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Byrne, P, Mayes, WM, James, AL, Comber, S, Biles, E, Riley, A and Runkel, RL (2024) PFAS river export analysis highlights urgent need for catchment-scale mass loading data. Environmental Science and Technology Letters, 11 (3). pp. 266-272.

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PFAS River Export Analysis Highlights the Urgent Need for Catchment-Scale Mass Loading Data

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Cite This: *Environ. Sci. Technol. Lett.* 2024, 11, 266–272



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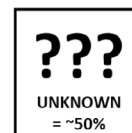
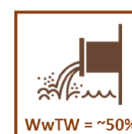


Supporting Information

ABSTRACT: Source apportionment of per- and polyfluoroalkyl substances (PFAS) requires an understanding of the mass loading of these compounds in river basins. However, there is a lack of temporally variable and catchment-scale mass loading data, meaning identification and prioritization of sources of PFAS to rivers for management interventions can be difficult. Here, we analyze PFAS concentrations and loads in the River Mersey to provide the first temporally robust estimates of PFAS export for a European river system and the first estimates of the contribution of wastewater treatment works (WwTWs) to total river PFAS export. We estimate an annual PFAS export of 68.1 kg for the River Mersey and report that the yield of perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) in the catchment is among the highest recorded globally. Analysis of river and WwTW loads indicates approximately one-third of PFOA emitted from WwTWs is potentially stored in the catchment and approximately half of PFOS transported by the River Mersey may not originate from WwTWs. As governments move toward regulation of PFAS in WwTW effluents, our findings highlight the complexity of PFAS source apportionment and the need for catchment-scale mass loading data. This study indicates that strategies for reducing PFAS loading that focus solely on WwTW effluents may not achieve river water quality targets.

KEYWORDS: PFAS, river, urban, loads, wastewater treatment works, point source, nonpoint source

PFOS Transport in Rivers



INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS) make up a class of >4700 chemical compounds first manufactured in the 1930s.¹ PFAS are extremely resistant to chemical and thermal breakdown, making them pervasive in everyday consumer products (e.g., oil and water repellent materials) and in industry (e.g., surfactants and polymer manufacturing). PFAS have been detected in environments^{2–4} and biota^{5–7} worldwide, and recent national-scale studies in the United States and England suggest PFAS are widespread in surface water and groundwater.^{8,9} PFAS have been detected in human serum¹⁰ and have been linked to cancer, birth defects, hormonal imbalances, obesity, fertility issues, and decreased vaccine response.^{11,12}

The highly persistent nature of PFAS and their ability to continuously cycle in the hydrosphere have facilitated transport of these chemicals globally,³ and it is likely that concentrations in certain environmental compartments will increase, even if emissions are curtailed.¹³ Consequently, the level of exposure of humans and wildlife to some PFAS may increase over time, potentially leading to additive and harmful effects when critical thresholds are reached. To understand and manage the exposure of humans and wildlife, we need to

quantify the loads through critical environmental systems. River basins and their anthropogenic and natural drainage systems ultimately control the fate of PFAS compounds by mobilizing PFAS from primary (manufacturing facilities) and secondary source areas (e.g., wastewater treatment works, landfills, airports, industry, and agriculture) and transporting them to the oceans. While recent studies have attempted source apportionment in river basins through analysis of riverine PFAS concentrations and catchment geodata sets,^{14–17} ultimately source apportionment that leads to targeted management interventions requires understanding of the mass loading (product of chemical concentration and river discharge) and transport pathways of PFAS from source areas to rivers.

A recent (2014–2019) national-scale study of PFAS in rivers (targeted analysis of 16 compounds; $n = 302$) in England¹⁸

Received: January 5, 2024

Revised: February 1, 2024

Accepted: February 1, 2024

Published: February 19, 2024



found detectable levels of 12 PFAS (PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFBS, PFPeS, PFHxS, PFOS, 6:2 FTS, PBSA, and PFecHS). It is noteworthy that PFOS and PFOA were detected at ~70% of sites, with the highest PFOS and PFOA concentrations found in northwest England in the River Mersey Basin. Effluents from wastewater treatments works (WwTWs) are thought to contribute substantial amounts of PFAS to rivers in England.¹⁹ While regulation of PFAS in most countries is currently limited to drinking water and surface water standards, others (e.g., United States and Australia) are moving toward restriction of commercial and industrial discharges to the environment.²⁰ In most countries, the focus of regulators is likely to fall on key point sources such as WwTWs.¹⁹ However, understanding the transport and fate of these chemicals at the river catchment scale is essential when developing strategic plans and source models. While some recent studies have shed light on the behavior of PFAS in river basins,^{14–16} there is a distinct lack of temporally and spatially variable mass loading data to establish the relative importance of different PFAS sources to overall PFAS river export.

