



Urban surface water flows contribute more PFAS to marine environments than treated wastewater

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ABSTRACT

Despite the increased number of studies on PFAS globally, our understanding of mass transport pathways remains limited. To address this, we investigated major rivers and creeks feeding into Port Phillip Bay, Melbourne, Australia, for 52 PFAS. We collected 76 grab samples and deployed 28 Polar Organic Chemical Integrative Samplers (POCIS) from 7 locations over 2-months to identify differences PFAS profiles across catchments, the influence of land uses and rainfall. There were 25 PFAS detected in grab samples and 26 in POCIS. Mean Σ_{52} PFAS for grab samples was 76.4 ng/L, with ~90 % made up of ten PFAS. PFOS was the most common but pre-cursors were also present. Our surface water flow model showed a wide range of land uses influenced PFAS profiles across catchments, including those not traditionally associated as point sources, highlighting further investigation is needed. We estimated 57.4 kg/year Σ_{52} PFAS were exported to Port Phillip Bay, with surface water flows exporting over twice the Σ_{19} PFAS compared to wastewater discharges. Our findings show the importance of monitoring a wide range of PFAS in combination with land use and surface water flow models is crucial for mitigating diffuse pollution sources to effectively safeguard both marine ecosystems and community health, worldwide.

1. Introduction

Understanding how per- and polyfluoroalkyl substances (PFAS) enter the environment is of global importance. Popularly known as 'forever chemicals', PFAS are a group of synthetic compounds that have been ubiquitously and widely detected around the world including in remote polar regions and the deep sea (Casas et al., 2023; Sanganyado et al., 2021; Xie and Kallenborn, 2023). PFAS have many applications, including coating non-stick cookware, smartphone screens, waterproof textiles and clothing; and are used extensively in industries such as aerospace, automotive, construction and electronics (Glüge et al., 2020; Lim, 2023). Due to their widespread use and ability to bioaccumulate, concentrations of PFAS have been reported in wildlife and domesticated animals, plants, including crops for humans and livestock, as well as humans, worldwide (Giesy and Kannan, 2001; Mikkonen et al., 2023;

Nilsson et al., 2023; O'Connor et al., 2022). As information on PFAS toxicity grows, it is crucial to understand how these chemicals enter the environment from various sources, as well as their movement and distribution in the environment (Sonne et al., 2023; Wang et al., 2024a,b).

Historically, point sources such as wastewater effluent from wastewater treatment plants (WWTPs), landfills and sites that undertook heavy use of aqueous-film-forming-foam (AFFF) firefighting foams have been the primary focus of studies examining PFAS emissions to freshwater and marine environments (Coggan et al., 2019; Currell et al., 2024; Hepburn et al., 2019; Novak et al., 2023). While the importance of contributions from other, more diffuse sources such as urban surface water flows and rainfall have received limited attention (e.g. Giglioli et al., 2023; Kim et al., 2014; Paige et al., 2024; Thompson et al., 2024). For example, in highly populated centres, urban surface water flows may be particularly vulnerable to PFAS loading, especially during high

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rainfall events, given the extent of impervious surfaces and potential abundance of diffuse PFAS sources (Pfotenhauer et al., 2022). The relative contribution of both known point and diffuse sources to the total export of PFAS from freshwater systems remains currently unknown or underestimated (Byrne et al., 2024; Grunfeld et al., 2024). Consequently, implementing effective policies or regulations to safeguard freshwater and marine environments continues to be a challenge.

At a landscape-scale, a further major challenge is the need to identify the mass transport of both 'legacy' and 'current use' PFAS in waterways (Viticoski et al., 2022). Worldwide, concerns about PFAS have led to establishment of national guideline limits and recommendations for the management of a limited range of longer-chain PFAS (e.g. ECHA, 2025; HEPA, 2025; US EPA, 2025). However, global phase-outs and restrictions have spurred the development of novel, short-chain PFAS ($C < 6$ for perfluoroalkane sulfonic acids, PFASs and precursors; $C < 7$ for perfluoroalkyl carboxylic acids, PFCAs; Brendel et al., 2018) that are now widely in use (Zheng et al., 2023). Reports of PFAS global pervasiveness indicate these chemicals are already widely present in environmental media (Grunfeld et al., 2024; Scheringer et al., 2024; Wee and Aris, 2023; Zheng et al., 2023). There are also developing concerns around potential bioactivity of shorter-chain PFAS, with evidence indicate these chemicals can bioaccumulate (Coy et al., 2022; Pickard et al., 2022). Recent studies in the US are showing environmental profiles of freshwater environments being dominated by the replacement, short-chain compounds (Smalling et al., 2023). Despite this, in most countries, there is still limited information on the presence or mass loadings of long-chain PFAS from riverine systems to marine environments (e.g. Byrne et al., 2024), let alone the presence and fate of their shorter-chain replacements.

Therefore, a detailed analysis of both legacy and current use PFAS levels in major river systems at a catchment level is necessary to determine loads of both short-and long-chain PFAS. In monitoring studies, both grab sampling and passive sampling techniques offer distinct advantages (Hawker et al., 2022; Valenzuela et al., 2020). Grab samples can provide high-resolution concentration data at specific time point, which can assess event-based variability during things like rainfall (Piniewski et al., 2019). In contrast, passive samplers like Polar Organic Chemical Integrative Samplers (POCIS) accumulate contaminants over extended time periods (28 days), capturing time-integrated concentrations (Gobelius et al., 2019) and enhancing the likelihood of detecting episodic or low-level PFAS discharges that grab sampling may miss (Hale et al., 2021; Kaserzon et al., 2019). Given that PFAS concentrations in surface waters can fluctuate due to rainfall, flow variability or intermittent releases, employing both methods can provide a more complete representation of environmental PFAS exposure in surface water.

For catchment monitoring studies, comparing land uses across multiple watersheds is essential to understand the different sources of PFAS to surface waters, and their impact in the environment. Although some studies comparing PFAS to coarse-grain land-use categories have been reported (Nguyen et al., 2022; Paige et al., 2024; Sardiña et al., 2019, 2024), examinations of an extensive suite of PFAS within a fine-grained land-use dataset (e.g., at resolutions $<100 \text{ m}^2$) across several catchments are scarce. Port Phillip Bay in Melbourne, south-eastern Australia, is a semi-enclosed, large shallow bay of $1,930 \text{ km}^2$ which receives run-off from both rural and major urbanised catchments, totalling almost $10,000 \text{ km}^2$ (DCCCEW, 2006). Rainfall strongly influences the delivery of sediments and nutrients, and the average exchange rate for Bay waters is mainly yearly, aside from the southern part closest to the Bass Strait (DCCCEW, 2006). Subsequently, this study aimed to address the following questions.

1. What types of PFAS are present in the major urban surface waters around Melbourne, Australia, and is there a difference between the catchments?

2. Are the PFAS compositions in surface waters influenced by different land uses or rainfall across the catchments?
3. Is the total load of PFAS exported from these surface waters to Port Phillip Bay higher than local point sources, like discharge from a local WWTP?

2. Materials and methods

2.1. Study area and sites

The study area, located in Melbourne (37.8136°S , 144.9631°E), Victoria, in south-eastern Australia, is a temperate environment with mean annual rainfall of 518 mm and temperatures ranging from 5.5 to 26.5°C between the austral winter months to summer (BOM, 2024). The greater Melbourne region, which surrounds Port Phillip Bay, has a population of approximately 5.2 million (ABS, 2024). We established 7 freshwater sampling sites along the key waterways, representing the major catchments that discharge into Port Phillip Bay. The sites included the Werribee, Maribyrnong and Yarra rivers, and Kororoit, Merri, Eumemmerring and Dandenong creeks (Fig. 1). Sites were selected, in part, based on their proximity to nearby flow and weather monitoring stations as well as accessibility. Details on the specific locations, land area, estimated population, land uses for each relevant catchment as well as the WWTP that discharges into Port Phillip Bay are detailed in the supplementary information (SI; section S1). Catchment information is provided in Table S1.1a.

