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Characterization of per- and polyfluoroalkyl substances (PFAS) and other constituents in MSW landfill leachate from Puerto Rico

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Abstract

Elevated per- and polyfluoroalkyl substance (PFAS) concentrations have been reported in municipal solid waste (MSW) landfill leachate with higher levels in wet and warmer subtropical climates. Information about landfill leachate characteristics is much more limited in tropical climates. In this study, 20 landfill leachate samples were collected from three MSW landfills on the tropical island of Puerto Rico and results were compared against landfills nationally and within Florida, USA. The samples collected in Puerto Rico underwent physical-chemical analysis, as well as a quantitative analysis of 92 PFAS. Samples described in this study include discrete leachate types, such as leachate, gas condensate, and leachate which has undergone on-site treatment (e.g., RO treatment, phytoremediation, lagoons). A total of 51 PFAS were detected above quantitation limits, including perfluorohexylphosphonic acid, a perfluoroalkyl acid (PFAA)

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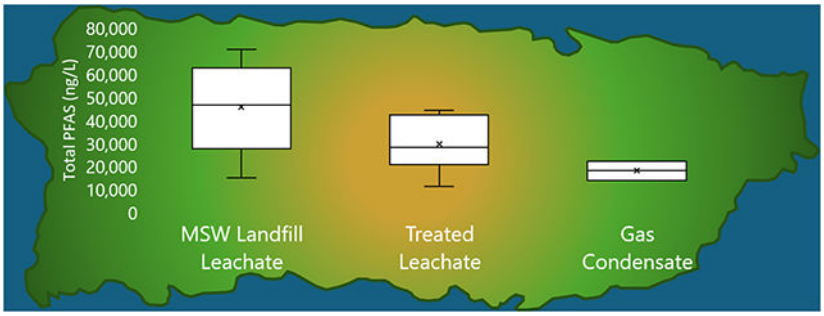
Declaration of competing interest
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data
Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2024.142141.

CRediT authorship contribution statement
Nicole M. Robey: Writing – review & editing, Writing – original draft, Visualization, Validation. **Yalan Liu:** Writing – review & editing, Investigation, Formal analysis. **Melitza Crespo-Medina:** Writing – review & editing, Investigation, Conceptualization. **John A. Bowden:** Writing – review & editing, Validation, Supervision, Methodology. **Helena M. Solo-Gabriele:** Writing – review & editing, Supervision, Methodology, Funding acquisition, Conceptualization. **Timothy G. Townsend:** Supervision, Resources, Project administration, Funding acquisition. **Thabet M. Tolaymat:** Writing – review & editing, Supervision, Resources, Funding acquisition, Conceptualization.

which has not been reported previously in landfill leachate. ∑PFAS concentrations in this study (mean: 38,000 ng L^{-1}), as well as concentrations of individual PFAS, are significantly higher than other reported MSW landfill leachate concentrations. The profiles of leachates collected from on-site treatment systems indicate possible transformation of precursor PFAS as a result of treatment processes – oxidizing conditions, for example, may facilitate aerobic transformation, increase the concentrations of PFAAs, and possibly increase the apparent ∑PFAS concentration. Extreme climate events, including rising temperatures and more frequent hurricanes, have placed additional strain on the solid waste management infrastructure on the island – adding complexity to an already challenging PFAS management issue. As concern grows over PFAS contamination in drinking water, these findings should inform solid waste and leachate management decisions in order to minimize PFAS emissions in island environments.

Graphical Abstract



1. Introduction

In recent years, extensive research has been conducted pertaining to the environmental and human health impacts of per- and polyfluoroalkyl substances (PFAS), as well as their persistence in the environment (Fenton et al., 2021; Garg et al., 2020; Ghisi et al., 2019). PFAS are a class of organic chemicals which provide stick- and stain-resistance and surfactant properties for many industrial applications and consumer products. Their near-ubiquitousness has resulted in reported exposure during product use and significant PFAS loading to municipal solid waste (MSW) and landfills (Coffin et al., 2022; Hamid et al., 2018; Ramírez Carnero et al., 2021; Tolaymat et al., 2023). A fraction of the PFAS which are disposed of in landfills will be emitted through landfill leachate, a complex wastewater formed when water interacts with waste materials. MSW landfill leachate is characterized by high concentrations of ammonia, dissolved organic matter, and various trace constituents derived from the waste, including PFAS (Chen et al., 2023; Gallen et al., 2016, 2017; Lang et al., 2017; Lu et al., 2023; Solo-Gabriele et al., 2020; Zhang et al., 2022). Numerous studies have aimed to capture the variability of PFAS concentrations and profiles in landfill leachates, considering factors such as waste type, climate, landfill age, and other parameters (Lang et al., 2017; Liu et al., 2020; Zhang et al., 2023).

The reported PFAS characterizations in these leachate studies suggest a wide range of concentrations and profiles, influenced by factors like climate, waste type, landfill conditions, and the employed analytical methods. Present reports indicate an average total

PFAS concentration of approximately 12,600 ng L^{-1} for US MSW landfills (Tolaymat et al., 2023), with landfill leachate from wet climates reportedly containing higher concentrations of PFAS (Lang et al., 2017). The most extensive published reports of PFAS in MSW landfill leachates are from (subtropical) Florida landfills (Chen et al., 2023; Zhang et al., 2022). Nonetheless, there is a lack of published data concerning leachate from US landfills beyond the contiguous US and in tropical climates. This is significant, as differences in waste composition, management practices, and climatic conditions will likely influence leachate compositions and PFAS profiles (Kjeldsen et al., 2002; Lang et al., 2017; Moody and Townsend, 2017; Tarafa Vélez, 1999)

The potential ramifications of landfill leachate emissions on water resources are particularly noteworthy for tropical island locations such as Puerto Rico, the location of this study, given that freshwater availability on the island, as well as on other island nations, is typically scarce. Considering recent calamities such as hurricanes, earthquakes, and the COVID-19 pandemic, which have strained solid waste management infrastructure (Brinton et al., 2022, 2023; Kennedy and Migaki, 2017), the US Environmental Protection Agency (EPA) and the Federal Emergency Management Agency (FEMA) have provided insights into solid waste generation, composition, and management data specific to Puerto Rico (US EPA and FEMA, 2021).

