



Coupling a pathway-oriented approach with tailor-made monitoring as key to well-performing regionalized modelling of PFAS emissions and river concentrations



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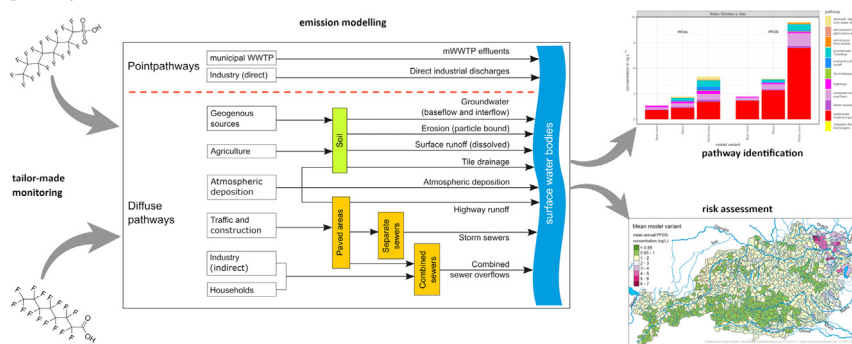
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HIGHLIGHTS

- MoRE performs well in modelling PFOA and PFOS concentrations in Austrian rivers.
- MoRE outperforms former models in predicting PFAS river concentrations.
- Regional pathways contributions to river pollution have been identified.
- Uncertainties in input data indicate possibilities for further improvement.
- MoRE is ready to be extended for emission modelling of PFAS of emerging concern.

GRAPHICAL ABSTRACT

PFOA and PFOS emissions via different pathways into surface water are modelled and used for identification of relevant pathways and risk assessment.



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ABSTRACT

Surface water pollution with poly- and perfluorinated compounds (PFAS) is a well-recognized problem, but knowledge about contribution of different emission pathways, especially diffuse ones, is very limited. This study investigates the potential of the pathway oriented MoRE model in shedding light on the relevance of different emission pathways on regional scale and in predicting concentrations and loads in unmonitored rivers. Modelling was supported with a tailor-made monitoring programme aimed to fill gaps on PFAS concentration in different environmental compartments. The study area covers the whole Austrian territory including some additional transboundary catchments and it focuses on perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS). These two PFAS are regulated and therefore their production and use in Europe are currently decreasing. Nevertheless, these compounds are still emitted into the environment via legacy pollution and as transformation products from other PFAS. These two compounds were selected for this study in view of the larger information availability compared to other PFAS. Despite considerable uncertainties in the input data, model validations show that this approach performs significantly better than previous modelling frameworks based on population-specific emission factors, population density and wastewater treatment plant information. The study reveals the predominance of emissions via municipal wastewater treatment plants for PFOS and a relevant role of diffuse emission pathways for PFOA. Results suggest that unpaved areas contribute the biggest share to total diffuse emissions, but the estimation of these pathways is affected by the highest uncertainty in the input data and requires better input data from monitoring. Once the currently growing substance-specific

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data sets on the concentration of PFAS, others than PFOS and PFOA, in different environmental compartments, will reach an adequate quality, the model presented here will be easily applicable to them.

1. Introduction

1.1. PFAS contamination of water bodies

Contamination of the aquatic environment with per- and polyfluoroalkyl substances (PFAS) is a well-recognized problem (Evich et al., 2022), but quantitative assessment of emission from different sources and via different pathways is scarce. Limited and fragmented data on PFAS pollution in media linked to emissions (e.g. soils or industrial discharges), confidential information on PFAS content in products and poor understanding of degradation and transformation of these substances in the environment are major challenges hindering a proper quantification of emissions (Gold and Wagner, 2020; OECD and IOMC, 2018; Wang et al., 2014).

Perfluorooctanoic acid (PFOA) and Perfluorooctanesulfonic acid (PFOS) have been produced since the late 1940ies (Paul et al., 2009; Prevedouros et al., 2006) and were in the focus of research on environmental issues related to PFAS in the past. Therefore, more knowledge is available about these two compounds than for the rest of the group comprising over 8000 substances (Evich et al., 2022). The focus on these compounds also led to their ban or limitation. Both substances are globally regulated under the Stockholm Convention (Stockholm Convention, 2019) and subjected to restrictions according to REACH in Europe. In the “Green Deal for Europe”, the European Commission defined a zero pollution ambition and the “chemicals strategy for sustainability towards a toxic-free environment” (European Commission (EC), 2020a) is one of the key elements. PFAS are recognized as a group of substances requiring special attention and the aim is to ensure that the use of PFAS is phased out in the EU unless a use is essential for the society (European Commission (EC), 2020a, 2020b). Furthermore the European Commission developed a possible way forward to address PFAS concerns by highlighting several options with reference to analytical method development or regulatory approaches (European Commission (EC), 2020b).

However, PFOS and PFOA are contained in older products still in use and are imported as impurities in products from other parts of the world, where these substances are not regulated. Further, other PFAS can be degraded to PFOA and PFOS (Eriksson et al., 2017; Mejia Avendaño and Liu, 2015; Zhang et al., 2022) and both – due to their high persistency – stay in environmental compartments like soil and groundwater as legacy pollution for a very long time. Therefore, it is no surprise that these chemicals are still found in many rivers (Jarvis et al., 2021; Kurwadkar et al., 2022; Podder et al., 2021). This applies to Austria as well, where levels of PFOS in some surface waters are still considerably above the water referred environmental quality standard (EQS, The European Parliament and the Council of the European Union, 2013) of 0.65 ng L^{-1} (Zoboli et al., 2019). Moreover, PFOA and PFOS were replaced in industry with other PFAS substances, which are being increasingly detected in the environment and in water bodies (Li et al., 2020).

To better assess the extent of surface water pollution beyond limited points of measurements in monitoring networks and to identify effective pollution mitigation measures, the contribution of different emission pathways on (sub-) catchment and on national scale need to be understood.

1.2. Regionalized modelling applied to PFOS and PFOA

Emission- and water quality models can help to shed light on which emission pathways are the most relevant and on how the pollution is distributed within river basins. Models of different complexity and with a different demand of input data are available to answer these questions. The choice of the right model is a trade-off between the effort for data

acquisition for model parametrisation and the necessary degree of model precision to answer the question of the modeler.

In the past, different approaches were developed to estimate regionalized emissions of PFOS and PFOA into surface waters.