2.2. Sample collection and analysis

2.2.1. Base flow and rainfall event grab samples

Surface water samples were systematically collected on a weekly basis from each site, utilising the grab sampling method. All collections occurred on the same day at each location throughout the austral autumn season, spanning from early March to late April 2023 ($n = 76$). Sampling was undertaken during base flow conditions and during two wet weather events (when rainfall $> 5 \text{ mm}$ in a single occasion). Samples were collected using $2 \times 500 \text{ mL}$ HDPE containers, which were first triple rinsed in the flowing water, then completely submerged $\sim 5\text{--}10 \text{ cm}$ below the surface for collection. Base flow samples were collected weekly from each location for six weeks, while two rainfall events exceeded 5 mm rainfall during the study period. During these rainfall events grab samples were collected from each location, daily, until flow conditions had returned to base flow levels. The first rainfall event consisted of daily grab samples collected from every location over 4 days ($n = 28$), while the second rainfall event, consisted of daily grab samples collected from each location over 2 days ($n = 14$). A summary of the sampling regime is in S1.1b. All samples collected were in accordance with handling procedures outlined in the PFAS National Environment Management Plan (HEPA, 2025) as well as standard EPA Victoria protocols IWRG 701 (EPA Victoria, 2009). Once collected, samples were stored on ice ($<4^\circ\text{C}$) and transported to the National Measurement Institute (NMI, Sydney, Australia) laboratory for analysis.

2.2.2. Passive samplers

Two round Polar Organic Chemical Integrative Samplers (POCIS) for the monitoring of perfluorinated compounds (90 mm diameter, Affinisep® AttractSPE® POCIS PFAS) were deployed at each study site over two 28-day periods (2–30 March 2023 and 2–28 April 2023; $n = 28$) following previous studies (e.g. Gobelius et al., 2019; Hale et al., 2021; Saaristo et al., 2024b). For deployment at each site, the POCIS discs were removed from individual foil packs and placed inside a single, stainless-steel cage that was tethered to a stable structure at a depth of $\sim 0.3 \text{ m}$ in the surface water body. For retrieval, the POCIS discs were returned to the same, individual foil packs which were then resealed and placed on ice ($<4^\circ\text{C}$) and transported to a laboratory. The POCIS sorbents were then removed by transferring $\sim 60 \text{ mg}$ to a blank SPE tube

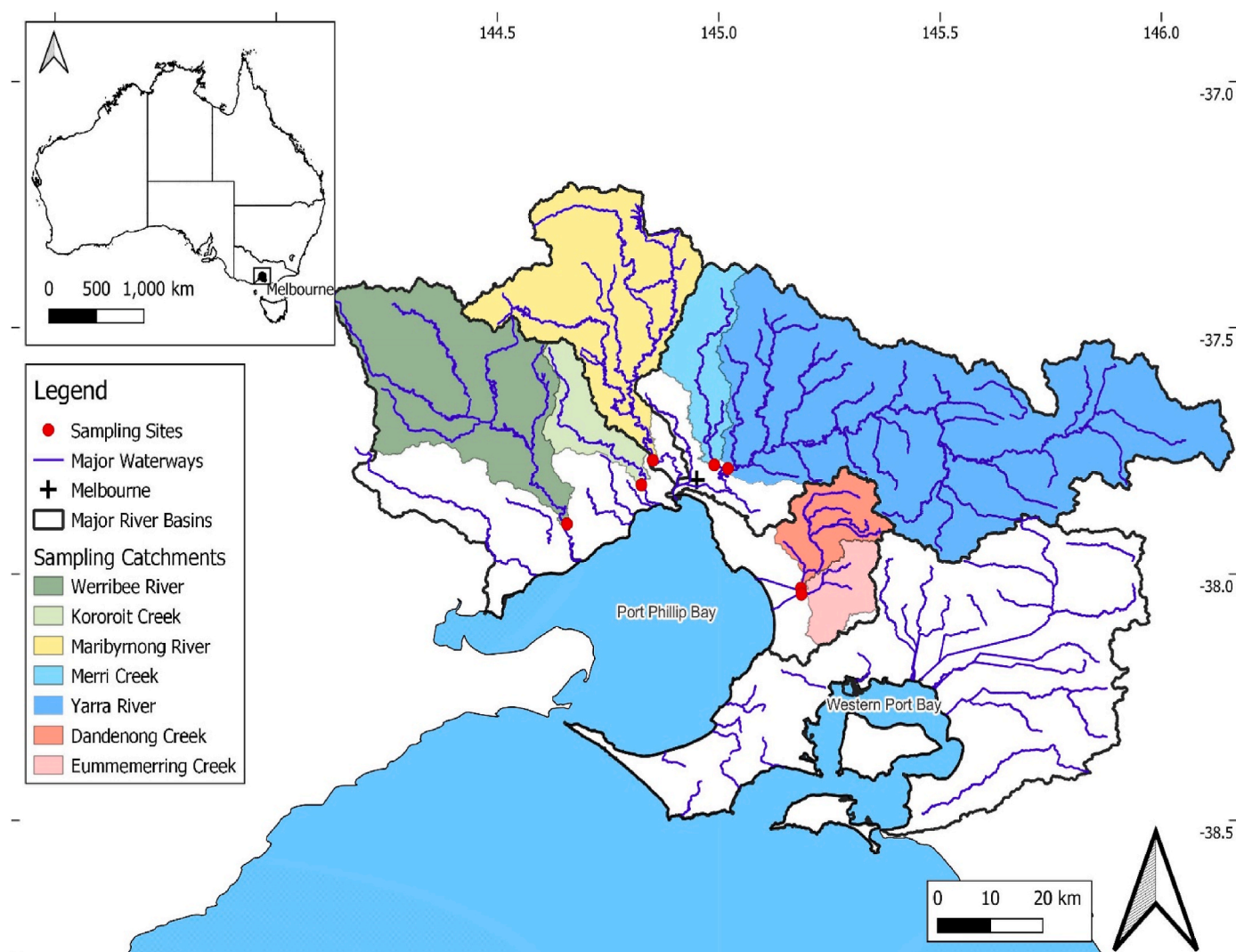


Fig. 1. Surface water sampling locations in Melbourne, Victoria, Australia (37.81°S, 144.96°E). Study sites were chosen as they encompass seven key waterways and their respective catchments servicing Port Phillip Bay.

with a fritted disk and evaporated to near dryness under nitrogen; sorbent samples were then sent to the National Measurement Institute (NMI, Sydney, Australia) for analysis.

2.2.3. PFAS analysis

Sample extraction and analysis was completed by NMI (Sydney, Australia), which is accredited under the ISO 17025 by National Association of Testing Authorities of Australasian (NATA) and ISO 9001 Quality Management Systems under the British Standards Institute (BSI). Samples were extracted and analysed based on US EPA method 1633 (US EPA, 2021). Briefly, water samples were spiked with isotopically labelled PFAS internal surrogate standard [^{13}C -PFAS], acidified with acetic acid and passed through a conditioned SPE cartridge (Strata XL-AW) before drying under vacuum. Samples were then eluted with 8 mL ammonia:methanol (0.4 %) and concentrated to 1 mL under nitrogen (40 °C). Concentrates were spiked again with isotopically labelled PFAS injection recovery standards [^{13}C -PFAS], then finally transferred to LC vials through a nylon filter (0.2 μm) for analysis.

A total of 52 PFAS analytes (Table S1.2) were quantified using ultra-performance liquid chromatography coupled to tandem mass spectrometry (UPLC-MS/MS) Sciex Triple Quad 6500+ instrument in negative electron ionisation using multiple reaction monitoring mode (MRM). The column (Luna Omega PS C18 16 μm 50 \times 2.1 mm) was run

at 50 °C with flow rate of 0.5 mL min⁻¹ and linear gradient (A = 10 mM ammonium acetate in water; B = 100 % LCMS methanol), with an injection volume of 8 μL . The linear gradient (%B) was 0 min 1 %, 0.25 min 1 %, 1 min 45 %, 9 min 85 %, 10 min 100 %, 11 min 100 %, 11.5 min 1 %, 12 min 1 % and 13 min 1 %. Method duration was 13 min.