The island of Puerto Rico, located between the Atlantic Ocean and Caribbean Sea, experiences mean annual temperatures of 20–32 °C in low lying coastal regions and 16–27 °C in the mountains, with 0.7–4.3 m yr^{-1} of precipitation (McCleary et al., 2022). The island is approximately 9000 km^2, with a population of over 3.2 million (population density: 350 people per km^2) (US Census Bureau, 2022). In 1990, per capita solid waste generation on the island was 7 % lower than on the mainland US (Miranda and Hale, 1999), while the most recent estimates indicate that current waste generation on the island exceeds that of the mainland US by 13% (US EPA and FEMA, 2021). This increase is in part due to significant contributions from disaster debris including an additional 2.3 million metric tons of debris generated in 2017 due to hurricanes Irma and Maria (US EPA and FEMA, 2021). Furthermore, the proportion of waste destined for landfill disposal is higher, with only 10% of solid waste being diverted through recycling, in contrast to nearly 24% in the US (US EPA, 2020). The strain on MSW disposal systems in Puerto Rico has also exacerbated historical patterns of waste being disposed of in unlined, open dumps (US EPA and FEMA, 2021). These sites lack the engineering controls utilized in sanctioned, sanitary landfills, which are designed to mitigate environmental impacts. Notably, the landfills participating in this study all employ leachate containment measures, along with varying degrees of on-site leachate treatment. Limited studies have reported characterizations of MSW landfill leachates and treatment systems from Puerto Rico, and none have analyzed samples for PFAS (Betancourt Moreno, 2011; Rivera-Santiago, 2019; Tarafa Vélez, 1999).

This study describes leachates collected from municipal solid waste (MSW) landfills in Puerto Rico, including results of PFAS analysis as well as other physical-chemical characteristics. Disparities in leachate quality and PFAS profiles within MSW landfill leachates can be attributed to varying waste and landfill management approaches influenced by geological conditions and the distinct climate of the region, which experiences more

frequent catastrophic weather events. Moreover, the relatively small island size and high population density impose constraints that further contribute to these differences. This analysis of MSW landfill leachates in Puerto Rico holds potential significance in informing the management of MSW landfill leachates for US island territories. Additionally, it offers a foundation for evaluating the effectiveness of specific management and treatment strategies aimed at curbing PFAS emissions from MSW landfills within island nations.

2. Materials and methods

2.1. Site information

The island of Puerto Rico is located in a tropical marine climate region which experiences warm temperatures and abundant rainfall and all three facilities are located in Moist Forest designated Holdridge Ecological Lifezones on the island (Torres-Valcárcel et al., 2014). All three facilities were actively receiving waste at the time of sample collection. Facility A began receiving waste in the 1960's, Facility C began receiving waste in 1970 and each receives approximately 550 metric tons of MSW per day; Facility B began receiving waste in 1994 and historically received MSW, but at the time of sample collection accepted exclusively vegetative waste. Additional facility details are included in Section S1 of the SI.

2.2. Sample collection

MSW landfill leachate samples were collected in clean HDPE sampling containers from 20 locations across three landfill sites in different regions in Puerto Rico during late 2020 and Spring of 2021. Samples were collected from several locations at each facility, including multiple points in the leachate collection systems, before and after on-site leachate treatment, and in discrete leachate sources such as gas condensate knock outs. While all samples are considered MSW landfill leachate, the discrete sampling sources from this study are divided according to a more specific matrix type. "Leachate" refers to untreated leachate collected from tanks or trenches, sometimes mixed with other types of water such as stormwater or gas condensate, "treated leachate" has undergone an explicit on-site treatment process (e.g., reverse osmosis or phytoremediation) or passive treatment such as open lagoon storage, and "gas condensate" is liquid collected from the landfill gas collection and control system. A description of all samples, labeled according to anonymized facility (i.e., A, B, C) and sequential sample number is included in Table S1 of the SI. In addition to PFAS analysis, samples were collected for physical-chemical characterization (see SI Table S2 for sample preservation and holding times). During sampling, an HDPE bottle with PFAS-free water was opened and poured into another HDPE bottle to serve as a field blank. Samples were transported between the field and laboratory on ice and stored at −20 °C until analysis.

2.3. Sample extraction, analysis, and quantitation

All samples were analyzed for pH, conductivity, total dissolved solids (TDS), total solids (TS), alkalinity, chemical oxygen demand (COD), ammonia-nitrogen, chloride, and trace metals. Physical-chemical analytical methods are included in the SI Table S2 (A.P.H.A., 2012, HACH Company, 2012, US EPA, 1992, US EPA, 1994). The sample extraction method for PFAS was adapted from Robey et al. (2020). The extraction process has been validated in subsequent studies of MSW landfill leachate (Liu et al., 2020; Smallwood et

al., 2023) and extraction efficiency for these matrices can be found in the literature. Details of the PFAS solid phase extraction protocol are included in the SI Section S2. Extracts were analyzed for 92 PFAS (full analyte list in the accompanying SI Table S3) using a Thermo Scientific Vanquish ultra-high pressure liquid chromatograph (LC) coupled to a TSQ Quantis triple quadrupole mass spectrometer (UHPLC-MS/MS).

2.4. PFAS quality control (QC)

Field blanks, extraction blanks, and solvent blanks were prepared and analyzed in a similar fashion as samples. Field blanks consisting of Optima water were exposed to ambient air and conditions at the landfills sites to capture potential contamination in the entire workflow. Extraction blanks were prepared with Optima water and extracted along with the leachate samples to identify contamination derived from the extraction process. A solvent blank was run within the instrument method queue every five samples to monitor potential carryover and instrument-derived contamination. To find PFAS-specific method detection limits (MDL) and minimum limits of quantification (MLQ), known concentration of native standards were spiked into the pooled sample before extraction. After applying the extraction workflow, data acquisition and analysis, the signal to noise ratio (S/N) of each individual PFAS was visually determined in the spiked sample. By knowing the concentration of spiked native standards and assigning the correspondent S/N to each PFAS, MDLs and MLQs were calculated by determining concentrations that would provide a S/N of 3 and 10, respectively.

2.5. Data analysis

To calculate summary statistics across samples, physical-chemical constituents (e.g., chloride, COD, ammonia-nitrogen, and trace metals) which were not detected, were given a value of one half the detection limit for each type of analysis. A value of zero ng L^{-1} was used for PFAS which were below detection or quantitation limits when calculating total PFAS. Relative concentrations of individual PFAS and PFAS classes were compared as a function of matrix type, facility, and on-site treatment techniques.