As governments look to upgrade WwTWs to reduce PFAS emissions to rivers²¹ and regulatory bodies begin to establish global inventories,²² the relative importance (loading) of WwTWs and other potential sources to PFAS riverine export remains unknown. To address this knowledge gap, we conducted a temporal analysis of PFAS concentrations and loads in the River Mersey Basin in northwest England to establish the first high-temporal resolution estimates of PFAS loading for a European river system. We then conducted a mass balance analysis of riverine and WwTW PFOS and PFOA loads to quantify, for the first time, the proportion of riverine PFOS and PFOA loads that can be attributed to WwTWs and unknown sources.

METHODS AND MATERIALS

Study Site and Sample Collection. The wider Manchester conurbation is the second most populous urban area (2.8 million people) in the United Kingdom. The region is located in the River Mersey Basin, comprising the upper River Mersey, River Irwell, River Glaze, River Bollin, and Sinderland Brook catchments (total catchment area of 2030 km²) (Figure S1). The drainage system is heavily modified and urbanized (29%), containing a mixture of land uses typical of many global river basins where high PFAS concentrations have been recorded.⁴ A notable modification of the drainage system is the Manchester Ship Canal (MSC), a navigable 58 km channel connecting central Manchester to the River Mersey Estuary.

River Mersey water samples were collected for PFAS analysis upstream of the tidal limit at Warrington Rowing Club (53°23'15"N, 002°34'00"W) on 32 occasions from August 2022 to July 2023. Unfiltered water samples were collected from below the water surface using a 2 L high-density polyethylene bottle (HDPE) and decanted into two 50 mL HDPE tubes for targeted analysis of 17 PFAS [nine perfluoroalkylcarboxylates (PFCAs), six perfluoroalkylsulfonates (PFSAs), perfluorooctanesulfonamide (PFOSA), and 6:2 fluorotelomer sulfonate (6:2FTS)] by liquid chromatography-tandem mass spectroscopy (LC-MS/MS) (Table S1). WwTW effluent samples were collected for analysis of perfluorooctanesulfonate (PFOS) and perfluorooctanoic acid (PFOA) from 2015 to 2021 as part of the UK Water Industry Research (UKWIR) Chemical Investigation Programme (CIP).²³ River water samples were also collected upstream

and downstream of effluent discharge locations. The numbers of CIP concentration data points for PFOS and PFOA are >1300 and >600, respectively. Further information about PFAS sampling and analytical procedures can be found in the Supporting Information.

River Mersey discharge data (15 min resolution)²⁴ at the time of PFAS sampling were obtained from an Environment Agency multipath ultrasonic flow monitoring station (River Mersey at Westy, station 69037; 53°23'25"N, 002°33'39"W) located ~800 m upstream of the water sampling location. The discharge data obtained from the Environment Agency gauge were verified on several occasions over the study period by independent discharge measurements at Warrington Rowing Club made by a remote-control boat equipped with an acoustic Doppler current profiler (ADCP) (Figure S2). Discharge measurements achieved good coverage across the flow regime from Q95 to Q10 flows (Figure S3). Discharge data for WwTW effluents were obtained from the UKWIR CIP,²³ and discharge data for the MSC were obtained from the Environment Agency.

Load Estimation. The daily loads (grams per day) of individual PFAS for the River Mersey at Westy were calculated as the product of the measured water sample concentrations and the observed river discharge at the time of sampling (river discharge data were within ±15 min of water sample collection). Using the observed relation between river discharge and PFAS loads ($n = 32$), the U.S. Geological Survey Load Estimator (LOADEST)^{25,26} was used to estimate daily PFAS loads for the River Mersey, from August 2022 to July 2023 (12 months). LOADEST has been used widely to simulate concentrations and loads of organic and inorganic contaminants in cases in which daily river discharge data exist, but water quality data are less frequent.^{26–28} In this study, the estimation of PFAS loads is constrained to PFAS transported in aqueous form and does not consider loads associated with suspended particulates. PFAS loads were also estimated for the MSC (using Environment Agency discharge data) and WwTW effluents (using UKWIR CIP discharge data) within the study area. Further information about the estimation of PFAS loads and LOADEST model development and performance is provided in the Supporting Information.

