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A source-based framework to estimate the annual load of PFAS in municipal wastewater

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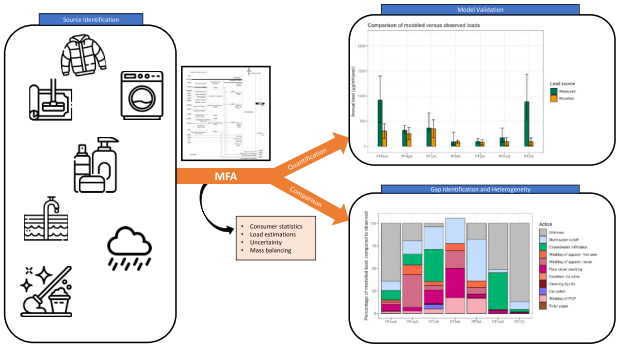
HIGHLIGHTS

- A source-based approach can reliably predict loads of certain PFAS in wastewater.
- Precursor transformation of PFAS in apparel plays a major role.
- Emission loads for PFCAs are explained to a larger extent than for PFSAs.
- Sources of PFAS vary in the magnitude of contribution with respect to the chemical in question.
- Large contribution of environmental, diffuse and unknown sources to loads of PFOS.

GRAPHICAL ABSTRACT



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ABSTRACT

Per- and Polyfluoroalkyl substances (PFAS) are a class of persistent chemicals, whose impact has been observed in various environmental compartments. Wastewater treatment plants (WWTPs) are considered a major emission pathway of PFAS, specifically in the context of the aquatic environment. The goal of this study was to develop a compartmentalized, source-based load estimation model of 7 PFAS within the municipal wastewater influent. Consumer statistics, data from literature on PFAS concentrations and release during use, and specific sampling activities for environmental flows in the related city were used to estimate per capita emission loads. Model results were compared with loads obtained through the monitoring campaign at the municipal WWTP influent. A wide range of discrepancies (≈5 % to ≈90 %) between loads observed in the WWTP influent and source based model estimates was noticed. The loads less accounted by the model were associated with sulfonic acids (PFSAs), whereas for carboxylic acids (PFCAs) most of the observed loads could be reasonably explained by the model, with even an overestimation of nearly 5 % noted for PFNA. Higher heterogeneity in sources was observed in the PFCA group, with a noticeable dominance in the share of consumer products. PFSAs had less of a consumer product input (<20 %), with the rest of the modelled load being attributed to environmental inputs. A large gap of unknown loads of PFSAs indicates a need for examination of other, not yet quantified activities that can potentially explain the remainder of the observed load. Especially commercial activities are considered as

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potential additional sources for PFSAs. These findings signify the importance of PFAS that originate from both consumer products, as well as environmental inputs in the overall load contribution into the sewage, while identifying the need for further investigation into commercial sources of PFAS emitted into the municipal wastewater.

1. Introduction

Per- and polyfluoroalkyl substances (PFAS) are an abundant class of synthetic chemicals whose structural properties have made them known for their environmental persistence (Buck et al., 2011), ubiquitous use (Glüge et al., 2020), and health effects (Starnes et al., 2022), among other characteristics. These attributes have made it possible for PFAS to be transported over long distances and affect multiple environmental compartments (Benskin et al., 2012). The main risk of such availability of PFAS can be the damaging human and environmental exposure (Sunderland et al., 2019). One of the major environmental emission pathways of PFAS are wastewater treatment plants (WWTP), with estimated emissions into the river from these sources reaching over 400 mg km^{-2} a^{-1} for some cases (Kittlaus et al., 2022). The presence of PFAS in wastewater can be due to a variety of processes. These may include commercial activities, release during use and maintenance of frequently used consumer products (Herzke et al., 2012), as well as due to loads introduced via recirculation such as rainfall (Cousins et al., 2022), tap water (Filipovic and Berger, 2015) and stormwater runoff (Houtz and Sedlak, 2012; Xiao et al., 2012). Adding to the significance of this pathway is the fact that these compounds have demonstrated either a retention or an increase in concentration during the wastewater treatment process in multiple studies (Lenka et al., 2021; Müller et al., 2023), making the task of conducting an in-depth research into the sources and pathways of PFAS emissions even more valuable for proper environmental management practice.

However, no research thus far has attempted to conduct an in-depth quantification of all the known sources and pathways that contribute to the PFAS loading into the municipal WWTP influent. Instead, the focus has been on either a single product of interest, or process (Chen et al., 2020; Thompson et al., 2023; Whitehead et al., 2021). This is further complicated by the fact that recent findings have shown that PFAS undergo a variety of chemical processes from production until disposal. One such case is an observed increase in the concentration of terminal PFAS during product use and maintenance, as in the case of PFAS-treated apparel (Schellenberger et al., 2022; van der Veen et al., 2022, 2020). This phenomenon was not taken into account in prior emission estimation studies (Vestergren et al., 2015). Additionally, some pathways, such as groundwater infiltration into leaky sewer systems have not been studied in terms of PFAS loads, despite groundwater showing susceptibility to PFAS contamination (Sharma et al., 2016), and groundwater intrusion being a significant contributor to the overall water inflow introduced into the sewers (Wittenberg and Aksoy, 2010). Stormwater runoff, although noted in multiple occasions (Houtz and Sedlak, 2012; Xiao et al., 2012), is geographically variable, and its loadings should be compared to the rest of the inputs into the system. Besides sources and pathways, sinks within the system need to be also accounted for. Combined sewer overflow (CSO) is one such case, where concentrations of PFAS have been noted on certain occasions (Clara et al., 2020, 2014; Nickel et al., 2021), but an overall framework for quantification of CSO flows on a regional scale has only been introduced recently (Quaranta et al., 2022), and not applied on a city-wide scale in terms of PFAS quantification. These missing aspects should therefore be investigated and incorporated into the mass balance calculations, in order to fully grasp the total PFAS load that is finally found at the influent of a municipal WWTP and to quantitatively assess the relevance of specific sources for different PFAS.

Material Flow Analysis (MFA) is an analytical method designed for such mass balance calculations, which enables the systematic evaluation of selected flows and stocks of matter, within defined spatiotemporal regions (Brunner and Rechberger, 2016). It has been used to analyse both the mass balances of single substances, such as phosphorus (Zoboli et al., 2016), as well as those of full composite goods, like in the case of plastic packaging (Lombardi et al., 2021), in both cases supporting diverse environmental and resource management efforts. Even though this method has been applied to various subjects, to the best of our knowledge, there are no instances of the model's application with respect to PFAS at city scale. The MFA approach used in this study allows for harmonization of the vast, but currently rather compartmentalized knowledge that exists on the topic of PFAS occurrence and release from individual sources. Namely, by considering the whole urban system and by applying the principle of mass conservation, the aim is to exploit the full information content and added value of such specialized investigations. This, in turn, allows for the clearer insight into inconsistencies, different ranges of variability with respect to phenomena, and scalability of the system that is being modelled.

The purpose of this study is to develop and validate a source-based modelling framework of annual loads for selected PFAS in the wastewater collection system of a large central-European city. The reason for such an endeavor is multifaceted, having both scientific and management connotations. From a scientific perspective, this study contributes to the clarification of a not well understood topic that is PFAS pollution in urban wastewater, by consolidating available information on all potential sources of PFAS emission, and quantifying it in a compartmentalized, unifying framework. Due to model's scalability, this approach can be applied on a wide array of spatiotemporal case studies, while its compartmentalization allows for the modification of the model to fit the user's needs, without impact to the overall quality of the model itself. Additionally, by using the MFA modelling technique to develop our framework, we can better represent the overview of the proportion and versatility of loads with respect to different sources and also assess their uncertainties. This also allows for the identification of sources that have so far been ignored in terms of magnitude, flows and sinks within the municipal wastewater system, as well as to identify potential gaps in sources that have so far been neither quantified, nor even considered. From a management perspective, the model serves as a valuable tool to policymakers and other stakeholders, in a sense that one can use it to compare the results with regulatory requirements, and make informed decisions on the topics of potential phaseouts, restrictions and alternatives to PFAS. To validate the results against observed annual loads, the modelling approach is complemented with a monitoring campaign targeting the influent of the wastewater treatment plant located in the study area as a flow representative for the whole city's activities.