3. Results and discussion

3.1. Physical-chemical parameters

The physical-chemical constituent profiles of the leachate samples shed light on the landfill conditions and environmental factors contributing to leachate formation. In Fig. 1, box-and-whisker plots depict bulk constituent concentrations across all matrix types, while Fig. S1 in the SI includes a scatterplot of bulk constituent concentrations as a function of conductivity —an indicator of total ions in solution. The normalization of analyte concentrations to another parameter, like conductivity, compensates for the dilution effect observed in highly variable leachate samples and aids in identifying genuine distinctions between matrix types.

Samples demonstrated the inherent variability typical of leachates. pH values spanned from 7.3 to 8.7, with an average of 7.9, indicating that all the sites were in the methanogenic decomposition phase (Kjeldsen et al., 2002). Conductivity, which serves as a proxy for the total ions in solution, ranged from 2300 to 22,700, with an average of 12,100 mS cm^{-1}.

For context, published studies have reported similar conductivity values for MSW landfill leachate ranging from 570 to 28, 000 mS cm^{-1} (Zhang et al., 2022). Table S7 in the SI includes the physical-chemical parameters for all the samples (excluding metals), along with the minimum, average, and maximum values for all analytes. Table S8 (SI) presents the minimum and maximum values for both leachate and gas condensate, along with values from the literature (two studies characterizing leachate and gas condensate from multiple Florida landfills) for comparative purposes. Metals concentrations are provided in Tables S9 through S11 of the SI.

The two landfill gas condensate samples had the lowest average values for conductivity, COD, and chloride while treated leachates exhibited the lowest averages for ammonia, TDS, TS, and alkalinity. Notably, chloride serves as a conserved indicator analyte for MSW leachate and is not anticipated to be present at high concentrations in gas condensate (Smallwood et al., 2023); while sample A-7 is designated as gas condensate, its chloride concentration of 1800 mg L^{-1} suggests that the condensate at this sampling point was likely mixed with leachate. This aspect is significant in the context of other analytes (such as PFAS) present. The other gas condensate sample, C-2, contained 200 mg L^{-1} of chloride, indicating that it primarily contained gas condensate.

The on-site leachate treatment systems are engineered to target the historical constituents of concern in leachate, such as ammonia, COD, and metals. Variations in these parameters before and after treatment are heavily contingent on the specific treatment mechanisms and offer insights into the chemical and biological processes taking place within the treatment systems. These processes could potentially influence the PFAS profiles present in the leachate.

3.2. PFAS characterization

3.2.1. Total PFAS—The cumulative PFAS concentrations ($\sum_{92}$PFAS) across all samples ranged from 11,200 to 70,300 ng L^{-1}. The box-and-whisker plots in Fig. 2 illustrate the $\sum_{92}$PFAS range by facility and matrix type: leachate, treated leachate, and gas condensate. These concentrations are, on average, higher than the average PFAS concentrations reported in the literature for both US MSW landfill leachate (Chen et al., 2022; Singh et al., 2021; Tolaymat et al., 2023) and landfill gas condensate (Smallwood et al., 2023). Higher total PFAS concentrations may be a result of the expanded suite of compounds included in this analysis. Additional comparison with other studies is included in Section 3.3.5 (Implications).

As mentioned previously, conductivity in these samples serves as a proxy for total ions in solution. The typical-for-leachate conductivity concurrent with high PFAS concentrations in these samples implies a higher normalized leaching of PFAS in comparison to inorganic constituents. Unlike inorganic elements such as chloride, which leach from MSW primarily based on water solubility, the leaching of PFAS is considerably influenced by landfill conditions that influence their transformation and degradation (Allred et al., 2015; Lang et al., 2016; Weber et al., 2022; Zhang et al., 2013).

Untreated leachate contained the highest average $\sum_{92}$PFAS, primarily due to the overall highest concentration observed among all samples, 70,300 ng L^{-1} in sample C-4. This was followed by treated leachate, and gas condensate had the lowest average $\sum_{92}$PFAS, although the sample with the lowest $\sum_{92}$PFAS concentration was A-5, a reverse osmosis (RO) permeate (treated leachate) sample with $\sum_{92}$PFAS of 11,200 ng L^{-1}. In Fig. S2 of the SI, $\sum_{92}$PFAS is plotted in relation to chloride, conductivity, and ammonia — proxies for leachate strength or dilution. This visualization offers further insights into the relationships between these variables and PFAS.

3.2.2. PFAS classes—The distribution of PFAS classes in terms of proportional fraction and total concentrations is depicted for each sample in Fig. S2 of the SI. On average $\sum_{15}$PFAAs accounted for just under half of the total PFAS (49%), ranging from 31% in gas condensate sample A-7 to 96% in leachate lagoon sample B-2. The leachate samples contained an average of 44% (±11%) PFAAs while treated leachates exhibited 63% (±30%) PFAAs – a profile characterized by the greatest variability – and gas condensates contained an average of 45% (±20%) PFAAs.

Among the terminal PFAS (PFAAs which do not degrade further in the environment; ITRC, 2023), perfluorocarboxylic acids (PFCAs) were more prevalent than perfluorosulfonic acids (PFSAs). Perfluorohexanoic acid (PFHxA; C7) emerged as the most abundant PFAA in 13 of the 20 samples and the overall most prevalent PFAS in three samples—B-1 and B-2 (both lagoon samples) and C-8 (a leachate trench sample), all originating from similar sampling locations. Perfluorobutanesulfonic acid (PFBS; C4) was the most abundant PFAA in six samples, while perfluorooctanoic acid (PFOA; C9) was the highest in a single sample (C-2).

Out of the 92 PFAS covered by the analytical method, each individual sample contained between 32 and 48 detectable PFAS, amounting to a total of 51 PFAS quantified across all samples. The specifics of these PFAS, encompassing detection frequency, median, and maximum concentrations (ng L^{-1}), can be found in Table 1 and concentrations in individual samples is included in Table 2. Among these compounds, 18 were measured in 100% of the 20 samples, including six PFCAs, three PFSAs, two fluorotelomer alcohols (FASAs), two fluorotelomer carboxylic acids (FTCAs), and five other precursors.

