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(54) **TREATING PER- AND
POLY-FLUOROALKYL SUBSTANCES IN
LANDFILL LEACHATE**

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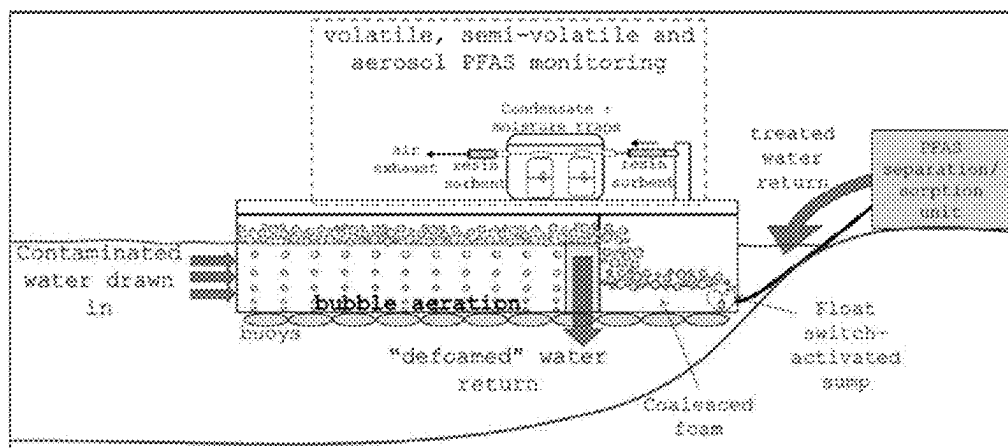
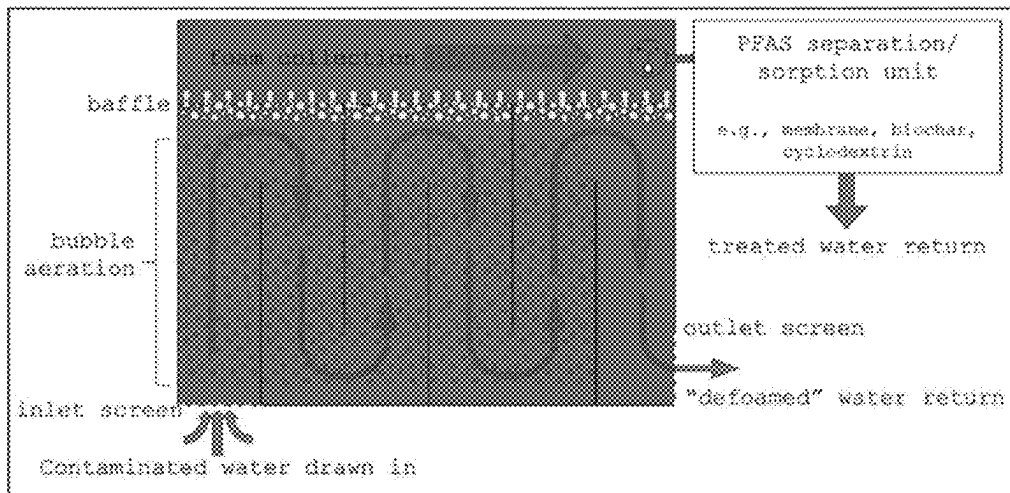
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022492 on Mar. 16, 2021, now Pat. No. 12,312,255.

(60) Provisional application No. 63/027,450, filed on May
20, 2020, provisional application No. 62/990,156,
filed on Mar. 16, 2020.

(57) **ABSTRACT**

The present disclosure provides for devices, systems, and methods of separating PFAS compounds from wastewater leachate. After separation, the PFAS compounds can be rendered less harmful. The present disclosure provides for devices, systems, and methods that uses aeration-induced foaming to isolate PFAS from landfill leachate into a concentrated, volume reduced liquid (coalesced foam), which can be separated and treated.



