



# Influence of urban land uses on per- and polyfluoroalkyl substances contamination in urban runoff and the receiving marine environment

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## ABSTRACT

Understanding the influence of urban land uses on PFAS contamination in urban runoff and receiving marine environments is critical for effective urban coastal contaminant management. However, data on PFAS contamination in urban runoff and marine receiving environments under low-flow (dry weather) conditions, which represent baseline contamination, are scarce. This study assessed the influence of urban land uses on PFAS occurrence and fate in urban runoff and adjacent marine environments under low-flow conditions. Water and co-located sediment samples were collected from five sites representing distinct land uses, including airport, residential, mixed port/agriculture, and mixed national park/residential areas, and analysed for 49 PFAS. Twenty-six PFAS were detected in water (including runoff and seawater), and seven in sediment samples. The median total PFAS concentrations were  $0.186 \mu\text{g L}^{-1}$  in low-flow urban runoff,  $0.0062 \mu\text{g L}^{-1}$  in seawater,  $0.69 \mu\text{g kg}^{-1}$  in runoff sediment, and  $0.58 \mu\text{g kg}^{-1}$  in marine sediment. PFAS distribution varied by environmental matrix. Ultrashort and shorter-chain PFAS dominated in water, while longer-chain compounds were more prevalent in sediments. Apart from the commonly regulated PFAS (PFOS, PFHxS, and PFOA), several PFAS including novel compounds bisperfluoroalkane sulfonimides (bis-FASI) and ultrashort ( $\leq 3$  carbons, C), short-chain (4-6C) perfluoroalkyl acids (PFAA), and perfluoroalkane sulfonamides (PFASA) were detected in at least 50% of water samples. In contrast, short- to long-chain ( $\geq 7\text{C}$ ) PFAAs were detected in at least 50% of sediment samples. PFAS profiles in runoff were influenced by land use, with regulated PFAS dominant in runoff from airport and industrial zones, while shorter-chain alternative PFAS more prevalent in runoff from residential areas, reflecting shifts in PFAS usage following regulatory phase-outs. These findings highlight the importance of considering land use in PFAS monitoring and the need to include a broader suite of PFAS, including novel, ultrashort, and other alternative compounds, in urban runoff and coastal environmental assessments.

## 1. Introduction

Per- and polyfluoroalkyl substances (PFAS) are a broad group of synthetic chemicals that are widely used across domestic and industrial applications (Wang et al., 2017). Many PFAS are mobile, chemically stable, and environmentally persistent, leading to their widespread occurrence in the environment (Buck et al., 2011). PFAS have been detected in almost all biotic and abiotic environments where they have been tested for, from urban to very remote regions (Xie and Kallenborn, 2023) including soil, water, air, food, biota, human matrices, and a wide range of consumer products (Evich et al., 2022). There is evidence that

PFAS pose complex risks to ecological and human health (Sunderland et al., 2019), and due to their potential for bioaccumulation and toxicity, PFAS contamination has become a global environmental concern (OECD, 2021). In response to growing evidence of PFAS-related health and ecological risks, many governments have introduced regulations and restrictions on the use and discharge of legacy compounds (Brennan et al., 2021; Industrial Chemicals Environmental Management Standard (ICEMS), 2025; Stockholm Convention), such as perfluorooctanesulfonic acid (PFOS), perfluorohexanesulfonic acid (PFHxS), and perfluorooctanoic acid (PFOA). In many countries including Australia, increasing efforts have been made to identify,

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monitor, and manage PFAS contamination across a range of environmental compartments (HEPA, 2025; Taskforce, 2025).

Understanding the influence of urban land use on PFAS contamination in urban runoff and receiving marine environments is essential to characterise PFAS occurrence, support risk assessment, and inform evidence-based decision making in coastal contamination management activities. Urban runoff is one of the major pathways through which PFAS enters receiving aquatic environments, especially coastal areas (Chen et al., 2025; Kim and Kannan, 2007). However, PFAS composition in urban runoff is highly variable depending on the surrounding land use (HEPA, 2025; Sardiña et al., 2024). Understanding this variability is necessary for effective monitoring, management, and remediation strategies.

