compounds. Toxicity assessment using Microtox bioassays indicated no acute toxicity from the treatment process.

The second objective focused on understanding the fate of PFAS during leachate evaporation, a common management practice in landfill operations. In this study, a bench-scale rotary evaporator operating at 77 °C and under a vacuum pressure of -650 mmHg was used to simulate the evaporation process for 1.6 liters of landfill leachate. Samples were collected at multiple stages of evaporation (0%, 12.5%, 25%, 50%, 75%, and 90%) to monitor changes in 44 water quality parameters alongside PFAS concentrations. Results revealed that while non-volatile PFAS like PFCAs and PFSAs accumulated in the residual leachate, volatile fluorotelomer alcohols (FTOHs) and other organic contaminants were largely transferred to the vapor phase or condensates. This highlights the potential for secondary emissions of PFAS during leachate evaporation and underscores the need for effective management strategies.

The third objective was to develop and validate analytical methods for measuring volatile PFAS in gaseous, liquid, and solid matrices. Solid-phase microextraction followed by gas chromatography/mass spectrometry (SPME-GC/MS) was optimized for detecting FTOHs in landfill gas and solid consumer products. This method offered a lower detection limit and minimized contamination risks compared to traditional approaches. The validated method was successfully applied to landfill gas emissions, revealing detectable levels of FTOHs in closed landfill sites and demonstrating the contribution of consumer products to volatile PFAS contamination.

Finally, this study examined the release and transformation of volatile PFAS from consumer products during simulated landfilling. A comprehensive survey of 81 consumer products identified FTOHs, fluorotelomer acrylates (FTAc), and fluorotelomer methacrylates (FTMAc) in various materials. 6:2 FTOH was the most common volatile PFAS, especially in food packaging papers and liquid and semi-liquid products, showing that these items are major sources of volatile PFAS emissions in landfills. Additionally, 6:2 FTMAc and 6:2 FTAc were found in 1.2% and 6.2% of the tested consumer products, respectively. Hydrolysis experiments confirmed the presence of PFAS precursors, which significantly increased the release of FTOHs over time. Simulated landfill experiments further revealed microbial activity as a potential factor influencing PFAS transformation and emissions.

Overall, this dissertation advances the understanding of PFAS behavior in landfills by providing critical insights into their release dynamics, partitioning during leachate evaporation, and the challenges associated with monitoring volatile PFAS. The findings contribute to the development of more effective PFAS management strategies and have important implications for regulatory policy and environmental remediation efforts. By integrating innovative treatment technologies with advanced analytical methodologies, this work lays a foundation for future research aimed at addressing both the removal of well-studied PFAS and the less understood volatile PFAS, thereby offering a comprehensive approach to mitigating the risks associated with these persistent contaminants.

Keywords:

Per- and polyfluoroalkyl Substances (PFAS), landfill leachate, volatile PFAS, evaporation, nonthermal plasma, fluorotelomer alcohols