A first approach, presented by Pistocchi and Loos (2009), was based on per capita emission factors, retrieved by disaggregation of river loads from the biggest European rivers. For PFOS the validation resulted in a R^2 of 0.34, while the R^2 for PFOA was only 0.19, with derived per capita PFOA emission factors being above PFOA emission factors reported in other studies. The authors interpreted this as the effect of inputs from industrial point sources and tried solving this issue by excluding river basins with PFOA loads above 0.5 t for the recalculation of the per capita emission factors. This resulted in an improved R^2 of 0.45 for PFOA. Building on the outcomes of Pistocchi and Loos (2009), Paul et al. (2012) applied the PFOS emission factor to model river loads and concentrations in the Rhine river: The model was matching the contamination pattern along the river but underestimating the observed concentrations. This was attributed to further emission pathways like industry and discharge from waste deposits. Another possible reason for this might be that Paul et al. (2012) did not include population from the whole catchment, but only from a 50 km buffer strip along the main river. When Earnshaw et al. (2014) used the same emission factor in the smaller catchment of the Aire/Calder river, the modelled concentration were significantly higher than the observed ones. These early attempts towards regionalized modelling of PFAS show the strong limitation and uncertainty range of approaches based on population specific emission factors and make clear that further differentiations between sources and pathways are necessary.

A step beyond was introduced by Müller et al. (2011a), who used the sweetener Acesulfame to differentiate between industrial point source emissions and diffuse emissions from products in use, while investigating PFAS concentrations in several rivers in Switzerland.

The contribution of different emission pathways during two rain events was investigated by Müller et al. (2011b) in a small rural catchment in Switzerland. While pollution generally was comparatively low, they found a significant share of total loads stemming from diffuse sources. As combined sewer overflows were not counted as diffuse sources in this study, the diffuse share of 29 % for PFOA and 44 % for PFOS is outstandingly high.

A more recent study modelled regionalized emissions of PFOS and PFOA in the Danube river basin by using population, wastewater treatment plant (wwtp) contribution, national economic performance and a combination of these variables (Lindim et al., 2015). In addition, the input via atmospheric deposition was calculated with a spatial homogenous deposition rate on soil and water of $2 \text{ ng PFOS m}^{-2} \text{ day}^{-1}$ and $8 \text{ ng PFOA m}^{-2} \text{ day}^{-1}$ according to data from Dreyer et al. (2010). For the population based approach, Lindim et al. (2015) adopted the emissions per capita from Pistocchi and Loos (2009). For the second regionalization approach based on wastewater emissions, Lindim et al. (2015) differentiated the per capita emissions by the wwtp technology based on data from Becker et al. (2008). In the third approach, they regionalized the emissions weighting them by the gross domestic product (GDP) per sub-catchment in relation to the overall GDP. Finally Lindim et al. (2015) extended the wwtp-based approach with the weighting by GDP into a combined approach. The regionalized emissions with these four approaches were fed into a water quality model (STREAM-EU, Lindim et al., 2016a, 2016b) and validated with measured concentrations from the Joint Danube Survey 3 (Liska et al., 2015). Only the combined approach was able to generate a Nash-Sutcliffe model efficiency coefficient (NSE) > 0 for PFOS, while none of them achieved a positive NSE for PFOA.

An estimation of PFAS emissions via different pathways to surface water, soil and groundwater was performed by Liu et al. (2017) for central

and eastern China. Many different pathways were quantified in this work, but unfortunately the emissions from soil and groundwater into surface waters were displayed but not quantified and a regionalization of emissions was not conducted on this large spatial scale.

Altogether these studies have greatly improved our understanding of PFAS pollution of water bodies and of the case-specific relevance of different sources and pathways. However, the so far poor performance in validation makes evident that more advanced modelling approaches are needed to provide: i) a more accurate quantification of different emission pathways to implement effective measures and ii) a more reliable prediction of PFAS concentrations in unmonitored river bodies for screening or risk assessment.

1.3. Purpose of the study

The hypothesis behind this study is that a pathway-oriented modelling approach, fed with data obtained via a tailor-made monitoring programme covering the main compartments linked with emissions, can achieve a much higher accuracy in the regionalized estimation of emissions, river loads and river concentrations of PFAS.

This hypothesis was tested on the entirety of river catchments in Austria. Besides evaluating the performance of the proposed approach, this study aimed to analyse the spatial pattern of pollution of surface waters with PFOA and PFOS as well as the contribution and relative relevance of different emission pathways in different regions. A further objective of the study was to apply the model to predict river concentrations in unmonitored rivers and thus to evaluate the potential risk of an exceedance of the water-referred environmental quality standard (EQS). PFOS and PFOA were selected in this investigation due to a significantly higher data availability, but they are considered as two examples of how well the proposed approach can be applied to a much broader spectrum of PFAS.

2. Material and methods

2.1. The MoRE model

The selected approach of emission modelling is based on the MoRE model presented by Fuchs et al. (2017) and implemented into the MoRE modelling framework (Fuchs et al., 2017). This pathway-oriented approach estimates the emissions for the different point and diffuse pathways presented in Fig. 1. The timestep is annual and the spatial resolution is at sub-catchment level.

The spatial model domain is the state of Austria. Transboundary river basins are partly included (small headwaters outside of Austria and the

whole Inn river including sub-catchments in Italy, Switzerland and Germany), while the Danube upstream of the confluence with the Inn river is considered as a boundary condition and thus its observed PFAS load is included as external input into the model domain (details on load estimation are reported in supplementary information (SI) A, table A1). From the March river (border to Slovakia and Czech Republic) only sub-catchments (e.g. Zaya) are included. The model domain (93,771 km²) is divided into 894 sub-catchments with an average size of 105 km² (map in SI A fig. A1).

The temporal coverage is chosen based on the available input and validation data. The tailor-made monitoring was carried out during 2016/2017 (Zoboli et al., 2019). Thus, the years 2016 and 2017 are modelled and all results presented are mean values of the results for these two years.

Based on data on land use, net discharge and sediment inputs per sub-catchment, the MoRE model calculates water and sediment balances at sub-catchment level. Since the model was originally developed in Germany, some adaptations from the MONERIS models (Venohr et al., 2011) and some revisions introduced by Zessner et al. (2011) for alpine regions are adopted to make the model applicable to the largely alpine Austrian territory.

PFOA and PFOS emissions via the pathways “municipal wastewater treatment plants”, “direct industrial discharges”, “groundwater (baseflow and interflow)”, “surface runoff”, “tile drainage runoff”, “atmospheric deposition onto water surfaces”, “combined sewer overflows” and “storm sewer outlets in separate sewer systems” are calculated by multiplying the water discharge of each pathway with its correspondent PFAS concentration for every single sub-catchment. Emissions via “runoff from overland roads and highways” are calculated by applying surface specific loads, while emissions via “soil erosion” are obtained by multiplying the sediment input with the respective PFAS content in top soils.