Overall, the fluorotelomer class (FTCA) of precursor PFAS dominated most samples (16 out of 20), particularly 5:3 FTCA. This compound, well-documented in landfill leachate and leachate-contaminated environments, is an intermediate transformation byproduct stemming from the anaerobic degradation of precursor PFAS (Hamid et al., 2020; Zhang et al., 2013). On average, this single compound constituted 38% of $\sum_{92}$PFAS, and it accounted for as much as 58% of $\sum_{92}$PFAS in sample C-4. Remarkably, perfluorohexylphosphonic acid (PFHxPA), a PFAA recently identified in street sweeping samples from Florida (Ahmadireskety et al., 2021), was present in all Facility A samples, with concentrations ranging from 72 to 210 ng L^{-1} but below detection limits (BDL) in samples from other facilities. PFHxPA and other perfluoroalkylphosphonic acids (PFAPAs) are used in pesticides and windshield washer fluids (Wellington Laboratories, 2014). Samples from Facility A had the most PFAS diversity, with all samples except the reverse osmosis (RO) permeate containing 40 or more PFAS above detection limits.

3.2.3. On-site leachate treatment—Each of the facilities incorporated at least one on-site leachate treatment method; either active treatment, such as RO separation, or passive treatment, like lagoon storage. Samples from Facility A included both leachate influent, RO permeate and concentrate, and leachate treated using phytoremediation. RO treatment, known for its effectiveness of 99% or higher with large organic molecules like PFAS (Liu et al., 2022a), is a common choice for leachate treatment (Renou et al., 2008). As shown in Fig. 3, $\sum_{92}$PFAS in RO permeate (A-5) was 24% lower than in the leachate influent (A-4). This reduction is comparatively less than those previously reported for RO-treated leachate (Chen et al., 2022; Zhang et al., 2023), indicating that this particular system or these samples might not accurately represent typical RO treatment efficiency. Parameters like total solids (TS), alkalinity, chloride, and ammonia exhibited a corresponding proportionate decrease (25% for all except ammonia, which was 24%) in the same samples (refer to Table S7 in the SI), also low compared to previously reported removal efficiencies (Ahn et al., 2002).

Sample A-1, originating from the leachate recirculation system containing both leachate and RO concentrate, had the highest $\sum_{92}$PFAS (46,000 ng L^{-1}) among samples from Facility A. Elevated PFAS (alongside other constituents) concentrations in recirculated leachate could potentially contribute to the progressive increases in leachate PFAS over time, due either to the accumulation of PFAS or enhanced biodegradation due to the additional moisture introduced or both (Lang et al., 2016; Reinhart and Townsend, 1997).

Furthermore, Facility A employs on-site phytoremediation as part of their leachate treatment approach (refer to the photo in Fig. S3 of the SI). Following phytoremediation, the PFAS concentration in leachate (sample A-6) reached 29,000 ng L^{-1}, surpassing the levels in any untreated leachates from Facility A. This could arise from the oxidative transformation of unmeasured precursor PFAS within the high-oxygen environment of plant root systems (Lott et al., 2023) or possibly due to inherent variability among grab samples.

Facility B included four samples: two derived from leachates collected from a storage tank (B-3 and B-4), and two from an on-site lagoon (B-1 and B-2) connected to visible leachate seepage. Specifically, one lagoon sample (B-1) was taken close to a leachate seepage site, while the other (B-2) was collected from the farthest point of the lagoon. These samples stood out as they demonstrated the most noticeable disparities between treated and untreated leachates across the entire study. On average, the cumulative PFAS concentration ($\sum_{92}$PFAS) was 33% lower in the lagoon samples. Notably, the profile of the lagoon samples exhibited significant differences (see Fig. 4). These samples contained higher concentrations of PFCAs, proportionally more PFCAs relative to other PFAS classes, and notably lower concentrations of precursor PFAS. On average, the reduction in cumulative precursor PFAS ($\sum_{36}$PrecursorPFAS) in the lagoon leachate was a substantial 94%. The reduced overall concentrations in the lagoon samples might be attributed to processes like volatilization or dilution with rainwater. Concurrently, oxidative and photodegradation processes could be transforming precursor PFAS present in the leachate into terminal PFCAs (Esfahani et al., 2022). The physical-chemical data suggest that both processes are occurring.

Chloride, which is typically conserved during many landfill leachate treatment processes, exhibited a significant decrease. Specifically, the average concentration of chloride in the

leachate from the tanks was 7200 mg L^{-1} and 1400 mg L^{-1} in the lagoon samples, representing an 85% reduction. This reduction suggests a dilution effect. Additionally, ammonia and COD, which can be reduced through oxidative mechanisms, are proportionally lower than chloride in the lagoon samples. In the leachate from the tanks, the average concentrations of ammonia and COD were 985 and 6250 mg L^{-1}, respectively. In the lagoon samples, these values decreased to 1.75 mg L^{-1} for ammonia and 460 mg L^{-1} for COD. This represents a significant 99.8% reduction in ammonia and a 93% reduction in COD. These findings collectively indicate a complex interplay of PFAS behavior, including dilution, volatilization, and transformation, contributing to the observed differences between the treated and untreated leachates in Facility B.

Facility C employs on-site phytoremediation as part of their leachate treatment approach, in addition to utilizing open-air leachate ponds and trenches from which samples were collected. Total PFAS concentrations in untreated leachates from Facility C ranged from 25,000 to 61,000 ng L^{-1} (mean: 47,000 ng L^{-1}). Notably, unlike the phytoremediation-treated leachate from Facility A, the treated leachate collected after undergoing phytoremediation at Facility C exhibited lower $\sum_{92}$PFAS than most of the untreated leachates from the same site (27,000 ng L^{-1}). Notably, three samples extracted from open-air leachate storage — samples C-3 (collected from a leachate trench), C-8 (collected from a leachate canal/trench), and C-9 (collected from an open-air pond) — contained higher PFAS concentrations compared to either the phytoremediation-treated leachate or any other leachate samples from Facility C (see Figs. S1 and S3 in the SI). The only exception was sample C-4, which was a mixture of leachate and gas condensate with the highest overall PFAS concentration at Facility C. In addition, samples C-8 and C-9 contained proportionally greater fractions of terminal PFAS than the other samples. These results highlight the intricate interplay between different treatment methods and leachate storage conditions at Facility C, affecting the concentration and composition of PFAS in the collected samples. Notably, across all treatment systems, PFAS were present in the treated leachate, indicating that even treatment processes which may remove nearly all PFAS under ideal conditions (i.e., RO) may not provide reliable removal due to system age, wear, and tear.