While PFAS in stormwater has been widely studied, most investigations have focused on wet weather conditions, where contaminant transport is dominated by episodic storm events (Codling et al., 2020; Houtz and Sedlak, 2012; Kali et al., 2025; Nguyen et al., 2011; Pramanik et al., 2020). In contrast, dry weather flows, which comprise baseflow contributions from groundwater intrusion (Das et al., 2024; Hort et al., 2024), leakage from urban infrastructure (Butzlaff et al., 2025), and other continuous inputs within developed catchments (e.g. illicit discharge) (Novak et al., 2023; Qi et al., 2016), remain comparatively understudied. Under these low-flow conditions, PFAS may be discharged more consistently to receiving environments, representing persistent sources of contamination. As a result, dry weather runoff has the potential to reveal chronic PFAS transport pathways that are not captured through storm driven sampling approaches. To date, limited information is available on the occurrence and composition of PFAS in dry weather urban runoff, or on its contribution to contamination of receiving marine environments, particularly within highly urbanised coastal catchments.

Botany Bay (or Gamay as referred to by Indigenous Australians), is located in New South Wales (NSW) in southeastern Australia and is a heavily urbanised and industrialised estuary that receives runoff from a range of land uses in its catchment, including residential, industrial, and seaport and airport zones. Gamay is also bordered by national park (Kamay Botany Bay National Park) and a Ramsar-listed wetland of international importance (Towra Point Nature Reserve) (DCCEEW, 1984; Heritage, 2023). Despite its ecological and economic importance, little is known about the PFAS contamination in the urban runoff entering Botany Bay or in the receiving marine waters or sediments. The aim of this study was to assess the influences of urban land uses on occurrence and fate of PFAS in urban runoff and adjacent marine environments within a heavily urbanised catchment under low-flow (dry weather baseline) conditions. By comparing PFAS occurrence and concentrations in both water and sediment matrices across areas representing diverse land uses, this work provides insights into PFAS fate, transport, and potential source characteristics under low-flow conditions. Low-flow conditions were specifically targeted to characterise PFAS inputs associated with continuous urban sources. In contrast to high-flow events (i.e., storm and/or heavy rain events), which are transient and highly variable, dry weather flows provide a more stable representation of PFAS occurrence and composition in urban runoff. As such, these conditions are critical for improving understanding of chronic contamination pathways and long term exposure risks to receiving environments.

## 2. Materials and method

### 2.1. Sampling

Grab samples of urban runoff discharge and co-located sediment together with adjacent seawater (i.e., within 0.5 m deep water of the intertidal zone) and co-located sea sediment were collected once per month over a four-month, low-flow (i.e., dry weather, low rainfall) period from January 2025 to April 2025. Samples were collected at low tide from five locations around the bay: Frenchmans Beach (a residential

area; New South Wales (NSW) Planning Portal (Planning, 2020) land-use class R2 Low Density Residential), Yarra Bay Beach (a mixed port and agricultural area; SP1 Seaport, RU4 Primary Production, RE1 Public Recreation), Foreshore Beach (an airport precinct; SP2 Airport), Ramsgate Beach (a residential area; R3 Medium Density Residential), and Kurnell Beach (a mixed national park and residential/environmental living area; C1 National Parks and Nature Reserves and C4 Environmental Living) (Fig. 1). It is important to note that based on the NSW Planning Portal, runoff at Kurnell and Foreshore beaches might also be impacted by industrial activities due large industrial land areas nearby.

Due to limited access, runoff discharge and sediment samples could not be collected at Ramsgate. Additionally, runoff discharge samples were not collected at Kurnell during the sampling period due to insufficient runoff flow. Sediment samples were collected by directly pushing polypropylene centrifuge tubes (Corning® 50 mL) into the substrate, while water samples were collected into high-density polyethylene (HDPE) containers. All sampling containers and equipment were pre-rinsed with methanol followed by ultrapure water (18 MΩ cm, Sartorius) prior to sample collection. There was no detection of any of the analysed PFAS in any blank samples using the same sampling containers or in the rinsate samples produced by rinsing the sampling gloves with ultrapure water, which were replaced between each sample.

