

Identification of Potential Sources of PFAS in the Gurabo Water Treatment Plant Watershed

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Abstract — *The drinking water treatment plant (WTP) of the municipality of Gurabo in Puerto Rico, is owned and operated by the Puerto Rico Aqueduct and Sewer Authority (PRASA). In its 2023 drinking water quality report, the WTP detected the presence of per- and polyfluoroalkyl substances (PFAS). Although there are thousands of PFAS compounds, the report specifically identified four: PFBA, PFHxA, PFOS, and PFPeA. This study aims to identify potential sources of PFAS contamination in the surface waters supplying the Gurabo WTP's watershed. Additionally, the research explores the relationship between PFAS concentrations and land use types within the watershed, comparing estimated PFAS levels from different land uses to the actual concentrations reported in 2023. The study identified 22 industry types within the watershed with potential PFAS contamination due to their use of these chemicals in their processes. The comparison between estimated and reported PFAS concentrations revealed an error margin of 10%, providing insights into the accuracy of land use association with contaminant concentrations under study.*

Key Terms — *Gurabo Water Treatment Plant, Land Cover/Use, NAICS Codes, PFAS, PRASA, Watershed.*

INTRODUCTION

Since the early 1940s, millions of citizens around the world have been exposed to per- and polyfluoroalkyl substances, commonly known as PFAS [1]. PFAS are man-made chemical substances that have proven to be excellent for the manufacture of over 5,000 products, such as fabrics, cosmetics, firefighting foams, and products resistant to grease,

water, and oil, among many others [2]. One of the most surprising characteristics of PFAS, evidenced in numerous studies, is their high persistence in the environment and, consequently, in the human body. This persistence is attributed to the molecules of PFAS being composed of a chain of carbon (C) and fluorine (F) atoms linked by a covalent bond. However, this is not just any covalent bond; it has been labeled as "the strongest bond in organic chemistry" [3]. This bond can have a bond dissociation energy of up to three times greater than the energy required to break a covalent bond such as carbon-halogens or carbon-hydrogen [4].

In recent years, PFAS have been detected in both surface and groundwater, posing risk to water quality, particularly for resources used in drinking water and agriculture. An example of this is the drinking water treatment plant (WTP) in the municipality of Gurabo in Puerto Rico. This plant is owned and operated by the Puerto Rico Aqueduct and Sewer Authority (PRASA) and during their 2023 quality report, they informed the presence of PFAS compounds in the drinking water. Hence, an effective watershed study is essential for identifying the main sources of PFAS contamination, understanding how these pollutants disperse, and determining the pathways by which they reach water bodies. According to Muir and Miaz in 2021 [5], worldwide, most PFAS pollution is released from human development activities into rivers where it is capable of being transported to oceanic environments. PFAS also transfers into the atmosphere where it diffuses long distances. However, given the widespread use of PFAS in products, elevated concentrations have been routinely detected in surface waters downstream from urban areas [5]. Understanding the key

anthropogenic land use activities associated with background PFAS pollution is crucial to gaining better insight into the sources and effects of PFAS contamination.

While many studies have focused on PFAS point sources, there is still limited knowledge about background levels in urban areas and the connection between diffuse pollution and different land use types (e.g., industrial, residential, and rural), particularly in freshwater systems. To date, research examining land use links to background PFAS pollution has primarily been conducted in the atmosphere or soil. Existing studies on surface waters have predominantly focused on the land use association with PFAS point sources [5]. Therefore, comparing PFAS concentrations between land uses within a watershed under study is important to improve understanding of the spatial distribution and background levels of PFAS, as well as to guide strategies to address major sources of PFAS.

This study aims to identify potential PFAS sources within the watershed that supplies the raw water intake of the Gurabo WTP. In addition, the study explores the development of a relationship between land use types within the watershed and their estimated contribution to PFAS concentrations. The analyses presented in this research utilized as reference two previous studies performed by Andrews et. al. [6] and Paige et. al. [5]. The study conducted by D. Andrews and collaborators in 2021 [6] focused on identifying point sources of PFAS in the United States and its territories, including Puerto Rico. As part of their findings, the researchers developed a table associating North American Industry Classification System (NAICS) and Standard Industrial Classification (SIC) codes to potential PFAS use and point source discharges.