3.2.4. Implications—As mentioned previously, the average $\sum_{92}$PFAS in this study, 38,000 ng L^{-1}, was higher than the average total PFAS reported for US MSW landfill leachate studies included by Tolaymat et al. (2023). It was also higher than concentrations reported for Australia (Gallen et al., 2016, 2017; Simmons, 2019), Canada (Benskin et al., 2012; Gewurtz et al., 2013; Li, 2009), or Europe (Busch et al., 2010; Eggen et al., 2010; Kallenborn et al., 2004; Perkola and Sainio, 2013; Harrad et al., 2019; Fuertes et al., 2017; Knutsen et al., 2019; Gobelius et al., 2018). However, MSW landfill leachate from China (Liu et al., 2022b; Yan et al., 2015) contained higher total PFAS concentrations. Furthermore, the average PFOA concentration for the Puerto-Rico landfills sampled in this study (3200 ng L-1) followed the same trend as the total PFAS content. The average PFOS concentration (60 ng L-1) was lower than most of the above-cited studies. Higher average concentrations of PFOA and other PFAS may be a result of inherent differences in waste composition, such as large quantities of carpeting disposed of as disaster debris (Lang et al.,

2016), or possibly climate influencing PFAS transformation and leaching behavior. Landfills in wet, warm climates are most likely to have higher PFAS concentrations in the leachate (Lang et al., 2017). The exact reason behind this variability is further complicated by the lack of historical data on the quantity and composition of landfilled wastes at these sites which makes this comparison challenging.

Chen et al. (2023) conducted a study measuring PFAS in 78 leachate samples from Florida landfills, providing data that are climatically and regionally comparable to the Puerto Rico landfill leachate data discussed in this study. The concentration range of 20 individual PFAS, which were analyzed in both studies, is presented in box and whisker plots found in Figs. S4, S5, and S6 of the SI. Additionally, Fig. 5 includes the sum of the 20 PFAS for each dataset, along with the five most prevalent PFAS (with mean leachate concentrations above 2000 ng L^{-1}), further highlighting the comparison.

For this comparison, PFPeS, which was analyzed in Chen et al. (2023) but consistently reported below detection limits in almost all leachate samples from the current study, and 4:2 FTS, which was measured in this study but fell below the detection or quantification limits in Chen et al. (2023), have been excluded. When comparing the two datasets, it becomes evident that the average $\sum_{20}$PFAS in the Puerto Rico (PR) leachate is significantly higher (with a p-value of less than 10^{-7}), largely due to higher concentrations of typically abundant PFAS. Particularly noteworthy are PFPeA, PFHxA, PFOA, PFBS, 5:3 FTCA, and 7:3 FTCA.

In terms of specific PFAS classes, concentrations of PFCAs were generally substantially higher in Puerto Rican leachates, especially among compounds with the highest concentrations. On the other hand, PFSA and FASA concentrations were lower in Puerto Rican leachates for all species except for PFBS, which was the most abundant PFSA in both the Florida leachates and the current study. Similarly, in terms of fluorotelomer PFAS, both 5:3 and 7:3 FTCAs included in the analysis were more abundant in Puerto Rican leachates, while both 6:2 and 8:2 FTSs were measured at higher concentrations in the Florida leachates. This comparison of 20 PFAS compounds included in both datasets accounts for an average of 92% of the $\sum_{92}$PFAS measured in this study across the 13 leachate samples (minimum 86%, maximum 96%).

Only a limited number of PFAS, both within the universe of PFAS and the specific PFAS analyzed in this study, have been subjected to comprehensive health-risk evaluations. Among these, 13 PFAS—comprising 12 perfluoroalkyl acids (PFAAs) and one replacement PFAS known as “GenX”—have been assigned risk-based thresholds as part of the United States Superfund program regional screening levels (RSLs) (US EPA, 2023). RSLs are often used as an initial screening tool to identify if further environmental evaluation is needed to protect human health and the environment. Nine of the 12 PFAAs with US EPA RSLs were quantified in these leachate samples; “GenX” was not quantified in this study.

More recently, in 2024, the US EPA released national primary drinking water maximum contaminant limits for five PFAS (PFOA, PFOS, PFHxS, PFNA, and GenX) as well as mixtures containing two or more of PFHxS, PFNA, GenX, or PFBS (US EPA, 2024). While

we are not suggesting that leachate should be used for drinking water, a comparison to the drinking water standard can provide an initial assessment of the extent of dilution and attenuation necessary for PFAS contamination (e.g., from unlined landfills) to be mitigated to safe levels at drinking water sources. All leachate samples exceeded the new MCLs for the four PFAAs as well as inherently exceeding the mixture limit. Table 2 includes leachate concentrations of PFAS measured in this study with corresponding RSLs and MCLs. PFOA concentrations were, on average, highest compared to both the RSL (THQ = 0.1) and MCL by an average ratio of 430 and 650, respectively. This observation aligns with previous findings from a review of landfill leachate studies, which reported that PFOA typically holds the highest ratio among PFAS in municipal solid waste (MSW) landfill leachate compared to its respective RSL (Tolaymat et al., 2023).

4. Conclusion

This study presents comprehensive data on PFAS concentrations and the physical-chemical characteristics of leachate collected from three municipal solid waste (MSW) landfills in Puerto Rico, USA. The sampled leachate types encompassed a range of scenarios, including gas condensate from landfill gas collection systems, leachate collected from facility leachate collection systems, leachate mixed with stormwater or gas condensate, and leachate treated on-site (such as through reverse osmosis and phytoremediation). Out of the 92 PFAS compounds analyzed, a total of 51 were detected, and 18 were detected in all samples. A notable finding was the presence of PFHxPA, a PFAA not previously reported in landfill leachate, which was detected across all samples from one of the facilities.

The study's results demonstrated that the total PFAS concentrations (average: 38,000 ng L^{-1}) were significantly higher compared to reported mean concentrations from MSW landfill leachate in other locations (e.g., the US MSW landfill leachate with an average of 12,600 ng L^{-1}, and 12,700 in Florida MSW landfill leachates). This could be attributed to the higher temperatures and more rainfall in Puerto Rico, leading to accelerated waste decomposition and subsequent PFAS transformation and leaching or differences in the composition of incoming waste. These findings underscore the critical significance of effective leachate management within island contexts. Puerto Rico, as a relatively small island territory with limited landfill space, high population density, continued reliance on unlined landfills, and scarce freshwater resources, faces unique challenges. The heightened impact of extreme climate events, including elevated temperatures and more frequent hurricanes, has added further complexity to the island's solid waste management infrastructure needs.