2.3. Quality assurance and quality control (QAQC)

Field blanks were collected at a rate of 1 in 10 for both grab sampling and POCIS deployment. Field blanks for grab sampling consisted of transferring 2 \times 500 mL of ultra-pure water into the same HDPE containers used for sampling. Field blanks for POCIS disks consisted of a clean disk removed from its package and exposed to the environment for the duration of POCIS deployment at the site on the day. Trip blanks consisted of 500 mL HDPE containers of ultra-pure water, at a rate of one trip blank per sampling day. Field duplicates for grab samples were also collected at a rate of 1 in 10 as per handling methods outlined in the PFAS NEMP (HEPA, 2025), while duplicates of POCIS disks were deployed at a single site during the deployment period. Field blanks, trip blanks and duplicates were treated and examined as normal samples, that is, they were kept on ice (<4 °C) until NMI Laboratories (Sydney, Australia) analysed them. The concentration of PFAS in field and trip blanks were below the limit of reporting (LOR) for every chemical. The

PFAS concentrations in the analysis of duplicate POCIS and grab samples were the same order of magnitude.

Quality of extractions were verified using laboratory control samples (LCS), analytical duplicates, matrix spikes and method blanks with each batch of samples (maximum 20 samples). Matrix spike concentrations of 20 ng/L were prepared by spiking 100 μ L of 100 μ g/L PFAS standard into 500 mL ultra-pure water. The LCS samples were prepared in the same way and used to assess the method precision and accuracy (US EPA, 2024, 2021). Acceptable LCS recoveries were between 64 and 134 %, matrix spikes between 50 and 150 % (Table S1.6). Method blanks showed no background contamination above the LOR for any chemical and analytical duplicates showed good agreement (Table S1.7). Concentrations of PFAS in samples were quantified and reported based on the following parameters: the signal/noise (S/N) ratio >10:1, the concentration was greater than the lowest calibration level, the retention time was within 5 % of the highest calibration result and where available, the qualifying ratio was within 20 % of the highest calibration result. Results which did not meet these parameters were reported as < LOR. All PFAS concentrations reported are internal standard corrected and reported as ng/L, all POCIS values are reported as ng/POCIS.

2.4. Data analysis

2.4.1. Land use/surface water flow model and PFAS loads

To classify land uses upstream of sample sites, a 10×10 -m digital elevation model (DEM) dataset was downloaded from Vicmap Elevation (State Government of Victoria, 2025). Initially, the DEM grid was cropped to the state of Victoria, landscape depressions were digitally filled to avoid spurious creek simulations, and flow accumulations and directions were calculated for all grid cells using the GRASS GIS function *r.watershed* in the R package *rgrass7*. Subsequently, watershed boundaries (i.e., catchments) were calculated for each sample site using the function *r.water.outlet*.

We applied a 2017 Victorian land use information system (VLUIS) dataset (Agriculture Victoria, 2017) and a 2016 VIC meshblock dataset from the Australian Bureau of Statistics (ABS, 2016). Cadastral (VLUIS) and meshblock (ABS) areas were counted if their centroid coordinates fell within watershed boundaries. To avoid double counting of areas that are covered by both land use datasets, we only included ABS meshblocks classified as “Residential”, “Commercial”, “Education” or “Industrial” and omitted VLUIS areas classified as “Urban residential”. Areas of all cadastra were summed by land use categories and then expressed as portions of total catchment areas. The top 40 land use descriptors and percent coverage for each catchment covered are summarised in Tables S1.3-1.4. Mass flows were calculated by multiplying the PFAS concentrations for each river with the relevant flow data (Nguyen et al., 2024). Detailed methods on how estimates of PFAS loads from surface water and wastewater were derived are provided in supplementary methods (Section S1.3).

2.4.2. Descriptive and inferential statistics

Descriptive statistics were calculated using pooled data from either all samples, or all samples within sites. The sum of total PFAS is denoted by $\sum_x \text{PFAS}$ where ‘x’ is the number of PFAS included in the concentrations summed. For descriptive and inferential statistics, compounds below the LOR were considered not detected in this study (i.e., <LOR were converted to 0). Statistical analyses and data visualisations were performed using R (R Core Team, 2020) and RStudio (RStudio Team, 2020). Key packages used were ‘ggplot2’, ‘vegan’, ‘corrplot’, ‘party’ and ‘partykit’.

Principal components analysis (PCA) in (‘prcomp’ in ‘stats’) was used to visually examine PFAS patterns among catchments. Library ‘vegan’ was used to check eigenvalues, screeplots and goodness of fit and are presented in the supplementary results. Exploratory analyses of catchment-level differences in PFAS were performed with conditional inferences trees (‘ctree’ in ‘party’/‘partykit’). Random Forests (‘cforest’

in ‘party’/‘partykit’) were used to examine relative importances of catchment land uses (as percentages) for predicting PFAS concentrations. We assessed accuracy of the Random Forests by comparing a pseudo- R^2 (detailed in supplementary results section S2.1 and Table S2.5) all parameters (except for n) were allowed to default to ‘partykit’ settings.

Kendall’s tau correlation tests (‘cor.test’ in ‘stats’) were used to compare the PFAS concentrations detected in both grab samples and POCIS. Kendall’s correlation values (‘corr’ in ‘stats’) were employed to examine relationships among dominant compounds (i.e. the 10 PFAS with highest overall detected concentrations) and the most important land uses (based on random forests). Kendall’s tau was chosen over Pearson’s *r* because data is non-parametric and it is generally preferred for its small-sample statistical properties (El-Hashash and Shiekh, 2022).

All statistical procedures, including PCA and regression trees were applied to the water grab and POCIS samples separately. The sampling methods have different temporal scales (i.e. POCIS capture PFAS over the entire sample window, whereas water grabs are ‘snapshots’ on a given day). The results showed strong correlation between water grab and POCIS (Supplementary Fig. S1A and B, & S2A and B) so that for the results and discussion, analyses of water grab samples are examined and discussed unless otherwise stated. The same analyses, but for POCIS, are in the Supplementary Material.

3. Results and discussion

Of the 52 PFAS screened, 25 PFAS were detected in grab samples for all sampling events (Table 1), while 26 were detected in the POCIS (Table 2). The contamination profiles were dominated by PFASs (47 %) and PFCAs (29 %), consistent with global studies on surface water (Grunfeld et al., 2024; Muir and Miaz, 2021). The most common PFAS were PFOS, PFHxS, PFHxA, PFOA and PFHpA across all sites (Table 1; 100 % detection frequency (DF) in Table S2.1), confirming the ubiquity of PFAS in these urban waterways. The mean sum of all 52 PFAS ($\Sigma_{52}\text{PFAS}$) between sampling locations showed the following trend: Maribyrnong River (213.6 ng/L) > Kororoit Creek (112.0 ng/L) > Merri Creek (76.1 ng/L) > Dandenong Creek (70.0 ng/L) > Eumemmerring Creek (54.0 ng/L) > Yarra River (12.4 ng/L) > Werribee River (9.5 ng/L). Maribyrnong River had a distinct profile of PFAS concentrations, compared to the other rivers (Fig. 2A and B). This was primarily driven by elevated concentrations of PFOS and PFHxS (Fig. 2C & Table 1). Concentrations of the other major PFAS detected including PFPeS, PFHxA, PFOA and PFPeA were similar when compared to the other sites.