On the other hand, the study conducted by T. Paige and collaborators in 2023 [5] focused on the Greater Melbourne watershed in Australia to determine the amount of diffuse PFAS pollution associated with land use. The researchers collected samples from surface water and sediments from various land uses within the catchment, including industrial, residential, and rural areas, as well as

streams receiving treated wastewater discharges. As part of their findings, the researchers developed a relationship between the average concentrations of each identified PFAS compound and the respective land use types within the watershed under study.

The study presented here, helps with the identification of industries or sites with potentially current use of PFAS for assessing the susceptibility of PFAS contamination within the Gurabo WTP watershed as a specific drinking water source. This analysis can help in the development of a strategy for local and state levels stakeholders for targeted PFAS monitoring of potential dischargers.

LITERATURE REVIEW

The following section presents a summary of the key concepts from the literature, offering context and insights relevant to the focus of this research.

Per and Polyfluoroalkyl Substances (PFAS)

PFAS are a group of synthetic chemicals that have been used in a variety of products for over 70 years. As mentioned before, PFAS are widely used in common consumer products such as stain-resistant, water-resistant, and non-stick products, coatings, food packaging, and outdoor clothing. Currently, PFAS in drinking water is an important emerging issue nationwide. Since some PFAS molecules are water soluble, over time PFAS from some firefighting foam, manufacturing sites, landfills, spills, air deposition from factories and other releases can seep into surface soils. From there, PFAS can leach into groundwater or surface water, and can contaminate drinking water [7].

There are thousands of PFAS compounds, and one way to classify them is by identifying them as either short-chain or long-chain. Short-chain PFAS typically have fewer than six to eight carbon atoms. These compounds are more hydrophilic, meaning they are attracted to water, and are more volatile compared to long-chain PFAS. Additionally, they are less effective at forming foams. On the other hand, long-chain PFAS generally have more than six to eight carbon atoms. These compounds are more

hydrophobic, meaning they dislike water, and are more effective at forming foams than short-chain PFAS [8]. This study focuses on four PFAS compounds identified in the WTP 2023 water quality report: PFBA, PFHxA, PFOS, and PFPeA. According to the PFAS chain classification outlined by the ITRC Regulatory Framework in 2021, PFBA, PFPeA, and PFHxA are classified as short-chain PFAS, while PFOS falls under the long-chain category.

According to the EPA in 2020 [9], existing drinking water treatment facilities in the U.S. lack the necessary technology and data for effective PFAS removal. Conventional treatment methods, low-pressure membranes, biological treatment, disinfection, oxidation, and advanced oxidation have been found to be ineffective for removing PFAS compounds. Currently, the technologies demonstrated to achieve between 90% and 99% removal efficiency for PFAS are anion exchange resin (IEX), high-pressure membranes, and powdered/granular activated carbon (with the best removal efficiency achieved when these systems are specifically designed for PFAS removal).

Gurabo Water Treatment Plant

The Gurabo Water Treatment Plant (WTP) is a compact plant with conventional unit operation and processes. The plant was installed in 1994 and as mentioned before, the facility is owned and operated by PRASA. The WTP uses the Gurabo River as its raw water source and has a design capacity of 4.0 MGD. The service area includes all the wards of the municipality of Gurabo, serving an estimated population of 40,622 inhabitants [10]. The facility uses a conventional treatment process comprising inline mixers, clarifiers for pre-sedimentation step, flocculation tanks, sedimentation tanks, filtration tanks, and chlorine contact chamber/distribution tank that also has portion for the backwash volume to clean filters. Additional to the drinking water process, the WTP has a sludge treatment system (STS) to manage and handle the sludge produced from the sedimentation processes.

In 2023, the WTP reported in its water quality report that PFAS were detected in the drinking water. Since the plant only provides a conventional treatment process, which removes suspended solids and ensures disinfection compliance for pathogenic microorganisms, the existing treatment lacks the capability to remove dissolved contaminants such as PFAS. According to EPA notice in 2024, public water systems will have three years (2024-2027) to complete the initial monitoring requirements. They must inform the public of the level of PFAS measured in their drinking water and they must implement solutions to reduce PFAS in their drinking water to levels below the standards within five years (starting from 2029).