Sampling dates, rainfall, longitude and latitude of sampling locations, and field readings (YSI ProDSS Multiparameter Water Quality Meter) of physicochemical parameters of water samples (i.e., pH, temperature (°C), salinity (ppt), dissolved oxygen (mg/L), specific conductivity (-mS/cm), turbidity (NTU)), are presented in Table S2 (SI). The multiparameter water quality meter was calibrated before each use.

### 2.2. Chemicals

Forty-nine native PFAS ( $\geq 98\%$  purity) covering a diverse range of PFAS classes were included in this study (Table S1, Supplementary Information, SI). These include perfluoroalkyl acids (PFAAs), perfluoroalkyl carboxylic acids (PFCAs) and perfluoroalkyl sulfonates (PFASs), perfluoroalkane sulfonamides (FASA), fluorotelomer sulfonates (FTSs), fluorotelomer carboxylic acids (FTCA), perfluoroalkane sulfonamido acetic acids (PFOSAA), fluorotelomer phosphate esters (PAPs), bisperfluoroalkane sulfonimide (bisFASIs), hexafluoropropylene oxide dimer acid, perfluoroalkyl ether carboxylic acid (PFECA), chloroperfluoroalkyl ether sulfonates (Cl-PFESA), perfluoroalkyl ether sulfonates (PFESA), perfluoroethylcyclohexane sulfonate (cyclic PFAS), chloroperfluoroalkane sulfonate, and several zwitterionic PFAS. Among the PFAS examined, ultrashort chain compounds included perfluoropropionic acid (PFPrA) and bisperfluoromethane sulfonimide (Bis FMeSI). Twenty-five isotopically mass labelled internal standards (IS) ( $\geq 98\%$  purity) were used for quantification. Compounds without matching internal standards were quantified using a surrogate standard, selected based on similarity in chemical structure and retention behaviour on the instrument (See Table S1). All native and internal standard PFAS were purchased from Wellington Laboratories (ON, Canada), except for those from bisFASI class, which were purchased from Sigma Aldrich (Merck). Unless otherwise stated, all solvents and other chemicals used for extraction and quantification were at analytical grade purchased from Sigma Aldrich (Merck).

### 2.3. Analysis method

Water and sediment samples were extracted following the US EPA Method 1633A for PFAS extraction and analysis (US EPA, 2024), with slight modifications. Specifically, the carbon clean-up step was omitted during the extraction of water samples. Internal standards were added directly to sample bottles prior to extraction in accordance with US EPA Method 1633, and samples were analysed without filtration; therefore, reported PFAS concentrations represent whole-sample measurements,