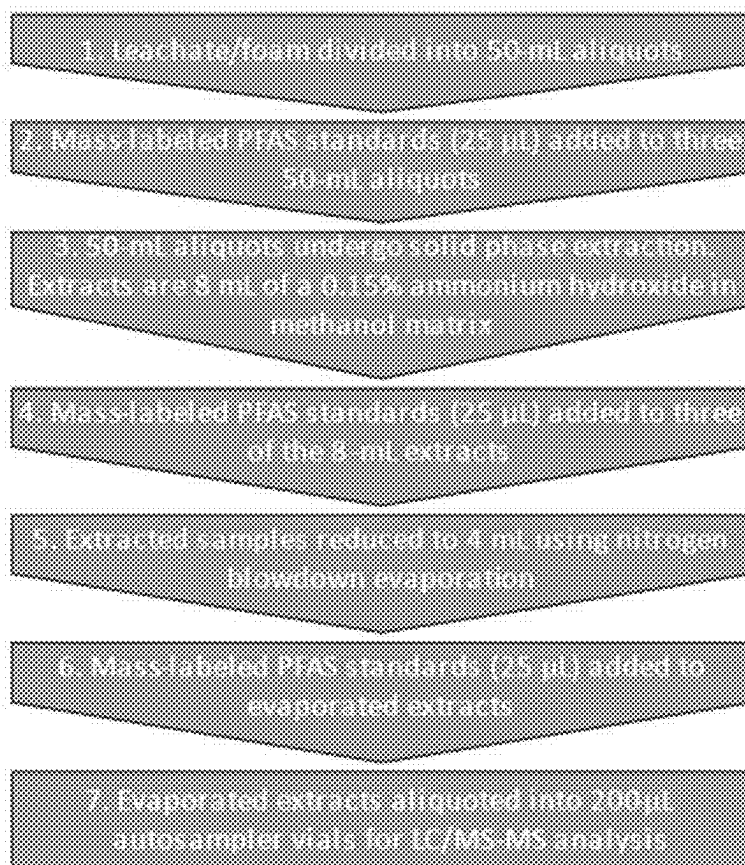


FIG. 1

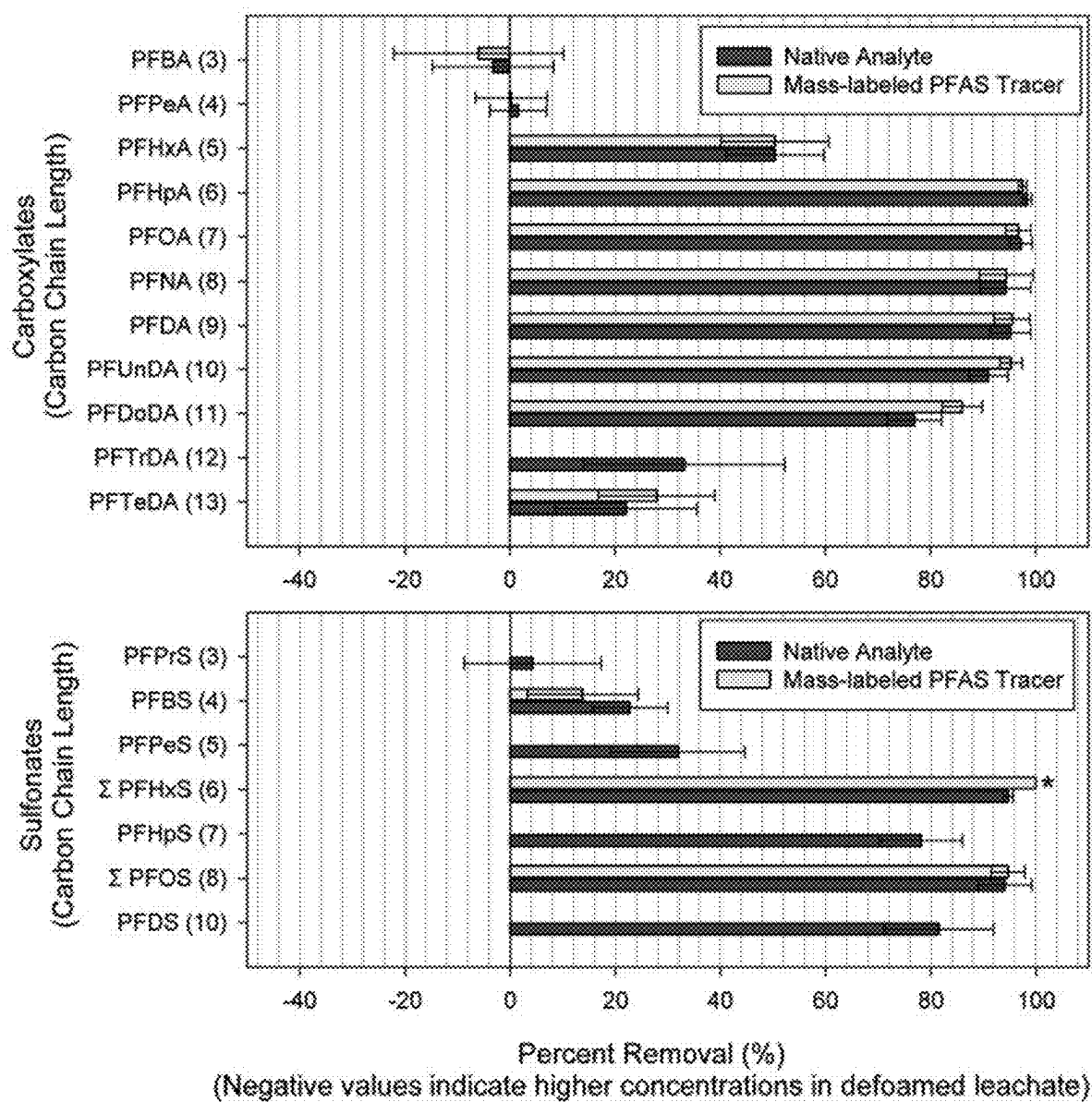


FIG. 2

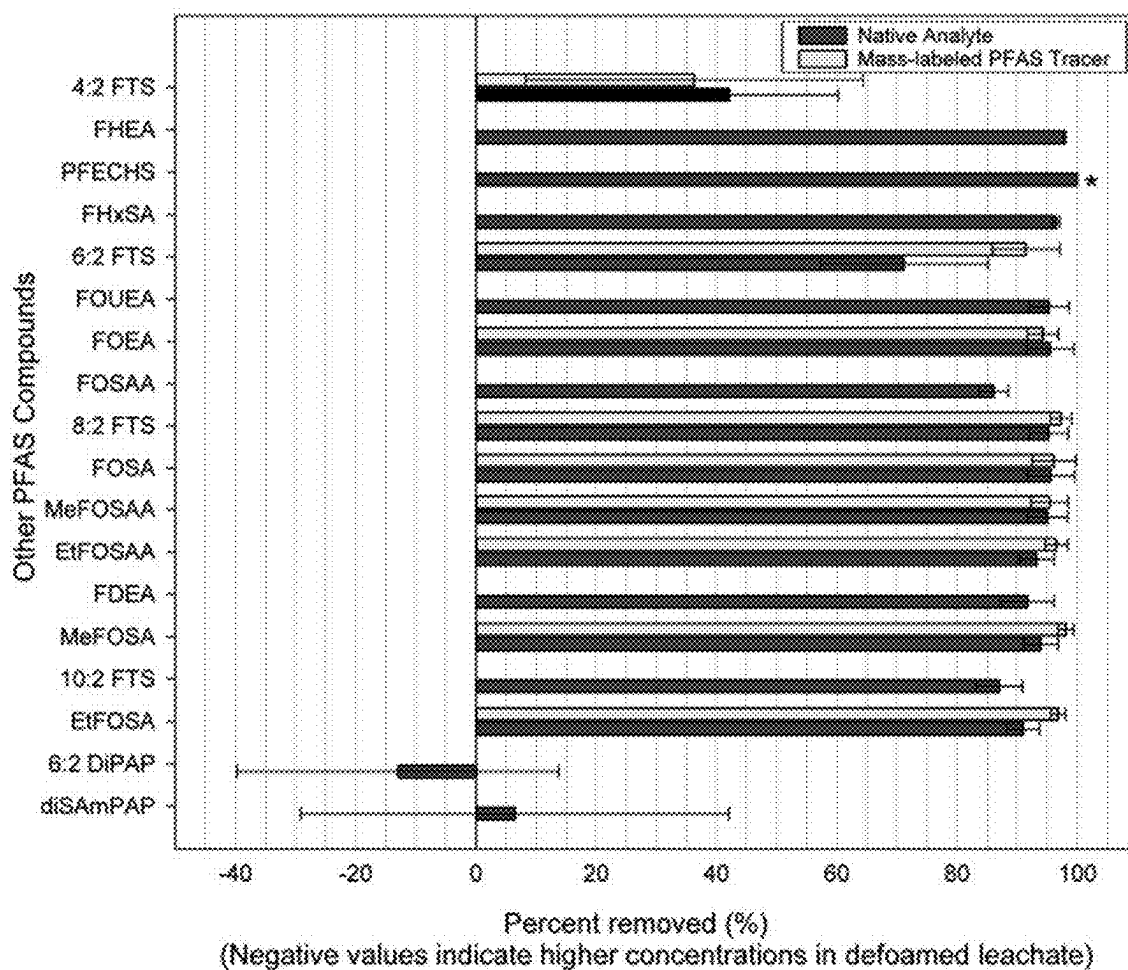


FIG. 3

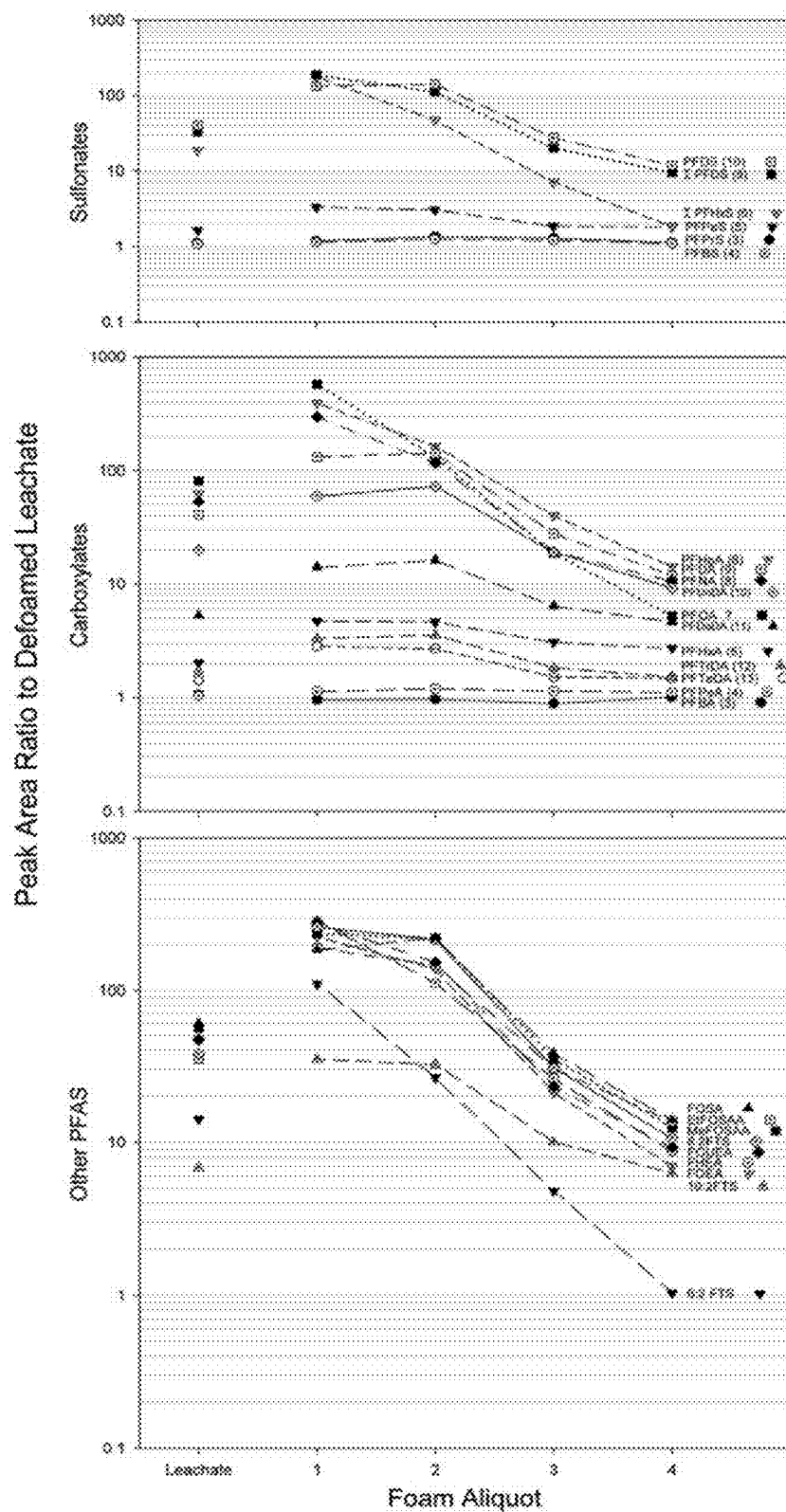
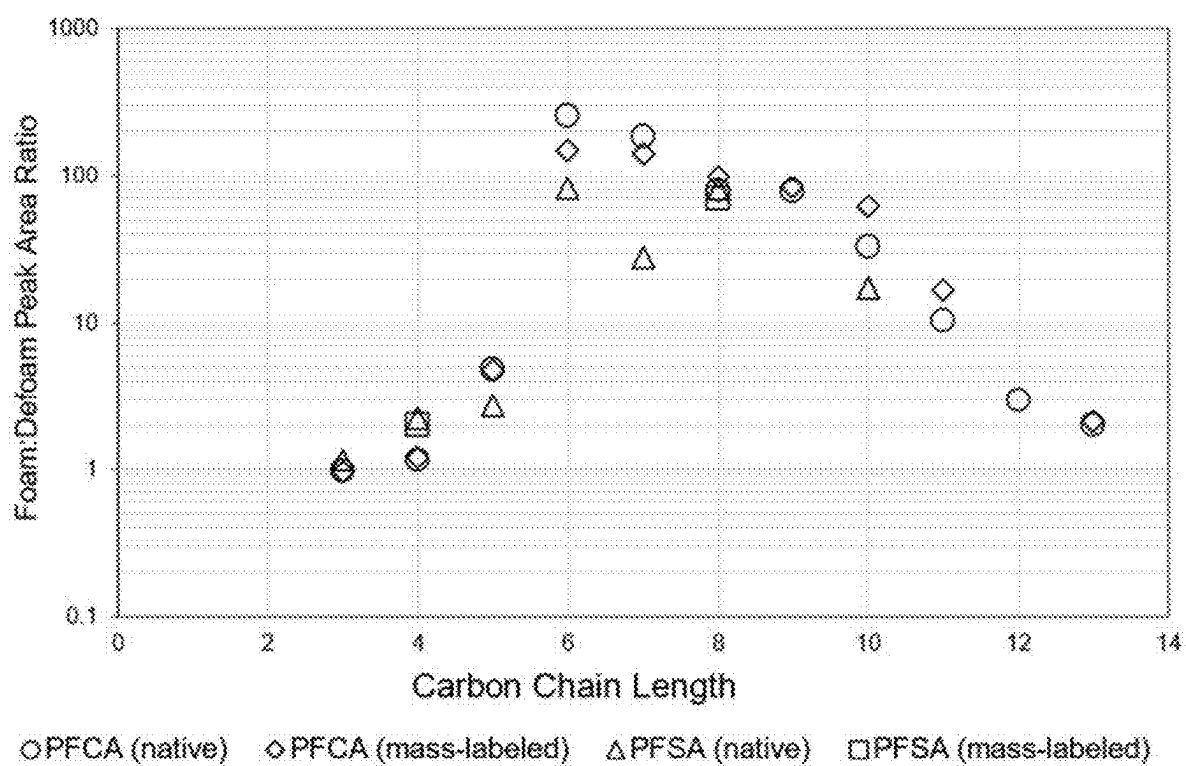