The EPA has established maximum contaminant levels (MCLs) that water treatment and distribution systems must comply with. For PFOA and PFOS compounds, the MCL for each individual compound is set at 4.0 parts per trillion (ppt or ng/L), while for PFNA, PFHxS, and HFPO-DA (GenX compounds), the MCL is set at 10 ppt. The concentration results presented in the Gurabo WTP water quality report 2023 were the following: PFBA with 7.3 ppt, PFHxA with 3.5 ppt, PFOS with 4.4 ppt, and PFPeA with 4.2 ppt.

Study Area

The Gurabo WTP watershed is located in the east region of Puerto Rico (refer to **Figure 1**). The watershed includes parts of the municipalities of Gurabo, Juncos, San Lorenzo and Las Piedras. It is bordered by the municipalities of Carolina, Canóvanas and Río Grande to the north, Naguabo to the east, Humacao and Yabucoa to the south, and San Lorenzo to the west. The centroid of the watershed is located at coordinates 18°13'0.35"N, 65°53'32.93"W. The total area of the watershed is approximately 60 square miles (mi²), equivalent to 155 km². According to the 2020 Census for this region, the population within the watershed is estimated to be around 12,800 inhabitants. Additionally, it contains approximately 310 km of river network that eventually drains into the watershed's outlet point, which is the WTP raw



Figure 1
Location Map of the Study Area

water intake. The watershed under study is part of the Grande de Loíza River watershed (primarily known for the Carraízo reservoir), which is the largest on the island, covering approximately 290 mi² [11]. The Gurabo WTP watershed comprises about 20% of this total area.

The main river in the watershed is the Gurabo River, with an approximate length of 6.2 km, and its tributaries include the Valenciano River, Honda River, among other streams and creeks. The study area is mostly composed of rural land, but also includes residential zones dominated by housing developments and industrial areas. Despite the presence of several industrial zones within the watershed, the literature review for this study found no evidence or reports of PFAS compound or polymer (such as Teflon) manufacturing. However, PFAS-containing products are imported and used daily for both domestic and industrial purposes.

North American Industry Classification System (NAICS)

According to the U.S. Census Bureau, 2024, the North American Industry Classification System (NAICS) is a standardized system used by the governments of the United States, Canada, and Mexico to classify and organize businesses and industries based on the type of economic activity they perform. Established in 1997, NAICS was developed to replace the older Standard Industrial

Classification (SIC) system and is designed to reflect the modern economy more accurately. NAICS assigns a unique six-digit code to industries, where each digit represents different levels of classification, from broad sectors (such as manufacturing or healthcare) to more specific industries. The system is widely used for collecting, analyzing, and publishing statistical data related to the economy, including employment, business trends, and market analysis. NAICS is updated periodically to reflect changes in the economy, ensuring it stays relevant as new industries emerge. Under this study, NAICS codes were utilized to identify facilities that are potentially PFAS sources.

In 2021, D. Andrews and colleagues [6] investigated to identify sources of PFAS in the United States, including Puerto Rico. They identified facilities that may currently use or may have used PFAS compounds, as well as those associated with PFAS discharges into the environment, by analyzing NAICS and SIC codes. To identify NAICS codes related to potential PFAS use, the investigators began with the codes listed by the US EPA in the Advance Notice of Proposed Rulemaking (ANPRM) for the potential regulation of PFOA and PFOS under the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) and the Resource Conservation and Recovery Act (RCRA), published on the EPA website on January 14, 2021 [12].

In addition to the NAICS codes listed by the US EPA in the ANPRM, the investigators incorporated potential industrial PFAS sources from three other sources: industries identified as potential contamination risks for drinking water aquifers in New England, industries known to use PFAS, and industries identified through a testing program developed by the state of Minnesota. As part of their findings, the researchers linked the NAICS and SIC codes from the U.S. Census Bureau's 2017 database to facilities potentially associated with PFAS. They identified approximately 41,862 facilities/sites, which were organized by NAICS industry codes, resulting in a list of 48 NAICS industry codes indicative of PFAS use.

METHODOLOGY

This section describes the procedure carried out to achieve the main objective of the study, which is to delimit the watershed supplying the Gurabo WTP to identify potential sources of PFAS contamination, which have already been detected at the plant. Two analytical methods were employed in this study. The first method focuses on identifying potential facilities that could contribute to PFAS contamination, using the study by D. Andrews et. al. [6], previously discussed in the literature review, as a reference. The second method seeks to establish a relationship between the land use classification of the watershed under study and PFAS concentrations, using the 2023 study by T. Paige and collaborators [5] as a reference. Finally, this second method compared the results obtained of PFAS concentrations with the PRASA PFAS concentration values reported in the water quality report 2023 of the Gurabo WTP.