2. Materials and methods

2.1. Conceptualization of the model and study area

The model was conceived with the main objective of determining a single-year total emission load of select PFAS into the municipal wastewater. The study area that was monitored and used for validation of the model is a large, post-industrial central European city. It is commercially active, and has a large population within the connected sewer area. The airport attributed to the modelled city, and airport-related activities, though thought of as a potentially major PFAS hotspot (Ahrens et al., 2015), are not included in the assessment, since the airport of the city that was used for validation has its own sewage treatment, which is under an administrative control of a separate

municipality. The majority of sample collection happened in the year 2022, with a few at the beginning of 2023. Therefore, the data sources used for modelling, and consequently the model's temporal boundary were adjusted to 2022 for ease of comprehension.

The initial step was to identify the direct PFAS sources that were geographically relevant to the study area, and within the given time-frame. The screening of relevant sources was based on the literature review of Glüge et al. (2020). The resulting conceptual model of identified contributors to the municipal sewage (Fig. 1), was produced using the STAN (subSTance flow ANalysis) software which offers graphical,

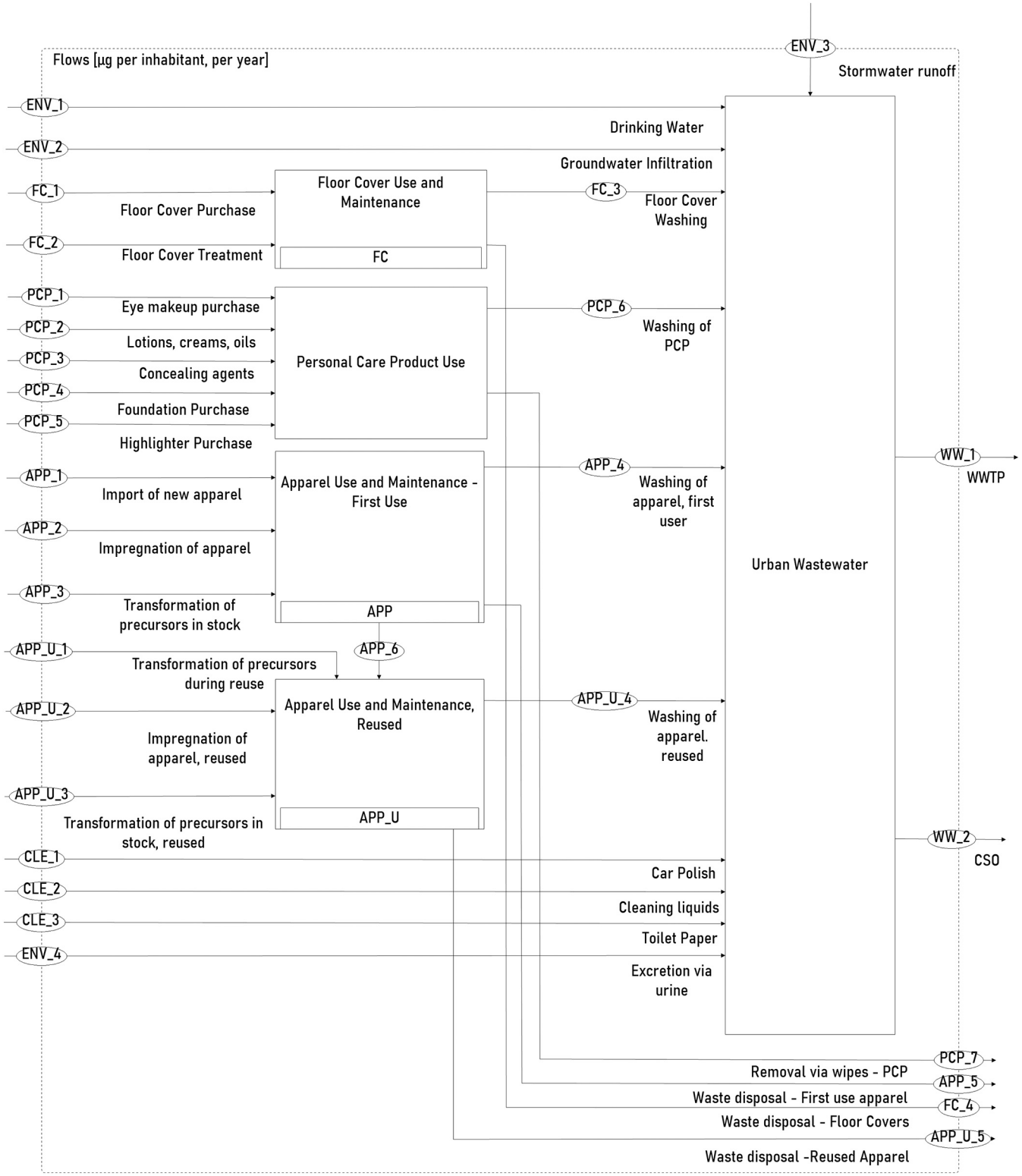

Fig. 1. Conceptual, STAN-generated MFA model used in this study. Arrows represent flows, i.e. imports into the system, inputs and outputs of a substance in and out a process and exports out of the system, respectively. Boxes represent processes, and the inner rectangles within them represent stocks. Abbreviations in oval represent the names of the flows of material. The full names and descriptions of the flows and processes is given in SI 1, along with calculations for each of them.

mathematical, and statistical support in MFA. Graphically, STAN visualizes flows via Sankey diagrams, providing a representation of the magnitude and distribution of flows within a system which eases comprehension of an MFA model. Additionally, STAN employs data reconciliation, a statistical method that calculates most likely values of uncertain quantities in a system subdivided into subsystems connected via flows under application of the principle of mass conservation for each single sub system (Cencic and Rechberger, 2008).The conceptual model was designed to represent a system boundary of the municipal wastewater system, and all the paths that lead to it, with respect to PFAS. Inputs into the system consider all the import flows that bring PFAS into a form that will eventually end up in the sewers.

Distinct PFAS were selected for evaluation, based on factors such as representativeness of different physicochemical characteristics, availability of data regarding concentration in consumer goods and other relevant information for the estimation of loads, as well as the percentage of PFAS during the monitoring campaign that were detectable, i.e. above the limit of quantification (LOQ) and that thus allowed a validation of the results. The two main groups observed in this case represent the carboxylic (PFCAs) and the sulfonic (PFSAs) groups of PFAS. The PFCAs (PFHxA, PFHpA, PFOA, PFNA, PFDA) represent the chemicals that are rather commonly researched in consumer products and are chosen in this way to represent the short-chained (six to eight carbon atoms) versus long chained (eight and more), and observe the behavior within the scope of the MFA. The same approach was taken for the PFSAs, albeit with two representatives – the short chained PFHxS and the long-chained legacy pollutant PFOS. As such, from the viewpoints of physicochemical properties, applicability and regulatory history, these seven PFAS represent a heterogenous group to be observed in the context of this study. No attempt was made to model the PFAS precursor compounds as individual cases. This was decided since precursor compounds are unpredictable in an uncontrolled environment in terms of the rate and frequency of transformation into terminal products (O'Connor et al., 2022). Instead, in this paper, the term "precursors" is used in order to explain an increase of the aforementioned seven PFAS during uses of consumables prior to the entrance of PFAS into the sewage system, based on empirical data from dedicated investigations.

It is important to note that some frequently mentioned potential sources were either excluded from this model as they were not applicable to the area of study, or were assimilated into a more general flow. For instance, Aqueous Firefighting Foam (AFFF), a frequently mentioned source of PFAS (Reinikainen et al., 2022) was considered in this case to be introduced via stormwater runoff into the sewers, and as such was not represented with a separate individual flow. Additionally, textiles other than apparel and floor coverings were omitted, due to their already proven lack of environmental emission loads for the substances modelled across all environmental compartments, regardless of the geographical location of manufacturing (Vestergren et al., 2015). Regarding apparel, the flow accounts for all the apparel types that have already shown to have a significant impact, namely outdoor clothes, as well as functional textiles. The area was chosen as such to allow for modelling of a case where exclusively municipal and commercial activities, as well as environmental processes impact the final annual load of PFAS in municipal wastewater. Moreover, by using such assumptions, it is expected that the model could be adjusted to fit other areas with the same geographical and socioeconomic structure characteristics.