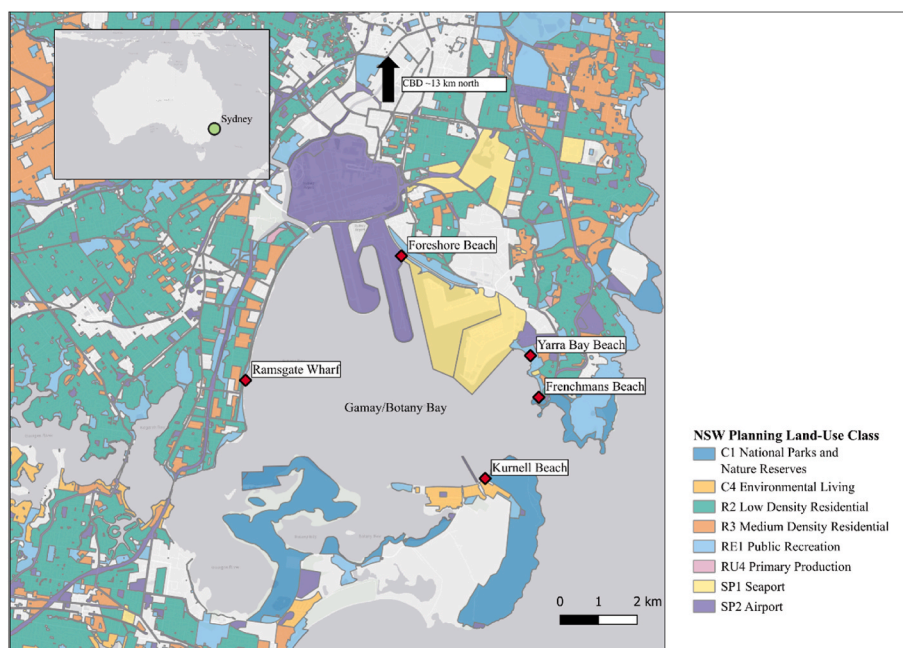


Fig. 1. Sampling locations (stormwater outlets and adjacent marine receiving environment) across multiple land uses (Botany Bay, NSW, Australia). Land use classifications are based on NSW Planning Portal (Planning, 2020).

including both dissolved and particle-associated fractions. The modified method was validated in-house using real sample matrices, and results showed no effect on extraction performance and analysis (i.e., recoveries of internal standards used for quantification are within the acceptable ranges specified in US EPA Method 1633A, and recoveries of spiked analytes of interest fall within acceptable analytical variations, see Table S1 for recovery ranges). PFAS were analysed using a Shimadzu 8060 Triple Quadrupole liquid chromatography-tandem mass spectrometry (LC-MS/MS) system equipped with an electrospray ionisation (ESI) interface, coupled to a Shimadzu Nexera high-performance liquid chromatography (HPLC) system. Samples were acquired in both negative and positive ionisation modes. Separation was achieved using an Ascentis® Express 90 Å C18 column (2.7  $\mu\text{m}$ , 5 cm  $\times$  1 mm) with a mobile phase gradient of 2-95% unbuffered acetonitrile, as described US EPA Method 1633A (US EPA, 2024). A Waters Isolator Column (5 cm  $\times$  1 mm) was used as a pre-injection column. The flow rate was set at 0.4 mL min<sup>-1</sup>. Mobile phase B was initially set at 2%, then increased linearly to 30% over 4 min, to 55% over 2 min, to 75% over 2 min, and to 95% over 1 min, before returning to 2% over 0.4 min and holding for 2 min to equilibrate the system. The total run time was 12 min. Data were acquired and processed using Lab Solutions 5.109. The method limits of reporting (MLR), recoveries of IS, and recoveries of spiked native PFAS for both water and sediment matrices are provided in Table S1 (SI). Analytical accuracy was also assessed using PFAS reference soil and water materials (National Measurement Institute, Australia), yielding recoveries from 78% for F53B major to 114% for PFHxS for soil matrix and from 75% for ADONA to 125% for PFDA for water matrix.