Given the growing concerns surrounding PFAS contamination of drinking water and the anticipated development of PFAS effluent guidelines (US EPA, 2021), the insights from this study have considerable implications for informed decision-making with regards to solid waste and leachate management strategies. This study highlights the effect traditional leachate treatment processes can have on PFAS in leachate and the importance of PFAS-targeted treatment methods tailored for leachate matrices. As PFAS loading at MSW landfills originates from widespread usage and their emissions have far-reaching consequences; addressing these concerns should be approached as a collective priority.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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Data availability

Data will be made available on request.

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HIGHLIGHTS

- Climate has been previously indicated as a factor in MSW landfill leachate PFAS.
- No PFAS data is published for leachate from landfills in tropical climates.
- 51 PFAS were quantified in 20 leachate samples from MSW landfills in Puerto Rico.
- Mean total PFAS concentrations (38,000 ng L^{-1}) were higher than other US studies.
- On-site leachate treatment may cause PFAS transformation, changes in PFAS profile.

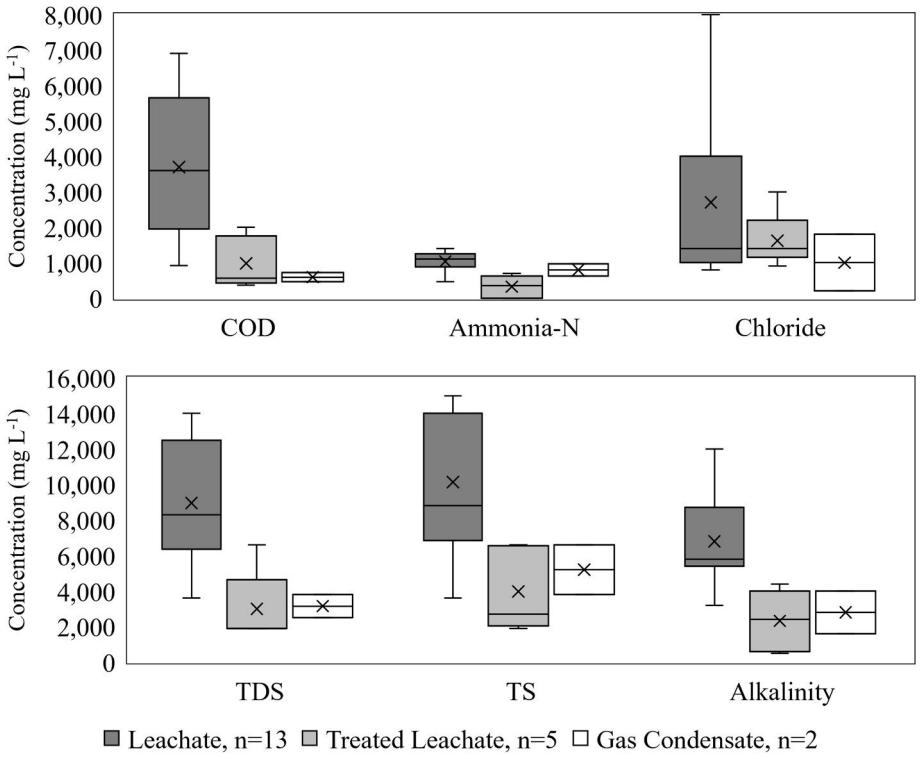

Fig. 1.

Physical-chemical parameter concentrations for four leachate types. Box-and-whisker plots represent mean (x), 10-, 25-, 50-, 75-, and 90th percentile values.

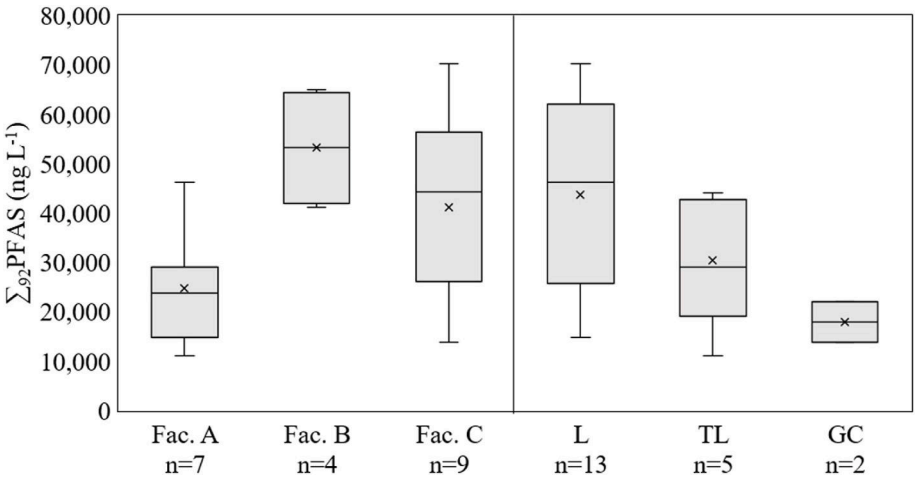

Fig. 2.

Total PFAS for three facilities (A, B, and C) and four leachate types (L = leachate, TL = treated leachate, GC = gas condensate). Box-and-whisker plots represent mean (x), 10-, 25-, 50-, 75-, and 90th percentile values.