2.2. Calculations

After identifying which consumer goods are suspected to contain PFAS, imports of these goods into the system were calculated based on consumer statistics. The PFAS loads considered as imports into the system were calculated based on prior findings on concentrations of PFAS in these consumer goods (e.g. purchase and maintenance of goods) as well as using hypothetical flows into the system, as in the case of precursor transformation stemming from apparel use and maintenance. For the quantification of imports via environmental (water) flows (e.g. drinking water, stormwater runoff, groundwater intrusion) into the system, a water balance of the city was calculated and together with PFAS concentrations in these water flows derived from monitoring campaigns PFAS loads have been assessed.

In the following examples, representative calculations are presented to signify a typical method of obtaining PFAS loads originating from goods and environmental processes, respectively.

With respect to consumer goods, after the import of PFAS into different processes (sub-systems) of the MFA (Floor Cover Use and Maintenance, Personal Care Product Use) was calculated, a partitioning coefficient was applied, which accounts for the amount presumed to be washed away from the goods into the sewer system in a year. A generalist, mathematical description is given in Eq. (1):

$$L_{PFAS,from\ consumptive\ use} = G \times e$$

Here, $L_{PFAS,fram\ consumptive\ use}$ represents the load of PFAS (in μg inhabitant^{-1} year^{-1}) emitted into the sewer system from a specific consumption pattern. G (μg inhabitant^{-1} year^{-1}) is the import into the system via purchase of a product or an undergone process within the system (e.g. precursor transformation during use), and before it is disposed into the sewer system via e.g. washing. Which fraction of the PFAS entering the system via consumer products or transformation finally enters the wastewater is quantified by multiplying G with e, the partitioning coefficient, which ranges from 0 to 1.

For environmental flows into the system, in order to calculate the loads in μg inhabitant^{-1} year^{-1}, water flow (m^3 inhabitant^{-1} day^{-1}) is multiplied with the concentration of PFAS in the water flow (C_{PFAS}), in μg m$^{3(-1)}$ (ng L^{-1}), and then the number of days in a year. This is generically described using Eq. (2) below.

$$L_{PFAS,Env} = Q \times C_{PFAS} \times 365$$

The details on the names of flows and processes, the individual calculation procedures for PFAS load quantification, sources of information, and the reasoning behind calculation approaches are described in Supplementary information A (SI_A).

Since the concentration data were skewed in all assessed sources, the median concentration value was used for the final load calculation, being more representative of the centre than the mean in such cases (Pagano and Favreau, 2018). In order to include the occurrence of censored data (values below the limit of quantification) in the calculation of the median, they were processed using the regression on order statistics (ROS) method (Helsel, 2012), with the aid of the NADA package (Lee, 2020) in the R programming environment (R Core Team, 2022).

2.3. Input data

The data was obtained from a variety of sources, including peer-reviewed experimental results, as well as results conducted by private or governmental entities. For consumer statistics, where reliable survey data was not available, assumptions were made based on third-party reports. The timeframe was varying, but limited to 10 years, i.e. 2012 as the earliest allowed dataset, albeit at a higher uncertainty. The spatial scale was aimed to not contain data outside of Europe, but in some cases that was unavoidable, yet still kept to a minimum. Where the datasets were not considered applicable or representative of the modelled case study, they were discarded. The reasons for discarding data were either due to old datasets in which the analysis was conducted, area of focus that is not relatable to the model's spatial assumptions, or the lack of a demonstrated limit of quantification (LOQ) which would introduce bias into the statistical analysis.

For environmental parameters (groundwater infiltration, stormwater runoff), a combination of on-site measured values and literature data was used. Specifically, all groundwater data that were used for the

quantification of inputs into the sewer via groundwater were taken in the geographical boundaries of the modelled city. This was done partly from our one-time sampling campaign (see Section 2.3), and partly from values that were available from the authorities responsible for the city. The data from surface runoff came from external sources, either originating from the city that was being modelled or from geographically and otherwise similar sampling campaigns. Values from the chosen literature datasets that did not correspond to our area of study were omitted from the model. For instance, there were a few measurement points pertaining to stormwater runoff results, that were set in a rural environment and not subject to a high percentage of impermeable surfaces (Clara et al., 2020), thus not applicable to the model's presumed spatial setting set forth in this study.

Table 1 reports the concentrations for the sources contributing to the WWTP influent, as well as the characteristics of goods used to calculate the loadings of separate sources. Not all flows are included, since some are inherently calculated by STAN. The column "associated flows" refers to the interrelation between the name of the phenomenon (process or flow, in depth explained in SI_A) in the model, and which good is considered under that phenomenon. The equations used to reach the final loading value for each flow represented in the MFA framework are noted and explained in the Supplementary information (SI_A), including the sources of the data used.

Aside from flow circulation within the system, a stock is an important component of any MFA study. The initial stocks for the processes "Floor Cover Use and Maintenance" and "Apparel Use and Maintenance" were calculated based on the presumed use and accumulation within the system boundaries within the years prior (SI_A, S1). The change in stock

Table 1
Descriptions of goods used to conduct the MFA model, their respective concentrations, as well as references pointing to their sources and calculation methods in the Supplementary information sheet A.

Modelled subject	Based on:	Relevant parameters***	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFHxS	PFOS	Associated flows	Details and References
Textile		Amount per capita (kg inh^{-1} yr^{-1})	Median concentration (μg kg^{-1})								
Apparel	Water repellent jackets	1	0.23	0.07	0.54	0.22	0.25	0.5	9.8**	APP_1–6	SI *A* 1.1, SI *A* 1.2
Treatment of apparel	Impregnated textile concentrations	1	3.05	1	3.64	0.5	2.37	–	–	APP_1–6, APP_U1–6	SI *A* 1.1, SI *A* 1.2
Floor cover	Nylon carpet face weight	4	12.5	2.2	6.1	2.7	0.92	1.4	2.3	FC_1 - FC_4, FC	SI *A* 1.3
Treatment of carpets	Treatment concentrations	4	19.5	4.7	22.3	13	0.82	1.4*	2.3*	FC_1 - FC_4, FC	SI *A* 1.3
Personal care		Consumption, if applied daily (mL inh^{-1} yr^{-1})	Median concentration (μg kg^{-1})								
Highlighting agents	Powders, highlighters	300	6	5.18	2.02	17.7	2.5	–	–	PCP_5, PCP	SI *A* 1.4
Concealing agents	Concealers, correctors	50	1935	860	2335	825	1675	–	–	PCP_3, PCP	SI *A* 1.4
Foundations	Blemishing/ corrective creams, foundations	200	81	6.13	4.1	35	6.34	–	–	PCP_4, PCP	SI *A* 1.4
Eye makeup	Eyeliner, eye cream, eye shadow	10	15	4.6	6	6.6	7.6	–	–	PCP_1, PCP	SI *A* 1.4
Lotions/creams/ oils	Sunscreens, moisturisers, shaving creams	2000	2.6	1.93	3	5.46	4.95	–	–	PCP_2, PCP	SI *A* 1.4
Car washing aides		Car surface per person (m^2 inh^{-1} yr^{-1})	Median concentration (μg kg^{-1})								
Finishing agent	Car polish	3	0.3	–	2.1	–	–	–	–	CLE_1	SI *A* 1.5.1
Cleaning aides		Amount used (L inh^{-1} yr^{-1})	Median concentration (μg kg^{-1})								
Cleaning liquids	Cleaning liquid	2.5	–	–	0.75	–	0.2	–	1.2	CLE_2	SI *A* 1.5.2
Paper		Amount used (kg $person^{-1}$ yr^{-1})	Median concentration (μg kg^{-1})								
Toilet paper	Toilet paper	12.5	0.13	–	–	–	–	–	–	CLE_2	SI *A* 1.5.3
Environmental parameters		Quantitative information	Median concentration (μg kg^{-1})								
Drinking water	Local sampling	See SI A,1.6	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	ENV_1	SI *A* 1.6.1
Groundwater	Measured groundwater concentration	See SI A,1.6	3.82	1.57	5.32	–	–	2.9	0.9	ENV_2	SI *A* 1.6.2
Stormwater runoff	Measured runoff data in central Europe	See SI A,1.6	4.00	2.00	4.00	1.00	1.91	0.25	3.00	ENV_3	SI *A* 1.6.3
Urine excretion	Human study in central Europe	See SI A,1.6	1.60	–	2.10	–	–	0.80	1.80	ENV_4	SI *A* 1.6.4

* No data available, hence assumed to be the same as the original concentration.
** Older median data used from Kotthoff et al. (2015) as to account for apparel still circulating in stock.
*** The abbreviation "inh" refers to "inhabitant".

during the modelled year itself was omitted, since the model in itself is assumed be operating in a steady-state scenario.