#### 2.4. Data analysis

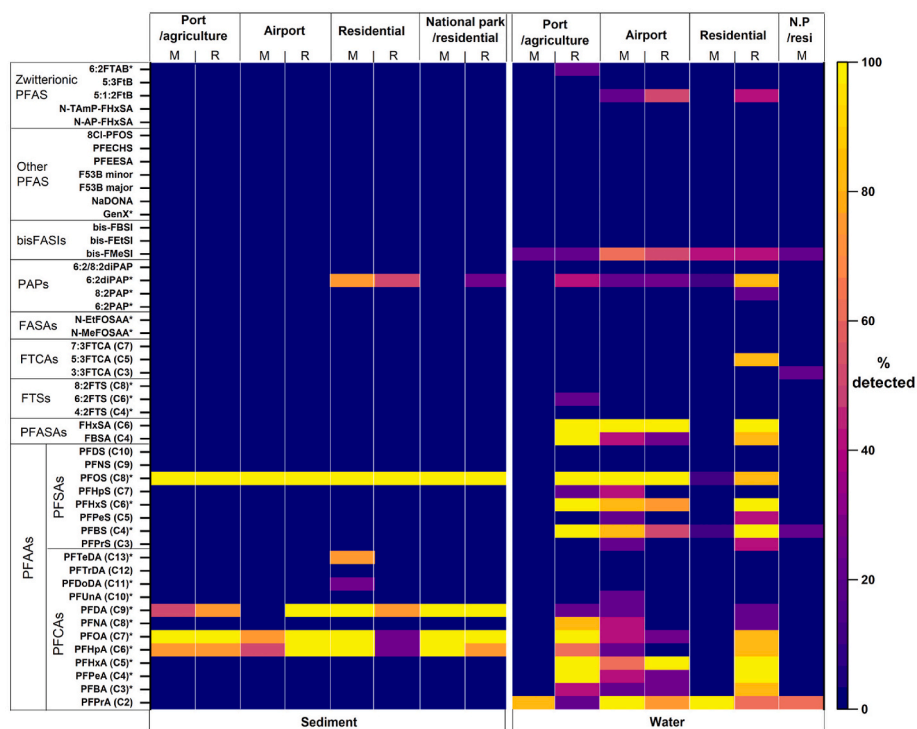
Statistical analyses were conducted to evaluate differences in PFAS occurrence across sites and matrices. Data contained a substantial proportion of left-censored values (i.e., concentrations below the MLR). To account for this, data below the MLR were treated using regression on order statistics (ROS), implemented in R (NADA package) (Helsel, 2011), to estimate values for non-detects while preserving the distributional characteristics of the dataset. Kruskal-Wallis test was used to test for significant differences in total detected PFAS concentrations

among locations, separately for water and sediment matrices. Where appropriate, *post hoc* comparisons were performed using Dunn's test. For compositional analyses (proportional contribution and principal component analysis (PCA)), values below the MLR were substituted with half MLR. As these analyses are based on relative proportions and the dataset contained a high proportion of non-detects, this approach was considered appropriate to preserve meaningful compositional patterns without introducing artefacts associated with modelled values. To explore compositional similarities and differences in PFAS profiles among sampling locations, PCA was performed on normalised relative concentrations (i.e., proportional contribution of each compound to  $\sum$ PFAS). Linear regression was applied to examine the relationship between sediment-to-water partitioning coefficients ( $K_d$ ) and PFAS carbon chain length. All analyses were performed in Origin (2023) and R (Version 4.3.3).

### 3. Results and discussion

#### 3.1. Impacts of environmental matrices on PFAS occurrence and fate

Detection frequency (DF) of PFAS in sediment and in water matrices are presented in Fig. 2. Of 49 PFAS analysed, 26 PFAS were detected in runoff discharge water while 5 were detected in sediment at the discharge point. A total of 22 PFAS were detected in seawater at the adjacent intertidal sampling sites, while 7 PFAS were detected in co-located marine sediment. Concentration of PFAS across all matrices, sampling locations, and sampling dates are shown in Table S3 (SI). The median total PFAS concentrations were 0.186  $\mu\text{g L}^{-1}$  in runoff discharge water and 0.0062  $\mu\text{g L}^{-1}$  in adjacent seawater. These concentrations are comparable to levels reported in urban runoff under dry weather conditions in moderately urbanised catchments (Kali et al., 2025) and are higher than those observed in open coastal waters (Ahrens et al., 2010; Khan et al., 2023; Muir and Miaz, 2021), but comparable to those observed in urban watersheds in developed nations (Ahrens et al., 2010; Kali et al., 2025; Lewis et al., 2025; Nguyen et al., 2011). PFAS profiles differed markedly between runoff discharge and seawater. In seawater, except near the airport site, PFAS were dominated by ultrashort and short-chain compounds, with PFPrA (C2) being the most frequently



**Fig. 2.** Detection frequency of PFAS in sediment (left) and water matrices (right) at runoff discharge points (R) and in the receiving marine environment (M) over four consecutive months (January to April, 2025) across different land uses around Botany Bay, NSW. C is the number of perfluorinated carbon. Compounds marked with an asterisk (\*) have a matching mass labelled internal standard for quantification.

detected (average DF 85%). However, runoff discharge water contained a more diverse suite of PFAS. The most detected compounds (DF  $\geq 50\%$ ) included the precursor FhXSA, long-chain PFAAs such as PFHxS, PFOA, and PFOS, and several ultrashort and short-chain PFAAs including FBSA, PFBS, PFPrA, PFPeA, and PFHxA.