The PFAS profiles in the POCIS broadly matched the profile seen in the grab samples for all sampling events. Kendall’s tau correlation tests of each detected PFAS as a percentage of total PFAS positively correlated both for all PFAS detected ($P < 0.001$, $\tau = +0.738$) and for the top ten PFAS detections by concentration ($P = 0.001$, $\tau = +0.956$; Fig. S2.6A&B). However, between the two sampling methods, there were some differences in the types of PFAS detected. There were 25 PFAS detected in grab samples, compared to 26 PFAS detected in POCIS (Table S2.1 & 2.2). Across the sites, PFAS like PFOSA and the pre-cursors N-MeFOSAA and N-EtFOSSA were detected in POCIS, but not in grab samples. In addition, site-specific differences were observed, for example, PFECBS was detected across three sites using grab samples (Kororoit Creek, Maribyrnong River and Merri Creek), while for POCIS samples, PFECBS was detected at the same three sites plus Dandenong Creek (Tables 1 and 2). These findings suggest that PFAS concentrations may be subject to fluctuations or released in pulses over a 28-day period, which may be missed by grab sampling (Hawker et al., 2022), and/or POCIS may be able to detect PFAS at low concentrations that were not detectable by the grab samples (Hayden et al., 2022; Metcalfe et al., 2014). The PFAS present in grab samples and not in the POCIS were most likely subject to stochastic effects, such as via flow conditions and dilution rates (Criquet et al., 2017; Miège et al., 2015). Overall, the combined grab sample and POCIS results are useful indicators of PFAS

Table 1

Summary of mean PFAS concentrations by location for surface water grab samples (ng/L ± standard deviation) collected from 7 freshwater sites (n = 76), representative of the 4 catchments that drain into Port Phillip Bay, Melbourne, Australia over March and April 2023. Mean concentrations for individual PFAS are reported in Table S2.1.

Catchment	Werribee		Maribyrnong	Yarra		Dandenong	
Site	Werribee River	Kororoit Creek	Maribyrnong River	Merri Creek	Yarra River	Eumemmerring Creek	Dandenong Creek
Perfluoroalkane carboxylic acids (PFCAs)							
PFBA ^a	0.5 ± 1.2	3.8 ± 2.9	1.5 ± 2.0	2.5 ± 2.6	0.9 ± 1.3	1.8 ± 2.2	2.8 ± 2.5
PFPeA ^a	0.2 ± 0.7	10.4 ± 2.7	5.8 ± 1.7	6.9 ± 2.2	0.5 ± 0.7	6.5 ± 2.4	4.6 ± 1.6
PFHxA ^a	1.8 ± 0.6	15.2 ± 4.3	16.8 ± 4.3	12.2 ± 3.7	2.5 ± 1.5	13.2 ± 4.9	9.7 ± 3.3
PFHpA ^a	0.9 ± 0.2	4.8 ± 1.4	2.7 ± 0.7	4.0 ± 1.0	0.9 ± 0.4	3.4 ± 1.3	3.2 ± 0.9
PFOA ^a	1.5 ± 0.4	11.0 ± 3.2	7.1 ± 1.3	9.4 ± 3.0	2.3 ± 1.5	6.9 ± 1.9	7.2 ± 2.0
PFNA ^a	<LOR	1.5 ± 0.3	0.7 ± 0.1	1.3 ± 0.3	0.2 ± 0.4	0.9 ± 0.2	1.3 ± 0.3
PFDA ^a	0.1 ± 0.2	1.9 ± 0.5	0.8 ± 0.3	1.9 ± 0.6	1.1 ± 1.0	1.6 ± 0.4	2.3 ± 0.7
Perfluoroalkane sulfonic acids (PFSA)							
PFPrS	<LOR	1.6 ± 0.7	3.0 ± 1.4	0.7 ± 0.5	<LOR	<LOR	0.1 ± 0.2
PFBS ^a	0.7 ± 0.3	10.4 ± 3.8	11.2 ± 3.5	4.1 ± 1.3	<LOR	2.1 ± 0.5	2.9 ± 0.8
PFPeS ^a	<LOR	4.4 ± 1.7	16.6 ± 6.3	2.3 ± 1.1	<LOR	0.3 ± 0.3	1.1 ± 0.7
PFHxS ^a	1.4 ± 0.2	18.4 ± 6.1	70.9 ± 19.6	9.8 ± 3.6	0.6 ± 0.2	2.6 ± 0.7	8.0 ± 4.0
PFHpS ^a	<LOR	0.7 ± 0.4	2.7 ± 0.9	0.3 ± 0.3	<LOR	<LOR	0.1 ± 0.2
PFOS ^a	2.4 ± 0.4	25.1 ± 5.6	67.9 ± 11.8	17.7 ± 4.8	2.1 ± 0.9	8.6 ± 2.5	19.9 ± 6.7
Perfluoroalkyl sulfonamides							
FBSA	<LOR	0.6 ± 0.5	1.4 ± 0.6	0.2 ± 0.4	<LOR	0.1 ± 0.3	<LOR
6:2 FTAB	<LOR	0.4 ± 0.4	<LOR	1.3 ± 1.2	<LOR	0.1 ± 0.3	0.4 ± 0.7
Perfluorocycloalkyl sulfonates							
PFECBS	<LOR	0.2 ± 0.3	1.6 ± 0.8	0.6 ± 0.4	<LOR	<LOR	<LOR
(n:2) Fluorotelomer sulfonic acids							
6:2 FTS ^a	<LOR	<LOR	<LOR	0.5 ± 0.7	<LOR	0.8 ± 1.7	2.9 ± 3.7
Polyfluoroalkyl phosphoric acid diesters							
6:2 diPAP	<LOR	1.5 ± 3.4	2.9 ± 4.7	0.1 ± 0.4	0.8 ± 2.7	3.9 ± 6.5	3.4 ± 7.7
Fluorotelomer carboxylic acids (FTCAs)							
5:3 FTCA	<LOR	<LOR	<LOR	<LOR	<LOR	1.1 ± 2.6	<LOR
Total PFAS							
Σ ₁₉ PFAS ^a	9.4 ± 2.7	107.6 ± 26.4	204.6 ± 44.6	73.0 ± 19.5	11.5 ± 7.1	48.7 ± 12.7	66.1 ± 19.5
Σ ₅₂ PFAS	9.5 ± 2.7	112.0 ± 25.0	213.6 ± 45.8	76.1 ± 20.2	12.4 ± 7.6	54.0 ± 15.8	70.0 ± 20.4

^a indicates PFAS included in the sum of the 19 PFAS reported in Coggan et al., (2019).

that the ecosystems and associated biota in these waterways were exposed to over the 2 months of this study.

3.1. Characterising PFAS present in urban surface waters

In grab water samples, the number of PFAS detected at all sites ranged between 10 and 23, however the major contribution to the sum concentrations were made up of just ten PFAS (89.9 %; Table 1). These were (from highest to lowest concentration): PFOS (C8) > PFOA (C8) > PFHxS (C6) > PFHxA (C6) > PFHpA (C7) > PFBS (C4) > PFDA (C10) > PFPeA (C5) > PFNA (C9) > PFPeS (C5). All had a detection frequency >60 % (Table S2.1). The profile found here is broadly similar to concentrations of 22 PFAS reported for the same study area (greater Melbourne), but focussed on urban stormwater treatment wetlands and streams from rural, residential and industrial land uses (Paige et al., 2024). The mean sum of Σ₅₂PFAS reported in our grab samples was 76.4 ng/L, which falls between the same values reported by Paige et al. (2024) for residential (76.2 ng/L) and industrial (129.4 ng/L). The profiles of the surface waters in both studies were dominated by longer chain PFAS (i.e. C ≥ 6), however their short-chain replacements were also present. Further, direct comparison of the PFAS profiles between each study suggest patterns in the region may be changing, as PFPeS was detected in only 31 % of wetlands and streams (n = 65; Paige et al., 2024), compared to being included in the top 10 PFAS from the major rivers and creeks sampled here (DF 62 %; Table S2.1). While this study targeted a wider range of PFAS compared to Paige et al. (2024), PFOS was most detected across both studies. The consistent presence of PFOS across all sites raises concerns in terms of its persistence and potential ecological impact. For example, PFOS has shown to be the largest contributor to total PFAS levels in freshwater fish, from a long-term study by the US EPA (Barbo et al., 2023). The implications here suggest there is higher risk for bioaccumulation, particularly in freshwater and marine biota that live in the Port Phillip Bay catchment areas and

monitoring is needed.