FIG. 4

**FIG. 5**

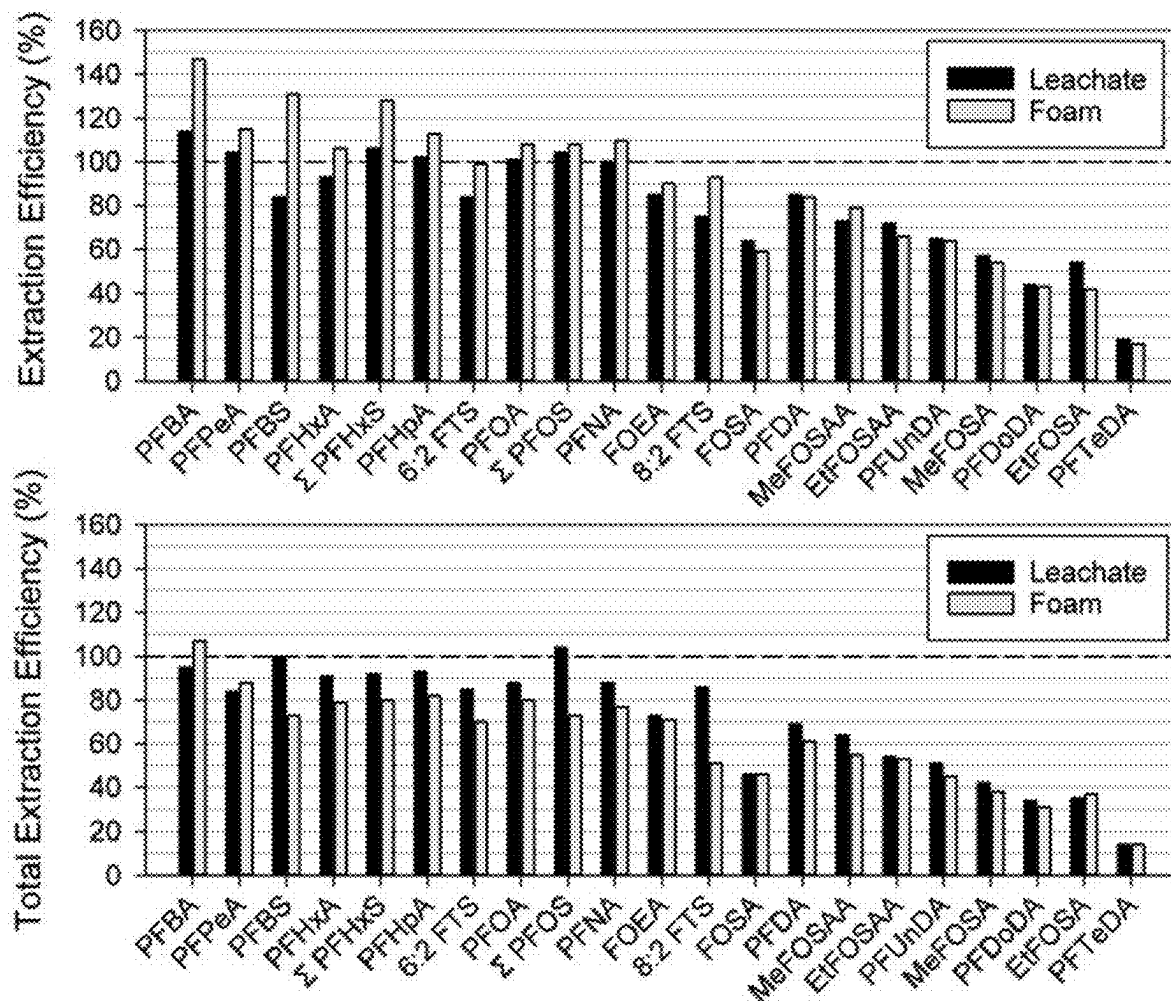


FIG. 6

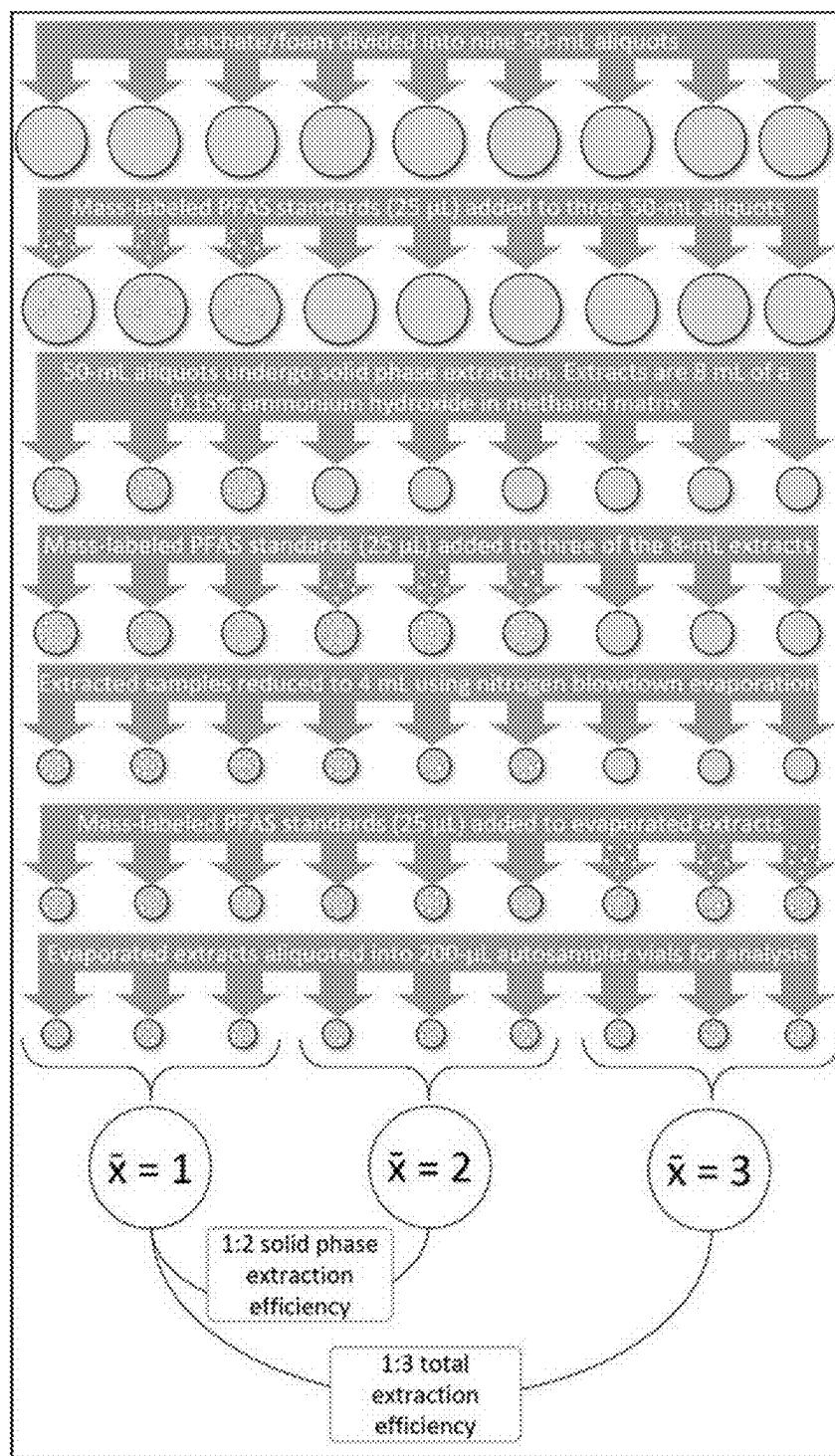


FIG. 7

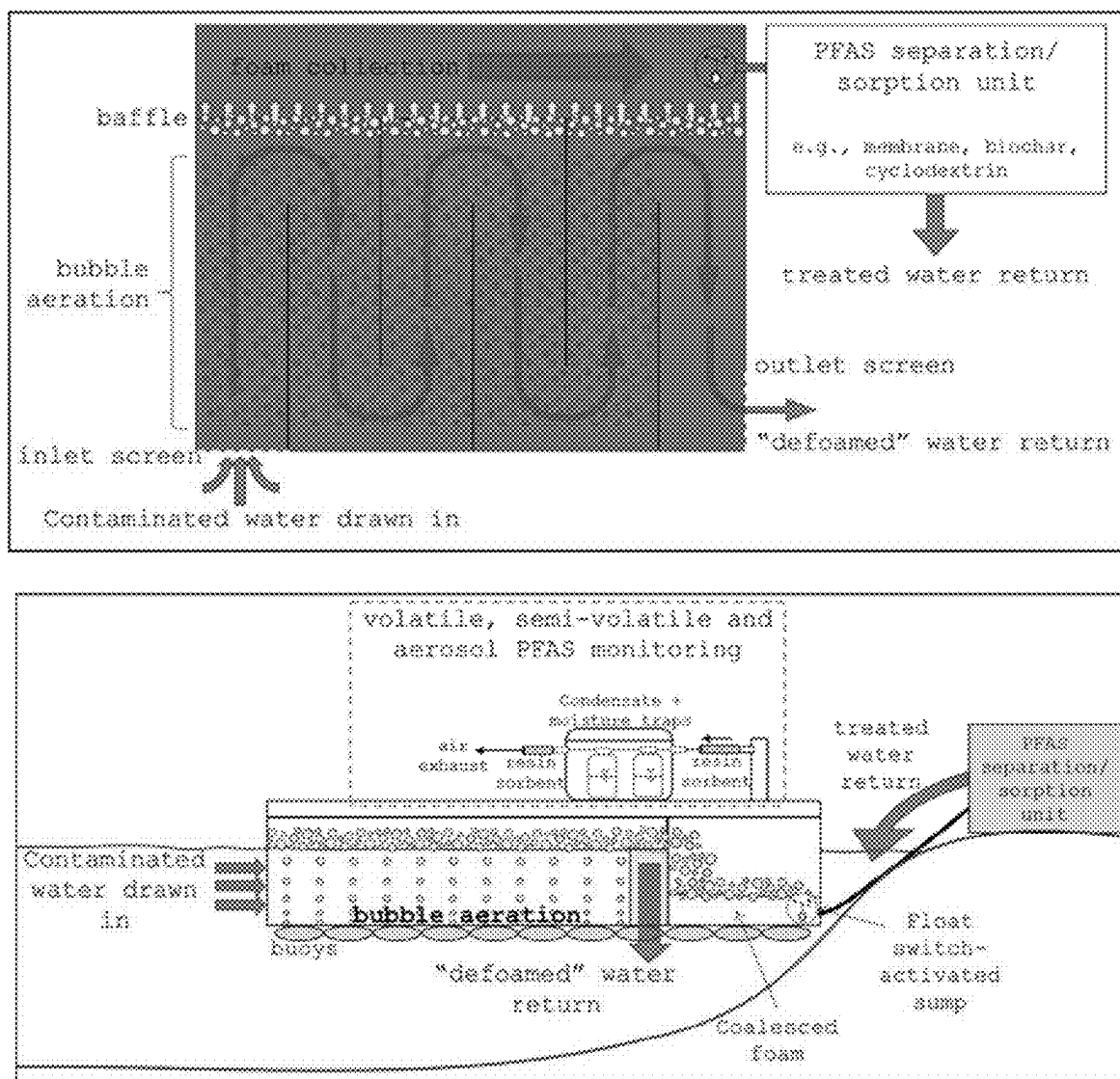


FIG. 8

**TREATING PER- AND
POLY-FLUOROALKYL SUBSTANCES IN
LANDFILL LEACHATE**

**CLAIM OF PRIORITY TO RELATED
APPLICATION**

[0001] This application is a divisional of U.S. patent application Ser. No. 17/911,903, filed Sep. 15, 2022, which is the 35 U.S.C. § 371 national stage of PCT application having serial number PCT/US 2021/022492, filed on Mar. 16, 2021. PCT/US 2021/022492 claims priority to U.S. provisional application entitled “TREATING PER-AND POLY-FLUOROALKYL SUBSTANCES IN LANDFILL LEACHATE,” having Ser. No. 63/027,450 filed on May 20, 2020, and to U.S. provisional application entitled “TREATING PER-AND POLY-FLUOROALKYL SUBSTANCES IN LANDFILL LEACHATE,” having Ser. No. 62/990,156 filed on Mar. 16, 2020, each of which are entirely incorporated herein by reference.

FEDERAL FUNDING

[0002] This invention was made with government support under grant number 83962001 awarded by the United States Environmental Protection Agency. The government has certain rights in the invention.

BACKGROUND

[0003] Large volumes of per- and/or polyfluoroalkyl-contaminated substances (PFAS-contaminated substances) wastewaters, such as municipal solid waste landfill leachates, pose a challenge for PFAS treatment technologies in practice today. While various techniques have been used, each of them possesses their own unique challenges as it pertains to wastewater leachate. Thus, there is a need to find alternative approaches.

SUMMARY

[0004] The present disclosure provides for devices, systems, and methods of separating PFAS compounds from wastewater leachate. After separation, the PFAS compounds can be rendered less harmful. The present disclosure provides for devices, systems, and methods that uses aeration-induced foaming to isolate PFAS from landfill leachate into a concentrated, volume reduced liquid (coalesced foam). The foam can then be separated and treated.

[0005] An aspect of the present disclosure provides for a method of separating per- and/or polyfluoroalkyl compounds (PFAS compounds) from a wastewater leachate contaminated with PFAS compounds, comprising: foaming the wastewater leachate contaminated with PFAS compounds for a period of time to form a foam layer on top of the wastewater leachate and a de-foamed wastewater leachate, wherein the foam layer comprises a concentrated amount of PFAS compounds relative to that present in the wastewater leachate, wherein the de-foamed wastewater leachate has a lower concentration of total PFAS compounds than the wastewater leachate; and separating the foam layer from the de-foamed wastewater leachate; and optionally processing the foam layer. The foaming can include bubble aeration of the wastewater leachate that can include artificial bubble aeration introduced using a bubble aeration system. The bubble aeration system can produce bubbles within the wastewater leachate for a period of time sufficient to form

the foam layer. The bubbles have a sufficient bubble size and air-to-liquid volume, and contact time with the wastewater leachate to form the foam layer. The PFAS compounds can include perfluorooctanoic acid (PFOA), perfluorooctanesulfonic acid (PFOS), or a combination thereof. The processing can include processing using an electron beam, processing using a plasma, processing by incineration, processing by oxidation, or a combination thereof. After processing any residual water can be returned, reclaimed, or recycled.

[0006] The present disclosure provides for a system for removing per- and/or polyfluoroalkyl compounds (PFAS compounds) from wastewater leachate contaminated with PFAS compounds, comprising: a bubble aeration system comprising an air flow device in communication with a bubble aeration device, wherein the bubble aeration device is within pre-foamed wastewater leachate contaminated with PFAS compounds, wherein the bubble aeration device is configured to produce bubbles from the air flow from the air flow device, wherein the bubbles form a foam layer on top of the wastewater leachate, wherein the foam layer comprises a concentrated amount of PFAS compounds relative to that present in the pre-foamed wastewater; a separating system configured to remove a portion of the foam layer from the surface of the wastewater leachate; and optionally a processing system includes a device that renders the PFAS compounds less hazardous relative to before processing than PFAS compound. The air flow device can be an air generator or pump and wherein the bubble aeration device is a structure that is configured to form bubbles as air is flowed through the bubble aeration device. The separating system can include a structure that is configured to skim the foam layer off of the surface of the wastewater leachate, optionally wherein the structure is a skimmer or a baffle. The processing system can include: an electron beam device, a plasma device, an incineration device, an oxidation device, or a combination thereof.

[0007] The present disclosure provides for a device for removing per- and/or polyfluoroalkyl compounds (PFAS compounds) from wastewater leachate contaminated with PFAS compounds, comprising: an air flow device in communication with a bubble aeration device, wherein the bubble aeration device is within pre-foamed wastewater leachate contaminated with PFAS compounds, wherein the bubble aeration device is configured to produce bubbles from the air flow from the air flow device, wherein the bubbles form a foam layer on top of the wastewater leachate, wherein the foam layer comprises a concentrated amount of PFAS compounds relative to that present in the pre-foamed wastewater; a separating device that is configured to remove a portion of the foam layer from the surface of the wastewater leachate; and optionally a processing system includes a device that renders the PFAS compounds less hazardous relative to before processing than PFAS compound. The air flow device can be an air generator or pump and wherein the bubble aeration device is a structure that is configured to form bubbles as air is flowed through the bubble aeration device. The separating device can include a structure (e.g., skimmer, baffle, and the like) that is configured to skim the foam layer off of the surface of the wastewater leachate, optionally wherein the structure is a skimmer or a baffle. The processing system can include: an electron beam device, a plasma device, an incineration device, an oxidation device, or a combination thereof.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] Further aspects of the present disclosure will be more readily appreciated upon review of the detailed description of its various embodiments, described below, when taken in conjunction with the accompanying drawings.

[0009] FIG. 1 illustrates landfill leachate PFAS extraction efficiency experiment flow diagram. The ratio between average peak area for aliquots spiked in step 2 and step 4 is the solid phase extraction efficiency, and the ratio between average peak area for aliquots spiked in step 2 and step 6 is the total preparation efficiency.

[0010] FIG. 2 illustrates graphs describing mean removal percentages for PFAS. Error bars represent standard deviation. In all ten foaming experiments, the mass-labeled tracer of PFHxS (*) was not found in defoamed leachate, therefore the removal percentage was assumed to be 100% (0% standard deviation). Σ PFOS and Σ PFHxS are shown as the sum of their respective isomers.

[0011] FIG. 3 illustrates graphs describing mean removal percentages for the remaining PFAS (a category which includes fluorotelomers and sulfonamides). Error bars represent standard deviation. In all ten foaming experiments, the labeled standard of PFECHS (*) was not found in defoamed leachate, therefore the removal percentage was assumed to be 100% (0% standard deviation). Compounds are displayed from top to bottom in increasing order of MS retention time.

[0012] FIG. 4 illustrates graphs describing sequential foam experiment results for select PFAS compounds: all detected sulfonates and carboxylates and the nine most prevalent (by peak area) "other" PFAS compounds. Peak area ratios were calculated using the mean peak areas of native and mass-labeled PFAS compounds in leachate, in 50-mL aliquots (approximately 14% of the initial leachate volume) of coalesced foam and in defoamed leachate from three experiments. The values reported in the figure are the peak area of the sample divided by the peak area of the defoamed leachate (the end point of PFAS reduction for this experiment). Σ PFOS and Σ PFHxS are shown as the sum of their respective isomers.

[0013] FIG. 5 illustrates graphs describing average foam: defoam peak area ratio among perfluoroalkyl acids (PFAA) relative to carbon chain length.

[0014] FIG. 6 illustrates graphs describing extraction efficiency comparison for solid phase extraction and total extraction (i.e., after nitrogen evaporation) for leachate and foam. Σ PFOS and Σ PFHxS are shown as the sum of their respective isomers. Compounds are shown in increasing order of retention time.

[0015] FIG. 7 illustrates extraction efficiency experiment details.

[0016] FIG. 8 is an aerial (top diagram) and elevation (bottom diagram) view of a device or system of the present disclosure that is a field scale PFAS removal treatment train.

DETAILED DESCRIPTION

[0017] This disclosure is not limited to particular embodiments described, and as such may, of course, vary. The terminology used herein serves the purpose of describing particular embodiments only, and is not intended to be limiting, since the scope of the present disclosure will be limited only by the appended claims.

[0018] Where a range of values is provided, each intervening value, to the tenth of the unit of the lower limit unless the context clearly dictates otherwise, between the upper and lower limit of that range and any other stated or intervening value in that stated range, is encompassed within the disclosure. The upper and lower limits of these smaller ranges may independently be included in the smaller ranges and are also encompassed within the disclosure, subject to any specifically excluded limit in the stated range. Where the stated range includes one or both of the limits, ranges excluding either or both of those included limits are also included in the disclosure.

[0019] As will be apparent to those of skill in the art upon reading this disclosure, each of the individual embodiments described and illustrated herein has discrete components and features which may be readily separated from or combined with the features of any of the other several embodiments without departing from the scope or spirit of the present disclosure. Any recited method may be carried out in the order of events recited or in any other order that is logically possible.

[0020] Embodiments of the present disclosure will employ, unless otherwise indicated, techniques of chemistry, polymer chemistry, material science, and the like, which are within the skill of the art. Such techniques are explained fully in the literature.

[0021] Prior to describing the various embodiments, the following definitions are provided and should be used unless otherwise indicated.

[0022] Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art of microbiology, molecular biology, medicinal chemistry, and/or organic chemistry. Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present disclosure, suitable methods and materials are described herein.

[0023] As used in the specification and the appended claims, the singular forms "a," "an," and "the" may include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to "a support" includes a plurality of supports. In this specification and in the claims that follow, reference will be made to a number of terms that shall be defined to have the following meanings unless a contrary intention is apparent.

DISCUSSION

[0024] Aspects of the present disclosure provide for devices, systems, and methods of separating PFAS compounds from wastewater leachate. After separation, the PFAS compounds can be rendered less harmful. The present disclosure provides for devices, systems, and methods that uses aeration-induced foaming to isolate PFAS from landfill leachate into a concentrated, volume reduced liquid (coalesced foam). Dilute waste streams are usually poor candidates for high energy destructive PFAS treatment methods (e.g., sonication, chemical oxidation, electron beam, plasma). Landfill leachate is a more concentrated waste stream, which can be further concentrated using this technique.

[0025] The surfactant properties of PFAS are exploited to concentrate the PFAS compounds in a foam layer that can be produced via the bubble aeration of landfill wastewater leachate. Initial testing shows that the effectiveness of the

foaming technique for concentrating PFAS varied by compound, with a mean removal percentage (the percent difference between PFAS in leachate before and after foam removal) of about 69% and a median removal percentage of about 92% among the ten replicate foaming experiments. The effectiveness can vary depending upon various factors such as the wastewater leachate contents, pH, presence of other materials in the leachate, and the like. An advantage of this technique is that it appears to be similarly effective at sequestering sulfonates and carboxylate PFAS compounds. The results suggest that for the pretreatment or preconcentration of landfill leachates, foaming to sequester PFAS is a practical approach that optionally could be strategically coupled to high energy PFAS-destructive treatment technologies. The process described herein is simple and could feasibly be applied at a relatively low cost at most landfills.

[0026] Per- and polyfluoroalkyl substances (PFAS) are man-made compounds that have been used to manufacture consumer products and industrial chemicals such as aqueous film forming foams (AFFFs). PFAS substances and related compounds such as PFAS precursors can be referred to as PFAS compounds. PFAS compounds can include perfluorobutyric acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorobutane sulfonate (PFBS), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorohexane sulfonate (PFHxS), 6:2 fluorotelomer sulfonate (6:2 FTS), perfluorooctanoic acid (PFOA), perfluoroheptane sulfonate (PFHpS), perfluorooctane sulfonate (PFOS), perfluorononanoic acid (PFNA), and 8:2 fluorotelomer sulfonate (8:2 FTS), as well other compounds and precursor materials used to make these compounds. The PFAS compounds can include perfluorooctanoic acid (PFOA), perfluorooctanesulfonic acid (PFOS), or a combination thereof.