The predominance of ultrashort and short-chain PFAS in seawater likely reflects dilution and mixing of runoff with seawater, as well as the greater mobility and persistence of these more hydrophilic compounds compared to long chained PFAS, which are more hydrophobic and prone to sorption or retention near the source (Ahrens and Bundschuh, 2014; Nguyen et al., 2020, 2022). Despite these differences, the detection of PFAS in seawater indicates that urban runoff discharge remains a contributor to nearshore contamination in Botany Bay. In addition, as a result of the phase-out of many long-chain compounds (for example, PFHxS, PFOA, and PFOS) (HEPA, 2025) shorter-chain alternatives including PFPrA and Bis-FMeSI among other ultrashort and short-chain compounds, are becoming more prevalent in surface water environments (Aro et al., 2021; Ghorbani Gorji et al., 2024; Hartz et al., 2023). However, data on their environmental fate and toxicological effects remain limited.

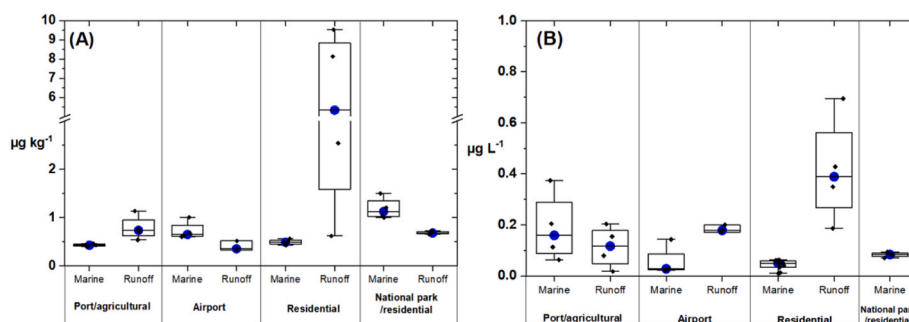
While water acted as the primary carrier, reflecting recent discharges and ongoing inputs of ultrashort- to long-chain PFAS, sediments appear to act as a long-term sink. Specifically, both discharge and marine sediment retained only a limited subset of long-chain PFAAs (C  $\geq 6$ ), including PFHpA (C7), PFOA (C8), PFDA (C10), and PFOS (C8) (Fig. 2). Those compounds were the most frequently detected PFAS in sediments across all sites, with average DF  $\geq 75\%$ . This is consistent with the greater sorption affinity of long-chain PFAS for sediments and particulate matter (Higgins and Luthy, 2006; Nguyen et al., 2020, 2022) making longer chain compounds more persistent with a tendency to accumulate in both discharge zones and the receiving environment once deposited (Ahrens and Bundschuh, 2014). In addition, for compounds detected in both matrices, the field-derived sediment-to-water partitioning coefficients ( $K_d$ ) (Fig. S1) generally increased with carbon chain length ( $p < 0.001$ ), in good agreement with reported trends from

controlled laboratory and field studies (Guelfo and Higgins, 2013; Milinovic et al., 2015; Nguyen et al., 2020).