Concentration Analysis. A spatial and temporal analysis of river and WwTW effluent PFOS and PFOA concentrations was conducted to investigate the effect of WwTWs on river water quality and to establish the potential presence of other unknown sources of these compounds in the River Mersey catchment. We also conducted a concentration–discharge (C–Q) analysis²⁹ of PFAS detected in the River Mersey at Westy. The C–Q relation characterizes chemical changes (dilution or concentration) in river water as a function of variability in river discharge and was applied in this study to investigate the control of catchment runoff processes on PFAS transport. Further information about the C–Q analysis methodology is provided in the Supporting Information.

RESULTS AND DISCUSSION

Eleven PFAS were detected in the River Mersey at Westy with detection frequencies between 6% and 100% (Table S2 and Figure S4). The observed peak concentrations were 19.9 ng/L for PFOA, 14.9 ng/L for PFBS, 14.4 ng/L for PFHxS, and 12.5 ng/L for PFOS, and mean concentrations (Table S2) were similar to those observed in other urban river systems.^{14,30–32}

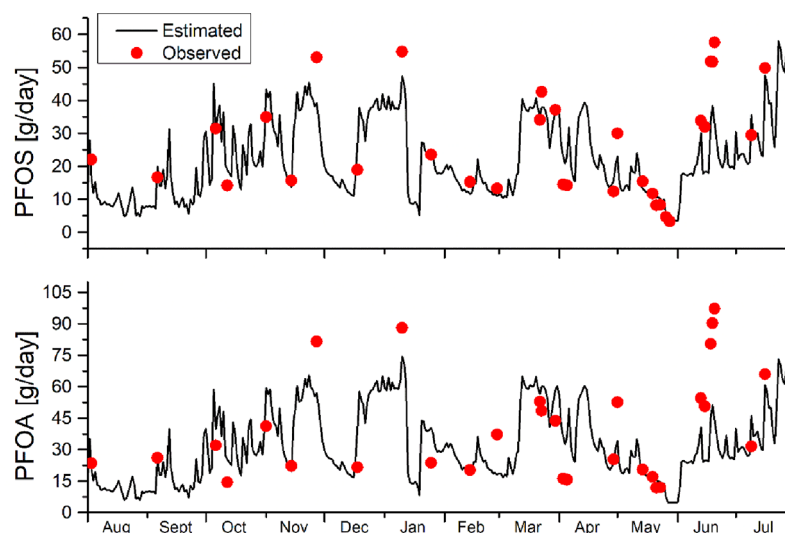


Figure 1. Observed and estimated (using LOADEST³³) PFOS and PFOA daily loads for the River Mersey at Westy (August 2022 to July 2023). The mean PFOS daily load was 22.45 g/day (95% CI of 4.08). The mean PFOA daily load was 32.48 g/day (95% CI of 9.89). Some observed loads exceeded simulated loads where the LOADEST calibration discharge data (15 min resolution) were different from the mean daily discharge value due to dynamic flow.

Mass Loading. Statistical measures of LOADEST³³ model performance for the River Mersey at Westy were within acceptable limits for eight of the 11 PFAS detected (Table S3), with a load bias of -0.05% to 2.5% , a Nash–Sutcliffe efficiency index of 0.5 – 0.9 , and a partial load ratio close to 1. Mean loads for PFOS and PFOA were 22.45 g/day [95% confidence interval (CI) of 4.08] and 32.48 g/day (95% CI of 9.89), respectively. The total \sum_8 PFAS load (PFOS, PFOA, PFBS, PFPeA, PFHxS, PFHxA, PFHpA, and 6:2FTS) in the River Mersey at Westy during the monitoring period (from August 2022 to July 2023, total of 365 days) was 51.1 kg. The largest loads were observed for PFOA (11.86 kg/year), PFBS (10.05 kg/year), and PFOS (8.19 kg/year) (Table S3). Considering also the PFAS load estimates for the Manchester Ship Canal, the total \sum_8 PFAS load for the Mersey Basin was ~ 68.1 kg/year, with loads for PFOS and PFOA estimated to be 9.81 and 14.36 kg/year, respectively (Figure 1 and Table S6). These data are the first temporally robust estimates of PFAS export for a European river basin and represent an essential baseline from which to evaluate the effects of future restrictions on PFAS use and catchment source control measures.