Globally, there are increasing reports of short-chain PFAS like PFBS and PFPeA being commonly detected across rivers in countries like China, the US and Europe (Li et al., 2020; Viticoski et al., 2022; Wang et al., 2024a,b). While short-chain PFAS are increasingly reported in global river systems, the continued dominance of longer-chain PFAS in Australian catchment areas here likely reflects regulatory timelines, with bans on PFOS, PFHxS and PFOA not taking effect until July 1, 2025 (DCCEEW, 2024), compared to PFOS production being phased out in the US since 2002 (Viticoski et al., 2022). As bans come into effect, the PFAS profiles found in future will reflect a more dominant presence of their short-chain replacements. Unlike Australia, where PFOS is the dominant PFAS, surface water profiles in major manufacturing regions such as the US and EU have historically been dominated by PFOA (e.g. Happonen et al., 2016; Loos et al., 2008). While the international literature is reporting on the presence of the Gen X (HFPO-DA) replacement for PFOA in freshwater environments globally (Feng et al., 2021), however in this study it was not detected (Table S2.1 & S2.2). To date, no studies have reported Gen X in the Australian environment, highlighting a key gap in national monitoring efforts.

3.2. Comparing PFAS profiles across catchments

Our study shows distinct differences in composition of PFAS at a site-level. Using the grab samples, a PCA of all detected PFAS indicated there was substantial differentiation along PC1 (35.3 % variance explained) and PC2 (17.4 % variance explained; Fig. 2A, loadings for PC1 & 2 Table S2.3). Specifically, there were three overall clusters identifiable, these were: 1) the Maribyrnong River (high levels of PC1), 2) Dandenong, Eumemmerring, Kororoit and Merri Creeks (intermediate PC1), and Yarra and Werribee Rivers (low levels of PC1). A conditional inference tree of PC1 and PC2, showed some additional classification splitting by PC1 and PC2, grouping Yarra and Werribee rivers as similar,

Table 2

Summary of mean PFAS concentrations by location for POCIS (ng/POCIS±standard deviation) collected from 7 freshwater sites (n = 28), representative of the 4 catchments that drain into Port Phillip Bay, Melbourne, Australia over March and April 2023. Mean POCIS concentrations for individual PFAS are reported in Table S2.2.

Catchment	Werribee		Maribyrnong	Yarra		Dandenong	
Site	Werribee River	Kororoit Creek	Maribyrnong River	Merri Creek	Yarra River	Eumemmerring Creek	Dandenong Creek
Perfluoroalkane carboxylic acids (PFCAs)							
PFBA	22.3 ± 44.5	302.5 ± 110	110.5 ± 40.2	97 ± 30	57.5 ± 43.1	165 ± 38.7	98 ± 20.1
PFPeA	54.3 ± 9.1	325 ± 56.9	260 ± 51.6	285 ± 71.4	54.5 ± 14.8	277.5 ± 22.2	217.5 ± 25
PFHxA	79.5 ± 9.1	582.5 ± 76.3	860 ± 241	557.5 ± 184.8	118.3 ± 17.5	512.5 ± 53.2	455 ± 111.2
PFHpA	48.8 ± 7.7	210 ± 18.3	177.5 ± 31	177.5 ± 60.8	43.8 ± 8.6	145 ± 12.9	162.5 ± 29.9
PFOA	97.5 ± 22.1	510 ± 21.6	505 ± 66.6	455 ± 156.1	117 ± 23.0	362.5 ± 39.5	407.5 ± 64.5
PFNA	15.8 ± 1.7	73.8 ± 11.6	59.3 ± 3.2	63.3 ± 15.4	19.3 ± 4.6	54.3 ± 9.6	66.5 ± 14.1
PFDA	24.5 ± 1.7	104.5 ± 20.5	78.0 ± 4.5	93.5 ± 25.8	45.5 ± 5.6	95.3 ± 12.5	124.5 ± 24.5
PFUdA	<LOR	10.3 ± 6.9	<LOR	14 ± 3.4	<LOR	8.0 ± 5.4	16.5 ± 5.3
PFDoA	<LOR	<LOR	<LOR	11.3 ± 1.3	<LOR	<LOR	10.8 ± 7.9
Perfluoroalkane sulfonic acids (PFSA)							
PFPrS	2.5 ± 5.0	31.8 ± 36.9	142.5 ± 33.0	17 ± 19.9	<LOR	5.8 ± 11.5	6.8 ± 7.9
PFBS	39.8 ± 5.9	437.5 ± 114.7	635 ± 193.6	212.5 ± 67.0	27.8 ± 5.3	115 ± 10	180 ± 16.3
PFPeS	21.8 ± 6.4	225 ± 12.9	915 ± 66.1	118.5 ± 26.2	7.5 ± 8.7	36.8 ± 11.9	113.8 ± 34.6
PFHxS	93.5 ± 12.2	817.5 ± 142.4	5300 ± 2221.1	477.5 ± 206.0	47.8 ± 18.5	160 ± 18.3	547.5 ± 38.6
PFHpS	<LOR	37.8 ± 8.0	187.5 ± 49.9	28 ± 10.5	<LOR	8.3 ± 5.6	25.8 ± 4.4
PFOS	170 ± 16.3	1225 ± 150	6475 ± 1806.2	990 ± 200.2	147.5 ± 33.0	532.5 ± 42.7	1192.5 ± 193.8
Perfluoroalkyl sulfonamides							
PFOSA	<LOR	2.5 ± 5	<LOR	5.8 ± 6.7	<LOR	<LOR	2.8 ± 5.5
FBSA	<LOR	22.8 ± 6.3	38.3 ± 5.7	9 ± 10.4	<LOR	<LOR	6.3 ± 7.3
6:2 FTAB	<LOR	22.5 ± 8.2	<LOR	82.5 ± 5.8	<LOR	11.5 ± 13.3	34.8 ± 14.2
Perfluoroalkyl sulfonamidoacetic acids							
N-MeFOSAA	<LOR	8.3 ± 5.6	<LOR	2.5 ± 5	<LOR	<LOR	5.8 ± 6.7
N-EtFOSAA	<LOR	15.8 ± 2.4	<LOR	18 ± 7.6	<LOR	<LOR	<LOR
Perfluorocycloalkyl sulfonates							
PFECHS	<LOR	18.5 ± 7.2	190 ± 0	43.3 ± 25.1	<LOR	<LOR	7.5 ± 8.7
(n:2) Fluorotelomer sulfonic acids							
4:2 FTS	<LOR	<LOR	15.0 ± 18.2	<LOR	<LOR	<LOR	<LOR
6:2 FTS	<LOR	27.3 ± 1.7	20.3 ± 2.6	58.3 ± 5.2	<LOR	34.3 ± 2.8	127 ± 67.1
8:2 FTS	<LOR	<LOR	<LOR	15.5 ± 12.8	<LOR	<LOR	<LOR
Fluorotelomer carboxylic acids (FTCAs)							
3:3 FTCA	3.3 ± 6.5	<LOR	<LOR	<LOR	<LOR	<LOR	<LOR
5:3 FTCA	<LOR	12 ± 1.2	<LOR	16.8 ± 3.9	5.5 ± 6.4	27.5 ± 4.0	23.8 ± 4.0
Total PFAS							
Σ ₁₉ PFAS	667.5 ± 68.2	4888.5 ± 589.6	15583 ± 4596.9	3654.3 ± 1033.8	686.3 ± 103.6	2506.8 ± 107.9	3745.3 ± 547.5
Σ ₅₂ PFAS	673.3 ± 72.2	5022.5 ± 644	15968.8 ± 4651.1	3849 ± 1113.8	691.8 ± 108.8	2551.5 ± 106.9	3832.8 ± 598.5

