Occurrence of per- and polyfluoroalkyl substances (PFAS) in the Philippine groundwater using a risk-based approach

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Abstract. In the Philippines, particularly in rural and remote areas, groundwater is the primary source of drinking water. Despite its abundance, the quality and availability vary across regions, emphasizing the dependence on distribution through local water districts and private suppliers. However, the characteristics of this water are not consistently monitored, thereby contributing to health and environmental risks. This study examines the occurrence of per- and polyfluoroalkyl substances (PFAS), also called forever chemicals, which are a global environmental concern. Using a risk-based monitoring approach in selected sites in Laguna, Philippines, groundwater samples (n=5) potentially contaminated with PFAS were analyzed using Liquid Chromatography-tandem Mass Spectrometry (LC-MS/MS) method following solid-phase extraction (SPE). Risk-based monitoring showed that the highest total PFAS concentrations were detected in areas located near a firefighting training facility and industrial parks, with an average of 36.77 ± 12.96 ng/L and 41.22 ± 0.35 ng/L, respectively. The detected concentrations surpassed the U.S. Environmental Protection Agency's Maximum Contaminant Levels (MCLs) of 4 ng/L, highlighting potential health concerns. These results underscore the importance of further research, integrated water resource monitoring and management, and the implementation of mitigation measures to minimize PFAS exposure in affected communities.

1 Introduction

Per- and poly-fluorinated alkyl substances (PFAS) are a group of fluorinated chemicals, which have been widely used for over 60 years in cosmetics, coatings, non-stick polymers, textiles, food packaging, insecticides, fluoropolymer manufacturing, medical devices, surfactants, enhanced oil recovery, aqueous film-forming foams (AFFFs: firefighting against oil fires), and other miscellaneous applications [1]. They are environmentally-persistent due to their surfactant-like properties, oil and water repellence, and high thermal and chemical

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stability attributed to its carbon-fluorine bond [2]. These properties caused many potential adverse health effects due to their non-susceptibility to natural degradation that resulted in bioaccumulation in humans as well as in wildlife [3].

Currently, the Philippines is not considered as a hotspot for PFAS occurrence in groundwater, simply because there are no recorded data on PFAS detection. Studies focused on bottled water [4], surface water [5], and blood serum [6] are some of the available data conducted locally. Meanwhile, PFAS occurrence in groundwater has not yet been explored.

This study examines the occurrence of PFAS in the groundwater from potentially contaminated sites. In the Philippines, industrial areas, agricultural areas, and highly urbanized sites were among the possible contaminated sites. However, the sampling points are limited to one area in a region as a preliminary assessment of the groundwater. The study utilized the testing procedure based on EPA's newly approved method 1633 Revised A [7].

2 Literature Review

PFAS contamination is detected in groundwater, surface water, soil, and sediment, which makes it an emerging threat to the quality of drinking water [8]. Major pathway of concern includes PFAS infiltration from industrial discharges such as AFFF, from landfill leachate [9], municipal sewage, and even from septic tanks, as the dominant wastewater treatment practice in some countries [5].

In a modelling study on the fate and transport of PFAS, it was noted that urban areas and agricultural areas are major sources of PFAS through surface runoff, highlighting the significant effect of topography, soil water retention and water-solid adsorption as major factors in the transport of PFAS [10]. A study also showed that PFAS is also present in pesticides and biowastes such as compost [11] and can be transported and end up in the food chain. PFAS may be present in food (eg, seafoods), indoor environments (e.g., interior dust, wall paints), personal care products (e.g., cosmetics), and consumption of contaminated water [12].

According to a National Toxicology Program (NTP) review, exposure to PFOA and PFOS is considered an immune hazard for humans. This determination is based on substantial animal evidence showing suppressed antibody responses, corroborated by a moderate level of evidence from human research [13]. As a consequence of the adverse health effects of PFAS, many countries are prioritizing the reduction of PFAS exposure as a critical step in safeguarding public health and ensuring access to clean, safe drinking water. However, in the Philippines, regulatory measures regarding PFAS in drinking water remain under developed, and research into PFAS contamination is still in its early stages. While there has been significant focus on the effects of endocrine disruptors on human health, policies and regulations for environmental management, particularly those targeting drinking water treatment and contamination, have not yet been established. In a previous study of Velarde et al. [6], 12 types of PFAS out of 41 endocrine disrupting compounds were found in 147 women (half of them were breast cancer patients), mostly in the Region IVA area in the Philippines. Their study highlights the needs for more researchers and policymakers to take action in the treatment, as well as in the regulation, of these harmful chemicals to protect the health of Filipinos.

3 Materials and Methods

The study area is located in Laguna, Philippines, wherein, sampling sites (n=5) were selected based on various categories published by Gluge et al. [1]. In particular, the site was selected based on the potential risk of contamination.