The modelled annual emission loads are transferred through the river network without considering retention or degradation processes in the river. As PFOS and PFOA are considered very persistent (Stockholm Convention, 2019; Vierke et al., 2012), these processes do not seem relevant for a mean annual load estimation. For each sub-catchment the mean annual load at the catchment outlet is divided by the mean annual river discharge to estimate a mean annual river concentration.

2.2. Input data

The basic input data (e.g. sub-catchments boundaries, land use, long-term average soil loss, point source data) were processed and supplied by Environment Agency Austria. Methodological details and data sources can be found in the SI (section A1.3).

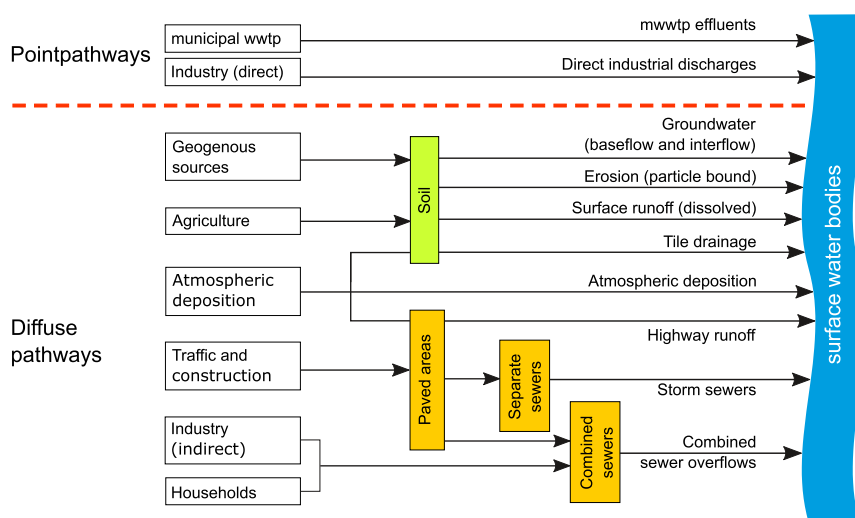


Fig. 1. Pathways of micro pollutant emissions into surface water bodies as modelled with MoRE (modified after Fuchs et al., 2010). mwwtp: municipal wastewater treatment plant.

The net runoff for each sub-catchment is used to derive surface, base flow and groundwater runoff for emission quantification and for the estimation of median annual river concentrations. As the network of river gauges is quite dense in Austria, Bavaria and Switzerland, a geostatistical approach called Top-kriging, developed by Skøien et al. (2006), was applied by Weber (2020) to generate this data set. Weber (2020) extended the Top-kriging approach available as an R package (Skøien et al., 2014) to consider the numerous trans-catchment diversions in the Alps. The final data set of net runoff contains a small but systematic bias (cp. fig. A2 in the SI), with modelled discharge values being slightly overestimated.

Concentrations of PFOA and PFOS in environmental compartments derived from monitoring are often close to or below the analytical limit of quantification (LOQ). Further, usually only a small set of measurement results are available with a rather high scatter of the data. To handle the values below LOQ while keeping the influence on the derived statistical descriptors to a minimum, “regression on order statistics” (ROS) was applied for the censored values according to Helsel (2012) using the NADA package (Lee, 2020) in R (R. Core Team, 2022). In cases where the application of this method was not possible because the data set contained only <3 values above the LOQ, values below the LOQ were replaced with 0.5 times LOQ (cp. SI section A1.3). To visualize the impact of the uncertainty derived from monitoring data on the model results, three model variants are calculated:

- Median: variant based on the most probable estimates of measurement data. The median of each data set is chosen to minimise the influence of outliers.
- Best-case: variant based on the lower boundary of probable values. The 25th percentile of each data set is used.
- Worst-case: variant based on the upper boundary of probable values. The 75th percentile of each data set is used.

The substance-specific input data used in our study is derived from the targeted monitoring program presented by Zoboli et al. (2019) and from further literature sources. Industrial direct dischargers were classified into different industrial sectors and each sector was parametrized with a different set of wastewater concentrations (cp. Table A3 in SI). The full detailed description of available data sets and of their statistical evaluation is reported in SI (section A1.3). Table 1 provides a summary of the resulting substance-specific data set used in the model variants.

2.3. The PFOA legacy site in Gendorf (Germany)

Within the Inn tributary catchment, precisely in the sub-catchment of the lower Alz river, a known legacy contamination site for PFOA exists. Close to the village Gendorf, a production site for polymers produced PFOA between 1968 and 2003 and used it until 2008 (Ulrich et al., 2019). The surrounding soils were contaminated with PFOA via emissions

into the air and subsequent atmospheric deposition (Hangen et al., 2010; Ulrich et al., 2019). Further, direct discharges into the underground at the production facility and via wwtp into surface water took place (Ulrich et al., 2019). After replacement of PFOA in the production process, concentrations in surface water and topsoil are decreasing due to washout. But this washout from the unsaturated soil zone is causing rising groundwater concentrations for the following decades (Herch et al., 2018).

To depict these emissions in the MoRE model, for this sub-catchment substantially elevated PFOA groundwater concentrations (Best-case: 100 ng L⁻¹, Median: 1000 ng L⁻¹, Worst-case: 2000 ng L⁻¹) were used as model input based on ERM (2018) and Ulrich et al. (2019).

2.4. Model validation

Modelled annual river loads and mean annual concentrations were validated against loads and concentrations derived from different monitoring programmes. Details about the monitoring results used for validation and how loads and median annual concentrations were calculated are given in the SI, section A2. Such calculations were also influenced by analytical results below LOQ. Thus, again ROS was applied for handling values below LOQ and three variants of data evaluation were used: Minimum (25th percentile), Median and Maximum (75th percentile).

Three quantitative indicators for model quality were selected, namely the Kling-Gupta model efficiency coefficient (KGE, Gupta et al., 2009; Kling et al., 2012), the Nash-Sutcliffe model efficiency coefficient (NSE, Nash and Sutcliffe, 1970) and the modified NSE with exponent 1 (mNSE). The KGE, together with its components (r = correlation, β = bias, γ = variability ratio), provide a better insight into the underlying quality components than the NSE and they are therefore primarily used in the discussion of the results.

3. Results and discussion

In the following sections, first the validation of the model results against observed values is presented and discussed. Then the model results regarding total emissions, river loads and concentrations, their spatial distribution and the resulting risk of exceedance of the environmental quality standards are presented. Finally, the contribution of different pathways to the pollution is assessed.

Where result values are given in the text, the Median model variant is given first, followed by the range between Best-case and Worst-case variant in brackets. The model results can be accessed from Kittlaus (2022).

3.1. Model validation by comparison with observed loads and concentrations

The calculated annual river loads were validated with loads calculated from monitoring data at 14 locations (Fig. 2).