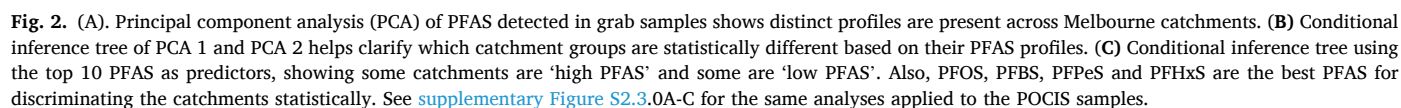
and the Dandenong, Eumemmerring, Kororoit and Merri creeks as similar (Fig. 2B). High values of PFSA, including PFOS, were the main drivers for PC1, as well as FBSA and PFECHS (Table S2.3). When a classification tree was applied using the dominant 10 PFAS as predictors of catchment, distinct groupings were also seen (Fig. 2C). Like the loadings for PC1, the groupings were driven by concentrations of PFSA: PFOS, PFHxS, PFBS and PFPeS. PFOS concentrations indicated significant groupings: >36 ng/L in the Maribyrnong, 3.6–36 ng/L in the Dandenong, Eumemmerring, Kororoit and Merri creeks, and <3.6 ng/L in the Werribee and Yarra rivers (Fig. 2C). Further splitting was driven by PFHxS concentrations in the Werribee (>0.83 ng/L) and Yarra rivers (<0.83 ng/L), while PFBS concentrations split out the Kororoit Creek (>6 ng/L). Finally, to a lesser extent, PFPeS concentrations were responsible for differences between Merri Creek (>6.3 ng/L) and the Dandenong and Eumemmerring (<0.63 ng/L; Fig. 2C). That PFOS occupied the first two nodes on the regression tree in Fig. 2C is not surprising given the ubiquitous concentrations in samples collected. Notably though, was the widespread presence of PFBS, which is a shorter-chain alternative to PFOS (UNEP, 2013). Previous studies have shown this contaminant to be a common presence in surface waterways in this region (Paige et al., 2024), suggesting its presence may increase as its use increases as an alternative to PFOS. The presence of both PFHxS and PFPeS can be attributed to their historical use in firefighting foams and current use in etching chemicals for electroplating, photolithography, and electronics manufacturing (NICNAS, 2015). Indicating industrial activities within these catchments may be impacting the types of PFAS found in waterways (Breitmeyer et al., 2023). Overall, clear patterns existed in the data, which may be related to the density and

range of land uses present in individual catchments.

3.3. Contribution of land uses and rainfall to explaining PFAS in waterways

When integrating land uses on a catchment scale to our analysis, a Random Forests model for PC1 and PC2 showed catchment as a land-use percentage was the second and seventh most important predictor for the axes, respectively (Fig. 3A and B). The rainfall events, described as ‘Weather’ (either ‘high’ rainfall, >5 mm, or no rainfall) showed no influence, being either worse than random (PC1) or approximately close to zero (PC2), in terms of its predictive power. This is likely due to only sampling 2 rainfall events, which may not have captured the initial ‘first flush’ of stormwater (Zushi and Masunaga, 2009). Given the amount of evidence linking PFAS mobilisation to rainfall (Cousins et al., 2022; Guerra De Navarro et al., 2024; Olney et al., 2023), sampling more rainfall events would be useful, particularly within an Australian context.

Despite the differences in PFAS profiles, the top 10 upstream percent land uses for PC1 and 2 were similar, both including ‘catchment’ and things like ‘production.native.forests’ (Fig. 3A and B). Kendall’s correlations were plotted to examine patterns among the top 10 PFAS and the land uses that appeared at least once in the top 15 predictors in the Random Forests analyses for axes PC1 and PC2 (Fig. 3C). The correlations showed these land uses were also all broadly negatively correlated with the presence of PFAS, particularly for PC2 (Fig. 3C; Figs. S2.10–S2.13). In contrast, positive (though weak; Fig. S2.11) associations with PFAS were found in a second, broad grouping of land use percentages,



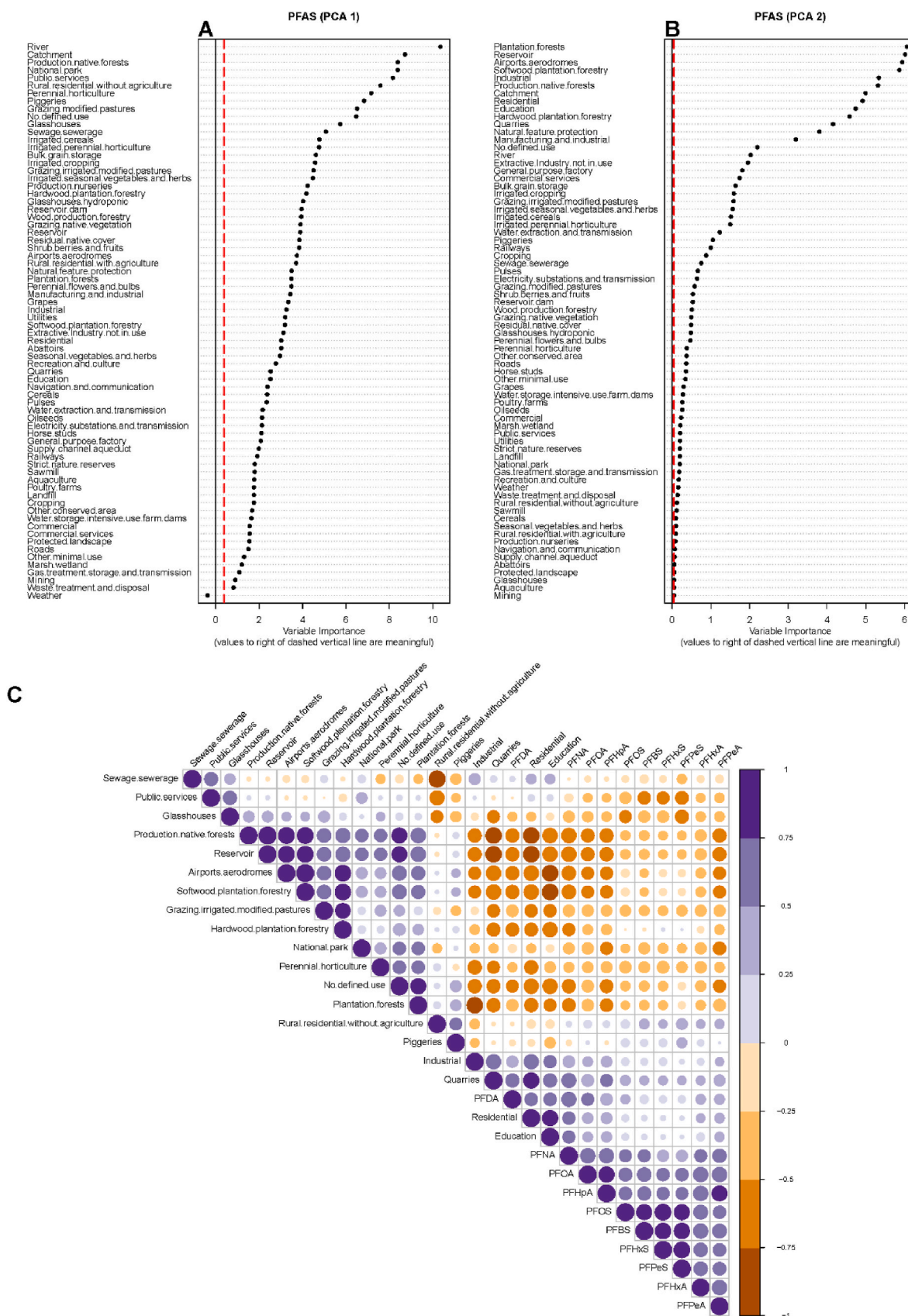


Fig. 3. Relative importance of various catchment land uses for predicting (A) PC1 [R^2 0.82] and (B) PC2 [R^2 0.74] for predicting PFAS concentrations using the grab sample data (ng/L); (C) Correlation matrix using the land uses that fell within the top 10 importances in either random forest. See [supplementary Figs. S2.10-13](#) for the same applied to the POCIS results and correlation coefficients and significance levels for both correlation matrices.

primarily those associated with more intensive human activity such as urban areas (e.g. 'residential' and 'rural residential without agriculture'), and industrial (Fig. 3C). These urban and industrial categories are heterogeneous and likely to reflect diffuse sources, including consumer products, legacy site contamination, stormwater runoff or infrastructure-related contributions (Breitmeyer et al., 2023). While individually weak, these relationships were consistent enough at the catchment scale to appear among the top 10 predictors in our models.