Watershed Delimitation

For the delimitation of the watershed supplying the WTP, QGIS version 3.38.1 software was used, employing a Digital Elevation Model (DEM) downloaded from the National Oceanic and Atmospheric Administration (NOAA) Data Access Viewer. The process began with loading the DEM,

ensuring it covered the entire area of interest. Subsequently, the river layer was added, generating a flow direction map that helped identify the main river courses. Once the rivers were identified, the watershed's outlet point, corresponding to the water intake of the treatment plant, was defined. With the outlet point established, the "Watershed" tool was used to delineate the catchment area, creating a polygon representing the watershed. Finally, the watershed was exported as a vector file for further analysis, including overlaying land cover, topography layers, and identifying facilities as potential sources of contamination.

Method 1 – Identification of Potential Facilities Utilizing PFAS

Once the watershed under study was delineated, data collection was performed. The EPA's Enforcement and Compliance History Online (ECHO) database was used to gather data. ECHO is a database that provides fast, integrated searches of EPA and state data for more than 800,000 regulated facilities. It focuses on inspection, violation, and enforcement data for the Clean Air Act (CAA), Clean Water Act (CWA), and RCRA, and includes data from the Safe Drinking Water Act (SDWA) and the Toxics Release Inventory (TRI). For the analysis conducted in this study, the ECHO data for the watershed under analysis was downloaded on September 01, 2024, and all data/location points presented in this report correspond to the available information from ECHO at that time. The data was downloaded in CSV format, which facilitated table analysis, and in GEOJSON format, which allowed for the geolocation of registered facilities within the study area.

With the facilities plotted within the watershed, each facility was identified with its respective NAICS code. After all facilities were classified under their corresponding NAICS numbers, a screening process was conducted to retain only those facilities with NAICS codes related to the use of PFAS in their processes, as identified in the study by D. Andrews et. al. [6]. The map created for the watershed was reviewed, maintaining only the

facilities whose NAICS codes are associated with PFAS use, thereby identifying potential sources of contamination.

Method 2 – Determination of Land Use and PFAS Concentration Relationship

The NOAA Data Access Viewer website was used to collect Land Cover data for the watershed under study. The Land Cover layer was downloaded in a raster format, which was then converted to vector format using QGIS tools and overlaid onto the delineated watershed. As part of the collected data, the classification of each Land Cover within the watershed was obtained from the list generated by the Coastal Change Analysis Program (C-CAP) 2010. For the WTP watershed, approximately 24 types of Land Cover were identified. To classify each Land Cover by type of Land Use, the following assumptions were made: for a Land Cover classified as "Developed-High Intensity," it was categorized as "Industrial Zone" Land Use; for a Land Cover classified as "Developed-Medium Intensity," it was identified as "Urban Residential" Land Use; for a Land Cover classified as "Developed-Low Intensity," it was classified as "Suburban Residential" Land Use; and the remaining Land Covers classified as "Forest/Grassland" without urban areas were identified as "Rural."

With the identification of each Land Use within the watershed, the percentage composition of each Land Use was calculated using QGIS tools. Once the composition of the different Land Uses was determined, an average PFAS concentration contribution value was assigned based on the research conducted by T. Paige et. al. [5]. These average values for each Land Use are presented in Figure 2. Using the assigned PFAS concentrations for each Land Use, a weighted average was

calculated using the Land Use composition values in the watershed to determine a total average concentration of PFAS contribution. This method assumes that each Land Use contributes an average PFAS concentration, as identified in the study by T. Paige et. al. [5], and that these concentrations are transported through surface runoff to the watershed's outlet, which corresponds to Gurabo WTP's raw water intake. The total average PFAS concentration obtained using this method was then compared to the actual PFAS concentration value reported in PRASA's 2023 water quality report.