Few robust PFAS daily and annual river load estimates exist in the literature, where PFAS load has been determined from co-located water samples and river discharge measurements and where loading data have been collected over the full range of river discharge conditions. More often, PFAS loads are based on long-term discharge or concentration means,^{30,34–39} potentially introducing error from temporal or spatial variability if concentration and discharge sample sites are not co-located. For these reasons, direct comparison of loading estimates from the River Mersey with other studies needs to be respectful of these differences in the load estimation methods. The levels of export of PFOS and PFOA in the River Mersey Basin are generally lower than estimates from other rivers worldwide (Table S4). However, PFOS yields (obtained by dividing the annual load by catchment area) in the River Mersey Basin are 2–28 times higher than those observed in the Rhone, Seine, and Danube rivers,^{30,34–36,38–40} and PFOA yields are 25 times higher than those observed in the

Danube.³⁹ PFAS yields in the River Mersey are exceeded in the Cape Fear River, United States (PFOA only), which is subject to a substantial point source of effluent from a fluorochemical plant, and in the Tokyo Basin, Japan (PFOS and PFOA), one of the most densely populated urban conurbations in the world. Thus, mobilization of PFOS and PFOA in the Mersey Basin is among the highest recorded, though there are currently few robust international estimates.

A number of studies have quantified PFAS concentrations or loads in WwTW effluents;^{41,42} however, we have found no studies in which the WwTW load contribution to overall river basin PFAS export has been established. In the River Mersey Basin, the cumulative PFOS and PFOA effluent loads for 44 WwTWs were 5.17 and 20.37 kg/year, respectively (Table S6), based on mean observed loads for 18 WwTWs and estimated loads for 26 WwTWs (Supporting Information). Wastewater treatment works contribute substantially more PFOA to the catchment (20.37 kg/year) than has been estimated at the catchment outlet at Westy (14.36 kg/year), indicating substantial potential storage of PFOA in the River Mersey Basin. Sorption of PFOA and PFOS to sediments has been widely reported,^{43,44} and PFOA sequestration in river channel sediments possibly explains the attenuation of PFOA loads in the River Mersey Basin. However, such large storage volumes in urban river basins are concerning, and these sediments may represent an important secondary nonpoint source of PFOA to river water and biota.⁴⁵ Unlike PFOA loads, PFOS loads from WwTWs (5.17 kg/year) were $\sim 50\%$ of the total export at the catchment outlet (9.81 kg/year). It is likely therefore that other point or nonpoint sources in the catchment explain the unaccounted for PFOS load. Although no other sources of PFOS to the river have been confirmed, potential sources of PFOS to the river are widespread in the catchment and include landfills, airports, and consented discharges from construction activities, chemical and textile manufacture, paper mills, metal fabricators, and contaminated land remediation projects (Figure S5). It is curious why the level of attenuation of PFOS in the system appears to be lower than that of PFOA. The geographic location of WwTWs in the River Mersey Basin