2.4. Model uncertainty

In MFA research, sources of information are usually heterogeneous in nature, with several different types of datasets, and sometimes lack of multiple values hindering the possibility to conduct conventional statistical analyses (Danius and Burström, 2001). Therefore, standard deviation and the interquartile range (IQR) that were calculated from the data sources themselves could not be used for a reliable uncertainty estimation. Instead, to quantify the percentage of uncertainty, a matrix

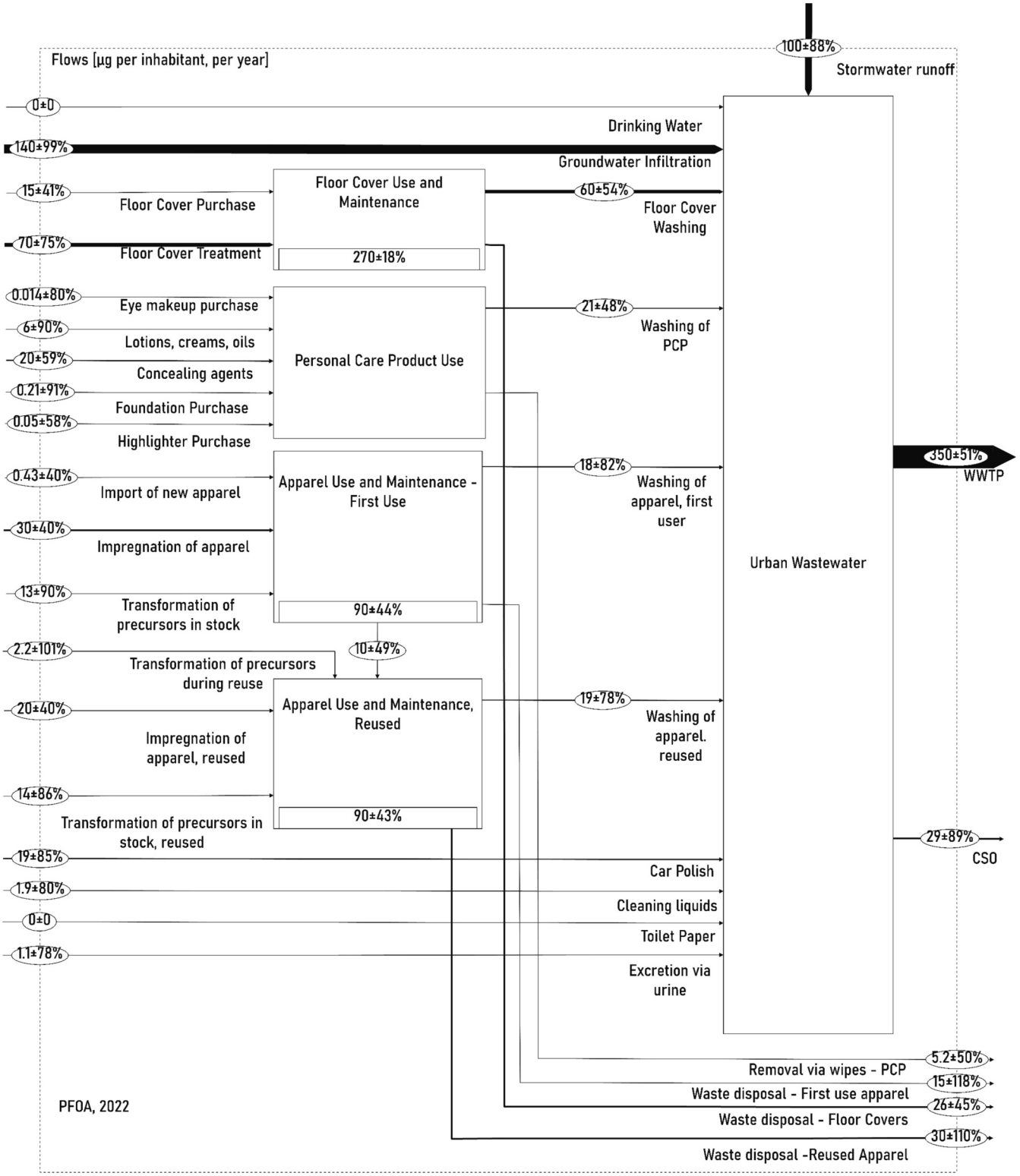

Fig. 2. Executed STAN based Sankey Diagram, representing PFOA mass balance within the spatial boundary of the case study city, representative for the year 2022. Results are represented in annual loads of ug of PFOA per inhabitant per annum.

approach conceptualized by Laner et al. (2016) was used. This approach, which in turn builds upon the earlier pedigree-based approaches (Hedbrant and Sörme, 2001; Weidema and Wesnæs, 1996), uses specific indicators with a scoring method applied based on the assessment of the chosen dataset, ultimately expressed as coefficients of variations (CVs). Such approach was selected in order to mitigate the impact of inherent individual data uncertainty and very strong heterogeneity that is commonplace in MFA studies. Consequently, such a matrix approach would result in consistency and robustness, otherwise not expected in uncertainty estimations.

For this study, CVs based on the work of Zoboli et al. (2016) were utilized. These CVs were representative of the indicators *Reliability*, *Completeness*, *Composition*, *Temporal correlation*, *Geographical correlation* and *Further correlation*. This way, various weaknesses of heterogeneous datasets were accounted for, that an otherwise purely statistical approach would not consider. When a CV could not be applied, such as in the cases of an educated guess or private correspondence, the *Expert judgment* scoring method was used, which is also a part of the aforementioned methodology. The scoring table, exponential graph, and the final estimated uncertainty percentages are shown in Supplementary information (SI_A, S2).

2.5. Model validation and sampling campaign

Modelled annual loads of PFAS in WWTP influent were validated against observed loads calculated based on data of annual municipal wastewater inflow multiplied with median concentrations obtained throughout a yearly sampling campaign. The WWTP influent was selected to correspond to the assumption of the model, and hence is located in a large, commercially active, post-industrial central European city. Water flow that was measured in the entry into the WWTP was used for the load quantification.

The monitoring campaign consisted of samples taken from the inflow of the municipal WWTP from January 2022 up to and including March 2023. The samples obtained varied in their characteristics. Namely, from January until end of December of 2022, for each month, a flow-dependent WWTP sample was composited, by combining weekly composite samples of one day collected through the month, with the inflow values on that day determining the fraction of the total volume of the composite sample. Additionally, from April 2022 up to and including March 2023, once a month, we have obtained additional daily composite samples from the inflow of the same WWTP. Given that our loads were calculated using a fixed, average per-person wastewater flow value, and that the annual median concentration value was of interest, it was decided to combine both types of datasets and use the median of the resulting combination for load estimation to be validated. For uncertainty values, the same approach was applied, by multiplying the 25th and 75th percentile of the concentrations for each compound with the average wastewater flow value.

lThe containers used for the sampling campaign were made from polypropylene, and kept in a refrigerated space at 4 °C until analysis. The analysis itself consisted of solid-phase extraction (SPE) and enrichment, after which liquid chromatography-mass spectrometry (LC-MS) was performed. The individual concentrations, and analytical descriptions of the LC-MS measurements are described in SI_A, S3-S4. As in the case of the modelled loads, the median concentration value was used for annual load estimation, along with the median annual wastewater inflow per person of the WWTP. For the uncertainty of the observed loads, the 25th and 75th percentile were used. To account for the groundwater infiltration in the model, a one-time, city-wide campaign was conducted, and groundwater stations were selected that were close to sewer lines, combined with prior, published research done in the same city where the model was set. The groundwater data details are described in SI_A, S1.6. The aim was to select sampling sites heterogenous in nature, with respect to population, permeability and surrounding activities within our model city. The groundwater samples were single-point, resulting in a very high uncertainty when the aforementioned uncertainty matrix was applied. The median values, which are a combination of monitoring efforts and data acquired from the literature in the same area, are noted in Table 1 while the description of the sites, and individual measurement results are reported in SI_A, S3.