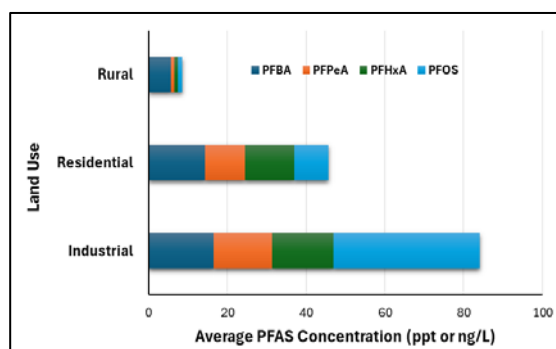


Figure 2
PFAS Concentrations Across Different Type of Land Uses

RESULTS

As part of the results obtained for **Method 1**, Table 1 presents a summary of the facilities/sites identified as potential sources of PFAS contamination, and Figure 3 shows their respective locations within the watershed. The results for **Method 2** are presented through the generated maps of land cover and land use, including their determined composition, and a comparison of the calculated PFAS concentrations with the actual values reported in the PRASA 2023 water quality report for the Gurabo WTP.

Table 1
Number of Potential PFAS Sources Identified in the Gurabo WTP Watershed as US EPA-Regulated Facilities Listed in ECHO Database

2022 NAICS	NAICS title or description	Municipality Registered			
		Juncos	Las Piedras	Gurabo	Grand Total
812320	Drycleaning and Laundry Services (except Coin-Operated)	3	2		5
325412	Pharmaceutical Preparations	1	1	2	4
339112	Primarily engaged in manufacturing medical, surgical, and ophthalmic.	2	2		4
922160	Fire Protection related	2			2
323111	Commercial printing (except screen printing, books printing)		2		2
212311-19	Stone Mining and Quarrying/Crushed and broken stone, dimension stone			2	2
335314	Electrical component manufacturing		1		1
562212	Solid Waste Landfill	1			1
423140	Motor Vehicle Parts (Used) Merchant Wholesalers			1	1
325510	Paint and coating manufacturing		1		1
335139	Electric Lamp Bulb and Other Lighting Equipment Manufacturing			1	1
325611	Soap and other detergent manufacturing	1			1
311613	Rendering and Meat Byproduct Processing		1		1
562219	Other Nonhazardous Waste Treatment and Disposal/Refuse System			1	1
423930	Recyclable Material Merchant Wholesalers/Scrap and waste material			1	1
312230	Manufacturing cigarettes or other tobacco products.	1			1
311615	Poultry Processing		1		1
334419	Other electronic component manufacturing	1			1
811192	Car washes	1			1
325998	All Other Miscellaneous Chemical Product and Preparation Manufacturing/Manufacturing Indus	1			1
332321	Metal Window and Door Manufacturing, Metal product manufacturing			1	1
334413	Semiconductor and related device manufacturing	1			1
Grand Total		15	11	9	35