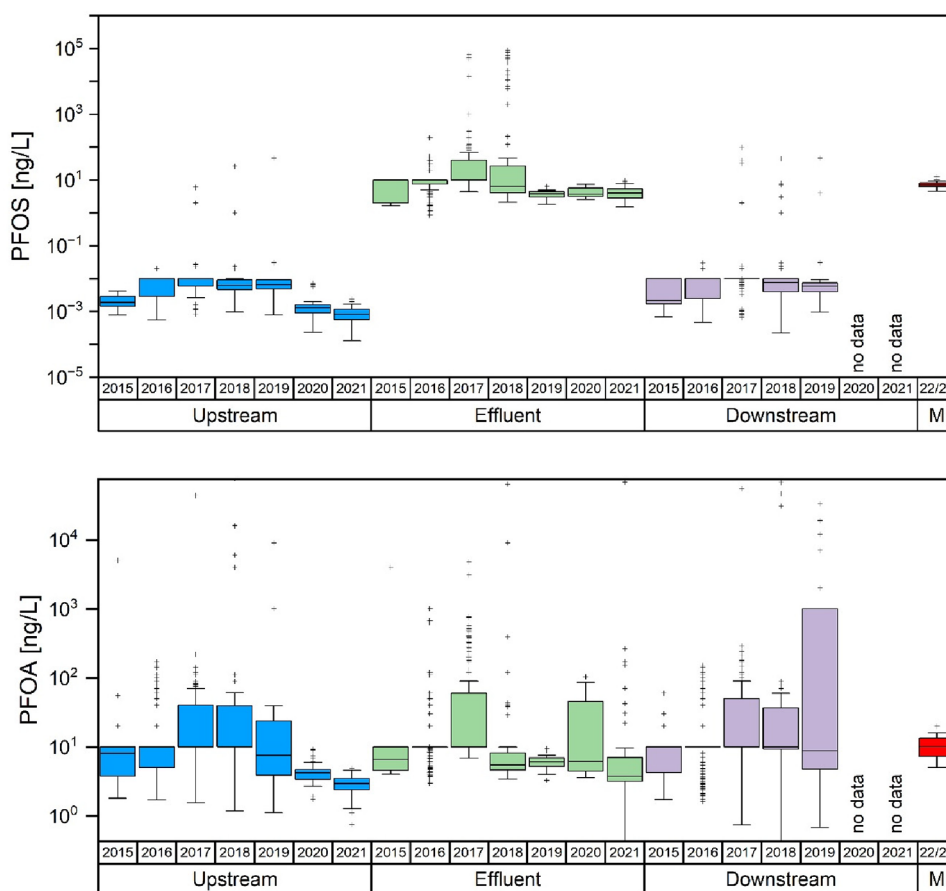


Figure 2. Temporal analysis of PFOS and PFOA concentrations in WwTW effluents in the River Mersey Basin, in river water upstream and downstream of WwTW effluents, and in river water at the River Mersey outlet at Westy. Boxes show the 25th and 75th percentiles, and data outliers are represented as black crosses. The symbol M on the x-axis for the years 2022 and 2023 represents the River Mersey at Westy.

may be important. Most of the PFOS input from WwTWs occurs in the lower part of the catchment and close to the catchment outlet at Westy, whereas most of the PFOA input occurs farther upstream (Figure S6), increasing the travel time for attenuation and storage of PFOA in the catchment.

Analysis of PFOS and PFOA Concentrations in River Water and WwTWs. Figure 2 summarizes the temporal variability (2015–2023) in PFOS and PFOA concentrations in WwTW effluents, in river water immediately upstream and downstream of the effluent discharges, and at the catchment outlet (River Mersey at Westy). Apart from PFOA in river water upstream of effluents, which saw a statistically significant ($p < 0.05$) decrease in concentration between 2015 and 2021, there were no significant increases or decreases in PFOS and PFOA concentrations in effluents or river water between 2015 and 2021 (Table S8). For both PFOS and PFOA, there is a clear pattern of detection of these compounds above the WwTWs, indicating possible unknown sources upstream. PFOS effluent concentrations are consistently diluted downstream of the effluent discharge points. However, PFOS concentrations in the River Mersey at Westy are notably higher than those observed downstream of WwTW effluents, suggesting unknown sources of PFOS downstream of WwTWs. These patterns confirm the findings of the loading analysis and provide further evidence that unknown sources make a large contribution to PFOS export in the catchment. Considering the PFOA data, concentrations in WwTW effluents and in river water upstream and downstream of

effluents frequently exceed concentrations in the River Mersey at Westy. The results of the loading analysis, where WwTW loads exceed Westy loads, confirm this decrease in concentration is not simply due to dilution but instead possibly due to loss of PFOA mass (attenuation) during transport.

Concentration–discharge ($C-Q$) analysis found all detected PFAS exhibited chemodynamic behavior ($CV_C/CV_Q > 0.2$) (Figure S7), confirming connectivity between PFAS source areas and the river is spatially and temporally variable. We identify two broad groups in the data. Group 1 includes five PFAS (PFBA, PFBS, 6:2FTS, PFOA, and PFHxS) that show moderately chemodynamic behavior ($b < \pm 0.1$; $1.0 > CV_C/CV_Q > 0.2$), indicating concentrations vary over time, but in a nonsystematic way (i.e., there is no flushing or dilution signal). Group 2 includes four PFAS (PFHxA, PFHpA, PFOS, and PFPA) that show moderately chemodynamic behavior where there is some evidence of systematic hydrologic controls on concentration ($b > \pm 0.1$). However, the R_2 values (concentration vs discharge) for group 2 PFAS are low, and the standard errors of the slopes are not statistically significant (Table S7), indicating nonsystematic behavior of this PFAS group also. In summary, hydrological processes of dilution and flushing are not apparent in the PFAS concentration data at the catchment outlet. This may be explained by the urbanized and highly regulated nature of the River Mersey drainage system, which may dampen any dilution or flushing signal in response to catchment runoff. However, discharge of effluent from

WwTWs operates independently of catchment runoff processes in a nonsystematic way and may explain the PFAS export patterns observed in the C–Q analysis.