[0027] The present disclosure provides for devices, systems, and methods of separating PFAS compounds from wastewater leachate contaminated with PFAS compounds and processing the separated PFAS. The wastewater leachate prior to foaming can be referred to as “pre-foamed wastewater leachate” or “wastewater leachate” while after foaming it is referred to as de-foamed wastewater leachate. It should be stated that the same volume of wastewater leachate can be subjected to the foaming process multiple separate times and/or continuously. The foaming process includes aerating the wastewater leachate that may be contaminated with PFAS compounds. In one instance, the wastewater leachate may be known to be contaminated while in another it may be suspected to be contaminated. The foaming process includes operating a bubble aeration device (e.g., fine bubble diffusers or microbubble diffusers) in contact (e.g., disposed within) with wastewater leachate using specified bubble size, air-to-liquid volume, and contact time, followed by physical separation of the foam from the leachate using a separating device or system that can include baffles or skimmers (e.g., industrial baffles or skimmers to process large volumes of wastewater). In an aspect, the wastewater leachate is flowed in a straight or serpentine, curving, winding, or sinuous path (e.g., see FIG. 8), where the wastewater leachate is subjected to the foaming process (e.g., exposed the bubble from the bubble aeration device) along portions or the entire path or at the end of the path. The separating device or system can be configured to separate the foam at various positions along the path and/or at the end of the path. The characteristics, volumes and manner of collection of landfill leachate differs from domestic water or

groundwater. Foam separation units can be placed at individual leachate collection points (pump station, sumps), at storage facilities, or inline with other treatment unit operations. Foam separation units can be fixed or can be mobile, where in some instances the unit can float on the surface of the wastewater leachate in a pond or other body of water.

[0028] During the foaming process, after a period of time (e.g., minutes to an hour or more), a foam layer is formed on top of the wastewater leachate (now referred to as de-foamed wastewater leachate). The foam layer comprises a concentrated amount of PFAS compounds relative to that present in the pre-foamed wastewater. The de-foamed wastewater leachate has a lower concentration (e.g., a reduction of about 10-90%, about 10-70%, about 10-50, or about 10-30%) of total PFAS compounds than the pre-foamed wastewater leachate. The reduction in the concentration can be obtained by measuring before and after foaming. Also, those measurements can be compared to what is found in the foam layer. The path which the wastewater leachate follows can be made longer to reduce the PFAS compounds and/or the wastewater leachate can be processed multiple times to reduce the PFAS compounds.

[0029] After foaming or even during the foaming process, the foam layer can be separated from the de-foamed wastewater leachate. The foaming process can be continuous or for set periods of time and the wastewater leachate can be foamed multiple times to reduce the amount of PFAS compounds down to the desired levels. The separation can be conducted by skimming off the foam layer manually or in an automated manner during the foaming process or after the foaming process is stopped.

[0030] Once the foam layer is separated, the foam layer (which may revert back to a liquid form after sufficient time) can be further processed on site or separately. Processing the foam layer renders the PFAS compounds less hazardous relative to before processing than PFAS compounds. The processing can include processing using an electron beam, processing using a plasma, processing by incineration, processing by oxidation, or a combination thereof.

[0031] Having described the present disclosure, additional details are provided below. The present disclosure provides for methods of separating per- and/or polyfluoroalkyl compounds (PFAS compounds) from a wastewater leachate contaminated with PFAS compounds. The method can include the following steps. The first step is foaming the wastewater leachate contaminated with PFAS compounds for a period of time (e.g., minutes to hours or more (e.g., 10 min to 24 hours)) to form a foam layer on top of the wastewater leachate and a de-foamed wastewater leachate. The foam layer includes a concentrated amount of PFAS compounds relative to that present in the wastewater leachate. In particular, the foam layer can include 10 to 90% of the PFAS compounds that were present in the wastewater leachate prior to treatment. The de-foamed wastewater leachate has a lower concentration of total PFAS compounds than the wastewater leachate. In other words, as the foam is made, the foam removes PFAS compounds from the wastewater leachate. The foam layer can be separated from the de-foamed wastewater leachate and optionally further processed.

[0032] The foaming step includes bubble aeration of the wastewater leachate. The bubble aeration includes artificial bubble aeration using a bubble aeration system. In other words, the foam is not formed using natural processes

caused by the natural flow of the wastewater leachate, where foam that might be generated is soon converted based to a fluid, so that an equilibrium naturally exists, whereas the foam layer described herein is formed using bubble aeration. The bubble aeration system includes producing bubbles within the wastewater leachate for a period of time sufficient (e.g., minutes to hours to a day or more) to form the foam layer. In particular, the bubbles formed have a sufficient bubble size (e.g., about 50 to 150 μm , or about 75 to 125 μm , or about 100 μm) and air-to-liquid volume (e.g., approximately about 10:1, about 7:1, or about 4:1), and contact time (e.g., about 1 to 10 minutes, or about 1 to 7 minutes, or about 2 to 5 minutes) with the wastewater leachate to form the foam layer.

[0033] The foaming step and the separating step can occur concurrently in that as soon as foam is formed the foam layer can be separated. Alternatively, the foaming step and separating step occurs sequentially, where in one aspect, the method includes alternating between forming and separation for a period of (e.g., time hour to days to weeks).

[0034] The separating step includes separating the foam layer from the wastewater leachate using devices such as baffles or skimmers such as those used in industrial processes. The baffle or skimmer can be positioned just above or just below the wastewater leachate to remove the foam layer, where the baffle or skimmer is moving across the wastewater leachate and/or the wastewater leachate is flowing past the baffle or skimmer.

[0035] Once the foam layer is separated from the wastewater leachate, the foam layer can be processed. In general, the foam quickly converts back into fluid. The foam (or fluid) can be subjected to processing to breakdown the PFAS compounds into less hazardous compounds. The processing that can be used to breakdown the PFAS compounds can include processing using an electron beam, processing using a plasma, processing by incineration, processing by oxidation, or a combination thereof.

[0036] The present disclosure also provides for systems for removing per- and/or polyfluoroalkyl compounds (PFAS compounds) from wastewater leachate contaminated with PFAS compounds. The system can include a bubble aeration system, a separating system, and optionally a processing system. Each component of the overall system can be in communication (e.g., via a computer or otherwise) with one another so that the foam layer is formed, separated, and optionally processed. The bubble aeration system can include an air flow device (e.g., air generator or pump) in gaseous communication with a bubble aeration device (e.g., fine bubble diffusers or microbubble diffusers). The bubble aeration device is within wastewater leachate that is contaminated with PFAS compounds and is configured to produce bubbles from the air flow from the air flow device. The bubbles cause the formation of a foam layer on top of the wastewater leachate, where the foam layer comprises a concentrated amount of PFAS compounds relative to that present in the pre-foamed wastewater.

[0037] The separating system is configured to remove a portion of the foam layer from the surface of the wastewater leachate using a device such as a baffle or skimmer. The separating system collects the foam layer, which can then be processed. The separating system can be in communication with the bubble aeration system so that the device can separate the foam layer at the appropriate time or can be operated in a continuous manner if the bubble aeration

system is continuously producing bubbles. The separating system can be in communication electronically or mechanically with the processing system so that the foam layer (or fluid therefrom) can be moved to an appropriate area to be processed.

[0038] The processing system includes a device(s) that renders the PFAS compounds less hazardous relative to before processing than PFAS compound. The processing system can include an electron beam device, a plasma device, an incineration device, an oxidation device, or a combination thereof, where each can decompose the PFAS compounds to less hazardous compounds.

[0039] The present disclosure also provides for devices for removing per- and/or polyfluoroalkyl compounds (PFAS compounds) from wastewater leachate contaminated with PFAS compounds. The device can include a bubble aeration device, a separating device, and optionally a processing device. Each component of the overall device can be in communication (e.g., via a computer or otherwise) with one another so that the foam layer is formed, separated, and optionally processed. The bubble aeration device can include an air flow device (e.g., air generator or pump) in gaseous communication with a bubble aeration device (e.g., fine bubble diffusers or microbubble diffusers). The bubble aeration device is within wastewater leachate that is contaminated with PFAS compounds and is configured to produce bubbles from the air flow from the air flow device. The bubbles cause the formation of a foam layer on top of the wastewater leachate, where the foam layer comprises a concentrated amount of PFAS compounds relative to that present in the pre-foamed wastewater.

[0040] The separating device is configured to remove a portion of the foam layer from the surface of the wastewater leachate using a device such as a baffle or skimmer. The separating device collects the foam layer, which can then be processed. The separating device can be in communication with the bubble aeration system so that the device can separate the foam layer at the appropriate time or can be operated in a continuous manner if the bubble aeration device is continuously producing bubbles. The separating device can be in communication electronically or mechanically with the processing device so that the foam layer (or fluid therefrom) can be moved to an appropriate area to be processed.

[0041] The processing device includes a device(s) that renders the PFAS compounds less hazardous relative to before processing than PFAS compound. The processing device can include an electron beam device, a plasma device, an incineration device, an oxidation device, or a combination thereof, where each can decompose the PFAS compounds to less hazardous compounds.

[0042] In an aspect, the bubble aeration device or system and the separating device or system are within a single structure. The single structure can include a straight flow path or can have a serpentine, curving, winding, or sinuous path flow path having an entrance for the wastewater leachate and an exit for defoamed water. The bubble aeration system (e.g., bubble aeration device) can produce bubbles along portions or all along the flow path. The separating system or device can be designed to skim the foam layer off of the surface of the wastewater leachate along the flow path or at or near the exit of the flow path. The single structure is configured to float in a body of wastewater leachate. In an aspect, the single structure including the bubble aeration

system or device and the separating system or device can be part of a single unit that is configured to float on a body of water and positioned within the body of water. The processing system or device can be part of the single unit or can be positioned on land, where when positioned on land, the processing system or device can be in fluidic communication with the separating system of the single unit so that the separated foam can be flowed from the single unit to the processing system or device and residual treated water can be flowed back to original body of water, for example, or otherwise processed. This configuration allows the single unit to be moved between bodies of water. In other aspects, the system or device for removing PFAS compounds can be constructed as a stationary unit and wastewater leachate is flowed into the system.

EXAMPLE 1

[0043] Per- and polyfluoroalkyl substances (PFAS) are an expansive family of manmade compounds used in many commercial and industrial applications. Concern regarding environmental and human exposure to PFAS has become the subject of extensive research 1-4, and the case has been consistently made regarding the value of continued PFAS research in numerous works detailing their presence (5-7), persistence (8-10), and fate and transport (11-14). Because they typically discharge to the environment, municipal wastewater treatment plants (WWTP) have been the subject of scrutiny over PFAS levels in their effluent (15-20). As a result, facilities increasingly refuse to accept high strength industrial wastewaters rather than attempt to treat or remove the PFAS and other contaminants from large volumes of comparatively dilute sewage. Landfill leachate—the liquid formed when moisture comes into contact with waste in a landfill—is one such industrial wastewater.

[0044] Modern, sanitary municipal solid waste (MSW) landfills are engineered to use space efficiently and to prevent excessive rainwater intrusion into the waste mass (21). To protect groundwater and the surrounding environment, water which does migrate into the landfill, now leachate, is collected on a low permeability liner system and removed for disposal or treatment. Often the leachate is sent to a WWTP, though in some cases it is treated and discharged on site, or disposed of using deep well injection (22). Landfill leachate is a complex matrix (23) containing the products of anaerobic decomposition and leaching from a wide variety of waste materials. Broadly speaking, landfill leachate from a mature MSW landfill contains high concentrations of ammonia, chemical oxygen demand (COD) and salts, with trace levels of many metals and metalloids such as arsenic and antimony (24). Leachates can also contain measurable levels of other contaminants of concern, such as pesticides (25), pharmaceuticals (26), and, of immediate interest, PFAS (27-29); if it is found in the waste, it is likely to be found in the leachate (30-32).

[0045] Due to their widespread use and resistance to degradation, several PFAS compounds have been found at elevated concentrations in leachates (33,34). Of the more than 5,000 individual compounds referred to as PFAS, only two—perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS)—have been sufficiently evaluated to receive risk-based exposure guidance by the U.S. Environmental Protection Agency (35,36), and some state agencies, including the State of Florida Department of Environmental Protection (FDEP), have released provisional risk-based

thresholds for non-drinking water, such as groundwater cleanup target levels (GCTLs) (37) based on the EPA guidance. Despite being phased out of use decades ago, both compounds are still routinely found in MSW landfill leachates at concentrations orders of magnitude higher than the 70 ng L⁻¹ (combined concentration of PFOA and PFOS) EPA Lifetime Drinking Water Health Advisory and FDEP provisional GCTL (34,38). While the implications of these elevated concentrations in leachate have yet to be determined, the need for treatment and/or pretreatment technologies is clear. Due to the high concentrations of PFAS and relatively low volume, which is typically a fraction of the flow rates for WWTPs serving the same population, landfill leachates can play an important role with respect to PFAS fate and transport from consumer products to the environment. Additionally, high concentrations of PFAS in leachate provide opportunities to implement advanced treatment technologies which may not be feasible for the larger volumes and lower concentrations typically observed in a WWTP or contaminated waterbodies (39). Wei et al. (40) reviewed the current understanding of PFAS in landfill leachate and the most common PFAS treatment technologies in terms of effectiveness and feasibility. Treatment methods can be categorized as either separation (e.g., reverse osmosis (RO), activated carbon adsorption) or destructive technologies (e.g., electron beam, plasma, incineration, oxidation, sonication). PFAS destruction is usually an energy- or chemical-intense process and may require large capital investments and operational costs, making them impractical for many landfill- or WWTP-scale applications. The most effective separation technologies described in the literature come with their own disadvantages—e.g., the complexity and chemical nature of landfill leachate can cause RO membrane fouling, and all separation methods produce a contaminated residual (such as highly concentrated RO retentate or spent activated carbon) which must then be further treated or disposed. Wei et al.'s review briefly describes an in-situ foam fractionation application—similar in principal to the work described in this manuscript—for extracting PFAS from groundwater in wells. The review describes the technology as infeasible for groundwater due to the limited access to PFAS-contaminated water in wells and uncertainty about the cost versus removal efficiency. Foam separation of PFAS has been described elsewhere in the literature. Meng et al. (41) reported removal of select PFAS (PFBS, PFHxS, PFOS, PFOA and OBS) from AFFF-contaminated water and a synthetic PFOS solution using bubble aeration, and Ebersbach et al. (42) investigated the role of foam partitioning and aerosolization as removal mechanisms for 6:2 FTS (as well as select PFAAs) in electroplating wastewaters.