Traditional land uses considered major PFAS sources, such as airports and sewage infrastructure did not rank as high in our analysis. For example, 'sewage and sewerage' were only not the top 10 important variables for PC1 (rank 11) and PC2 (rank 29), which may be due to the limited presence of this land use in the Maribyrnong catchment (e.g. was not listed in the top 40 land uses with highest percentage land cover; Table S1.3). In addition, the Melbourne International Airport, Australia's second-largest, is in the same catchment and upstream of the sampling point. When the PFAS correlation values were examined, they were also overall negative (Fig. 3C). Airports are well known sources of ongoing PFAS contamination due to the long, historical and continued use of firefighting foams (Ahrens et al., 2015; Liu et al., 2023; Milley et al., 2018). Both the Maribyrnong and Werribee catchments having approximately equal percentage of land covered by airports and aerodromes (~0.1 % Table S1.3). These results suggest that on a catchment scale, other, diffuse land uses, with a higher percentage land cover, may have more influence on PFAS compositions in surface waters compared to traditional point sources like WWTPs or airports. However, we note the model does not take into account the intensity of activity for each site, nor any facility-specific inputs, for example, the concentration of specific PFAS that may be discharged from individual sites with a history of AFFF use (Kibbey et al., 2021). These findings highlight that, at a catchment-wide scale, diffuse land sources may play a greater role in PFAS contamination patterns compared to traditional point sources. Further studies could incorporate land use modelling with targeted sampling of point sources (for example, via WWTP presence/absence, proximity to discharge points or flow-based weighting) to enable quantification of specific discharge pathways to help validate model outputs and prioritise management actions.

When the catchment land-use data is regressed using the water grab and POCIS values for the most common PFAS in this study, most PFAS showed similar relationships with land uses upstream as seen in the correlational result above (Fig. S2.14-S2.53). Further, water grab and POCIS results tended to agree on the whole. For example, higher PFOS values from the both the water grab and POCIS were associated with the 'piggeries' land use (Fig. S2.15 & 2.17). Piggeries also positively associated with PFBS, PFHxS, and PFPeS (Fig. S2.21; S2.35 & S2.37; S2.51 & S2.53). The positive associations with these PFAS with the upstream presence of piggeries could be due to the use of agrochemicals, irrigation via recycled water, as well as biosolid or compost amendment to crops used for feed (Ghisi et al., 2019; Jha et al., 2021; Müller et al., 2007; Saliu et al., 2024; Shi et al., 2022), waste treatment processes for manure (Girard et al., 2014; Lam et al., 1993) or the use of recycled materials which have become available for use as fertilisers, soil conditioners or animal bedding (Death et al., 2021; Sobhi et al., 2024). There is limited research around piggeries or animal husbandry as sources of PFAS to surface waters, and more research is needed. The land use model was not adjusted for proximity to sampling sites or any proxies for passive transport of PFAS (such as percentage impervious area) in surface water. Based on the present observations, future sampling regimes and locations could be designed to better locate more diffuse and previously un-investigated sources of surface water PFAS. Future studies could exploit these observations to inform targeted sampling and establish land uses as predictors of PFAS in surface waters, also incorporating targeted source attribution tools or compound ratios, particularly in catchments where industrial or legacy point sources are suspected, to distinguish between consumer product-derived PFAS and site-specific emissions (Charbonnet et al., 2021; Hu et al., 2016).

3.4. PFAS loads to Port Phillip Bay from surface water flows and treated wastewater

We compared surface water PFAS loads to those from WWTPs because WWTPs represent a well-monitored, continuously discharging point source with established direct inputs into Port Phillip Bay (Melbourne Water, 2018). Estimating annual PFAS loads to the bay from both WWTPs and surface waters provides a means to identify and prioritise the dominant sources of contamination. The load of PFAS discharged into Port Phillip Bay was estimated to be 57.4 kg/year (Σ_{52} PFAS; Table 3). The contribution of each waterway followed the trend: Maribyrnong River > Yarra River > Dandenong Creek > Merri Creek > Kororoit Creek > Eumemmerring Creek > Werribee River, which was slightly different to the PFAS profile groupings discussed previously. Outside of land uses, contaminant concentrations, and consequently estimates of contaminant loads can be strongly influenced by water flow (Rafiei and Nejadhashemi, 2023; Saaristo et al., 2024a). As a result, surface water flow can either over- or underestimate contaminant loads, depending on the context. For example, the Maribyrnong River had a higher mean Σ_{52} PFAS than any other waterway sampled (213.6 ng/L; Table 3), leading to a higher PFAS load under lower flow conditions when compared to the Yarra River (120.1 GL/year compared to 892.2 GL/year; Melbourne Water, 2023). In contrast, the mean Σ_{52} PFAS in the Yarra River was comparatively low (12.4 ng/L; Table 3) but annual flow was more than quadruple other waterways sampled, leading to a higher calculated yearly load. The loads estimated here are much lower compared to mass loads estimated for the Danube River in Europe of 4.5 t/year for just four PFAS: PFHxA, PFHpA, PFOA and PFNA (McLachlan et al., 2007). Despite the much wider analytical screen of PFAS used, we still measured a lower annual load compared to previous European studies (McLachlan et al., 2007; Zarebska et al., 2024). However, in the UK, PFAS loads from the Mersey Basin for just 8 PFAS were estimated 68.1 kg/year (Byrne et al., 2024), which is closer to the values reported here. Also, like the Bryne study, the loadings analysis indicates that unknown sources are making a larger contribution than wastewater to the total export of PFAS to the marine environment.

Comparing the PFAS loads entering Port Phillip Bay from urban surface water flows those from WWTP effluent, we estimate the total annual load for Σ_{19} PFAS to be 81.6 kg/year (Table 4), consisting of 54.9 kg/year from concentrations reported here (~67 %) and an additional estimated 8.3 kg/year from other waterways (~8 %). This is compared to treated WWTP discharges, which were estimated to contribute 26.7 kg/year (~32 %) into Port Phillip Bay. Only half of Melbourne's

Table 3

Estimated annual Σ_{52} PFAS loads (kg/year) into Port Phillip Bay per year based on PFAS concentrations in surface water grab samples (n = 90) collected from 7 freshwater sites, representative of the 4 catchments that drain into Port Phillip Bay, Melbourne, Australia.

Catchment	Waterway	Mean Σ_{52} PFAS (ng/L)	Mean annual flow (GL/year) ^a	Estimated annual load Σ_{52} PFAS (kg/year)
Werribee	Werribee River	9.5	78.2	0.7
	Kororoit Creek	112.0	19.8	2.2
Maribyrnong	Maribyrnong River	213.6	120.1	25.7
Yarra	Merri Creek	76.1	95.6	7.3
	Yarra River	12.4	892.2	11.1
Dandenong	Eumemmerring Creek	54.0	40.5	2.2
	Dandenong Creek	70	118.3	8.3
Total annual Σ_{52}PFAS exported to Port Phillip Bay				57.4

^a Mean annual flow monitoring data from August 2020 to August 2023 (Melbourne Water, 2023).

Table 4

Estimated annual Σ_{19} PFAS loads (kg/year) entering Port Phillip Bay from surface water flows and wastewater. Contribution by sampled waterways was determined using site specific data reported in Table 3.