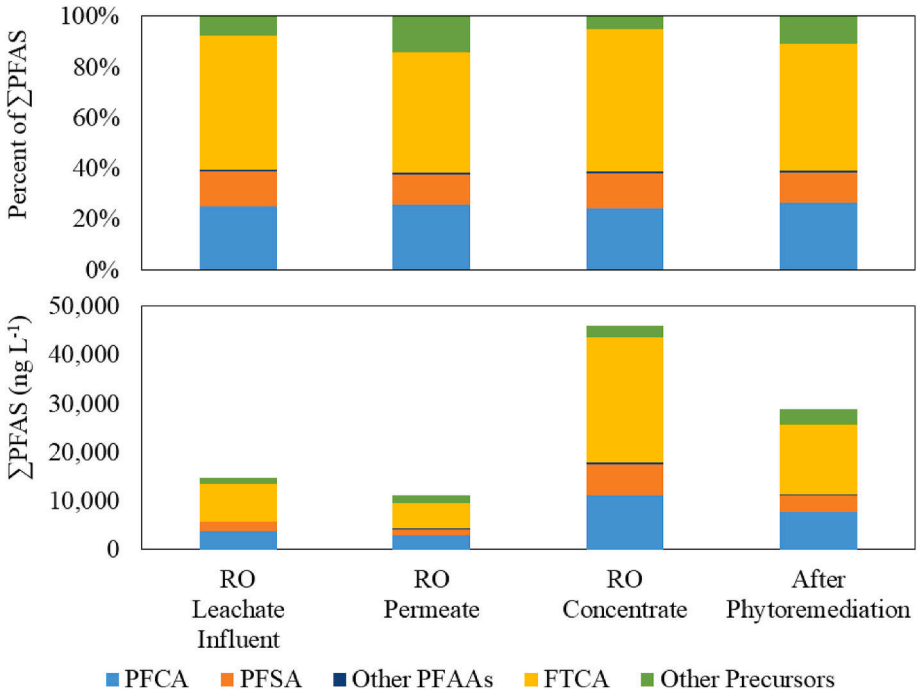

Fig. 3.

PFAS concentrations in leachate, RO permeate and concentrate, and phytoremediation effluent samples collected from Facility A.

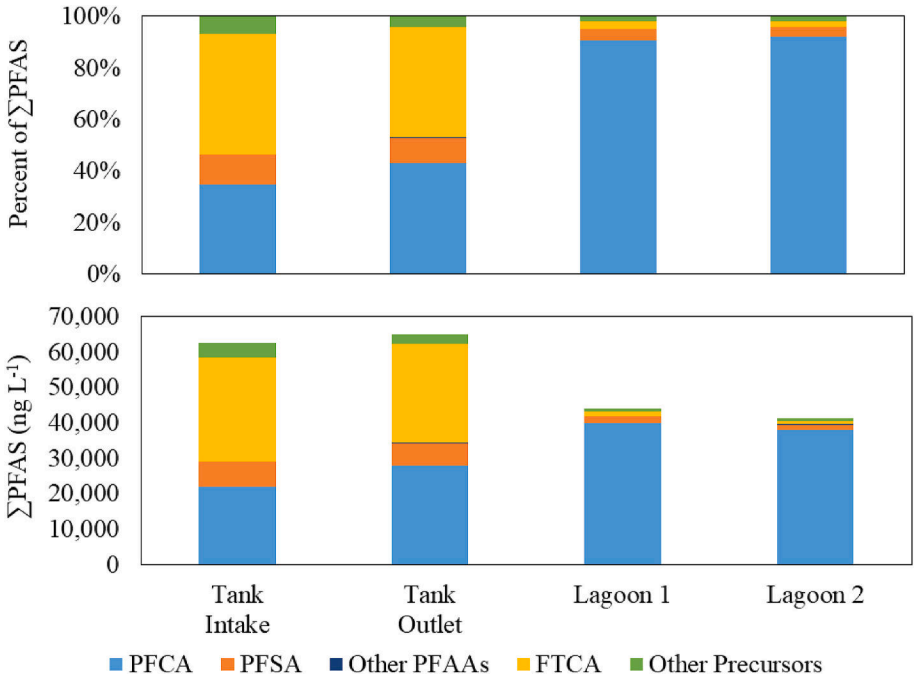

Fig. 4.

PFAS concentrations in storage tank leachate and leachate lagoon samples collected from Facility B.

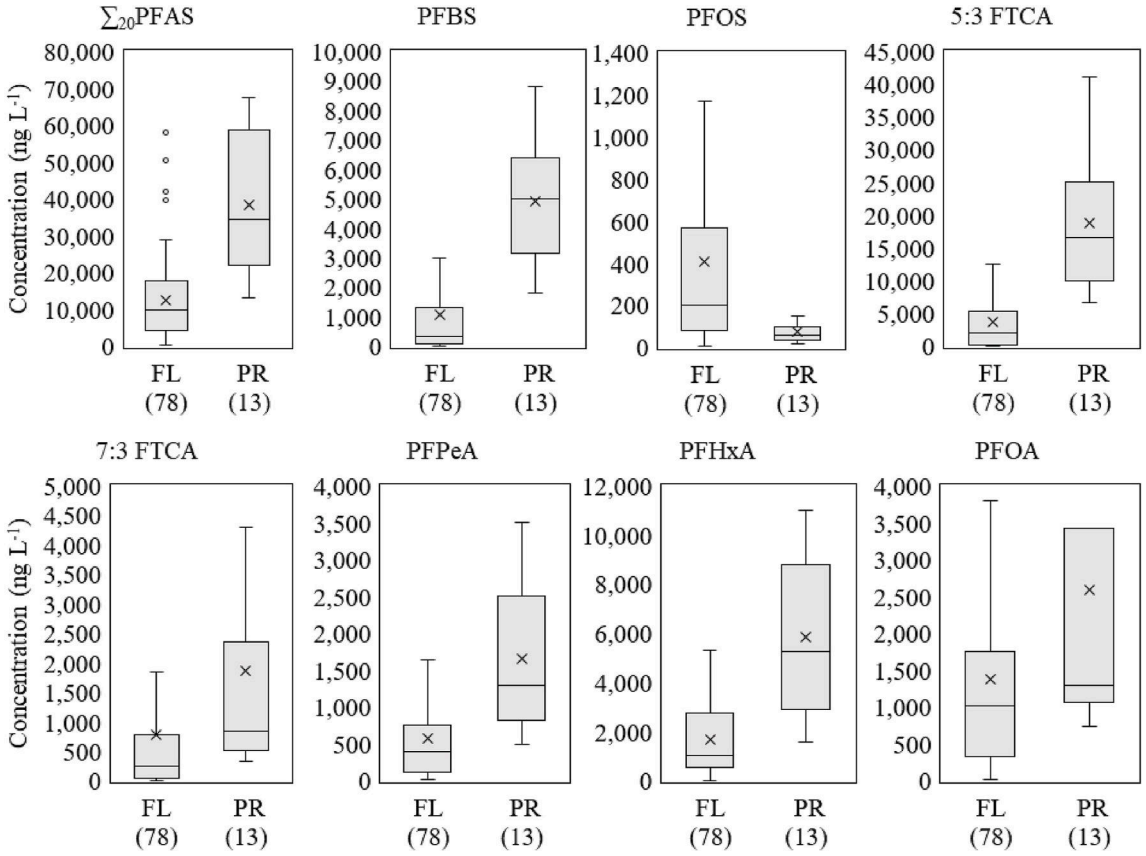

Fig. 5.