[0046] Here, we explore a treatment approach that takes advantage of the surfactant properties of several PFAS compounds to remove PFAS from MSW landfill leachate and explore PFAS characteristics associated with the phenomenon. Many species of PFAS tend to partition to the interface between air and water, oil and water and water and solids (43,44) and the surfactant properties of a few select PFAS species have been described in the literature (45-48). Surfactants, such as PFAS, are often used to generate foam for applications such as fire-fighting, sometimes referred to as aqueous film-forming foams, or AFFFs, a frequent source of PFAS contamination (49-51). Landfill leachates, like many wastewaters, are known to have foaming issues. By

inducing leachate foaming (i.e., generating a high air-water interfacial area) and separating the foam from the “defoamed” leachate, PFAS may then be concentrated in the foam, which subsequently coalesces back into a liquid form. Pretreatment methods common in landfill leachate collection systems include aeration, which has proven ineffective by itself for the treatment of PFAS (52). Previous studies and our findings suggest that existing treatment technologies such as dissolved air floatation (DAF) might be an effective component of a treatment train for PFAS in leachate, producing a low volume, high concentration residual which could be further subjected to stabilization or possible thermal treatment (similar to concentrated residuals from membrane technologies).

[0047] The primary objectives of this study were to (1) investigate the partitioning of mass-labeled PFAS “tracers” from leachate into foam in ten replicate experiments (reported as percent removed from leachate); (2) describe the partitioning rate of PFAS into the foam by assessing sequential foam fractions; (3) relate the partitioning results to structural characteristics of both the native and mass-labeled PFAS (e.g., implication of chain length, functional groups); (4) examine the extraction efficiency (and quantified levels for a triplicate set) of both landfill leachate and foam; and (5) and provide context regarding the implications of how foam sequestration of PFAS from leachate may lead to better overall PFAS removal solutions.

Materials and Methods

Mass-Labeled PFAS Tracer Experiment

[0048] Ten replicate experiments were designed to promote the foaming of landfill leachate, followed by the systematic removal and collection of the foam for subsequent PFAS analysis. The pre-foamed leachate, as well as defoamed leachate were also analyzed for PFAS. The leachate was collected from a 20-year old cell of an active MSW landfill in central Florida, U.S.A., via leachate lift station in a 20-L HDPE carboy and homogenized gently, with care taken not to agitate and induce foaming, before aliquots were collected for this experiment. In brief, the setup included 1,000-mL glass beakers with 750 mL of leachate added, in addition to a 750 μ L spike of a mass-labeled PFAS mixture (see Supplemental Table S1 for more information; ~20 ng/g in methanol; derived from Wellington Laboratories using two retail mixtures-MPAC-C-ES and MFTA-MXA and several individually purchased compounds). The mass-labeled PFAS spike served as a “tracer”, providing a means to follow the fate of each PFAS during the foaming process. The spike was gently added and stirred into the leachate for 60 s. Prior to the initiation of the experiment, one 50-mL aliquot of the spiked leachate was collected from each beaker as the untreated leachate sample and was saved for later analysis via ultra-high performance liquid chromatograph-tandem mass spectrometry (UHPLC-MS/MS). One sintered glass aquarium air stone, spherical and approximately 4 cm in diameter with a pore size of 100 μ m, connected to an 8 watt, four-outlet air pump using methanol-rinsed polypropylene tubing, was submerged into each leachate beaker. The air stones were used to bubble air and, subsequently, induce substantial foaming in the landfill leachate. All materials were washed using laboratory cleaner and decontaminated with HPLC grade methanol prior to use.

[0049] When the air pump was turned on, air was bubbled through the leachate at approximately 2.6 L min⁻¹ and foam began to form immediately. A stainless-steel mesh skimmer was used to collect foam as necessary to prevent foam from overflowing from the beaker, approximately every 10-15 seconds, and was transferred to an HDPE funnel mounted on a pre-weighed 250 mL HDPE bottle. Foam quickly coalesced back into a liquid form and once foam generation slowed, the air pump was turned off, the sintered glass stone was removed and a “defoamed” 50-mL aliquot of leachate was collected from the beaker and saved for later analysis. The bottles were weighed after collection to determine the mass of foam collected from each beaker. This process was repeated for ten beakers-seven as described, and three modified to collect the foam sequentially in 50-mL aliquots to compare PFAS in the first foam collected versus subsequent 50-mL fractions.

Extraction and LC-MS/MS Analysis

[0050] Leachate, foam, “defoamed” leachate samples and blanks underwent solid phase extraction developed specifically for landfill leachate samples. One 50-mL aliquot of leachate, “defoamed leachate” and foam (subsampled from the 250-mL bottles of coalesced foam) was extracted for each replicate experiment. Each full 50-mL sample bottle was weighed before and after extraction to normalize concentration and/or peak areas during data processing. Before extraction, sample pH was adjusted to 4-5 using glacial acetic acid (Fisher Scientific) and samples were centrifuged to remove/isolate suspended solids. Samples were extracted using Phenomenex solid phase extraction cartridges (Strata-X-AW 100 μ m Polymeric Weak Anion 500 mg/6 mL). The cartridges were conditioned with 4 mL of 0.3% ammonium hydroxide in methanol, 3 mL of methanol and 4 mL of an ammonium acetate buffer before samples were loaded using a 60 mL reservoir attachment. The loaded cartridges were rinsed with 4 mL of ammonium acetate buffer, then eluted into 15-mL HDPE tubes using 4 mL each of methanol and 0.3% ammonium hydroxide in methanol. Eluted extracts were evaporated from approximately 8 mL to 4 mL using a Biotage TurboVap nitrogen evaporator at 28° C.

[0051] To monitor potential sources of contamination in this process, one quality control sample was collected in the field (field blank), and the foaming procedure was repeated in triplicate using 750 mL of reagent grade water (no mass-labeled PFAS tracer added). For these three control experiments, a 50 mL aliquot was collected from the beaker, then air was bubbled using identical air stones for a period of 15 min. No foam was generated in any of the control tests, and 50 mL “after” aliquots were collected at the end of the 15 min process. Additional blanks were included throughout the extraction and analytical process.

[0052] The analyses of the samples were conducted using a Thermo Scientific Vanquish ultra-high-pressure liquid chromatography coupled to a TSQ Quantis triple quadrupole mass spectrometer (UHPLC-MS). Chromatographic separation was achieved using a Gemini C18 (100x2 mm; 3 μ m) column from Phenomenex. Water [A] and methanol [B] both containing 5 mM of ammonium acetate were used as the mobile phase. Optima grade water, methanol and ammonium acetate used in this study were purchased from Fisher Scientific. The gradient elution was set as 0-3 min 10% B, 3-4.5 min 10-35% B, 4.5-12.5 min 35-95% B, 12.5-12.51 min 95-99% B, 12.51-19 min 99% and then equilibrated to

initial conditions in 30 min. The autosampler temperature was 4° C., the flow rate and injection volume were 0.5 mL min⁻¹ and 10 µL, respectively. Each PFAS (native and/or mass-labeled) was detected using scheduled selected reaction monitoring scan (SRM) mode (monitoring two transitions, if possible). Additional LC-MS/MS analytical conditions are detailed in Table S2 (SI) and the scan parameters for all target analytes are found in Table S3 (SI).

PFAS Extraction Efficiency and Quantification Experiment

[0053] Because mass-labeled internal standards were added as “tracers” in the foam treatment study, quantification of PFAS compounds in those samples was not possible. Thus, nine additional 50-mL samples of leachate were collected from the 20-L carboy for a quantification and extraction efficiency experiment where mass-labeled P FAS internal standards (IS) were added to three 50-mL leachate samples before solid phase extraction (samples 1-3), three samples where IS was added after extraction but before evaporation (samples 4-6) and three samples where IS was added after evaporation down to 4 mL (samples 7-9). Approximately 3,000 mL of leachate was then added to a 5,000-mL glass beaker and aerated to produce approximately 500 mL of coalesced foam, which was then divided into nine 50 mL HDPE bottles for a similar foam concentration and extraction efficiency experiment (as described above for leachate). FIG. 1 describes the extraction efficiency experiment and details of the solid phase extraction and evaporation protocol are included in the “Extraction and LC-MS/MS Analysis” section. A more detailed diagram of the extraction efficiency experiment is included in FIG. 7. PFAS concentrations were calculated for three leachate and three foam aliquots (samples 1-3). For extraction efficiency calculations, the ratios between the mass-adjusted peak areas (peak area per gram of leachate) of the mass-labeled PFAS compounds were compared between the samples where IS was added before any extraction (samples 1-3), after solid phase extraction (samples 4-6) and after evaporation (samples 7-9). Results were compared between foam and leachate aliquots using a paired two-sample t-test to determine if there is a statistically significant difference in extraction efficiency.

[0054] For quantification, a calibration curve (14 levels, spanning from 10 ng/L to 100,000 ng/L) was developed for all 51 PFAS compounds (listed in Supplemental Table S4) through serial gravimetrically-weighted dilutions of primary standard solutions. Calibration information for each PFAS was derived and tailored using the prepared calibration levels. Each calibration level also contained a mixture of 24 mass-labeled P FAS internal standards (see Supplemental Table S1) at a concentration of ~ 1000 ng/L). The mass of all reagents and standards was recorded to report the most precise concentration. All mass-labeled P FAS compounds found in the mixtures and their respective gravimetric concentrations are detailed in Table S1 (SI). All PFAS standards were purchased from Wellington Laboratories Inc. (Guelph, ON, Canada).

Data Analysis

[0055] Scheduled selected-reaction monitoring (SRM) transitions were used to detect and quantify P FAS in a total of 56 samples and seven controls. The most intense transition was used to quantify PFAS while the second transition

was used to confirm identification (if possible). Acquisition and peak integration were performed using Xcalibur v.4.1 (Thermo Fisher Scientific). P FAS were quantified in three leachate and three foam samples following integration of the peak area for the most intense transition of each analyte. A linear regression model was used to build the calibration curves, with intercept, slope and correlation coefficient values calculated over the linear dynamic range for each PFAS species. Instrument detection and quantification limits (LOD and LOQ, respectively) were calculated for each compound using calibration curve and visual signal-to-noise (S/N) determination (S/N of 3 and 10 for LOD and LOQ, respectively). Detection limits were also calculated using the method described by U.S. EPA 53, however, for most compounds, the visual method produced a higher (i.e., more conservative) LOD, and 7-replicates of each limit showed higher reproducibility (RSD<15%) than the EPA approach, so the visual method was employed in this study. LOD and LOQ for all 51 compounds are included in the supplemental Table S4. For the foam experiment, we examined the intra-sample variations between leachate before and after foaming and the coalesced foam for individual replicates. Each native and mass-labeled PFAS had a percent removed calculation (i.e., percent difference between the peak area of the “pre-foam” leachate aliquot and the “defoamed” leachate aliquot) as well as a concentration factor calculation (i.e., the ratio of the foam peak area to the defoamed leachate peak area). All peak areas were normalized to the mass of sample extracted e.g., peak area g⁻¹.

Results and Discussion

Leachate Foaming Experiment

[0056] The results of this study suggest that foam sequestration is an effective technique for concentrating several P FAS compounds in landfill leachate. The average amount of foam produced among the ten replicate experiments was 153 mL of foam from 700 mL of leachate, approximately 22% of the initial volume. The percent removal was calculated for 21 mass-labeled and 37 native compounds measured above detection limits. The effectiveness of the foaming technique for concentrating P FAS varied by compound, with a mean removal percentage of 69% and a median removal percentage of 92% among the ten foaming experiments (FIGS. 2 and 3). These removal rates, in a matrix which is likely more organically complex than the wastewaters used in other studies (23), are comparable to other foam removal studies, such as Meng et al. (41) and Ebersbach et al. (42). Results for native analytes and their corresponding mass-labeled compound were similar in most cases. The mean and median difference between the percent removal of native and mass-labeled compounds were 3.8% and 2.4%, respectively, and the difference was greater than 10% for only one compound, 6:2 FTS (FIGS. 2 and 3).

[0057] The percent of each compound removed can be found in FIGS. 2 (carboxylate and sulfonate PFAS compounds) and 3 (all other PFAS compounds measured above LOD, including fluorotelomers, sulfonamides and others). In several cases, a compound was detected in the leachate and foam but not in the defoamed leachate. When this happened (for native compounds PFHxS, FHEA, FHxSA, FOUEA, FOSAA, 8:2 FTS, FDEA and EtFOSA, and mass-labeled tracers 4:2 FTS, PFHpA, PFOS, FOEA, 8:2 FTS and FOSA), the average peak area of the other replicates was

used instead. This results in a more conservative estimate than using a value of zero which would result in 100% compound removal for those replicates. Two compounds, PFECHS and the mass-labeled PFHxS tracer, were not found in any of the defoamed leachate samples, although they were found in all leachate and foam samples, so the percent removal was designated as 100%. PFHpS and 6:2 diPAP were not found in several leachate and defoamed samples but were found in the foam for all replicates, so the measured peak areas for leachate and defoamed samples for the remaining replicates were averaged to provide a substitute value and allow for an estimation of percent removal.

[0058] Two compounds, PFBA (a PFCA with carbon chain length of three) and 6:2 diPAP (a high molecular weight phosphate ester) were found, on average, in slightly higher concentrations in the defoamed leachate than in leachate, resulting in negative percent removal. However, in all of these cases, the value was close to zero with high variability (i.e., positive removal percentage was within one standard deviation). These compounds, as well as others with low, positive removal percentages (e.g., low molecular weight PFPeA (n=4) and PFPrS (n=3), and high molecular weight diS AmPAP) represented the lowest and highest molecular weight compounds, and showed some of the highest variability in removal percentage among all compounds. These compounds should be prioritized in future optimization studies; for example, Ebersbach et al. were able to increase removal of PFBS using lower air flow rates and longer treatment times (up to 120 min) 42 and Meng et al. reported improved removal of PFOS at higher ionic strengths and higher and lower adjusted pH (41).