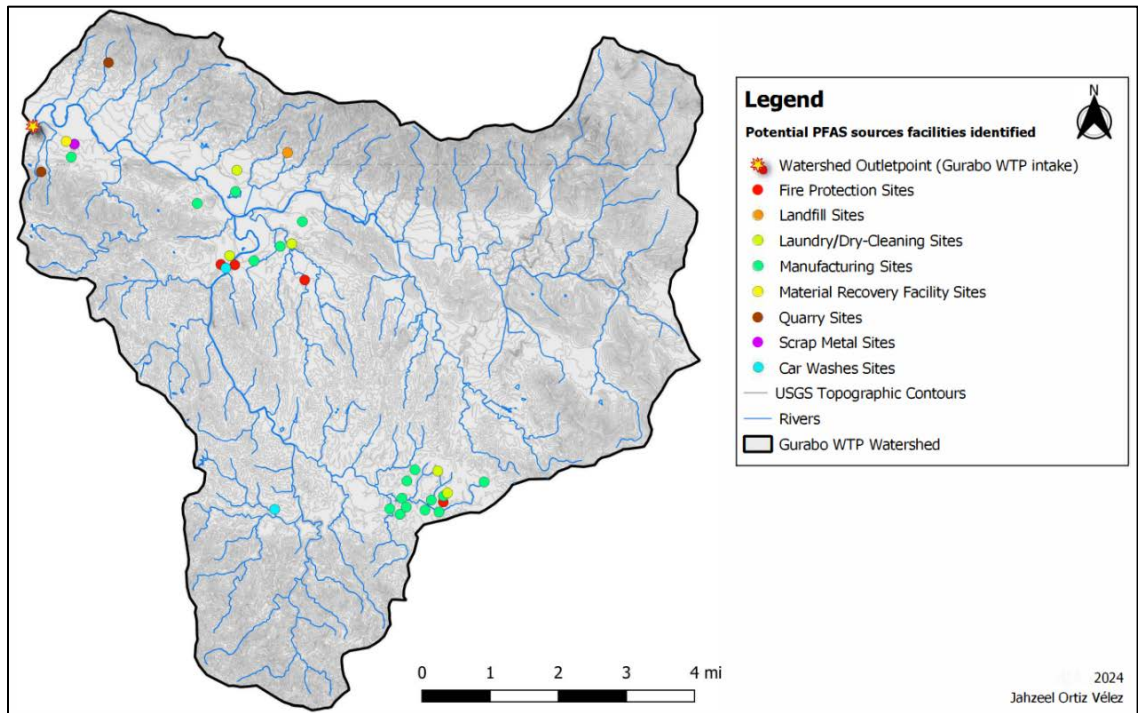


Figure 3
Potential PFAS Sources Identified in the Gurabo WTP Watershed and Classified as per NAICS Description

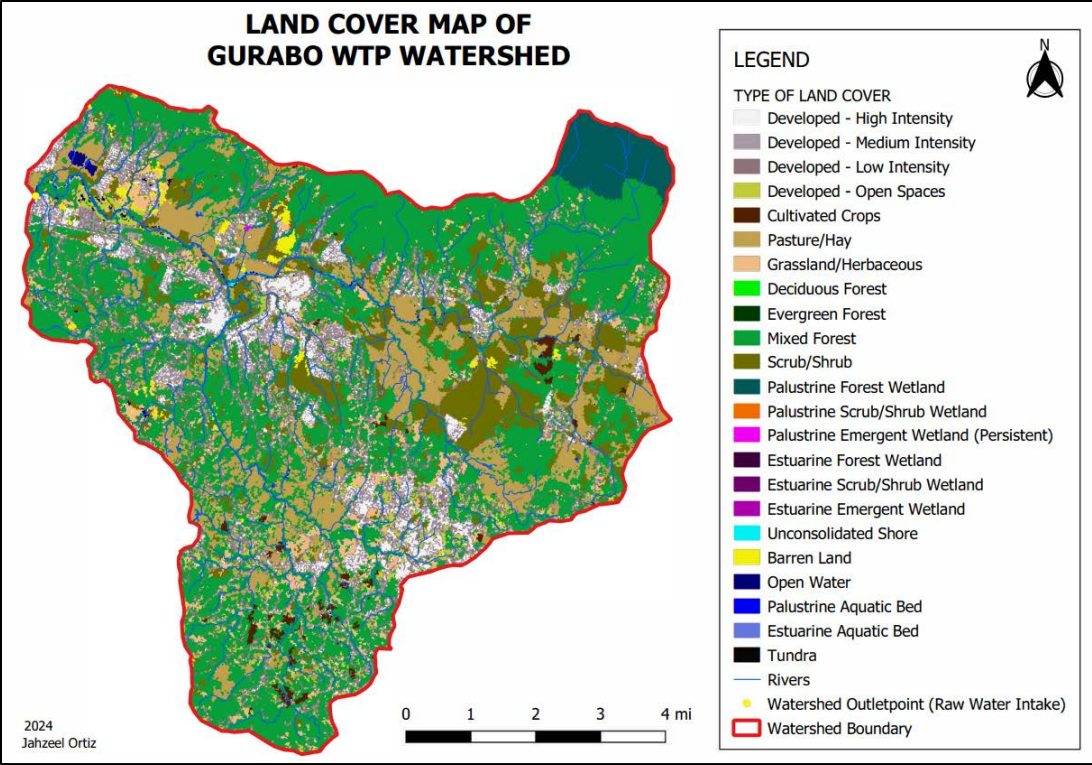


Figure 4
Land Cover Map of the Gurabo WTP Watershed Generated with the NOAA Data Access Viewer