Limit of quantification (LOQs) and limit of detection (LODs) were determined according to EPA Method 1633/1633A. The lowest concentration that can be detected with acceptable accuracy for PFOS is LOQ=1.68 ng/L, and for PFOA, LOQ=1.28 ng/L. The LOD for both analytes is 0.71 ng/L.

Reference standards used for the analysis within the study are M-PFOS (with 13C4) and M-PFOA (with 13C4). Acetonitrile (LC-MS grade) and Methanol (LC-MS grade) were obtained from commercial suppliers. Ammonium acetate (>99%) of LC-MS grade was used in the mobile phase. Milli-Q water was used throughout the experiments.

Groundwater samples were collected from the selected sites using pre-rinsed polypropylene (PP) sampling bottles. The preparation protocol for the bottles involved washing with surfactant free detergent, air drying, sequential rinsing with LC-MS grade water and methanol, followed by air drying. During the sampling, groundwater sample was allowed to flow freely before the collection. The water samples were ice-preserved during transport and stored in the laboratory at 4 °C until extraction.

All samples were extracted in triplicate using solid phase extraction (SPE) based on EPA Method 1633/1633A [7]. The extracted analytes were analyzed using the liquid chromatograph (LC) from Agilent Technologies (USA) coupled with an Agilent 6475 Triple Quadrupole tandem mass spectrometer (MS/MS). Separation of analytes was achieved using a Zorbax Eclipse Plus C- 18 Reverse Phase column.

4 Results and Discussion

Sampling sites were selected according to several criteria, including topography, historical waste management practices, prevailing economic activities, and the source of water samples, with preference given to commercial deep wells. Multiple locations in Laguna, Philippines met these criteria and underwent preliminary assessment prior to sampling. Each site was subsequently evaluated based on its potential risk of pollution. Criteria and evaluation for the selection of the sampling sites are summarized in Table 1. The area with a potential direct source was assigned a High Risk rating (e.g., firefighting training sites and industrial areas), whereas areas with a history of agricultural activities were classified as Moderate to Low Risk.

Table 1. Evaluation of the selected sites based on potential risk of pollution

Site	Coordinates/ Elevation	Description	Potential Source of Pollution	Risk
Site 1	14.18124 N, 121.24223 E / 16 m	A residential village with private pumping well	History of agricultural activities	Moderate
Site 2	14.15286 N, 121.13402 E/ 135 m	A residential village with private pumping well	Nearby manufacturing companies (without specific knowledge of PFAS production or use)	High
Site 3	14.21636 N, 121.11804 E/ 51 m	A training site for fire-fighting activities with private pumping well	Fire-fighting activities	High
Site 4	14.28608 N, 121.05078 E/ 47 m	A residential village with private pumping well	History of agricultural activities, with nearby industrial park	Moderate
Site 5	14.34065 N, 121.05188 E/ 22 m	A residential village with private pumping well	History of agricultural activities, with nearby industrial park	Low-Moderate

Identifying the sources of PFAS in groundwater is critical for evaluating the extent of contamination, while characterizing their composition provides valuable insights into pollution origins. Fig. 1 shows the total PFAS (PFOS + PFOA) in ng/L measured in selected sites of Laguna, Philippines. Site 3 which is a training ground for firefighting activities, exhibited the highest level of PFOS contamination, with an average value of 29.84 ± 12.96 ng/L. This outcome was anticipated, as the site has served as a training facility for firefighting personnel for over three decades. The continued presence of PFOS is attributable to the historical use of Aqueous Film Forming Foam (AFFF), which has long been recognized as a major source of PFOS contamination. Also, due to its extended shelf life, residual AFFF may persist in existing stockpiles and legacy fire suppression systems, thereby contributing to the observed contamination level.

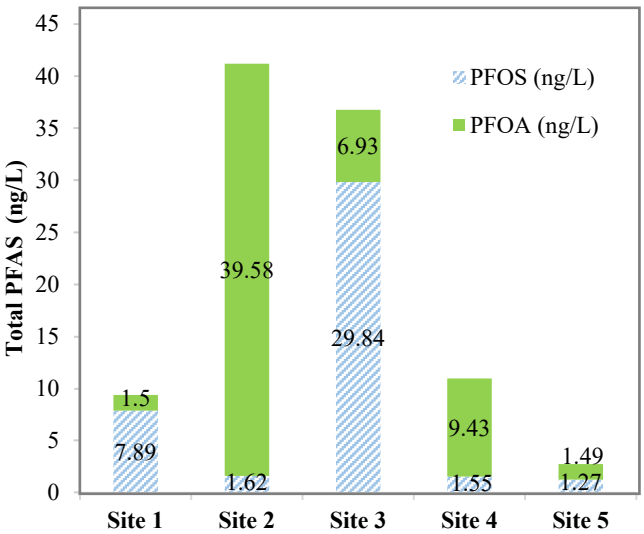

Fig. 1. Total PFAS (PFOS and PFOA) measured in selected sites in Laguna, Philippines.