Table 1

Substance-specific input data for the MoRE model and the three model variants (Best-case, Median and Worst-case). For spatial variable data the range is given. For details see SI section A1.3. wwtp: wastewater treatment plant.

Environmental compartment	PFOA			PFOS		
	Best-case	Median	Worst-case	Best-case	Median	Worst-case
Atmospheric deposition/surface runoff (ng L ⁻¹)	0.0	0.5	1.0	0.0	0.5	1.0
Soil on arable land (µg kg ⁻¹)	0.0	0.13	0.44	0.00	0.13	0.25
Soil on pastures (µg kg ⁻¹)	0.93	1.3	1.55	0.38	0.38	2.9
Soil in forests (µg kg ⁻¹)	0.86	1.0	1.2	0.06	0.39	5.3
Groundwater ^a /tile drainage discharges (ng L ⁻¹)	0.3	0.7	1.5	0.2	0.6	1.4
Highway surface load (mg m ⁻² a ⁻¹)	0.75	0.86	1.4	0.34	0.57	0.75
Combined sewer overflow (ng L ⁻¹)	1.7–9.2	2.8–12	4.9–21	1.0–7.4	2.4–13	5.3–31
Storm sewer outlets (ng L ⁻¹)	1.3–9.6	2.4–17	4.1–30	0.7–5.1	1.8–13	4.0–29
Industrial direct dischargers (ng L ⁻¹) ^b	0.8–270	1.1–730	1.5–1950	0.4–99	0.5–310	0.7–480
Municipal wwtp effluent (ng L ⁻¹)	5.1	7.1	7.8	12.4	25.5	30.5

^a Except the lower Alz catchment, see Section 2.3.

^b Different concentrations were applied for different industry branches, for details see SI table A3.

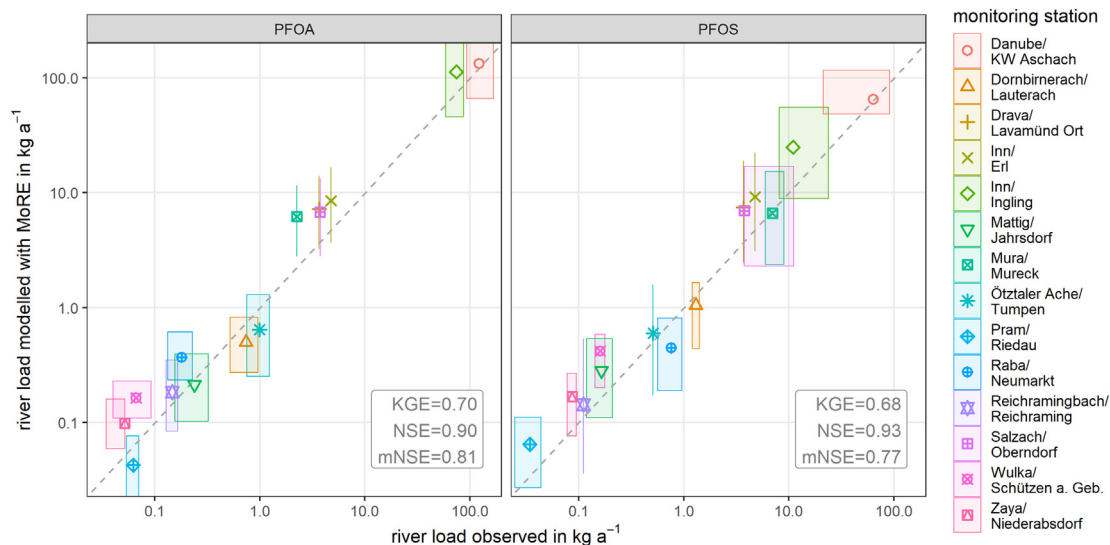


Fig. 2. Validation of modelled annual river loads against loads calculated from observation data. The points represent the validation of the Median model variant against the Median evaluation of the observation data. The surrounding coloured boxes show the uncertainty of model results (Best- to Worst-case variant) and of the loads based on observation data (Minimum to Maximum evaluation). KGE: Kling-Gupta model efficiency coefficient, NSE: Nash-Sutcliffe model efficiency coefficient. mNSE: modified NSE.

The validation of modelled river loads against loads calculated from observation data yields a satisfactory KGE (PFOA = 0.7, PFOS = 0.68). The components of the KGE reveal that the correlation ($r_{\text{PFOA}} = 0.98$, $r_{\text{PFOS}} = 0.98$) is very high, the variability ratio ($\gamma_{\text{PFOA}} = 0.93$, $\gamma_{\text{PFOS}} = 0.83$) is reasonable but for both substances with values of β being 1.3 for PFOA and 1.27 for PFOS the model is biased and overestimates the loads. This can be partly attributed to the overestimation of the discharge (cp. SI Fig. A2).

For all validation stations, the area of uncertainty, defined by the Best-case and Worst-case variant of the modelled data and by the Minimum and Maximum evaluation of the observation data, is close or intersects the 1:1 line. Therefore, there is no clear objection against the model results. A better hydrological data set might further improve the load estimation. Nevertheless, this version of the model is capable of predicting loads in a satisfactory way on an annually averaged basis and for this purpose a well-performing extension to further PFAS is conceivable.

The validation of modelled mean annual concentrations against median observed concentrations (Fig. 3) yields good results, taking into consideration that the area of uncertainty defined by the Best-case and Worst-case variant of the modelled data and the Minimum and Maximum evaluation of the observation data in nearly all cases intersects the 1:1 line, there is no clear objection against the modelled concentration range.

The KGE with 0.80 for PFOA and 0.86 for PFOS is higher than for the loads. Its components reveal that, for both substances, correlation of the modelled and simulated concentrations is rather high ($r_{\text{PFOA}} = 0.84$, $r_{\text{PFOS}} = 0.86$), but the correlation coefficient is the factor limiting the KGE, while there is no systematic bias ($\beta = 0.98$ for PFOA and $\beta = 1.04$ for PFOS) and the variability ratio for PFOS ($\gamma = 1.0$) is optimal, while it is lower for PFOA ($\gamma = 0.88$), which yields a less favourable overall KGE.