3. Results

The STAN-based model was executed for all the selected PFAS with the results expressed as μg per inhabitant in a year. The final results,

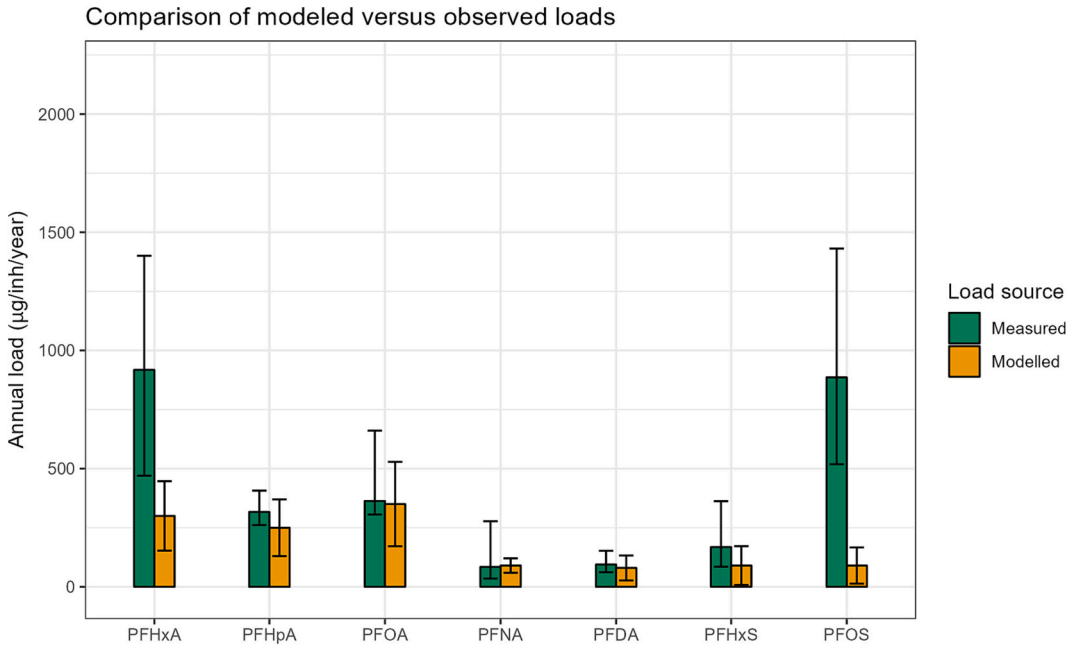

Fig. 3. Comparison of median-based annual loads (ug/inhabitant) for the selected PFAS groups. Errors from the measured data are based on the 25th and 75th percentile, while the modelled errors are based on the error propagation algorithm of the software STAN, which in turn is an accumulation of the individual uncertainties conducted via the matrix principle.

including stocks, flows and individual uncertainty percentages are presented in SI_C. As a demonstration, in Fig. 2 the MFA model representing the mass balance of PFOA is presented.

The final modelled loads as compared to the measured loads in the WWTP influent are presented in Fig. 3. Highest percentages explained by the model were achieved in long-chained carboxylic-based PFAS (PFCAs), with an overestimation slightly above 100 % noted in the modelled PFNA loads, above 90 % for PFOA, while PFDA and PFHpA accounted for about 80 % of the observed load, albeit with overlapping uncertainties. Less amount of explanation was available for PFHxA (30 %). From the PFSA, PFHxS was explained to a degree of 50 %, with tenuous certainty, whereas the least explained was PFOS at 10 %.

Within the modelled loads, the proportion of PFAS source contribution varied among substances. The graphical representation of the ratios of separate modelled PFAS source loads with respect to different compounds is depicted in Fig. 4.

Consumer products, at least in the case of PFCAs, constitute a significant portion of the overall composition of the modelled load. In all observed PFCAs, consumer product use could account for at least 50 % of the modelled load, with the highest fraction being attributed to apparel- or floor cover use and maintenance processes. Though present in each instance of selected chemicals in the PFCA group, personal care products (PCP) were deemed higher contributors in the longer-chained PFCAs, with shorter chained ones having 5 % or lower of their overall

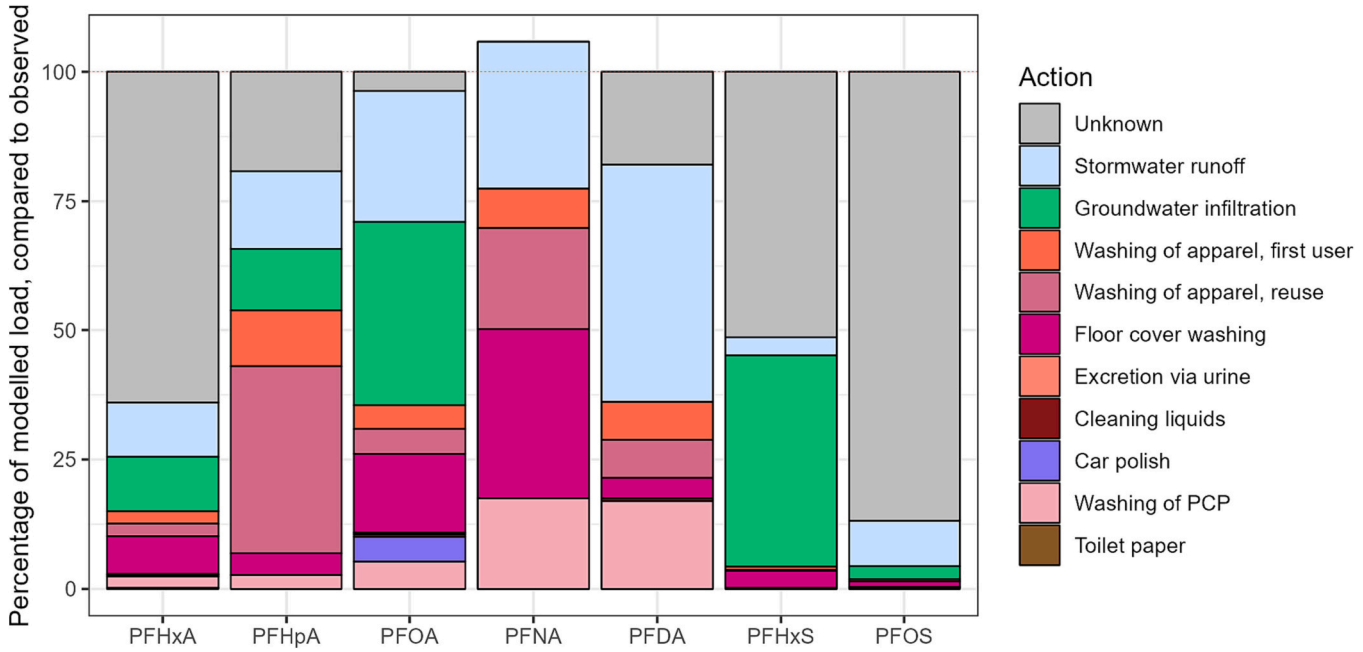

Fig. 4. Proportion graph describing the ratio of identified and quantified possible sources and to what extent are they modelled to have contributed to the WWTP influent loads in the studies area. The grey area titled "Unknown" is the unexplained portion of the model, when compared to the annual load observed. Because of PFNA, which the model has overestimated, a red-line has been given to signify a threshold after which a model is deemed to overestimate.