Partitioning Behavior of PFAS into Foam

[0059] For three of the ten foaming experiments, the collection of foam was modified to collect the foam sequentially into separate 50-mL aliquots to compare PFAS concentrations in the first foam collected versus subsequent 50-mL fractions. Thus, when foam was collected in these 50-mL aliquots, percent removal for each aliquot could not be determined in the same manner. The ratio between the defoamed leachate (i.e., the endpoint of these experiments) and each aliquot can illustrate the partitioning behavior as a function of foam removed and point towards an optimum fraction of leachate to remove as foam for PFAS removal and volume reduction. In this portion of the experiment, we derived the ratio between the peak areas for each compound found in the leachate (before foaming), then in each aliquot of coalesced foam, to the defoamed leachate. As shown in FIG. 4, the peak area ratio (a proxy for relative concentration) for some compounds is significantly higher in the first and second aliquots than in the third and fourth. These highest concentration aliquots combined account for approximately the first 100 mL of coalesced foam, or 14% of the initial leachate volume (100 mL of coalesced foam divided into 700 mL initial leachate volume). Compounds with low or negative removal percentages (e.g., PFBS, PFPrS, PFBA, PFPeA, 6:2 diPAP and diS AmPAP) in FIGS. 2 and 3 showed little or no change across any of the aliquots. These compounds partition to the foam to some extent, but not preferentially compared to water (leachate) partitioning.

Foam Sequestration Effectiveness as a Function of PFAS Structure

[0060] Goss et al. (47) and Campbell et al. (45) compared air-water interface partitioning coefficients for select PFAS

compounds (fluorotelomer alcohols/olefins and perfluoroalkyl acids (PFAA), respectively) and in both cases, found a positive relationship between the number of carbons in the compounds' carbon-fluorine chains and interfacial partitioning. Using foam removal of PFAAs, Ebersbach et al. also reported an increase in elimination rate as the carbon chain length increased (42). The results of this experiment suggest a similar trend for short-chain PFAS, which reverses among longer chain species. Sequestration peaks for the carboxylates at PFHpA (carbon chain=6) and for the sulfonates at PFOS (carbon chain=8), and the ratio declines for all longer-chain compounds, although the shortest chain species (PFBA, PFPrS, n=3; and PFPeA and PFBS, n=4) remain the lowest in terms of relative concentration in the foam. FIG. 5 compares the foam: defoam peak area ratio for PFAS of different carbon chain lengths, and the same trend is demonstrated in FIGS. 2, 3 and 4—more effective foam sequestration, whether measured as the percent removed from leachate or the relative abundance in foam, as molecular weight increases within each PFAS class, to a point, then less effective among the largest compounds. Variability, measured as standard deviation among ten replicated experiments, was highest among the lowest and highest molecular weight compounds as well. This could suggest instability of the compound or a matrix interference, and this experiment was not performed to account for PFAS transformations within the leachate (e.g., due to aeration) or transportation of aerosols outside of the experimental setup (14,42).

PFAS Extraction Efficiency and Quantification Experiment

[0061] Solid phase (comparing samples 1-3 to samples 4-6) and total preparation (comparing samples 1-3 to samples 7-9, as described in Methods) efficiencies for the 22 mass-labeled PFAS are presented in FIG. 6. Mass-labeled PFAS standards of the 22 compounds listed in Table S1 (SI) were used, although one, 4:2 FTS (a fluorotelomer), was unable to be detected at the concentrations used in the standard. Total preparation efficiency was between 70% and 130% for 11 and 12 of the 21 compounds for leachate and foam, respectively. Extraction efficiency was lowest for the largest molecular weight compounds, particularly PFTeDA at less than 20% for both matrices and both extraction endpoints. Where SPE efficiency of PFTeDA in landfill leachate has been reported elsewhere, results ranged between 8% 54 and 155% 55. Additional comparison between these extraction efficiency results and selections from the literature can be found in Table S6 (SI). The paired sample t-test results suggest a significant difference between extraction efficiencies (for both solid phase extraction and total extraction) between leachate and foam ($\alpha=0.05$). On average across all 21 compounds, foam extraction efficiency was 8% higher than leachate extraction efficiency for both solid phase and total extraction. Perhaps, constituents found in the leachate matrix which interfere with PFAS extraction do not partition to the foam, making coalesced foam a "cleaner" matrix for extraction; this hypothesis would necessitate a follow-up study to confirm. The average loss during evaporation (i.e., the difference between extraction efficiency of solid phase extraction and total extraction efficiency) is 18% for both leachate and foam. Despite these losses, the nitrogen evaporation process is an important part of extraction in order to concentrate the sample and improve quantification of trace species. A thorough evaluation of PFAS loss during evaporation versus improved mass spec-

trometric response for low-concentration compounds has yet to be published. The differences between leachate and foam extraction efficiencies and evaporation loss for individual compounds is included in Table S5 (SI).

[0062] Of the 51 native PFAS measured in the quantification experiment, 32 and 36 were present in leachate and foam, respectively, at levels above the detection limit. Landfill leachate is notoriously heterogeneous, with a diversity of PFAS, wide concentration ranges and high standard deviations of concentrations reported in the literature (29,34). Based on what has been published previously, the PFAS concentrations determined from the leachate samples used in this study align with what is typical for MSW landfill leachate. Mean concentrations and standard deviations for each PFAS detected at concentrations above the detection limits, in both the foam and leachate are included in Table 1. Two compounds, 6:2 FTS and 6:2 diPAP, were measured in every field and control blank, so the average peak area of the blanks was subtracted from the samples.

TABLE 1

Mean PFAS concentrations and standard deviation in leachate and coalesced foam. A complete list of the compounds included in this study, as well as full names and classification details is found in Table S4 of the Supplemental Information.		
Compound	Mean Concentration (Standard Deviation)	
	Leachate (ng/L) n = 3	Foam (ng/L) n = 3
PFBA	+1,021.4 (437.6)	660.5 (200.2)
PFPeA	837.1 (118.5)	930.2 (111.4)
PFHxA	+2,178.6 (16.2)	+7987.7 (259.5)
PFHpA	454.1 (13.1)	+3034.3 (112.1)
PFOA	950.9 (58.1)	+5,659.4 (151.9)
PFNA	63.8 (2.1)	272.3 (7.5)
PFDA	86.9 (4.2)	249.7 (40.7)
PFUnDA	11.5 (0.9)	28.2 (5.0)
PFDoDA	11.2 (1.5)	29.4 (1.9)
PFTTrDA	BDL	2.4 (0.2)
PFTeDA	*0.9 (0.2)	*1.5 (0.2)
PFPrS	10.8 (1.7)	12 (3.3)
PFBS	+752.6 (119.7)	+1,806.1 (116.6)
PFPeS	24.6 (4.5)	+62.5 (1.4)
Σ PFHxS	2,058.9 (280)	+10,630.3 (583.9)
PFHpS	BDL	*2.9 (0.7)
Σ PFOS	103.9 (13.6)	199.7 (5.6)
PFDS	BDL	*2.6 (0.5)
4:2 FTS	BDL	4.3 (0.8)
6:2 FTS	+134.7 (29.1)	+820.7 (146.3)
8:2 FTS	22.8 (2.1)	+32.4 (11.8)
10:2 FTS	6.2 (0.1)	31.6 (2.2)
FHEA	329.4 (8.5)	+1,799.5 (72.3)
FOEA	131.9 (10.7)	377.6 (71.4)
FDEA	*11.5 (0.8)	57.3 (14.4)
FOUEA	5.9 (0.9)	+16.1 (3.6)
PFECHS	*0.4 (0.1)	3.1 (0.4)
FHxSA	*2.1 (0.7)	5.8 (0.3)
FOSA	7.6 (0.9)	17.4 (2.6)
FOSAA	3.4 (0.2)	5.5 (0.4)
MeFOSAA	111.5 (16.1)	269.9 (45.9)
EtFOSAA	85.5 (4.2)	180.1 (35.3)
MeFOSA	*0.7 (0)	*1.3 (0.1)
EtFOSA	6.2 (0.7)	11.9 (2.6)
6:2 diPAP	4.2 (0.3)	3.6 (0.3)
diSAmPAP	4.3 (1.8)	+8.5 (3.9)

BDL indicates compounds for which the peak area was below the instrument detection limits

*compounds found above detection limits but below the limit of quantification (LOQ) in at least one of the three samples

+denotes concentrations above the highest point of the calibration curve.

Implications

[0063] The experimental results presented here have implications for the analysis of PFAS in water as well as wastewater treatment applications. This foam generation and collection technique can be used to concentrate several PFAS within a matrix (in this case, landfill leachate), which can enhance PFAS measurement in complex matrices, particularly species of interest which occur in low concentrations. With respect to engineering applications, the results suggest that the separation of PFAS chemicals into a volume-reduced, highly concentrated, coalesced foam may prove a valuable addition to leachate treatment strategies at MSW landfills. A common practice at landfills sites is aeration of leachate in lagoons or similar storage units, typically using surface aerators. Occasionally, operators will include a dissolved air flotation unit, which by their nature include removal of a foam fraction. The process described herein is simple and could feasibly be applied at a relatively low cost at most landfills, even in discrete locations within a landfill site, optimized to address specific leachate streams.

[0064] A majority of the dominant PFAS species detected in a typical active MSW landfill leachate were removed at levels well over 80%. This includes the two PFAS species with EPA-recommended exposure guidances, PFOS and PFOA. If we apply the mean percent removal from the foam experiment to the initial concentrations of these compounds, the defoamed leachates would contain 26.3 ng L⁻¹ PFOA and 3.4 ng L⁻¹ PFOS, well below the EPA drinking water guidance and FDEP GCTL threshold of 70 ng L⁻¹ combined. Low molecular weight compound PFBA was one of the most highly concentrated compounds in this leachate and did not respond to foam separation. This low response has been reported for other sequestration methods, such as granular activated carbon³⁹. It is possible that a modification of this experiment, for instance pH adjustment, may change the partitioning behavior of highly mobile species.

[0065] Additional research is required to optimize foaming strategies that both maximize PFAS concentration (particularly for PFAS which did not partition to the foam under the conditions of this study) and minimize foam volume (as sequential foam collection found that the highest rate of removal occurs in the initial generation of foam, approximately the first 14% of leachate removed). While PFTeDA exhibited the lowest extraction efficiency and poor foam partitioning, other PFAS with low recoveries (e.g., FOSA, MeFOSA, PFDODA, EtFOSA) had high foam partitioning and thus would be good candidates for foam-augmented analysis. Partitioning tendencies of most precursor species and some of the less common PFAAs are not well understood, and more research may shed light on the behavior of these compounds in this experiment. Strategies for managing concentrated leachate streams (to align with the foaming approach) require further investigation, whether they be destructive technologies such as plasma, sonication, or chemical oxidation, or stabilization techniques that will allow the material to be disposed of in the landfill in a manner such that PFAS is not released back into the leachate.

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Supplemental Information

TABLE S1

Mass-labeled PFAS tracer compounds. The molecular formula includes deuterated/ ¹³ C information from the manufacturer (Wellington Laboratories).				
Abbreviation	Compound	Molecular Formula	PFAS Type	Concentration (ng/g)
M4PFBA	perfluorobutanoic acid	¹³ C ₄ HF ₇ O ₂	carboxylate	22.118
M5PFPeA	perfluoropentanoic acid	¹³ C ₅ HF ₉ O ₃	carboxylate	22.118
M5PFHxA	perfluorohexanoic acid	¹³ C ₅ ¹² CHF ₁₁ O ₂	carboxylate	22.118
M4PFHpA	perfluoroheptanoic acid	¹³ C ₄ ¹² C ₃ HF ₁₃ O ₂	carboxylate	22.118
M8PFOA	perfluorooctanoic acid	¹³ C ₈ HF ₁₅ O ₂	carboxylate	22.118
M9PFNA	perfluorononanoic acid	¹³ C ₉ HF ₁₇ O ₂	carboxylate	22.118
M6PFDA	perfluorodecanoic acid	¹³ C ₆ ¹² C ₄ HF ₁₉ O ₂	carboxylate	22.118
M7PFUdA	perfluoroundecanoic acid	¹³ C ₇ ¹² C ₄ HF ₂₁ O ₂	carboxylate	22.118
MPFDoA	perfluorododecanoic acid	¹³ C ₂ ¹² C ₁₀ HF ₂₃ O ₂	carboxylate	22.118
M2PFTeDA	perfluorododecanoic acid	¹³ C ₂ ¹² C ₁₂ HF ₂₇ O ₂	carboxylate	22.118
M8FOSA	perfluorooctane sulfonamide	¹³ C ₈ H ₂ F ₁₇ NO ₂ S	sulfonamide	22.118
d3-N-MeFOSAA	n-methylperfluoro-1-octanesulfonamidoacetic acid	C ₁₁ D ₃ H ₃ F ₁₇ NO ₄ S	sulfonamidoacetic acid	22.118
d5-N-EtFOSAA	n-ethylperfluoro-1-octanesulfonamidoacetic acid	C ₁₂ D ₃ H ₃ F ₁₇ NO ₄ S	sulfonamidoacetic acid	22.118
M3PFBS	perfluorobutyl sulfonate	¹³ C ₃ ¹² CHF ₉ O ₃ S	sulfonate	20.547
M3PFHxS	perfluorohexyl sulfonate	¹³ C ₃ ¹² C ₃ HF ₁₃ O ₃ S	sulfonate	20.923
M8PFOS	perfluorooctyl sulfonate	¹³ C ₈ HF ₁₇ O ₃ S	sulfonate	21.167
M2-4:2FTS	4:2 fluorotelomer sulfonate	¹³ C ₂ ¹² C ₄ H ₄ F ₉ O ₃ SNa	fluorotelomer	20.680
M2-6:2FTS	6:2 fluorotelomer sulfonate	¹³ C ₂ ¹² C ₆ H ₄ F ₁₃ O ₃ SNa	fluorotelomer	20.990
M2-8:2FTS	8:2 fluorotelomer sulfonate	¹³ C ₂ ¹² C ₈ H ₄ F ₁₇ O ₃ SNa	fluorotelomer	21.189
MFHEA	6:2 fluorotelomer carboxylic acid	¹³ C ₂ ¹² C ₆ H ₃ F ₁₃ O ₂	telomer acid	23.002
MFOEA	n-2-perfluorooctyl ethanoic acid	¹³ C ₂ ¹² C ₈ H ₃ F ₁₇ O ₂	telomer acid	23.002
MFDEA	n-2-perfluorodecyl ethanoic acid	¹³ C ₂ ¹² C ₁₀ H ₃ F ₂₁ O ₂	sulfonamidoacetic acid	23.002
M3HFPO-DA	hexafluoropropylene oxide dimer acid (Gen-X)	¹³ C ₃ ¹² C ₃ HF ₁₁ O ₃	n/a	111.026
d3-N-MeFOSA-M	n-methylperfluorooctane-1-sulfonamide	C ₉ D ₃ HF ₁₇ NO ₂ S	sulfonamide	118.144
d5-N-EtFOSA-M	n-ethylperfluorooctane-1-sulfonamide	C ₁₀ D ₃ HF ₁₇ NO ₂ S	sulfonamide	111.379

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TABLE S2

LC-MS/MS Analytical Conditions	
Chromatography Conditions - Thermo Scientific Vanquish UHPLC	
LC conditions	Column: Gemini Phenomenex 100 × 2 mm 3 μm Gradient elution using Water and methanol both containing 5 mM of ammonium acetate Oven temperature 40° C. Flow rate: 0.5 mLmin ⁻¹

TABLE S2-continued

LC-MS/MS Analytical Conditions	
Injection volume: 10 μ L	
Mass Spectrometry Analysis - Thermo Quantis	
Ion Source	Electrospray - negative mode
parameters:	Ion Spray: 1500 V
	Sheath Gas: 50 Arb
	Auxilliary Gas: 10 Arb
	Ion Transfer tube Temperature: 250° C.
	Vaporizer temperature: 550° C.