The observed concentration of PFOS at two stations is considerably higher than the modelled one. A common trait of these two catchments (Raba, Dornbirnerach) is the significant contribution from industrial direct

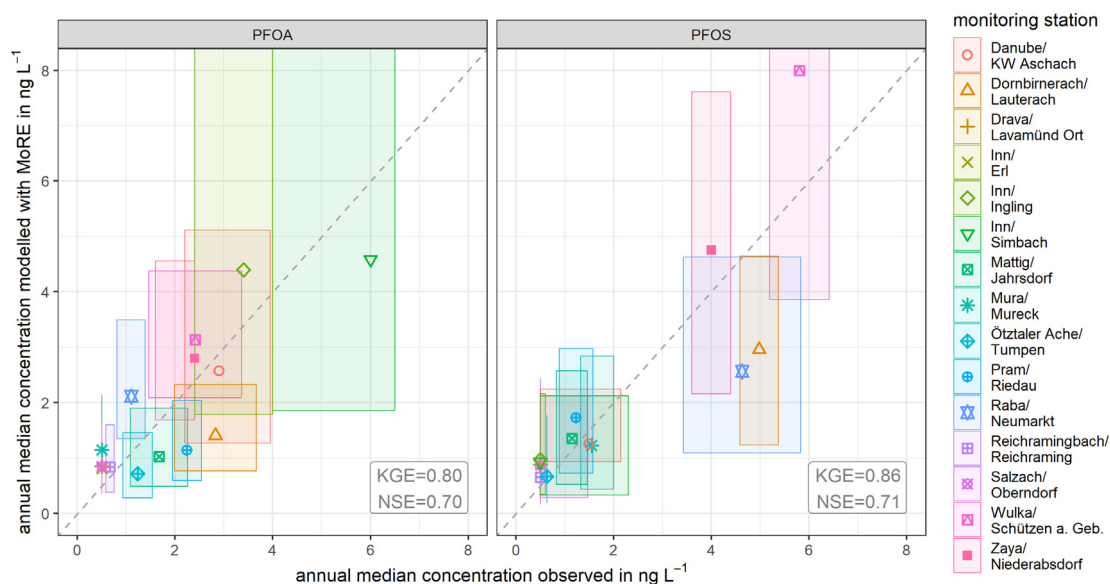


Fig. 3. Validation of modelled annual median concentrations against annual median concentrations calculated from measured river concentrations. The surrounding coloured boxes show the uncertainty of model results (Best- to Worst-case variant) and of the concentrations based on observation data (Minimum to Maximum evaluation). KGE: Kling-Gupta model efficiency coefficient, NSE: Nash-Sutcliffe model efficiency coefficient.

dischargers. This indicates that extrapolating average concentrations in discharges for industrial categories from measurements in some facilities and from literature data is a too coarse approach and that more specific observation data are needed as model input. Contrary, at the two stations in the Zaya and Wulka catchments the modelled median concentrations exceed the observed ones by 1–2 ng L⁻¹. These two catchments are both situated in regions with lower annual precipitation and therefore a higher share of municipal wastewater in the runoff. Therefore, it can be hypothesised, that the wastewater born PFOS emissions are currently slightly overestimated in the model.

For PFOA concentrations the uncertainty in modelled and observed concentrations is high. As diffuse emission pathways are more relevant for PFOA than for PFOS and the input data for these pathways (surface runoff and groundwater) have a high uncertainty caused by majority of measurements below LOQ, the model cannot predict the concentrations precisely. Better input data for diffuse emissions with a lower uncertainty range are needed to retrieve more precise estimates of the river concentrations. But the data used for validation show a high uncertainty as well. This can be exemplarily seen in the case of PFOA, for the two stations Simbach and Ingling along the Inn river. Both stations are situated downstream the Gendorf contamination site, first Simbach and then Ingling with only medium size tributaries in between these two stations. The drop of the median concentration from 6 ng L⁻¹ to 3.4 ng L⁻¹ between these stations can only be explained to a small share by dilution from the tributaries. The remaining difference is most likely due to a rather small sample size and to different sampling times at the two stations, which hinder the estimation of an accurate representative median concentration for both stations.

Under the assumption that no significant change in emissions occurred between the model period of Lindim et al. (2016a) (2009–2013), and the time of validation measurements for the work presented here (2016/2017), we compared simulated concentrations using their fourth “mixed contributions” emission estimates to the same dataset of observed concentrations. As the original concentrations modelled by Lindim et al. with the STREAM-EU model were not available, regionalized emissions by Lindim et al. were fed to the STREAM-EU model as reported by van Gils et al. (2020), using the substance characteristics as reported by Lindim et al. (2016a). The modelled daily mean concentrations for the years 2009–2013 were aggregated into annual mean concentrations. Fig. 4 shows the comparison of these annual mean concentrations with the observed mean concentrations. As the modelled concentration from the year 2013 was extremely high (very dry year), the median of the annual mean concentrations of

the 5 years was used for the comparison to remove the influence of this extreme year.

In Fig. 4 it can be seen that for all catchments with significant population density (not the case for Reichramingbach and Ötztaler Ache) the STREAM-EU model overestimates the concentrations. For PFOA in the Danube at Hainburg, the overestimation is smaller, which can be attributed to the PFOA-emissions of the Gendorf legacy site, which is not explicitly included in the model.

This comparison shows that combining regionalized pathway analysis with to a certain degree regionalized input data yields much better predictions than basin wide homogenous approaches based on very few input data.

3.2. Spatial distribution of modelled emissions, river loads and concentrations and associated risk

The total emissions for the model domain of MoRE were estimated as 157 (67–305) kg PFOA and 79 (29–170) kg PFOS per year. The higher emission load for PFOA is heavily influenced by the legacy contamination in Gendorf (cp. Section 2.3). Without emissions from this sub-catchment, 66 (31–123) kg PFOA emissions per year were estimated. Expressed as area specific emission rates, these loads correspond to mean values of 1680 (715–3260) mg PFOA km⁻² a⁻¹ (including Gendorf sub-catchment) and 838 (312–1810) mg PFOS km⁻² a⁻¹.

With about 9.9 million inhabitants living in the modelled area (Batista e Silva et al., 2021), this means per capita emission factors of 44 (19–85) µg PFOA cap⁻¹ day⁻¹ and 22 (8–47) µg PFOS cap⁻¹ day⁻¹.

A detailed comparison of these per capita emission factors with factors estimated by other studies is reported in SI (Table A10). The emission factors from Pistocchi and Loos (2009) are in a similar range for PFOA and PFOS. The emission factors derived by Müller et al. (2011a) are lower for PFOA, but still within the range given by Best- and Worst-case model variants in this study (excluding the Gendorf legacy emissions). For PFOS Müller et al. (2011a) give a higher emission factor than this study and Pistocchi and Loos (2009), but still within the range given by Best- and Worst-case model variants of this study.

Modelled river loads exported from the model domain into different river basins (Danube, Rhine) and large lakes (lake Constance, lake Neusiedl) are listed in table A9 in the SI. The modelled loads can be used to investigate the built-up of stocks or degradation in sinks like e.g. lake Neusiedl, which has no regular outflow (Zessner et al., 2019).