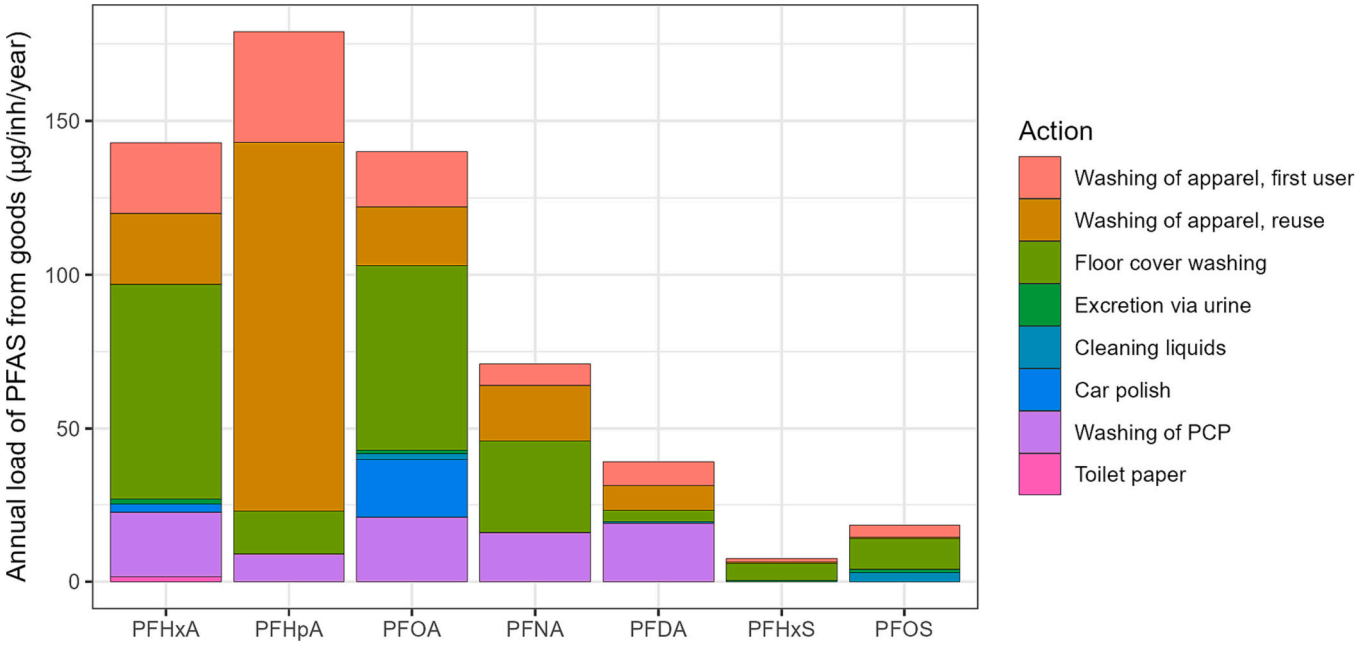

Fig. 5. Modelled loads of PFAS attributed to the use of consumer goods.

fraction attributed to this group. In Fig. 5, a quantitative depiction of the loads attributed to consumer products is depicted to reflect the findings and provide for a better comparison of source allocation with respect to different PFAS.

In the case of PFSAs, both PFHxS and PFOS exhibited smaller fractions that could be attributed to consumer products, and were in fact mostly dictated by the aforementioned environmental recirculation events. This was in spite of this paper accounting for the discontinuation of PFOS in consumer products, by using the source data that are much older compared to the rest of the PFAS modelled.

Sources attributed to environmental recirculation, in this case being stormwater runoff and groundwater leakage into sewer system, constitute a noticeable fraction of the overall modelled mass load. The stormwater runoff loading accounts for at least 10 % of the modelled load across all substances, while groundwater exhibits a range of 10 % to 25 % in short-chained PFCAs, but is nevertheless not noticed in longer chain PFCAs, as seen in PFNA and PFDA. In the case of PFSAs, both PFHxS and PFOS modelled loads are majorly dictated by environmental, diffuse and other, so far unknown sources in our case study (>70 %).

4. Discussion

4.1. Modelling

The results of this source-based modelling framework indicate that such a technique has potential to predict the annual load of certain PFAS. If uncertainties are considered, modelled loads are, for the most part, within the range of the observed ones. However, the less-explained percentages of other compounds that have been subject to this modelling process indicate that there are caveats to this approach, especially in the case of PFOS. In the following section, the separate source components of the framework are discussed in terms of their plausibility and potential improvement suggestions.

4.1.1. Consumer products

The maintenance and use of consumer products can be seen as a significant contributor to the overall load estimation across the spectrum of PFAS examined in this paper. All of the consumer products that were considered have had some form of peer-reviewed, substance-specific research done beforehand. However, none of the products have thus far been subject to a city-wide mass balance annual load estimation with respect to municipal sewer loading. Hence, a combination of PFAS concentration, prior experimental results and location-specific consumer statistics was needed in order to reach the finalized version that is discussed in the following subsections.

4.1.1.1. Apparel (APP, APP_U and related flows). The calculations performed for this study's MFA signify the high level of complexity involved when estimating the final value of apparel-based flows. Previous work has demonstrated that PFAS stemming from apparel during the washing cycle can indeed contribute to the overall sewage PFAS load (Knepper et al., 2014), but that was deemed negligible in the overall loading of PFAS into the environment (Vestergren et al., 2015). However, only recently has there been research conducted with respect to the complexity of PFAS originating from apparel treatment and maintenance. More specifically, results of certain experiments indicate that, aside from partitioning of PFAS, there are differing levels of increase of PFAS concentrations during the use of originally bought outdoor apparel and functional textiles (Schellenberger et al., 2022; van der Veen et al., 2020). This phenomenon is thought to occur due to the precursor compounds found in impregnation agents, as well as the weaving of the fabric allowing for release of the compounds during wear-and-tear. Thus, instead of assuming that there is a straightforward partitioning mechanism that would ultimately result in the depletion of PFAS concentration in apparel, one had to consider the magnitude by which the PFAS concentrations would increase during the product life cycle, as well as the amount of impregnation and the amount of depletion of PFAS during each washing cycle.

It is also important to signify the importance of stock within the apparel use and maintenance process. It needs to be considered that a certain household has multitude of such apparel for different uses. This means that within a year, the sum of all purchased jackets from prior years in the system were accounted for as being impregnated, washed, and transformed. Combined with the fact that a significant number of used clothing that is intended to be further reused by another person, adds to the overall number of jackets in circulation (Klepp et al., 2020). This accumulation of apparel inside the system leads to a complex representation of the emission of PFAS into the sewer in the given year. The full depiction of the stock estimation for apparel is represented in SI_A, S1.1 and S1.2 respectively.

The degrees of variability between different processes that occur during the lifetime of a jacket therefore posed a risk of high uncertainty when estimating the final load that reaches the municipal sewer. Mitigation was conducted by relying on reproducible and quantifiable methods, in order to make the process more scalable. This was true for the quantification method of the removal of PFAS per wash, which was originally conducted in this work by using the parameter XLogP (Wang et al., 1997), but was based on the fact that the structure of individual PFAS molecules dictate their functional properties (Su and Rajan, 2021). Other aspects need further investigation in order to automate the calculation, as in the case of the amplification of PFAS during use and maintenance. In this model, the calculations of this flow were based on values obtained from prior experimental settings (van der Veen et al., 2022) and implemented directly into the model (SI_A, S1), with no ability to automate or mathematically quantify them, based on their chemical structure. It is important therefore, to conduct a further insight into the direct mechanism of precursor transformation in items of clothing, finalized with a mathematical model to explain the chemical processes. Until such progress is made, the equations and this portion of the modelling framework serve as an improved version of apparel-based load estimation into the municipal sewers. A major consideration in the modelling process needs to be given to the frequency of impregnation of apparel conducted on a yearly basis. While this is a rather individual preference, case studies, based on manufacturer experience and recommendations, assumed two impregnations per year (W.L. Gore & Associates GmbH, 2013). When comparing the overall PFAS loading apparel with one impregnation assumed instead of two, a difference is noted, but overall not to a high extent, and certainly not to an extent that affects the total PFAS loading modelled for the entire sewer system.

4.1.1.2. Floor coverings (P_FC, and related flows). Assuming that floor covers are treated with a PFAS-based solution every time after a cleaning service, and assuming such a cleaning service is conducted every 2 years, floor coverings can be a significant contributor of PFAS emissions into the WWTP, based on the results of this modelling framework. More specifically, the fraction of PFAS emission from cleaning was ever present, ranging from 10 % to 25 % of the total modelled load for individual substances. This is even more significant to consider when noted that precursor transformation does not occur in this range of consumer products, due to a lack of wear-and-tear or exposure to the elements, meaning that the PFAS-treated floor covering presents a large load upon entry into the system, instead of through years of use. All of the formulas, as well as the stock estimation, which follows the same pattern as for the apparel, can be found in SI_A, S1.3.

Dust is also considered an important part of the human-carpet interactions in terms of PFAS (Hall et al., 2020). In recent years, floor covers were not looked at individually as a PFAS contributor within a household, but coupled with dust, which can be a significant component of overall household emissions of PFAS. However, so far the risk of dust exposure has been deemed to be higher from inhalation or ingestion in

close proximity (Savvaides et al., 2021; Winkens et al., 2018; Wu et al., 2020), rather than via the introduction into the wastewater system. This is further backed by the fact that, in general, household vacuum cleaners are an efficient alternative to professional high volume surface samplers (Colt et al., 2008), most likely leaving insignificant amounts of dust during the cleaning process that ultimately enters the sewage. Therefore, dust as a flow was omitted from the framework.