TABLE S3

Target PFAS Analytes SRM experiment - Scan parameters				
Analytes (abbreviation)	Precursor Ion (m/z)	Fragment Ion (m/z)	Collision Energy (V)	RF Lens (V)
PFBA	213	168.9	11	75
M3PFBA	216	172	11	75
M4PFBA	217	172	11	75
L-PFPrS-1	249.05	79.9	28.84	138
L-PFPrS-2	249.05	98.9	25.68	138
PFPeA	263	219	11	64
M5PFPeA	268	223	11	64
FBSA-1	297.95	77.9	24.8	144
FBSA-2	297.95	118.9	17.97	144
L-PFBS-1	298.975	79.9	32	152
L-PFBS-2	298.975	98.9	28.46	152
M3PFBS	302	99	29	152
PFHxA	312.9	269	10	73
M5PFHxA	318	273	10	73
4:2FTS-2	326.962	81	28.5	138
4:2FTS-1	326.962	306.8	17.97	138
M2-4:2FTS	329	81	17.97	138
HFPO-DA	329	285	7	65
PFPeS-1	348.975	79.9	34.28	174
PFPeS-2	348.975	98.9	31.45	174
PFHpA-1	362.9	169	17	81
PFHpA-2	362.9	318.9	11	81
M4PFHpA	367	322	11	81
FHEA	376.9	293	20	100
NaDONA	377	251	10	280
FHxSA-1	397.96	77.9	28.42	185
FHxSA-2	397.96	377.9	20.33	185
L-PFHxS-2	398.975	79.9	37.48	174
L-PFHxS-1	398.975	98.9	34.95	174
M3PFHxS	402	99	35	151
PFOA-1	413	169.0	19	94
PFOA-2	413	368.9	11	94
M2PFOA	415	370	11	94
M8PFOA	421	376	11	94
6:2FTS-2	426.962	80.9	29.94	166
6:2FTS-1	426.962	406.9	21.39	166
M2-6:2FTS-2	429	81	21.39	166
M2-6:2FTS-1	429	376	21.39	166
PFHpS-1	448.925	79.9	39.2	223
PFHpS-2	448.925	98.9	37.56	223
FOUEA	456.9	392.9	12	100
PFECHS-2	460.925	98.9	28.76	171
PFECHS-1	460.925	380.9	26.15	171
PFNA-1	463	218.9	16	101
PFNA-2	463	418.9	12	101
M9PFNA	472	427	12	101
FOEA	476.9	393	18	100
MFOEA-1	479.01	394	11	107
N-AP-FHxSA-1	483.05	168.9	26.57	244
N-AP-FHxSA-2	483.05	318.9	21.55	244
FOSA-I-1	497.962	77.9	30.44	206
FOSA-I-2	497.962	477.9	23.16	206
L-PFOS-1	498.925	79.9	40.26	214
L-PFOS-2	498.925	98.9	40.55	214
MPFOS-2	502.925	79.9	41.86	266

TABLE S3-continued

Target PFAS Analytes SRM experiment - Scan parameters				
Analytes (abbreviation)	Precursor Ion (m/z)	Fragment Ion (m/z)	Collision Energy (V)	RF Lens (V)
MPFOS-1	502.925	98.8	41.86	266
M8FOSA-I-2	505.95	77.9	30.4	196
M8FOSA-I-1	505.95	485.9	22.94	196
M8PFOS-1	507	80	44	259
M8PFOS-2	507	99	44	259
N-MeFOSA-M-2	511.962	168.9	26.23	187
N-MeFOSA-M-1	511.962	219	23.62	187
PFDA	513	469	11	94
8Cl-PFOS-1	514.925	79.9	41.44	273
8Cl-PFOS-2	514.925	98.9	40.3	273
d-N-MeFOSA-M-2	514.995	168.9	26.23	194
d-N-MeFOSA-M-1	514.995	218.9	23.74	194
MPFDA	515	470	11	94
M6PFDA	519	474	11	94
N-EtFOSA-M-2	525.962	168.9	26.69	209
N-EtFOSA-M-1	525.962	219	24.04	209
8:2FTS-2	526.988	486.8	30.57	179
8:2FTS-1	526.988	506.8	24.76	179
M2-8:2FTS	529	81	24.76	179
9Cl-PF3ONS-1	530.838	350.9	24.71	155
d-N-EtFOSA-M-3	530.925	169	26.69	203
d-N-EtFOSA-M-2	530.925	219	24.76	203
L-PFNS-1	548.975	80	42.99	280
L-PFNS-2	548.975	98.9	42.78	280
FOSAA-2	555.95	418.9	23.45	210
FOSAA-1	555.95	497.8	26.06	210
FDUEA	557	493	21	280
PFUnDA	563	518.9	11	116
N-MeFOSAA-1	569.975	418.8	18.18	178
N-MeFOSAA-2	569.975	482.8	14.39	178
M7PFUnDA-2	570	525	11	116
d3-N-MeFOSAA-1	572.962	418.9	18.56	174
d3-N-MeFOSAA-2	572.962	482.8	14.06	174
FDEA	576.8	493	8	100
N-EtFOSAA-2	583.962	418.9	18.52	179
N-EtFOSAA-1	583.962	525.9	18.1	179
d5-N-EtFOSAA-2	589.012	418.9	19.15	176
d5-N-EtFOSAA-1	589.012	530.9	19.36	176
L-PFDS-1	598.925	79.9	44.51	280
L-PFDS-2	598.925	98.9	46.87	280
PFDoDA-2	612.925	318.9	17.51	129
PFDoDA-1	612.925	568.9	9.8	129
MPFDoA	615	570	9.8	129
10:2FTS-2	626.95	80.9	34.19	280
10:2FTS-1	626.95	606.8	29.01	280
HCl-PF3OUdS	630.95	450.8	27.2	225
SAmPAP-1	650	526	25	280
PFTTrDA-2	662.812	318.9	18.98	136
PFTTrDA-1	662.812	618.9	10.73	136
L-PFDoS-1	698.925	80	55	280
L-PFDoS-3	698.925	99	55	280
6:6PFPI	700.9	400.9	55	188
PFTeDA	713	669	12	107
M2PFTeDA	715	670	12	107
6:2diPAP-2	788.925	96.9	29.3	216
6:2diPAP-1	788.925	442.9	17.05	216
6:8PFPI-2	800.9	400.9	55	188
6:8PFPI-1	800.9	500.8	55	188
PFHxDA-2	812.875	418.9	20.42	167
PFHxDA-1	812.875	768.8	11.95	167
6:2/8:2diPAP	889	443	20	280
PFODA-2	912.888	318.8	25.05	188
PFODA-1	912.888	868.8	13.3	188
8:2diPAP-2	988.888	522.9	27.11	280
8:2diPAP	989	543	20	280
diSAmPAP	1202.95	525.9	25	280

*-1 and -2 means first and second transition of the analyte—first transition used for quantitation and second transition for confirmation.

TABLE S4

PFAS standard compounds and corresponding mass-labeled compounds used to develop calibration curves.					
Abbreviation	Compound	PFAS Type	Correlative Labeled Compound	LOD (ng/L)	LOQ (ng/L)
PFBA	perfluorobutanoic acid	carboxylate	M4PFBA	4.18	8.09
PFPrS	perfluoropropane sulfonate	sulfonate	M5PFPeA	1.66	6.42
PFPeA	perfluoropentanoic acid	carboxylate	M5PFPeA	20.92	182.15
PFBS	perfluorobutyl sulfonate	sulfonate	M3PFBS	3.70	18.52
FBSA	perfluorobutane sulfonamide	sulfonamide	M3PFBS	80.74	398.28
4:2FTS	4:2 fluorotelomer sulfonate	telomer sulfonate	M24:2FTS	3.91	19.56
PFHxA	perfluorohexanoic acid	carboxylate	M5PFHxA	4.18	20.92
PFPeS	perfluoropentane sulfonate	sulfonate	M3HFPO-DA	3.93	19.67
PFHxS	perfluorohexyl sulfonate	sulfonate	M3PFHxS	19.08	35.46
PFHpA	perfluoroheptanoic acid	carboxylate	M4PFHpA	4.18	20.92
NaDONA	dodecafluoro-3H-4,8-dioxanonoate	other	M4PFHpA	76.85	379.09
FHEA	6:2 fluorotelomer carboxylic acid	telomer acid	M4PFHpA	35.40	165.86
AP-FHxSA			M26:2FTS	32.48	362.66
PFECHS	n-decafluoro-4-ethylcyclohexanesulfonate	cyclic	M26:2FTS	3.32	16.59
FHxSA	perfluorohexane sulfonamide	sulfonamide	M3PFHxS	9.76	36.26
6:2FTS	6:2 fluorotelomer sulfonate	telomer sulfonate	M26:2FTS	3.97	19.87
PFHpS	perfluoroheptane sulfonate	sulfonate	M26:2FTS	9.94	36.93
PFOA	perfluorooctanoic acid	carboxylate	M8PFOA	10.46	38.88
PFOS	perfluorooctyl sulfonate	sulfonate	M8PFOS	19.36	81.44
PFNA	perfluorononanoic acid	carboxylate	M9PFNA	4.18	20.92
Cl-PFOS	8-chlorohexadecafluoro-3-oxaactane-1-sulfonate	other	M8PFOS	17.06	71.76
FOEA	n-2-perfluorooctyl ethanoic acid	telomer acid	MFOEA	35.92	168.30
FOUEA	2H-perfluoro-2-decanoic acid	unsaturated telomer acid	MFOEA	3.18	6.14
Cl-PF3ONS	9-chlorohexadecafluoro-3-oxanonane-1-sulfonate	other	M28:2FTS	3.30	6.38
FOSAA	2-perfluorooctanesulfonamido acetic acid	sulfonamidoacetic acid	M28:2FTS	8.83	17.65
PFNS	perfluorononane sulfonate	sulfonate	M28:2FTS	10.04	84.48
8:2FTS	8:2 fluorotelomer sulfonate	telomer sulfonate	M28:2FTS	20.08	37.32
FOSA	perfluoro-1-octanesulfonamide	sulfonamide	M8FOSA	8.09	38.88
PFDA	Perfluorodecanoic acid	carboxylate	M6PFDA	1.62	8.09
N-MeFOSAA	N-methylperfluoro-1-octanesulfonamidoacetic acid	sulfonamidoacetic acid	d3-N-MeFOSAA	8.09	88.00
PFDS	perfluorodecane sulfonate	sulfonate	d5-N-EtFOSAA	20.19	84.92
PFUnDA	perfluoroundecanoic acid	carboxylate	M7PFUnDA	4.18	20.92
N-EtFOSAA	N-ethylperfluoro-1-octanesulfonamidoacetic acid	sulfonamidoacetic acid	d5-N-EtFOSAA	20.92	88.00
FDUEA	n-2-perfluorodecyl ethanoic acid	unsaturated telomer acid	M7PFUnDA	1711.28	13092.94
FDEA	n-2-perfluorodecyl ethanoic acid	saturated telomer acid	M7PFUnDA	35.67	167.14
Cl-PF3OUdS	11-chloroeicosafluoro-3-oxaundecane-1-sulfonate	other	d5-N-EtFOSAA	3.39	6.55
N-MeFOSA	N-methylperfluorooctane sulfonamide	sulfonamide	d-N-MeFOSA	3.58	33.29
PFDoDA	perfluorododecanoic acid	carboxylate	MPFDoDA	4.18	8.09
10:2FTS	10:2 fluorotelomer sulfonate	telomer sulfonate	MPFDoDA	8.68	32.24
6:6PFPi	sodium bis(perfluorohexyl)phosphinate	perfluoroalkyl-phosphinate	MPFDoDA	3.45	17.23
N-EtFOSA	N-ethylperfluorooctane sulfonamide	sulfonamide	d-N-EtFOSA	17.43	32.39
PFDoDS	perfluorododecane sulfonate	sulfonate	MPFDoDA	17.13	31.83
PFTriDA	perfluorotridecanoic acid	carboxylate	d-N-EtFOSA	6.97	8.09
6:2diPAP	6:2 fluorotelomer phosphate diester	phosphate ester	M2PFTeDA	3.66	18.29
PFTreDA	perfluorotetradecanoic acid	carboxylate	M2PFTeDA	4.18	20.92
6:8PFPi	sodium perfluorohexylperfluoro-octylphosphinate	perfluoroalkyl-phosphinate	M2PFTeDA	1.78	8.89
6:2/8:2diPAP			M2PFTeDA	6.94	33.34
PFHxDA	perfluorohexadecanoic acid	carboxylate	M2PFTeDA	3.16	6.12
8:2diPAP	6:2 fluorotelomer phosphate diester	phosphate ester	M2PFTeDA	9.00	33.46

TABLE S4-continued

PFAS standard compounds and corresponding mass-labeled compounds used to develop calibration curves.					
Abbreviation	Compound	PFAS Type	Correlative Labeled Compound	LOD (ng/L)	LOQ (ng/L)
PFODA	perfluorooctadecanoic acid	carboxylate	M2PFTeDA	3.51	6.80
diSAmPAP	sodium bis-(2-N-ethylperfluorooctane-1-sulfonamido)ethyl	phosphate ester	M2PFTeDA	15.68	29.13

When the same compound was not available as mass-labeled, the closest retention time labeled compound was selected.