The median total PFAS concentrations in sediments were  $0.69 \mu\text{g kg}^{-1}$  at runoff discharge points and  $0.58 \mu\text{g kg}^{-1}$  in adjacent marine intertidal zones. The concentrations observed here are comparable to those reported in coastal sediments in other urbanised environments in Australia (Paige et al., 2024) and elsewhere (Groffen et al., 2025; Pulster et al., 2022), though lower than those measured near heavily contaminated sites in Australia such as firefighting training areas or industrial hotspots (Grimison et al., 2023). Except for discharge sediments from the residential site, no significant differences in total PFAS concentrations were observed between marine and discharge sediments (Fig. 3). This similarity suggests that coastal urban runoff discharge is a contributor to both regulated (PFOS, PFOA) (HEPA, 2025) and non-regulated long-chain PFAS in intertidal sediments. With no sediment quality guidelines currently available for PFAS in Australia due to limited ecotoxicity data (HEPA, 2025), their frequent detection in Botany Bay sediments suggests both their persistence and the need for research on marine ecotoxicity and ecological impacts.

### 3.2. Influences of land-use on PFAS profiles

Land use appeared to influence PFAS contamination patterns across the study sites; however, no statistically significant differences in total PFAS concentrations among land uses were observed (Kruskal–Wallis test,  $p > 0.05$ ). Among runoff discharges (where runoff enters the bay), median total PFAS concentrations were highest at the residential catchment (i.e., Frenchmans beach) with  $0.39 \mu\text{g L}^{-1}$  and  $5.34 \mu\text{g kg}^{-1}$  in water and sediment, respectively. Among marine receiving sites (intertidal areas receiving the runoff), median total PFAS concentrations were highest at the port/agriculture site (i.e., Yarra Bay) in seawater ( $0.16 \mu\text{g L}^{-1}$ ) and at the national park/residential site in marine sediment ( $1.12 \mu\text{g kg}^{-1}$ ) (Fig. 3). These differences should be interpreted cautiously given the lack of statistical significance. With the exception of runoff from the residential catchment, total PFAS concentration remained



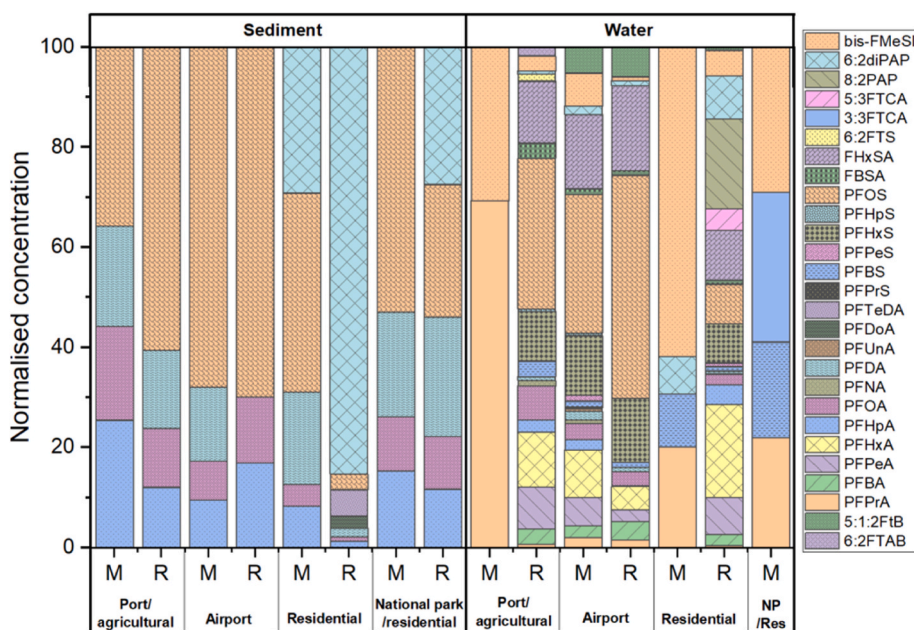
**Fig. 3.** Total PFAS concentrations in (A) sediment matrices and (B) water matrices collected over four consecutive months (January to April 2025) across different land uses around Gamay (Botany Bay), NSW. Total PFAS concentrations are based on ROS-treated data. Boxes represent the interquartile range (25th –75th percentiles), with whiskers indicating minimum and maximum values and blue circles denote median values. Water data for the marine residential category combine results from the Frenchmans and Ramsgate sites. No significant differences in total PFAS concentrations among land uses were observed (Kruskal–Wallis test,  $p > 0.05$ ). Only compounds with a detection frequency  $\geq 10\%$  were included in the analysis.