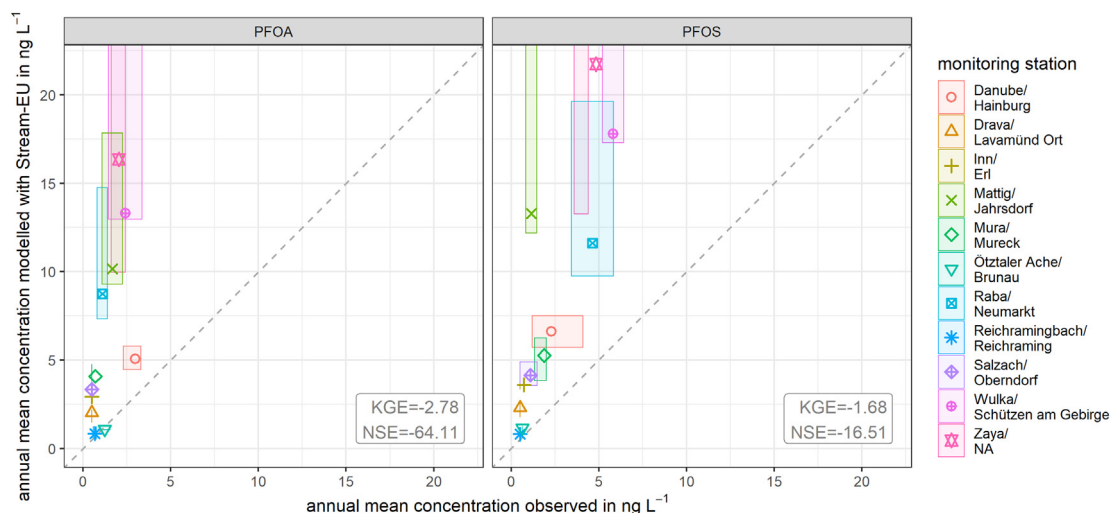


Fig. 4. Comparison of concentrations modelled by Lindim et al. (2016a) for 2009–2013 with the concentration data used for validation in this study from 2016/2017. Median of the modelled annual mean concentrations of the 5 years 2009–2013 is plotted against mean observed concentration in 2016/2017. The coloured boxes display the range of annual mean concentration for the modelled data and the uncertainty of the observed concentration caused by values below LOQ. KGE: Kling-Gupta model efficiency coefficient, NSE: Nash-Sutcliffe model efficiency coefficient.

In Fig. 5 maps of the modelled PFAS concentrations are shown for all three model variants. For PFOA in all three model variant, the emissions from the legacy contamination site can be clearly seen with increasing dilution along the Inn and Danube river. The pollution of this site with these “forever chemicals” is still polluting the downstream rivers and will probably continue to do so for many decades, in case no decontamination measures are taken.

For PFOS in the Median model variant the highest annual mean concentrations ($> 4 \text{ ng L}^{-1}$) appear only in the eastern part of the model domain, where the precipitation and consequently the river discharges are rather low compared to the precipitation rich western and alpine regions and therefore the emissions from municipal and industrial point sources are less diluted. Nevertheless, for the Median model variant most sub-catchments show concentrations above 0.65 ng L^{-1} , which is the environmental quality standard (AA-EQS) for PFOS as annual average concentration in inland surface waters in Europe (The European Parliament and the Council of the European Union, 2008). When considering the Best-case model variant, PFOS concentrations are still above the EQS at the outlet of 17 % of

all sub-catchments, which indicates a problem with a high certainty in these cases.

3.3. Contribution of different pathways to surface water pollution

The PFAS emissions via different pathways for the whole model domain are listed in Table 2. For the Median model variant the highest emissions were estimated from the pathways “groundwater + interflow + tile drainages” for PFOA and “municipal wwtp” for PFOS. The quantification of the diffuse pathways is especially affected by high uncertainty and for the Best-case variant their emissions are significantly smaller than for the Worst-case variant. Emissions via municipal wwtp can be quantified with a much lower uncertainty and are higher than other urban emission pathways (sewer systems, industrial direct dischargers), especially for PFOS.

The relative contribution of different pathways to total emissions largely diverges in catchments of different size and characteristics, as presented by way of example for eight catchments in Fig. 6. The Wulka catchment shows the highest contribution of municipal wwtp emissions