Unlike in the case of apparel, no portion of the floor covering process flows could be mathematically validated based on individual PFAS properties, hence the removal of PFAS was attributed to experimental carpet cleaning results (Hubbard et al., 2012), rather than an automated chemical descriptor. Nevertheless, the geographically relevant consumer statistics, lack of precursor transformation, relevant experimental results and the amount of knowledge that exists on the topic of PFAS in floor coverings, render this process and its associated flows a reliable portion of the modelling framework.

4.1.1.3. Personal care products (PCP, and related flows). The types of personal care products that contributed to the overall emission load into the wastewater varied greatly, depending on the consumer statistic used, the targeted bodily area of treatment, and the geographical area used as a reference. Our findings confirm already strong scientific opinion that this range of products can contribute to the emission load during use to a rather noticeable level (Ministry of Environment and Food Denmark, 2018; Pütz et al., 2022; Whitehead et al., 2021), though smaller in effect when compared to the likes of apparel use. PFSA groups of compounds were not accounted for with respect to this portion of the modelling framework, as they were almost universally found below censoring limit.

The large variety of personal care products in terms of naming, purpose and frequency of use made this process in the framework one of the most uncertain ones. A clearer distinction is needed in defining the purpose of the different makeup products, as well as the area it is applied to. This will allow for a higher resolution model in terms of wastewater emissions. Experiments regarding PFAS removal efficiency from consumer products during washing are also of importance, as are more advanced numerical models in terms of absorption via skin or ingestion. However, given the very high variability of potential exposure pathways (De Silva et al., 2021), the relatively long time of PFAS retention in humans (Zhang et al., 2015), and the narrow temporal scope of the modelling framework presented here, one can omit the calculation of a stock representing bodily absorption.

4.1.1.4. Toilet paper (CLE_3). When limiting the findings of Thompson et al. (2023) to the relevant spatial boundaries of the model (Europe), only PFHxA becomes a noticeable contributor, with other compounds of interest being consistently placed below the limit of detection. Even though toilet paper alone should disintegrate relatively easily in normal sewage conditions (Mertoglu Elmas and Bekiroglu Ozturk, 2019), this rather new and so far unexplored topic opens new questions that need to be addressed, in terms of actual solubility of PFAS in toilet paper before wastewater treatment. Until such a study, that is related specifically to PFAS is conducted, toilet paper should be considered as adding to the total influent loading of PFAS and should be analyzed in a large study on the European continent.

4.1.1.5. Cleaning aides (CLE_1, CLE_2). Chemicals used for cleaning, as in this case detergents and car waxes, did not contribute a large portion to the overall modelled load. In fact, in most of the cases, PFAS were seldom detected in these products (Borg and Ivarsson, 2017). This model nevertheless included them, as their significance in terms of city-wide loadings has not been assessed thus far. Given the ever-changing regulations on PFAS in consumer products, a repeated measurement of PFAS is needed for a more accurate insight into the current state of affairs with respect to these substances, though it is highly unlikely that they would constitute a significant part of the load in any scenario.

4.1.2. Environmental inputs

Inputs associated with external environmental influences, especially stormwater runoff and groundwater intrusion into leaky sewer systems, constitute an important fraction of the modelled load across all the examined PFAS compounds. Considering that the combined share of this group of contributors ranges from a third of the modelled load to over 70 %, and that these activities are accompanied with rather high uncertainty, it is imperative to discuss the overall procedure, evaluation, shortcomings and points to be considered for future modelling efforts.

4.1.2.1. Stormwater runoff (ENV_3). The results of the model confirm the notions of previous studies, that the impact of the load of PFAS from stormwater runoff can be rather high in an urban setting (Xiao et al., 2012). From a modelling perspective, the contribution of the stormwater runoff to the overall sewage load can be described as twofold. For one, PFAS have been recorded globally in rainwater itself in various areas, ranging from rural to urban and from scarcely to densely populated ones (Cousins et al., 2022). Other than that, PFAS have been recorded in many instances of coatings, paints and varnishes, as well as other forms of outdoor protective coverings (Glüge et al., 2020), potentially allowing for more PFAS to be washed away during rain events, in addition to already being present in rainwater.

The issue with the estimation of this specific substance flow arises in the lack of real-time data, as well as the geographically-specific lack of consistent datasets. Importance, as well as the lack of PFAS-oriented studies that have stormwater runoff within their scope is noticeable (O'Connor et al., 2022), and even separate sewer overflows, which can be used as an alternative to direct stormwater runoff measurements are not considered enough (Nickel et al., 2021). This study has managed to obtain high-quality datasets that match the geographical boundaries of the model (SI_A, S1.6.2). However, the characteristics of the modelled area, compared to the sampling points do not completely match, since there are some rural, and non-commercially intensive areas included. An intensive sampling campaign is thus needed, which takes into account exclusively the heterogeneity of a large central European city, as was done in other continents beforehand (Houtz and Sedlak, 2012).

In the cases where stormwater runoff was found to be the majority of the identified load, such as in the case of PFHxS and PFOS, a correlation could not be observed between the magnitude of the average inflow of the WWTP and the concentration of the two PFSAs, meaning that a rainfall event is not the sole responsible driver behind higher incidence of these substances in the influent. Possibly, the discrepancy between the inflow and the detected concentration can be attributed to the amount of precursor transformation that had occurred on impermeable surfaces in the time prior to entering the sewage. More specifically, PFAS precursors have been shown to be reactive to ambient photolytic events, especially when combined with engineered nanomaterials (ENMs) which are usually concurrently found in the same products (Dai et al., 2020). To a lesser extent, and over a longer exposure time, microbial degradation of precursors has also been considered another noted pathway to ambient precursor transformation (Liu and Mejia Avendaño, 2013; Royer et al., 2015). Atmospheric deposition is also a contributor to the uncertainty of the flow, given the rather far distance that PFAS can traverse, evident by the findings of high concentrations of PFOS and certain other PFAS in remote regions (Benskin et al., 2012).

In general, a simple modelling approach to stormwater overflow as applied here could be used for immediate influent load estimation if appropriate data is applied. For a more precise quantification of yearly loads, the chemical pathways of precursor transformation, and atmospheric models signifying the dynamics of PFAS in rainwater are needed, but go beyond the scope of this study.

4.1.2.2. Groundwater infiltration (ENV_2). Groundwater infiltration

into leaky sewer systems was modelled solely based on water balance calculations, combined with groundwater concentrations within the examined area. Nevertheless, this modelling method for the quantification of the intrusion of groundwater itself is plausible (Wittenberg and Aksoy, 2010), and with the addition of groundwater concentrations near sewage lines, constitutes a reliable attempt at the PFAS load estimation of this portion of the modelling framework. In this form, the modelled substance flow has demonstrated a large portion of the overall modelled load for most of the substances examined.

Exceptions to the consistency of this substance flow were the long-chained PFCAs, specifically PFNA and PFDA, which were not detected in any of the groundwater samples. This is in concert with other case studies on the topic of PFAS in groundwater (Vierke et al., 2014), where their mobility was found to be dictated by the respective compounds' water solubility and lower adsorption to soil particles, characteristics dictated in turn by the chemical structure (McKenzie et al., 2015). It could therefore be suggested that this portion of the model has room for interpolation, based on physicochemical characteristics of individual compounds.

4.1.2.3. Urinary excretion (ENV_4). Urinary excretion had a minimal effect on the overall modelled value, at least on the substances for which the data was available. This can be attributed to the fact that initial concentrations were not high enough to contribute to the load via urine excretion (Hartmann et al., 2017), and that the retention time of PFAS in the body can extend beyond the set temporal boundary of one year (Zhang et al., 2015).

4.1.2.4. Combined sewer overflow (WW_2). The model indicates that the export flow of CSO out of the system should be included as a factor whenever a WWTP mass balancing effort is conducted. Depending on multiple factors, such as precipitation, area, and water consumption (Quaranta et al., 2022), it can divert a significant amount of the load away from the WWTP directly into the waterbody. Thus, exclusion of CSO can lead to a rather imprecise estimation of final loads. The calculation method itself, requires concentrations of PFAS in rainwater, as well as from the WWTP (SI_A, S1.6.5), and therefore it is recommended that this data is available when attempting to apply this modelling framework on other case studies.

4.1.3. Model limitations

The findings indicate that there are still emissions that are unaccounted for, if currently quantifiable sources of PFAS contributing to municipal wastewater are considered. This in turn, caused a bias in the values obtained via the usage of our model. We believe this is a result of a number of factors that we suggest below, and which future studies should focus on, in order to reduce such a bias. The summary of the limitations and the proposed resolutions for future modelling efforts are presented in Table 2.