Range of $\sum_{20}$PFAS, PFBS, PFOS, 5:3 FTCA, 7:3 FTCA, PFPeA, PFHxA, and PFOA concentrations among 78 samples of MSW landfill leachate collected from Florida landfills (Chen et al., 2023) and 13 samples of MSW landfill leachate collected from landfills in Puerto Rico (this study). The plots represent the 10th, 25th, 50th, 75th and 90th percentiles, while "x" indicates the mean.

Table 1

Percent (%) of samples in which each PFAS was detected and median and maximum concentrations (ng L^{-1}) of PFAS quantified in leachate samples.

Class	Analyte	DF[a]	Median	Max	Class	Analyte	DF[a]	Median	Max
PFCAs	PFBA	90%	920	3300	Fluorotelomer PFAS	4:2 FTS	75%	2	7
	PFPeA	100%	1200	7600		6:2 FTS	95%	155	1000
	PFHxA	100%	4650	14,000		8:2 FTS	90%	17	200
	PFHpA	100%	510	4800		10:2 FTS	75%	6	33
	PFOA	100%	1300	12,000		6:2 FTCA	90%	165	1800
	$PFNA_{linear}$	100%	68	580		8:2 FTCA	85%	46	230
	$PFNA_{Br}$	35%	BDL[b]	83		10:2 FTCA	20%	6	27
	PFDA	100%	102	1800		8:2 FTUCA	80%	7	550
	PFUdA	90%	6	30		10:2 FTUCA	25%	BDL	280
	PFDoA	90%	8	36		3:3 FTCA	90%	210	620
	PFTrDA	55%	3	17		5:3 FTCA	100%	12,000	41,000
PFSAs	$PFPrS_{linear}$	50%	2	60		6:3 FTCA	100%	75	350
	PFBS	100%	3400	14,000		7:3 FTCA	100%	600	7700
	$PFPeS_{linear}$	20%	BDL	1900		8:3 FTCA	70%	5	170
	$PFHxS_{linear}$	100%	115	150		7:2sFTOH	25%	BDL	510
	$PFOS_{linear}$	100%	51	200		5:2sFTOH	25%	BDL	180
Other PFAAs	PFHxPA	35%	BDL	210	Other Precursor PFAS	PFECHS	80%	5	24
	PFBSI	100%	51	110		6:2 diPAP	80%	13	150
FASAs	FBSA	30%	BDL	2		Syn40	35%	BDL	1300
	FOSA	75%	3	17		Syn41	75%	130	1500
	FOSAA	60%	7	25		Syn45	20%	BDL	490
	N-MeFOSAA	100%	19	92		Syn53	100%	1150	2000
	N-EtFOSAA	100%	47	300		Oak6	100%	20	1500
	N-MeFOSE-M	30%	BDL	380		Oak8	95%	150	280
	N-EtFOSE-M	75%	10	210		Oak10	100%	7	43
	N-CMAmP-6:2 FOSA	30%	BDL	80	Not detected: PFTeDA, PFHxDA, PFODA, PFHpS, $PFOS_{branched}$, PFNS, PFDS, PFDoDS, 6:6 PFPi, 6:8 PFPi, 6:2 FTUCA, MeFBSA, FHxSA, N-Ap-FHxSA, N-TAmP-FHxSA, FDSA, MeFOSA, EtFOSA, EtFHxSA, EtFHxSE, Oak36, 8:2 diPAP, 6:2/8:2 diPAP,				

Class	Analyte	DF[a]	Median	Max

Class	Analyte	DF[a]	Median	Max
	diSAmPAP, Syn72, Syn32, 9Cl-PF3oNS, 11Cl-PF3OUdS, HFPO-DA, HFPO-TA, HFPO-TeA, Syn62, NaDONA, Syn38, Syn71, Oak37, PF4OPeA, 3,6-OPFHpA, Syn43, PFECHS, Syn28, Syn35, 8Cl-PFOS, Syn12, Syn46			

[a]DF = detection frequency.

[b]BDL = below detection limits.

Table 2

Concentrations (ng L^{-1}) of PFAS identified by US EPA with corresponding regional screening levels (RSLs) and maximum contaminant levels (MCLs), Σ_{92}PFAS, and number of PFAS quantified in each of thirteen leachate samples. Sample concentrations in bold text exceed their respective RSL and MCL.

Sample ID	PFOA	PFOS	PFBA	PFHxA	ΣPFNA	PFUnDA	PFDoDA	PFBS	PFHxS	Σ_{92}PFAS	# PFAS
EPARSL (THQ = 0.1)	6	4	1800	990	5.9	600	100	600	39	–	–
EPA MCL	4.0	4.0	–	–	10	–	–	–	10	–	–
A-1	**1400**	41	810	**6300**	**54**	3.0	5.4	**6200**	**100**	46,000	44
A-2	**940**	21	1000	**2900**	**39**	BDL	BDL	**3300**	**140**	24,000	40
A-3	**1100**	80	640	**2900**	**150**	7.0	8.0	**3000**	**130**	26,000	48
A-4	**740**	57	380	**1600**	**97**	5.0	5.1	**1800**	**93**	15,000	46
B-3	**7100**	17	BDL	**8400**	**190**	7.6	17	**7000**	**120**	63,000	36
B-4	**8200**	200	**3300**	**10,000**	**240**	15	31	**6000**	**150**	65,000	34
C-1	**1880**	150	620	**2900**	**110**	9.6	10	**3200**	**120**	31,000	38
C-3	**1100**	55	1300	**8400**	**110**	1.5	2.3	**6000**	**140**	51,000	35
C-4	**2200**	77	BDL	**11,000**	**89**	4.7	7.5	**8800**	**110**	70,000	35
C-5	**1200**	46	1000	**4200**	**63**	1.2	1.4	**4000**	**130**	25,000	34
C-7	**780**	3	1200	**5100**	**45**	2.1	4.7	**7200**	**78**	44,000	35
C-8	**5700**	**91**	**1800**	**14,000**	**210**	11	20	**14,000**	**140**	61,000	37
C-9	**1300**	**56**	1600	**9400**	**57**	7.1	13	**3500**	**100**	46,000	37
Ave. Ratio to RSL	430	17	0.6	7.0	19	0.1	0.1	9	3		
Ave. Ratio to MCL	650	17	–	–	11	–	–	–	12		