Source	Mean Σ_{19} PFAS (ng/L)	Mean annual flow (ML/year)	Annual Σ_{19} PFAS load (kg/year)
Contribution from sampled waterways	9.4–204.6	1,364,610 ^c	54.9
Other waterways not included in this study	74.4 ^a	111,690 ^c	
Treated wastewater	145.4 ^b	183,333 ^d	26.7
Total annual Σ_{19}PFAS exported to Port Phillip Bay			81.6

^a Estimated from mean of Σ_{19} PFAS in sampled waterways from this study.

^b Σ_{19} PFAS calculated from Coggan et al. (2019).

^c Total mean annual flow between August 2020 and August 2023 (Melbourne Water, 2023).

^d Wastewater discharged to Port Phillip Bay (Melbourne Water, 2018).

wastewater is discharged into the bay (Melbourne Water, 2018; supplementary methods S1.2), however even if we were to double the WWTP output estimated here, it is still less than the estimated total PFAS (kg/year) in surface water. Per person (based on total population estimate Table S1.1a), this equates to emissions of ~ 24 mg/year of Σ_{19} PFAS released via surface water flows and 9.4 mg/year released via treated wastewater. These estimates are significantly less than northern hemisphere studies, where per capita emissions of just PFOS and PFOA from European surface waters were estimated to be 9 and 27 mg/year, respectively (Pistocchi and Loos, 2009). However, overall, these findings suggest that Australian urban surface water flows are an important source of PFAS to receiving marine environments compared to WWTP effluent.

Findings here indicate PFAS are primarily transported via freshwater pathways, as the main source of PFAS compared to treated effluent discharges. The loads delivered via the two mechanisms considered here are mediated by the volume of water (either waste or surface) discharged. Wastewater discharges only made up 11 % of the volume of water received into the bay. Wastewater discharges, however, may deliver higher loads to a smaller area which may be significant for the health of species and ecosystems in their receiving environments. In contrast, the mass of PFAS delivered by freshwater flows would be subject to dispersal throughout the bay (Murray et al., 2001; Parry and Black, 2023). The sampled waterways were a significant source of PFASs (particularly PFOS and PFHxS) to the bay, contributing to ~ 50 % of the total loads calculated (Fig. 4). Due to this, surface water flows were

estimated to deliver 4.7x more PFASs than wastewater discharges, annually. PFASs have declined recently in treated wastewaters from Australia (Gallen et al., 2018). Indeed, recent findings from 75 Australian WWTPs showed while PFOS was the major contributor of mass loads discharged (48 kg/year), the second highest was 6:2 FTS (38 kg/year) (Nguyen et al., 2024). For our surface water findings, this suggests there are other significant sources of these contaminants being transported to aquatic environments that must be identified.

While there is value in detecting a wide range of PFAS to identify risks marine environments, it is also clear that regulated PFAS remain a significant issue. As previously discussed, PFOS was the most common PFAS detected in surface waters. Recently, reports of PFOS in dolphins from the study area were found to be the highest in the world, and the primary contributor to PFAS burden (Foord et al., 2024). Australian fur seals known to frequent the same waters in the bay also have elevated PFOS concentrations, compared populations common along Australia's southern coast (Taylor et al., 2021). Our findings indicate that the elevated PFOS levels in local wildlife are due to PFAS influx from major freshwater sources flowing into the bay, rather than a single point source. Information on further PFAS contamination in Australian marine or freshwater species in this region is sparse, especially concerning recreational marine fish species, which are commonly targeted by both humans and wildlife, given the area's high recreational value. Further work is needed to understand the ecological risk of both legacy and current use PFAS to these species as well as to protect human health, given the similar exposure routes via recreationally caught fish.

4. Conclusion

This study provides clear evidence that surface water flows in urban catchments are a major source of PFAS to Port Phillip Bay, exporting more than double the annual PFAS load compared to wastewater discharges. Using a combination of grab sampling and POCIS, we identified over 25 different PFAS, including precursors not covered by current guidelines. These findings show PFAS are widespread in urban waterways, suggesting standard monitoring may underestimate environmental PFAS burdens. The dominant PFAS for all sites was PFOS, highlighting an ecological risk and potential for bioaccumulation. Land use is a key determinant of PFAS distribution, underscoring the need for catchment-scale strategies for effective PFAS management. It's clear that future studies could identify further, non-traditional point sources of PFAS via hydrological modelling to inform targeted sampling, utilising both grab and passive sampling techniques. An integrated monitoring and modelling framework offers a powerful tool for understanding

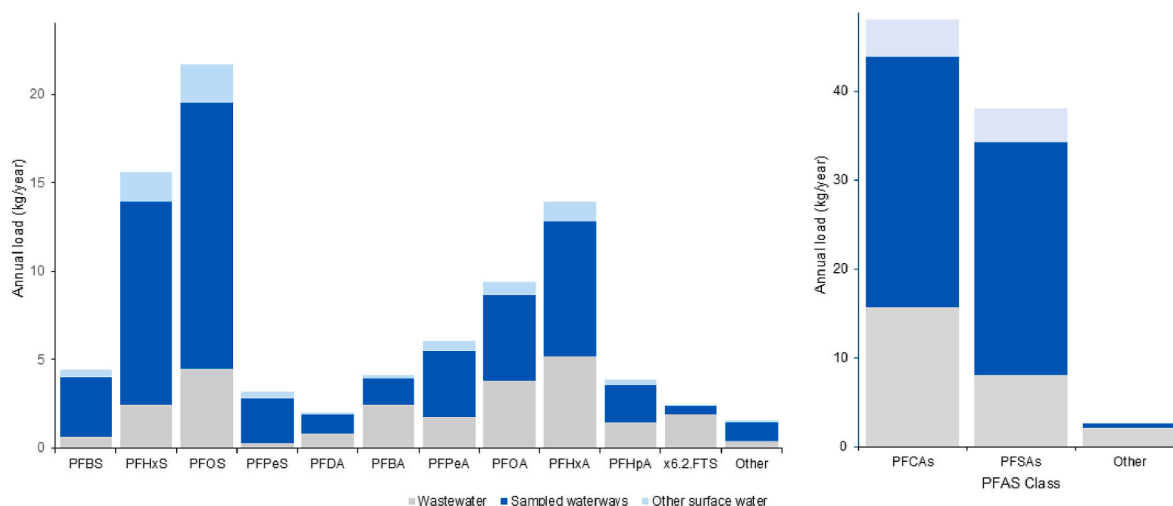


Fig. 4. Distribution of (A) the top detected PFAS as percentages of the total estimated loads of Σ_{19} PFAS (kg/year) and (B) the major PFAS classes detected entering Port Phillip Bay from wastewater and surface water flows (kg/year).

catchment-scale contaminant transport and identifying diffuse sources of PFAS. This supports targeted management strategies to protect coastal ecosystems and guide environmental policy. Future studies that integrate these catchment-scale findings with direct measurements from Port Phillip Bay itself, alongside hydrodynamic modelling will be critical to better resolve fate, transport, and risk to marine biota. Such work would build upon the present findings to develop a more comprehensive understanding of PFAS dynamics from land to sea.

CRedit authorship contribution statement

Phoebe Lewis: Writing – original draft, Project administration, Methodology, Investigation, Data curation, Conceptualization. **Erica Odell:** Writing – review & editing, Writing – original draft, Visualization, Formal analysis, Data curation. **Christopher P. Johnstone:** Writing – review & editing, Writing – original draft, Visualization, Formal analysis, Data curation. **Timothy Chaston:** Writing – review & editing, Formal analysis, Data curation. **Daniel MacMahon:** Visualization, Methodology, Investigation. **Tanya Paige:** Methodology, Investigation. **Simon Sharp:** Methodology, Investigation. **Mark Patrick Taylor:** Writing – review & editing, Resources. **Vincent Pettigrove:** Writing – review & editing, Supervision, Resources, Methodology, Conceptualization. **Minna Saaristo:** Writing – review & editing, Supervision, Resources, Conceptualization.

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.2025.122751>.

Data availability

Data will be made available on request.

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