Detection and quantification limits (LOD and LOQ) reflect concentrations in the 4-mL solvent-eluted samples.

In order to compare these values to leachate concentrations, multiply the instrument detection limit by the ratio between volumes, in this case, 4 mL divided by the extracted volume of each leachate sample (approximately 50 mL).

TABLE S5

Extraction efficiency experiment result details. Compounds are listed in increasing order of retention time.								
Compound	Extraction Efficiency (%)			Total Extraction Efficiency (%)			Evaporation Loss (%)	
	Leachate	Foam	Δ	Leachate	Foam	Δ	Leachate	Foam
PFBA	114	147	34	107	95	-12	6	52
PFPeA	104	115	11	88	84	-4	16	31
PFBS	84	131	47	73	100	27	11	31
PFHxA	93	106	14	79	91	11	14	16
PFHxS	106	128	21	80	92	12	26	36
PFHpA	102	113	11	82	93	11	21	20
6:2 FTS	84	99	16	70	85	15	13	14
PFOA	101	108	6	80	88	7	21	20
PFOS	104	108	5	73	104	31	31	4
PFNA	100	110	10	77	88	11	22	22
FOE A	85	90	5	71	73	2	14	16
8:2 FTS	75	93	18	51	86	35	24	7
FOSA	64	59	-4	46	46	0	17	13
PFDA	85	84	-1	61	69	8	24	14
N-MeFOSAA	73	79	6	55	64	10	18	15
N-Et-FOSAA	72	66	-7	53	54	1	20	12
PFUnDA	65	64	-1	45	51	6	20	13
N-MeFOSA	57	54	-3	38	42	5	20	12
PFDoDA	44	43	-1	31	34	3	13	9
N-EtFOSA	54	42	-12	37	35	-2	16	7
PFTeDA	19	17	-2	14	14	0	6	3
MEAN	80.1	88.3	8.2	62.4	70.8	8.4	17.7	17.5

TABLE S6

Comparison of landfill leachate extraction efficiency results from previous reports, values are in %.					
The comparison was made for PFAS evaluated in common with this study, most of these studies included additional compounds not listed here. Current solid phase extraction methods for PFAS in leachate vary between researchers. The procedure used in this study features commonly employed materials, such as WAX cartridges ^{1,2} , methanolic ammonium hydroxide ^{1,2} (however, the concentration varies), and methanol, which was used in some portion of all SPE approaches referenced. Other efficiency experiment results in the literature, which were not included in this table, such as Li et al. ⁵ , which reported a range of recoveries (20% to 120%) for all compounds and no individual PFAS, and Gonzalez-Barreiro et al. ⁶ , which also reported similar recoveries for two SPE methods (ranging from 11% to 96% for Method A and 8% to 102% for Method B) using wastewater effluent, had comparable results. Optimization of PFAS extraction protocols for multiple compounds with a wide variety of extraction behaviors is a challenge, and thus, solid phase extraction efficiency for different compounds varies widely (i.e., from 8% to 160%) among these studies; this method resulted in a comparable range (19% to 114%). Community-wide efforts aimed at harmonizing/standardizing PFAS measurement in leachate (e.g., development of a Standard Reference Material) would provide a means to better evaluate these workflows.					
	This study	Benskin et al. (2010) ¹	Busch et al. (2010) ²	Huset et al. (2011) ³	Allred et al. (2014) ⁴
Extraction Type	SPE	SPE	SPE	SPE	LLE
PFBA	114	54	53 ± 21	25 ± 5	11

TABLE S6-continued

Comparison of landfill leachate extraction efficiency results from previous reports, values are in %.					
The comparison was made for PFAS evaluated in common with this study, most of these studies included additional compounds not listed here. Current solid phase extraction methods for PFAS in leachate vary between researchers. The procedure used in this study features commonly employed materials, such as WAX cartridges ^{1,2} , methanolic ammonium hydroxide ^{1,2} (however, the concentration varies), and methanol, which was used in some portion of all SPE approaches referenced. Other efficiency experiment results in the literature, which were not included in this table, such as Li et al. ⁵ , which reported a range of recoveries (20% to 120%) for all compounds and no individual PFAS, and Gonzalez-Barreiro et al. ⁶ , which also reported similar recoveries for two SPE methods (ranging from 11% to 96% for Method A and 8% to 102% for Method B) using wastewater effluent, had comparable results. Optimization of PFAS extraction protocols for multiple compounds with a wide variety of extraction behaviors is a challenge, and thus, solid phase extraction efficiency for different compounds varies widely (i.e., from 8% to 160%) among these studies; this method resulted in a comparable range (19% to 114%). Community-wide efforts aimed at harmonizing/standardizing PFAS measurement in leachate (e.g., development of a Standard Reference Material) would provide a means to better evaluate these workflows.					
	This study	Benskin et al. (2010) ¹	Busch et al. (2010) ²	Huset et al. (2011) ³	Allred et al. (2014) ⁴
PFPeA	104	68*		39 ± 8	41
PFBS	84	68*		54 ± 2	
PFHxA	93	121	47 ± 17	64 ± 9	92
PFHxS	106	102*	49 ± 19	80 ± 3	100
PFHpA	102	137*		110 ± 12	
6:2 FTS	84			74 ± 2	100
PFOA	101	136	50 ± 19	72 ± 16	100
PFOS	104	96	60 ± 24	69 ± 1	110
PFNA	100	139	54 ± 23	120 ± 18	100
FOEA	85	103	45 ± 22		110
8:2 FTS	75			94 ± 7	
FOSA	64	132*		110 ± 8	
PFDA	85	146*	48 ± 22	73 ± 7	110
MeFOSAA	73	123*		71 ± 4	100
EtFOSAA	72	116*		65 ± 3	110
PFUnDA	65	160*	47 ± 20	44 ± 3	100
MeFOSA	57		60 ± 23		
PFDoA	44	144*	45 ± 20	34 ± 6	100
EtFOSA	54		54 ± 18		
PFTeDA	19	155*		8 ± 3	

*Results for these compounds are for non-mass-labeled standards, the remaining extraction efficiencies are for mass-labeled. References for supplemental information

¹Benskin, J. P.; Ikonomou, M. G.; Woudneh, M. B.; Cosgrove, J. R. Rapid Characterization of Perfluoroalkyl Carboxylate, Sulfonate, and Sulfonamide Isomers by High-Performance Liquid Chromatography-Tandem Mass Spectrometry. *J. Chromatogr. A* 2012, 1247, 165-170. <https://doi.org/10.1016/j.chroma.2012.05.077>.

²Busch, J.; Ahrens, L.; Sturm, R.; Ebinghaus, R. Polyfluoroalkyl Compounds in Landfill Leachates. *Environ. Pollut.* 2010, 75(5), 1467-1471. <https://doi.org/10.1016/j.envpol.2009.12.031>.

³Huset, C. A.; Barlaz, M. A.; Barofsky, D. F.; Field, J. A. Quantitative Determination of Fluorochemicals in Municipal Landfill Leachates. *Chemosphere* 2011, 82 (10), 1380-1386. <https://doi.org/10.1016/j.chemosphere.2010.11.072>.

⁴Allred, B. M.; Lang, J. R.; Barlaz, M. A.; Field, J. A. Orthogonal Zirconium Dioxide/C18 Liquid Chromatography-Tandem Mass Spectrometry Analysis of Poly and Perfluoroalkyl Substances in Landfill Leachate. *J. Chromatogr. A* 2014, 1359, 202-211. <https://doi.org/10.1016/j.chroma.2014.07.056>.

⁵Li, B.; Danon-Schaffer, M. N.; Li, L. Y.; Ikonomou, M. G.; Grace, J. R. Occurrence of PFCs and PBDEs in Landfill Leachates from Across Canada. *Water, Air, Soil Pollut.* 2012, 223 (6), 3365-3372. <https://doi.org/10.1007/s11270-012-1115-7>.

⁶González-Barreiro, C.; Martínez-Carballo, E.; Sika, A.; Scharf, S.; Gans, O. Method Optimization for Determination of Selected Perfluorinated Alkylated Substances in Water Samples. *Anal. Bioanal. Chem.* 2006, 386 (7), 2123-2132. <https://doi.org/10.1007/s00216-006-0902-7>.

EXAMPLE 2

[0121] The laboratory experiment described in Example 1 was used to design a field application of foam separation of PFAS in landfill leachate. The field unit includes a simple, portable, two-stage PFAS separation unit which will use foam flotation followed by either membrane or sorbent separation to concentrate PFAS in a low volume waste stream. Additional laboratory studies will be used to optimize (based on site-specific matrix characteristics and PFAS contamination) the design and construction of a deployable unit which uses bubble aeration to produce and separate a P FAS-rich foam, which will be separated and undergo additional separation, stabilization and/or destructive treatment. In the field unit, PFAS concentrations in the treated water as well as air effluent will be monitored. The schematic included in FIG. 8 includes an additional apparatus similar

to that described in EPA OTM-45, a method in development for the measurement of volatile and semi-volatile PFAS in gases.

[0122] It should be noted that ratios, concentrations, amounts, and other numerical data may be expressed herein in a range format. It is to be understood that such a range format is used for convenience and brevity, and thus, should be interpreted in a flexible manner to include not only the numerical values explicitly recited as the limits of the range, but also to include all the individual numerical values or sub-ranges encompassed within that range as if each numerical value and sub-range is explicitly recited. To illustrate, a concentration range of “about 0.1% to about 5%” should be interpreted to include not only the explicitly recited concentration of about 0.1 wt % to about 5 wt %, but also include individual concentrations (e.g., 1%, 2%, 3%, and 4%) and the sub-ranges (e.g., 0.5%, 1.1%, 2.2%, 3.3%, and 4.4%)

within the indicated range. In an embodiment, the term “about” can include traditional rounding according to significant figures of the numerical value. In addition, the phrase “about ‘x’ to ‘y’” includes “about ‘x’ to about ‘y’”.

[0123] It should be emphasized that the above-described embodiments of the present disclosure are merely possible examples of implementations, and are set forth only for a clear understanding of the principles of the disclosure. Many variations and modifications may be made to the above-described embodiments of the disclosure without departing substantially from the spirit and principles of the disclosure. All such modifications and variations are intended to be included herein within the scope of this disclosure.

1. A system for removing per- and/or polyfluoroalkyl compounds (PFAS compounds) from wastewater leachate contaminated with PFAS compounds, comprising:

a bubble aeration system comprising an air flow device in communication with a bubble aeration device, wherein the bubble aeration device is within pre-foamed wastewater leachate contaminated with PFAS compounds, wherein the bubble aeration device is configured to produce bubbles from the air flow from the air flow device, wherein the bubbles form a foam layer on top of the wastewater leachate, wherein the foam layer comprises a concentrated amount of PFAS compounds relative to that present in the pre-foamed wastewater; and

a separating system configured to remove a portion of the foam layer from the surface of the wastewater leachate to form defoamed water.

2. The system of claim 1, wherein the air flow device is an air generator or pump and wherein the bubble aeration device is a structure that is configured to form bubbles as air is flowed through the bubble aeration device.

3. The system of claim 1, wherein the separating system comprising a structure that is configured to skim the foam layer off of the surface of the wastewater leachate.

4. The system of claim 2, wherein a single structure includes has a winding flow path having an entrance for the wastewater leachate and an exit for defoamed water, wherein along the winding flow path the bubble aeration device produces bubbles

5. The system of claim 4, wherein along the winding flow path the separating system is skimming the foam layer off of the surface of the wastewater leachate or wherein the separating system skims the foam layer off at the exit of the winding flow path.

6. The system of claim 5, wherein the single structure is configured to float in a body of wastewater leachate.

7. The system of claim 6, wherein bubble aeration system and the separating system of in a single unit that is configured to float on a body of water and positioned within the body of water.

8. The system of claim 1, wherein the bubble aeration system includes a path configured to flow the wastewater leachate, wherein the path is a serpentine path, a curving path, a winding path, or a sinuous path.

9. The system of claim 1, wherein the separating system configured to remove a portion of the foam layer from the surface of the wastewater leachate at multiple points along the path.

10. The system of claim 1, wherein the separating system includes a skimmer, a baffle, or both, wherein the separating occurs as the de-foamed wastewater leachate flows past the skimmer or baffle along the path.

11. The system of claim 1, further comprising a processing system includes a device that renders the PFAS compounds less hazardous relative to before processing than PFAS compound.

12. The system of claim 1, wherein processing system includes: an electron beam device, a plasma device, an incineration device, an oxidation device, or a combination thereof.

13. A device for removing per- and/or polyfluoroalkyl compounds (PFAS compounds) from wastewater leachate contaminated with PFAS compounds, comprising:

an air flow device in communication with a bubble aeration device, wherein the bubble aeration device is within pre-foamed wastewater leachate contaminated with PFAS compounds, wherein the bubble aeration device is configured to produce bubbles from the air flow from the air flow device, wherein the bubbles form a foam layer on top of the wastewater leachate, wherein the foam layer comprises a concentrated amount of PFAS compounds relative to that present in the pre-foamed wastewater; and

a separating device configured to remove a portion of the foam layer from the surface of the wastewater leachate to form defoamed water.

14. The system of claim 13, wherein the bubble aeration system includes a path configured to flow the wastewater leachate, wherein the path is a serpentine path, a curving path, a winding path, or a sinuous path.

15. The system of claim 13, wherein the separating system configured to remove a portion of the foam layer from the surface of the wastewater leachate at multiple points along the path.

16. The system of claim 13, wherein the separating system includes a skimmer, a baffle, or both, wherein the separating occurs as the de-foamed wastewater leachate flows past the skimmer or baffle along the path.

17. The system of claim 13, further comprising a processing system includes a device that renders the PFAS compounds less hazardous relative to before processing than PFAS compound.

18. The system of claim 13, wherein the air flow device is an air generator or pump and wherein the bubble aeration device is a structure that is configured to form bubbles as air is flowed through the bubble aeration device.

19. The system of claim 13, wherein the separating system comprising a structure that is configured to skim the foam layer off of the surface of the wastewater leachate.

20. The system of claim 13, further comprising a processing system includes a device that renders the PFAS compounds less hazardous relative to before processing than PFAS compound, wherein processing system includes: an electron beam device, a plasma device, an incineration device, an oxidation device, or a combination thereof.

* * * * *