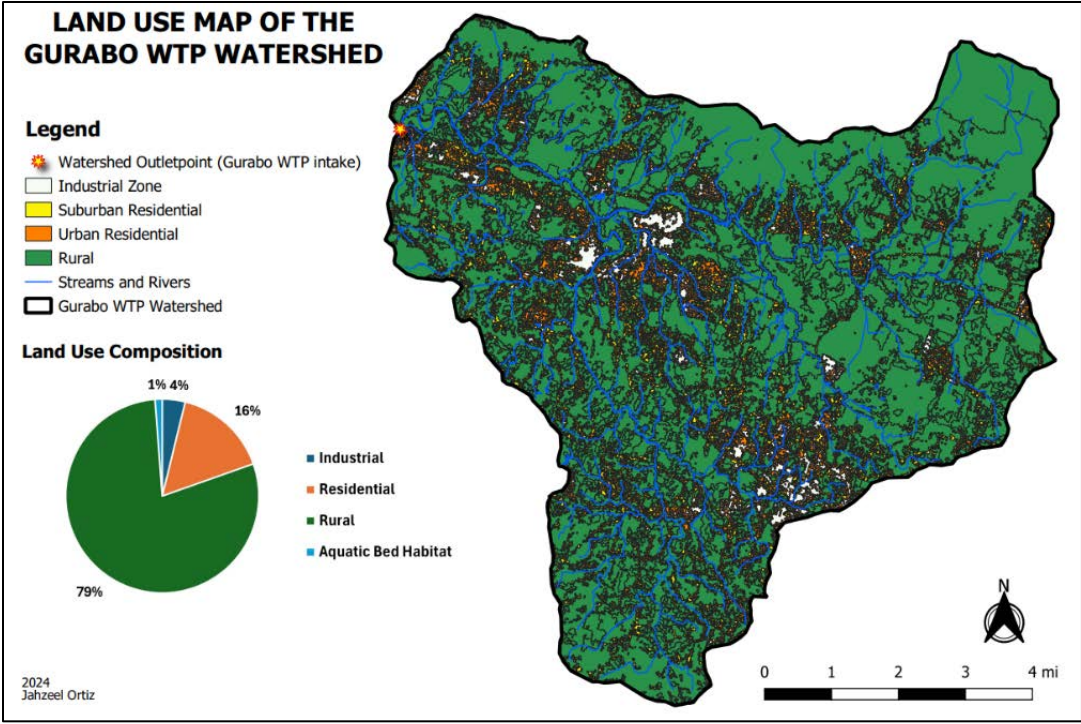


Figure 5
Land Use Map of the Gurabo WTP Watershed and Its Determined Land Use Composition

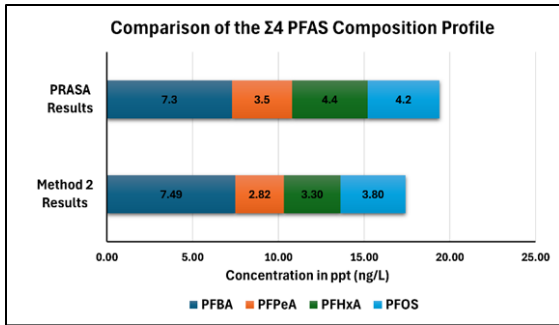


Figure 6
Weighted Average Results of PFAS Concentrations by Land Use in Comparison with the PRASA Results in the 2023 Water Quality Report

DISCUSSION

This study presents a preliminary analysis for identifying potential sources of PFAS contamination within the watershed that supplies the Gurabo WTP. The focus was on identifying facilities within the watershed that are registered under EPA ECHO and classified with NAICS codes known or suspected of using PFAS in their processes (**Method 1**). Additionally, the study developed an analysis to determine the relationship between different types of land use and the contribution of PFAS concentration (**Method 2**). According to the results obtained for Method 1, a total of 35 facilities were identified within the watershed under study as potential PFAS contamination sources. This total is distributed as follows: 9 facilities in the municipality of Gurabo, 11 facilities in Juncos, and 15 facilities in Las Piedras. The identified facilities or sites are categorized as follows: 4 fire protection sites, 1 landfill site, 5 laundry/dry-cleaning sites, 1 material recovery facility, 3 quarry sites, 1 scrap metal site, 2 car wash sites, and 18 manufacturing facilities. It is important to highlight that all the identified facilities are located adjacent to rivers or streams, suggesting potential point or non-point discharges through runoff into these water bodies within the watershed. One of the limitations encountered during this method was the inability to obtain information on NPDES discharge permits issued by the EPA for the identified facilities, likely due to privacy restrictions

on public information associated with these facilities.