relatively consistent across the four sampling months (Fig. 3), suggesting stable baseline inputs under dry-weather conditions. By contrast, the higher variability in total PFAS concentrations in residential runoff water and sediments potentially reflects irregular inputs from localised domestic activities (e.g., washing and cleaning) involving PFAS-containing products (Dewapriya et al., 2023; Glüge et al., 2020).

Relative compositions of PFAS in both sediment and water at each site, expressed as proportional contribution of individual compounds to the total PFAS concentration ( $\Sigma$ PFAS) are shown in Fig. 4. The PCA biplot of normalised PFAS profiles across land-use types is shown in Fig. 5. In runoff discharge waters, distinct patterns were identified in both residential and airport /port /agriculture (Fig. 4). Discharges from airport and mixed port/agricultural sites were dominated by regulated PFAS (e.g., PFOS, PFOA, and PFHxS) and FHxSA. On the other hand, residential catchments displayed more diverse profiles compared to the above catchments, characterised by shorter-chain compounds and dominated by PFHxA and PAPs (e.g., 6:2 diPAP and 8:2 PAP), with comparatively lower relative abundances of regulated compounds. These findings align with previous reports of PFAS releases from airports (Milley et al., 2018), industrial/manufacturing sites (Carlson and

Andersen, 2025), agricultural sites (Islam et al., 2025), and residential catchments (Dimitrakopoulou et al., 2024; Eichler and Little, 2020). In addition, distinct differences were observed between residential /mixed residential runoff sediment and other sites (Figs. 4 and 5) due to the presence of 6:2 diPAP. This could be attributed to the strong retention of 6:2 diPAP in the sediment matrix due to its strong sorption potential in soils/sediments (Lämmer et al., 2022). Compounds such as shorter chain PFAS and PAPs are commonly found in commercially available household products (e.g., cleaning chemicals, food packaging, etc) (Dewapriya et al., 2023; Glüge et al., 2020). However, it is also important to note that the PCA clustered runoff discharge water from airport, port/agriculture, and residential land uses together (Fig. 5), indicating strong compositional overlap despite the apparent catchment differences.

Seawater exhibited distinctive PFAS profiles, with the airport site differing markedly from the others (Fig. 5). Despite the expected dilution in seawater, the airport site displayed a diverse PFAS profile closely resembling its runoff discharge, even though the total PFAS concentration (Fig. 3) in runoff was significantly lower than that from the residential catchment (Fig. 3). This pattern may indicate pronounced



**Fig. 4.** Proportional contribution of individual compounds to the total PFAS concentration ( $\Sigma$ PFAS) across different land uses around Gamay (Botany Bay), NSW. (M = marine, R = runoff). Values below the method limit of reporting (MLR) were substituted with half MLR for compositional analysis. Only compounds with detections across the dataset are shown.



## CRedit authorship contribution statement

**Hong T.M. Nguyen:** Writing – original draft, Validation, Methodology, Investigation, Formal analysis, Data curation. **Apoorva Prabhu:** Writing – review & editing, Investigation. **Kia Billings:** Investigation. **David P. Bishop:** Writing – review & editing, Funding acquisition, Conceptualization. **Justin Seymour:** Writing – review & editing, Funding acquisition, Conceptualization. **Martina A. Doblin:** Writing – review & editing, Project administration, Funding acquisition, Conceptualization.

## Declaration of generative AI use

Generative artificial intelligence (AI) Microsoft Copilot was used to assist with language refinement and formatting during manuscript preparation. No AI tools were employed for data analysis, interpretation, or generation of scientific content. The authors take full responsibility for the accuracy and integrity of all content presented.

## 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.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envres.2026.124539>.

## Data availability

Data will be made available on request.

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