One of the explanations for the missing fraction of the observed load could be that there are sources that have still not been quantified. For that purpose, the descriptions of commercial applications found in CHEMSEC (2023) were cross-checked with the city's chamber of commerce business registry, in order to see which commercial entities within the city are potentially contributing to emission of the monitored PFAS that were not originally considered. The results of the commercial applications that could potentially explain the remainder of the observed load are presented in SI_A, Table 7. Commercial activities include sectors from the chemical, textile, paper processing and building materials industry. A remarkable finding is that for PFOS, the compound that was least explainable by our modelling approach, all of the commercial activities found within the city boundary could be applicable, meaning that a large fraction of PFOS could most likely originate from these, yet unquantified sources. In contrast, the PFAS compounds that our model better explains, such as PFOA and PFNA, are found more in consumer products than in commercial processes themselves (Glüge et al., 2020).

Table 2
Identified limitations of the model, causes and proposed resolutions for future modelling efforts.

Issue	Root causes	Proposed resolutions
Certain amount of the load for PFAS remains unaccounted by the model	- Lack of quantifiable emission datasets from commercial activities in urban environments	- Intensification of monitoring efforts in urban sub-catchments that are suspect of including commercial PFAS emitters - Improved reporting by authorities and data availability regarding PFAS emission by commercial activities
Loads are modelled with high uncertainty	- High variability of data sources pertaining to identical goods or processes - Consumer statistics are vague and inherently carry large uncertainties with them - Mechanistic description of PFAS partitioning from goods is missing	- Analysis of PFAS in suspect goods on a regular basis and with each change in legislation - Application of cheminformatics or other techniques to predict fate of different PFAS contained in products
Unknown behavior of PFAS during transport within sewage	- Lack of sufficient datasets of PFAS occurrence and concentrations in sewage system - No scientific consensus on the behavior of PFAS precursors during sewage transport	- Intensification of targeted wastewater monitoring efforts in the sewer system - Examination of precursor behavior within raw sewage
Environmental inputs into the sewage are underrepresented	- Publications are missing for long-term stormwater monitoring results - Precursor transformation on surfaces prior to stormwater events is poorly understood - Actual data on groundwater infiltration into leaky sewer systems is lacking	- Intensification of stormwater and groundwater monitoring, with inclusion of factors that might contribute to PFAS release - Examination of precursor transformation on impermeable surfaces

Another possible explanation is the phaseout that producers have voluntarily committed over the years. This aspect can explain the discrepancy in the case of PFHxA. In general, shorter-chain PFAS can replace longer chained ones in manifold applications (Brendel et al., 2018). Since PFOA was restricted under POPs regulation since 2020 (European Comission, 2020), there is a chance that the consumer datasets used in this study do not fully reflect the actual content of newly purchased consumer products in the examined area, and that PFOA-based products are in fact replaced by shorter-chained substitutes (PFHxA). This was accounted for by increasing the uncertainty of the respective parameters. Nevertheless, more analytical data from consumer products are needed, in order to compare the incidence of banned or phased out substances, versus the ones that are still allowed.

There was a lack of inclusion of precursor transformation processes during the transport of chemicals from the point of entry into the sewage until the arrival at the WWTP influent. This could have contributed to the bias of the model. It has been demonstrated, albeit under simulated laboratory conditions, that certain PFAS species may undergo processes such as retention or precursor transformation (Li et al., 2022). Nevertheless, the retention was not deemed to be large in this stage of the PFAS transportation, and the mechanisms by which certain PFAS may have undergone transformation prior to reaching the influent are so far

not understood. Hydrolysis, photolysis, biodegradation and oxidation are the main mechanisms by which precursor transformation may occur in the context of water (O'Connor et al., 2022). However, in untreated sewage, these processes are unlikely to have a big impact, due to the relatively long time (days), and the accommodating environment needed for these processes (Dai et al., 2020; Dinglasan et al., 2004; Zhang et al., 2021). Additional limitations included the number of samples in the wastewater matrix, values below the limits of detection, the selection of PFAS examined in such an area, and the additional information that is needed in order to infer a conclusion, such as the concentration of interacting parameters (Lenka et al., 2021). With these limitations in mind, it was therefore not possible to consider the inclusion of transformation of precursors during the transports of PFAS in sewer systems.

The level of quality assurance of analytical results was not used as a criterion in the final selection of the concentration datasets used for the model. This was decided due to the heterogeneity of techniques used, as well as the different amount of information provided by each analyzing entity. It should be noted however, that the concentration values that were used in the model were obtained from peer-reviewed publications, and other reliable datasets, where quality assurance is ultimately required. Therefore, it could be argued that the heterogeneity of the datasets with respect to analytical quality and overall yield could be responsible for a part of the missing load in the model. To dampen such an impact, the uncertainty matrix was adjusted for each parameter accordingly, based on the other quality parameters related to the dataset.

4.2. Monitoring

A limitation of the WWTP monitoring campaign was the low number of samples used to represent the yearly average of PFAS concentrations. This hindrance was due to the limited availability of samples provided by the WWTP and sewer channels operators. The fixed date and time at which samples could be obtained also meant that there were no possibilities to select timeframes in outstanding circumstances, such as for instance, a stormwater event. This was mediated with the inclusion of monthly composite samples, which increased the chance of occurrence of higher flow events. For future studies, it is recommended that research is expanded to include a higher number of samples per month, allowing for more statistical precision and potentially for assessment of temporal variability as well. In addition, purposeful selection of sampling time when rainfall events occur should be included in future sampling campaigns, given the impact that the stormwater runoff might have on the overall PFAS loading in the wastewater.

5. Conclusions

This study has assessed the possibility of estimating the load of certain PFAS using a comprehensive modelling framework. For PFCAs, a much higher percentage could be explained compared to either of the examined PFSAs, the latter group, specifically PFOS, yielding the less percentage of explained modelled load. PFOS, a compound that is presumed to have very limited sources in current time period, has exhibited one of the highest yearly influent loads. This prompts the question of an unidentified stock within the city boundaries, the role of precursor transformation prior to reaching the WWTP, or an emission that was not accounted for in any of the literature thus far. Given the ubiquitous use of PFAS in modern life, it cannot be said with certainty that this framework represents the final list of processes that contribute to the system, but should rather serve as a proof of concept onto which one can add and adapt. Therefore, a comprehensive review of experimental and monitoring results, as well as quantitative concentration values in products, would be beneficial for the further betterment of the model and the topic in general. Furthermore, the results clearly show the significance external environmental factors have on the overall influent load, as in the case of stormwater runoff and groundwater infiltration into leaky sewer systems. This means that more intensive monitoring campaigns need to be conducted in terms of these potential PFAS entry points, in order to increase model resolution and performance. Therefore, there needs to be a better understanding of the system for this fraction of pollutants, in terms of atmospheric, chemical and groundwater modelling and quantification efforts. Such a high fraction of the load that does not stem from consumer products indicates that a ban on PFAS would not lead to an immediate, complete reduction of PFAS in municipal wastewater, and that PFAS will continue to be emitted from previously purchased consumer products as long as there is a stock of such material within households, impermeable urban surfaces or the groundwater below the city. Additionally, industrial and commercial activities within an urban environment are much less covered in literature, in spite of there being sources that could be attributed to such emitters. A comparative study between commercial and non-commercial urban areas would be beneficial to assess the impact different processes have on the overall PFAS loading in sewage systems. Nevertheless, until such efforts are made, this modelling framework represents a reliable opportunity to model certain PFAS in municipal WWTP influent within the scope of an urban environment, and identify the gaps in potential sources for other PFAS of interest.

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CRediT authorship contribution statement

N. Krlovic: Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Software, Validation, Visualization, Writing – original draft, Writing – review & editing. **E. Saracevic:** Formal analysis, Investigation, Resources, Writing – review & editing. **J. Derx:** Funding acquisition, Project administration, Writing – review & editing. **C. Gundacker:** Funding acquisition, Project administration, Writing – review & editing. **J. Krampe:** Project administration, Resources, Writing – review & editing. **M. Zessner:** Conceptualization, Methodology, Supervision, Writing – review & editing. **O. Zoboli:** Conceptualization, Funding acquisition, Methodology, Project administration, Supervision, Writing – review & editing.

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.

Data availability

Data will be made available on request.

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