One of the most recognized sources contributing to PFAS contamination is fire protection activity sites, which store and use fire extinguishing foam for training, equipment testing, and emergency response events. As mentioned earlier, fire protection-related sites were identified within the watershed. Another potential source identified in the watershed was a landfill. In Puerto Rico, a study by N. Robey, et. al. [13], analyzed leachate from three landfills to identify PFAS concentrations. The investigators detected 51 PFAS compounds, including one that had never been detected before in landfill leachate. The researchers noted that extreme climate events, including rising temperatures and more frequent hurricanes, have placed additional strain on the island's solid waste management infrastructure, adding complexity to an already challenging PFAS management issue.

Laundry/Dry-Cleaning sites were also identified within the watershed, and although these facilities are not widely recognized as significant sources of PFAS contamination, studies are beginning to focus on them. For example, in 2019, the Florida Department of Environmental Protection conducted a study to gather information on whether PFAS could be a contaminant of concern at these facilities [14]. In this study, 15 dry-cleaning facilities across Florida were sampled for PFAS in their effluents. The results showed that 10 of these facilities had PFAS concentrations above the state's Groundwater Cleanup Target Levels.

Facilities such as material recovery facilities, scrap metal sites, and quarry sites are currently being studied regarding PFAS contamination [15]. Studies have shown that automobile shredder residue contains industrial materials manufactured with PFAS and how the use of PFAS in quarry activities has long been employed as part of their operational processes [16].

As part of the results obtained from **Method 2**, the watershed supplying the Gurabo WTP showed a land use composition predominantly characterized by rural areas, which accounted for 79% of the total composition. This highlighted that the highest PFAS concentration contribution under the analysis was attributed to rural land use, which was presented with an average PFAS concentration below 10.0 ppt (ng/L). This was reflected in the results obtained through the weighted average calculation for each PFAS compound, with values of 7.49 ppt, 2.82 ppt, 3.30 ppt, and 3.80 ppt for PFBA, PFPeA, PFHxA, and PFOS, respectively. The total PFAS concentration obtained through this method was 17.71 ppt. When compared to the total PFAS concentration reported by PRASA in 2023, which was 19.4 ppt, the experimental value shows a 10% error relative to the theoretical value. Although a few studies have analyzed the relationship between land use types and PFAS concentration contributions, these results highlight the association between land use and PFAS and how these contaminants can be transported via surface waters. This method can serve as a preliminary and conceptual analysis that may be applied to other watersheds across the island and help estimate PFAS concentrations during the planning process of new projects.

As part of the study's limitations, it is important to mention the need for surface water and sediment sampling in various catchments within the identified industrial, residential, and rural land uses. Additionally, a fate and transport model for PFAS within the watershed could be developed using advanced contaminant modeling software such as the Soil & Water Assessment Tool (SWAT) and MODFLOW. These tools can be employed to create watershed analyses and simulate surface and groundwater quality, enabling predictions of behavior and potential environmental impacts.

CONCLUSIONS

Two analysis methods were performed in this study to evaluate potential PFAS sources and behavior within the watershed: the identification of

facilities registered under the EPA ECHO system with NAICS codes associated with PFAS use (Method 1) and the analysis of the relationship between land use types and their respective PFAS concentration contributions (Method 2). The results show that there are multiple industrial facilities potentially related to PFAS contamination, including fire protection activities, landfills, and the agglomeration of manufacturing sites, all located near water bodies. Additionally, the land use analysis revealed that, although rural areas dominate the watershed, these areas can contribute significant amounts of PFAS, suggesting that contamination may not be limited to industrial sources alone.

The statistical technique performed for PFAS concentrations based on land use demonstrated reasonable accuracy when compared to the actual water quality data reported by PRASA in 2023, with a 10% margin of error. This analysis represents an initial effort, it highlights the importance of continued investigation into the relationship between land use types and PFAS concentrations. The approach presented here may be useful as a preliminary tool for future project planning in drinking water and wastewater infrastructures and environmental impact assessments.

The limitations identified, such as the lack of direct sampling of surface water and sediments, as well as the absence of detailed and calibrated contaminant fate and transport models, emphasize the need for more in-depth studies and the use of advanced modeling tools to obtain a more accurate and comprehensive assessment of PFAS behavior within the watershed. Since PFAS sources are starting to be studied and identified, it is recommended that stakeholders use this type of analysis to targeted PFAS monitoring and reduce the concentrations from those industries and sites.

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