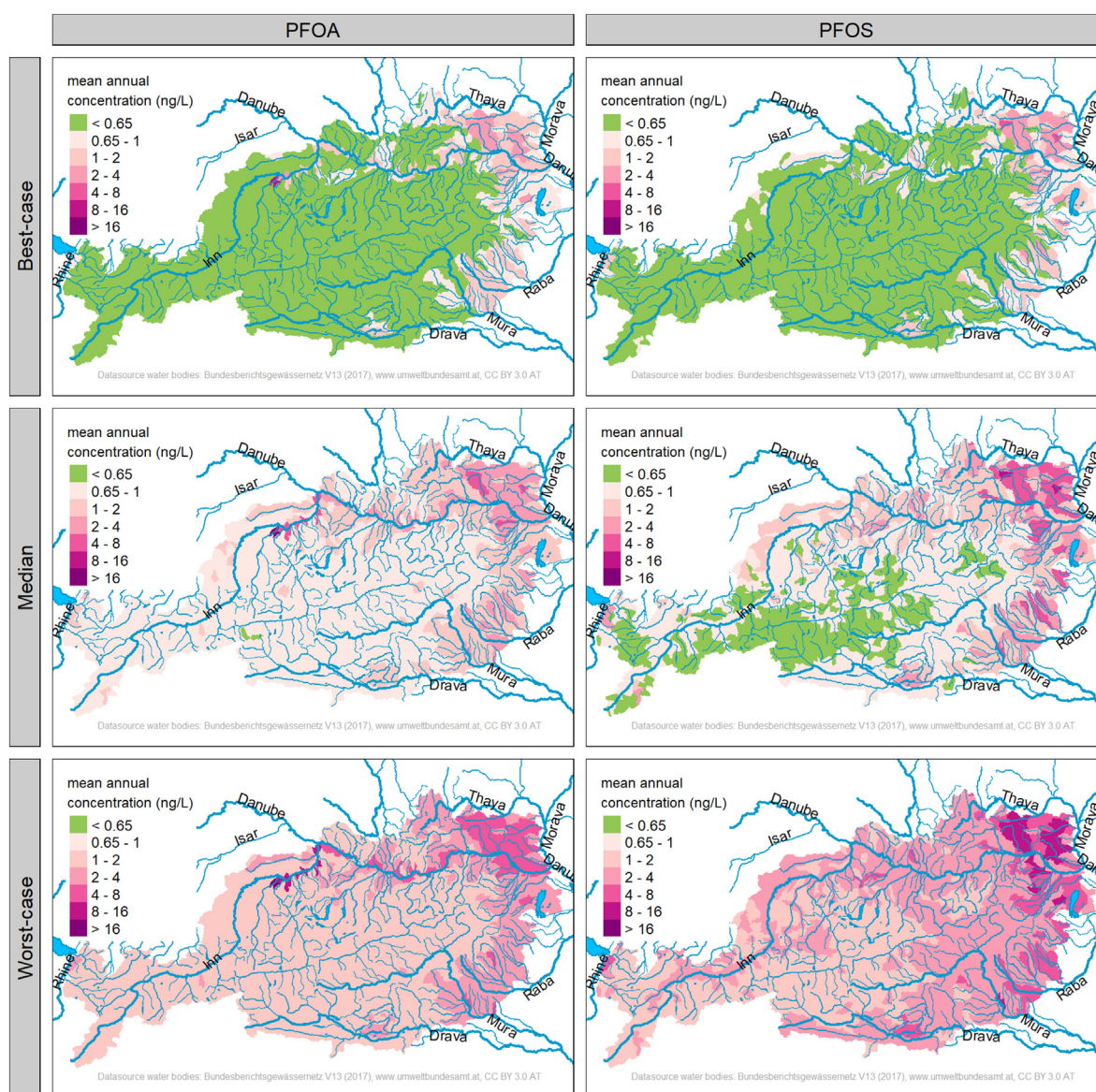


Fig. 5. Map of the annual mean PFAS concentration at the outlet of each sub-catchment for PFOA and PFOS and the three model variants “Best-case”, “Median” and “Worst-case”. Values below the water-referred environmental quality standard for PFOS of 0.65 ng L^{-1} are shown in green. Catchment borders are not shown to increase readability, they can be found in Fig. A1 in the SI. A bigger version of the maps can be found in the SI (Fig. A4-A5).

Table 2

Modelled emissions of PFOA and PFOS via different pathways in the total model domain. For better comparability the emissions are given as area specific values (divided by the area of the whole model domain) in $\text{mg km}^{-2} \text{a}^{-1}$. As the pathway “tile drainages” was quantified based on the same concentration as “groundwater + interflow” and did not result in significant emissions, these pathways were combined in the table. Wwtp: wastewater treatment plant.

	PFOA ($\text{mg km}^{-2} \text{a}^{-1}$)			PFOS ($\text{mg km}^{-2} \text{a}^{-1}$)		
	Best-case	Median	Worst-case	Best-case	Median	Worst-case
Atmospheric deposition onto water surfaces	0	9	18	0	9	18
Overland surface runoff	0	77	153	0	77	153
Overland streets + highways	18	20	33	8	14	18
Combined sewer overflow	8	12	19	10	17	38
Storm sewers	22	38	67	15	31	62
Municipal wwtp	67	94	103	164	337	403
Industrial direct dischargers	12	32	59	5	15	28
Soil erosion	38	46	54	3	18	233
Groundwater + interflow + tile drainages (contribution of Gendorf legacy site)	550 (72 %)	1348 (70 %)	2751 (70 %)	107	323	861

to the total emissions for PFOA and PFOS. This is caused by a high amount of treated wastewater in a catchment with high population density and rather low annual precipitation, thus with a low area specific runoff. In the Zaya catchment similar patterns can be seen, but the wastewater load is lower and therefore other diffuse pathways contribute to a larger degree to the total emissions. As the annual total runoff is very low in the Zaya catchment, emissions via “overland surface runoff” are negligible and emissions via “groundwater + interflow” are rather small. Other catchments like Pram, Mattig, Raba and Mura show a more balanced contribution of different pathways, with a major share coming from diffuse pathways. The Ötztaler Ache is an alpine catchment with low settlement density. Therefore, the main emission inputs stem from the natural runoff components (groundwater, interflow and overland surface runoff).

Comparison of PFOA and PFOS emissions show that PFOS emissions are dominated to a larger degree by municipal wwtp emissions, while for PFOA diffuse pathways play a bigger role. Consequently, total emissions of PFOS are higher in wastewater dominated catchments (e.g. Wulka, Zaya, Dornbirnerach), while PFOA and PFOS emissions are of equal magnitude in catchments without strong wastewater influence (e.g. Ötztaler Ache, Mur). High concentrations of PFOS can be found especially in rivers with a high share of contribution from wwtps. That means that even emissions from wwtps in the context of the overall country do not have the highest

share of emissions (these are emissions from unsealed areas), wwtp effluents are the drivers in case of high concentrations in rivers.

Past studies on the regionalization of PFAS emissions mostly either did not deliver information about the contribution of different emission pathways (Müller et al., 2011a; Pistocchi and Loos, 2009) or only differentiated between wwtp emissions and the remaining diffuse emissions considered as black box (Earnshaw et al., 2014; Huset et al., 2008; Paul et al., 2012).

In comparison to the results presented by Müller et al. (2011b), significantly higher contributions of diffuse pathways are estimated here. This is explained by the fact that the catchment investigated by Müller et al. (2011b) was much smaller ($\sim 5.9 \text{ km}^2$) and the population density in the catchment ($\sim 2100 \text{ in. km}^{-2}$) is much higher than in this study ($\sim 105 \text{ in. km}^{-2}$).

Lindim et al. (2015) only differentiated between input via atmospheric deposition and other emissions directly caused by the population. The deposition rates applied by Lindim et al. (2015), based on data from Dreyer et al. (2010), of $8 \text{ ng PFOA m}^{-2} \text{ day}^{-1}$ and $2 \text{ ng PFOS m}^{-2} \text{ day}^{-1}$ are quite similar to the rates calculated in this study (based on Zoboli et al., 2019) of $1.5 (0.0\text{--}7.2) \text{ ng PFOA m}^{-2} \text{ day}^{-1}$ and $1.5 (0.0\text{--}7.2) \text{ ng PFOS m}^{-2} \text{ day}^{-1}$. The higher deposition rates from Dreyer et al. (2010) might be explained by the fact, that sampling was done some years earlier than for this study, when the use of these PFAS was still more common.