Implications. Our PFAS loading and concentration analysis confirms that WwTWs are an important source of PFOS and PFOA to the River Mersey Basin. Unfortunately, river export estimates for fluorotelomers and short-chain, more mobile PFAS cannot be compared with WwTW loads as only PFOS and PFOA effluent data were collected for the CIP. However, routine monitoring of these compounds in effluents is vital due to the low efficacy of conventional water treatment technologies and the greater potential for long-range transport of short-chain PFAS.³⁷ Our findings indicate ~50% of the total PFOS export in the River Mersey may originate from unknown (point and nonpoint) sources. The supporting evidence for the importance of unknown sources is presented in the spatial and temporal analysis of PFOS and PFOA in WwTW effluents and river water, which shows both compounds are frequently detected upstream of WwTW effluents throughout the Mersey Basin. Our findings also suggest that a large proportion of the PFOA discharged by WwTWs (and potentially from other sources) could be stored within river channels, presumably in sedimentary environments.⁴⁶ However, there may be some uncertainty in the PFOS and PFOA WwTW effluent loads, where these data were estimated. We consider the River Mersey Basin to be typical of many other highly regulated, urbanized, and industrialized river basins with high population densities and would therefore expect high load contributions from point and nonpoint sources, and PFAS storage and release from sediments, to be observed more generally. This complicated PFAS export regime is reflected in our concentration–discharge analysis, where transport of PFAS from source areas to rivers may be buffered by anthropogenic flow controls (including WwTW discharges).

Considering the complexity of PFAS loading in urban river basins, large-scale investments in upgrades to WwTWs to remove PFAS and improve river water quality need to be carefully weighed against the potential effects of unknown (point and nonpoint) sources of PFAS in river basins. Despite numerous studies and reports documenting potential sources of PFAS to rivers (e.g., landfill leachate, contaminated groundwater, runoff from agricultural land, airports, and military bases),^{30,32,47,48} the actual load contribution of these sources to total river PFAS export remains unknown. Our findings highlight the urgent need for catchment-scale mass loading data at high temporal resolution that can locate and “bracket” PFAS sources to rivers and quantify the loads associated with those sources. These data, in turn, could underpin effective source control measures (catchment management) and use restrictions. This study indicates that strategies for reducing the load of PFAS in urban rivers that focus mainly or solely on WwTW treatment may not achieve river water quality improvement targets or prevent the transport of PFAS to the oceans.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.estlett.4c00017>.

Detailed information about the sampling methods and materials and the modeling approach (Methods and Materials), location of WwTWs in the River Mersey

Basin (Figure S1), relationship between river flow measured by a remote-control ADCP and an ultrasonic gauge (Figures S2 and S3), PFAS compounds detected in the River Mersey (Figure S4), map of all potential sources of PFAS in the River Mersey Basin (Figure S5), PFAS loads of WwTW effluents (Figure S6), concentration–discharge analysis (Figure S7) (PDF)

PFAS limits of detection (Table S1), PFAS concentrations (Table S2), summary of the LOADEST model output (Table S3), comparison of PFAS loads measured in the River Mersey and elsewhere (Table S4), PFAS concentrations and loads in WwTW effluents in the River Mersey Basin (Table S5), estimation of WwTW effluent loads to overall PFAS loads in the River Mersey (Table S6), summary of concentration–discharge analysis results (Table S7), and summary of statistical analysis comparing river water and WwTW PFAS concentrations (Table S8) (XLSX)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported by the Liverpool John Moores University Strategic Research Development Fund. R. L. Runkel's contribution was funded by the U.S. Geological Survey through the Environmental Health Program of the Ecosystem Mission Area. Discharge data for River Mersey at Westy and the Manchester Ship Canal were provided by the Environment Agency (of England). Wastewater treatment work effluent discharge and PFOS and PFOA concentration data were sourced from the United Kingdom Water Industry Research Chemical Investigation Programme.

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NOTE ADDED AFTER ASAP PUBLICATION

The version of this paper that was published ASAP February 19, 2024, was missing a Supporting Information file (excel file with supporting tables). This was added, and the revised version was reposted February 23, 2014.