Site 2, situated at an elevation of approximately 135 m above sea level (Fig. 2), recorded the highest PFOA concentrations, with average value of 39.58 ± 0.35 ng/L. The area is currently a residential village with an unknown land-use history; however, the observed contamination may be influenced by its proximity to a nearby industrial park located within a 3-kilometer radius at an elevation of 143 m above sea level, which is slight higher than Site 2. Additionally, the presence of nearby water bodies may have contributed to the groundwater contamination observed in samples collected from this area.

Based on the literature, a wide range of PFAS contributors from industrial activities, including fluorochemical, petrochemical, fine chemical, paper industries, metallurgical machinery processing, and the discharge of domestic sewage into surface waters [2] account for the largest proportion of PFAS releases, particularly PFOA and PFOS. However, agricultural practices also contribute significantly to the PFAS occurrences [14]. Table 2 summarized the average PFOS and PFOA measured from the 5 sites.

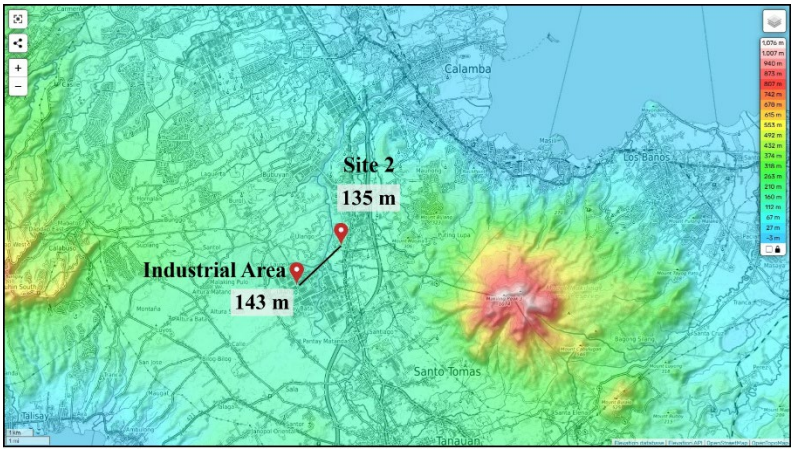

Fig. 2. Topographical location of Site 2 (Generated from OpenTopoMap).

Table 2. PFAS measured from five sites in Laguna

Site	Description	Average PFOS (ng/L)	Average PFOA (ng/L)
1	A residential village with private pumping well	7.89 ± 0.15	1.50 ± 0.05
2	A residential village with private pumping well	1.62 ± 0.06	39.58 ± 0.35
3	A training site for fire-fighting activities with private pumping well	29.84 ± 12.96	6.93 ± 2.44
4	A residential village with private pumping well	1.55 ± 0.02	9.43 ± 0.16
5	A residential village with private pumping well	1.27 ± 0.02	1.49 ± 0.04

Sites 1, 4, and 5 share a history of agricultural activities, though the duration of such practices varies depending on the number of years since each area was converted to residential use. These differences in land-use history may influence the extent and nature of contamination, as longer periods of agricultural activity could contribute to greater accumulation of PFAS or other pollutants, while more recent conversions may reflect transitional impacts associated with mixed residential and agricultural practices.

5 Conclusion

Groundwater contamination by per- and polyfluoroalkyl substances (PFAS) has emerged as a pervasive global concern, driven largely by the extensive and prolonged use of PFAS-containing products such as oil- and water-repellent materials, non-stick cookware, treated textiles, and food packaging. The Philippines reflects this global pattern, with similar pathways of PFAS use and disposal contributing to contamination risks. Yet, despite the growing recognition of PFAS as an environmental and public health issue, the country presently lacks the institutional capacity to integrate PFAS monitoring within its regulatory frameworks.

PFAS levels detected across the five sites in Laguna exceeded the United States Environmental Protection Agency (USEPA) maximum contamination levels of 4 ppt (4 ng/L) for PFOS and PFOA in drinking water [15], indicating potential risks to public health, particularly given that groundwater serves as a primary source of drinking water. In this study, the occurrence of PFAS contamination in selected groundwater samples underscores the urgent need for enhanced environmental monitoring. Importantly, the use of a risk-based approach for site selection proved effective in identifying areas of concern, demonstrating the value of strategic site prioritization in resource-limited contexts. Given that the dataset is limited in scope, both in terms of the number of sites and the compounds targeted, there is a considerable risk of underestimating the true extent of contamination. Future efforts should broaden the analyte scope to include emerging PFAS variants, particularly short-chain alternatives, to achieve a more comprehensive characterization. Routine sampling and analysis in areas with known or suspected PFAS sources (e.g., firefighting facilities, industrial zones) are essential to track contamination trends and assess long-term exposure risks.

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