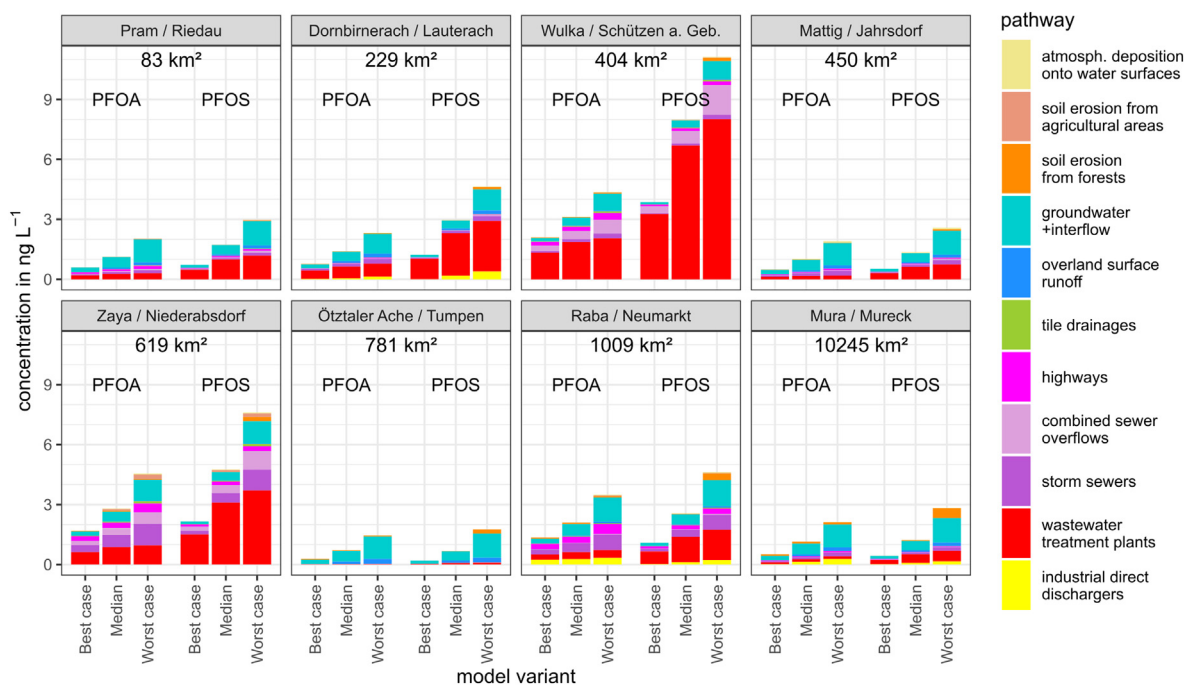


Fig. 6. Concentration of PFOA and PFOS at the outlet of selected catchments for the three model variants. Contribution of different emission pathways to total emissions is shown by the colours of the bars.

Owing to the very different regulatory situation regarding PFAS in China, a direct comparison with the results from Liu et al. (2017) is not meaningful. Production and use of PFOA and PFOS in industry and agriculture (via use of insecticide Sulfluramid) is still ongoing. However, the results of Liu et al. (2017) highlight landfill leachate as an important pathway, which might also play a relevant role in Europe. In this study it could not be fully considered. Only landfill sites, in which landfill leachate is treated by a treatment plant and for which data are reported within the Austrian emission registry, could be considered (cp. Table A3 in SI). Contaminated sites, in which no collection or no treatment is in place yet and which probably emit PFOA and PFOS via leachate collection and disposal or via groundwater into surface waters, should be considered in the future. Currently data about sites, discharge volumes and concentrations are missing. The same applies for sites with firefighting activities, either at trainings or real fire accidents, involving the use of aqueous film forming foam. Sites with a higher probability of such activities are airports, waste handling sites and firefighting training grounds. Data regarding their location, PFAS emission factors or PFAS concentrations and discharge volumes, necessary to include such sources in the model, are currently unavailable. Further efforts are needed to collect such information by means of monitoring and inventorying, which could further improve the model's prediction capabilities.

4. Conclusions and outlook

We combined the MoRE model with parametrisation of substance-specific data obtained from literature and a tailor-made monitoring programme in different environmental compartments. With this approach we achieved a model performance for prediction of river loads and concentrations which is clearly better than the performance obtained with regionalization approaches based on population-specific emission factors, population density and wwtP information. Thus, it can be concluded that the additional effort dedicated to targeted monitoring and data processing is rewarded with significantly better results.

The Austrian territory is very heterogenous regarding precipitation amounts, land use, population density and geomorphology, therefore the successful model application in this area proves, that the model is capable to handle very different emission situations and therefore the application in other spatial domains will be possible.

Model results can be used for estimating environmental concentrations in unmonitored rivers, assessing the relevance of different emission pathways and the effectiveness of measures for pollution reduction. These investigations are a promising basis for an extension of the MoRE application to PFAS of emerging concern, other than PFOS and PFOA. The model approach is mainly based on monitoring input data and less on substance properties. Therefore, PFAS with different chemical structures, showing differences in substance properties and environmental behaviour, can be implemented in the model, provided the monitoring data for parametrization of all relevant pathways for these substances become available. Adaptations of the model approaches might be necessary to describe processes like degradation to other PFAS, creation by the degradation of precursor substances, or adsorption on particulate matter in the aquatic environment. Such quantification algorithms already exist in the model from other organic trace substances. As soon as monitoring data and knowledge about the processes becomes available, the model can be extended for further PFAS.

Current results show that in water-rich catchments like the western and central part of Austria, diffuse emission pathways, like overland surface runoff, interflow and groundwater exfiltration, might play a significant role for PFOA and PFOS emission loads. To reduce uncertainty of the results for diffuse emission pathways, sample measurements with lower analytical limits of quantification are necessary as they have been available in the past.

For PFOS municipal wwtP effluent is a more important pathway than for PFOA, which shows higher contributions from diffuse pathways. WwtP effluents are the drivers in case where highest PFAS concentrations in rivers have been found. Potentially overlooked pathways like landfill leachate and runoff from sites contaminated with aqueous firefighting

foam should be further investigated and approaches for their quantification still need to be developed.

The results of this investigation clearly show the relevance of action against PFAS contamination in surface waters, given that the current pollution level causes a high risk of exceedance of the water referred EQS especially in the eastern part of Austria in regions with high shares of wastewater effluents in river flow.

CRedit authorship contribution statement

Steffen Kittlaus: Conceptualization, Methodology, Software, Validation, Data curation, Writing - original draft, Writing - review & editing, Visualization. **Manfred Clara:** Conceptualization, Methodology, Writing - review & editing, Project administration, Funding acquisition. **Jos van Gils:** Methodology, Software, Data curation, Writing - review & editing. **Oliver Gabriel:** Methodology, Data curation. **Marianne Bertine Broer:** Methodology, Writing - review & editing. **Gerald Hochedlinger:** Data curation. **Helene Trautvetter:** Methodology, Data curation. **Gerold Hepp:** Data curation, Writing - review & editing. **Jörg Krampe:** Resources, Project administration, Writing - review & editing. **Matthias Zessner:** Conceptualization, Methodology, Writing - review & editing, Supervision, Project administration, Funding acquisition. **Ottavia Zoboli:** Conceptualization, Methodology, Writing - review & editing, Supervision.

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Data availability

Data are available from <https://doi.org/10.48436/jpzv9-c8w75>.

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.scitotenv.2022.157764>.

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