



Implications of the transition towards water-wise approaches in urban areas: Elucidating the risk from micropollutants release

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ABSTRACT

The transition towards circular and sustainable urban water systems, embracing a water-wise city approach, results in highly interconnected systems, introducing complexities in managing water quality due to the intricate interplay of pollutant sources, pathways, and receptors in urban environments. This study focuses on assessing the impact of transitioning to a water-wise city approach on water quality. The analysis employs an integrated model-based approach to evaluate the release of micropollutants (PFOA, PFOS, pyrene) in the urban water system, considering potential future changes. We considered Milan (Italy) as a case study and explored sustainable urban water management strategies related to the hydraulic reconnection of canals, including (i) the use of groundwater for energy purposes, (ii) the establishment of a separate stormwater sewer system, and (iii) the indirect reuse of reclaimed water for crop irrigation. Acute and chronic environmental risks were assessed at various locations of the recipients, under different water management and climate change scenarios. Uncertainties on projections related to rainfall and runoff concentrations were also considered. The model accurately predicted average micropollutants concentrations in the current situation. PFOA and PFOS exhibit chronic, but not acute risks in all scenarios; high removal efficiency is required to reduce the risk at acceptable levels. Pyrene poses higher risks for increasing separation fractions of the sewer system, with further increase for climate change, but concentration uncertainty has more influence than precipitation uncertainty on the risk extent. This study provides a water management framework, identifying critical sources and locations under current, future, and climate change scenarios.

1. Introduction

Urban water systems are shifting from a linear concept of pump-use-treat to more circular approaches to address the multiple challenges and trends (often exacerbated by climate change) affecting the urban water infrastructure. Growing population density and water scarcity ask for alternative water sources, such as reclaimed water [1]. Changes in industrial activities or increased annual rainfall result in increasing groundwater levels, creating the need to handle these additional water fluxes. Increases in intense rainfall events, together with increased environmental awareness and higher demands for good status of urban waters, are promoting the implementation of separated stormwater systems [2] and the adoption of decentralized green infrastructures [3]

to reduce flooding risks and to prevent the release of untreated wastewater through combined sewer overflows.[2,3] The increasing demand for livable spaces in urban areas lead to requalification and restoration of urban water rivers, included in a planning perspective combining green and blue solutions [4]. As a result of these transformations, new water fluxes, serving diverse purposes across urban areas, are appearing in accordance with a water-wise city approach [5].

However, the transition towards an interconnected system can have a side effect, with the creation of new challenges for water quality management, due to the intricate interplay of pollutant sources, spread pathways, and receptors. Contamination sources encompass point sources, such as industrial discharges and wastewater treatment plants [6], as well as non-point sources, such as urban runoff from streets,

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roofs, and construction sites [7]. A wide range of micropollutants is discharged and enters water bodies through diverse pathways, including direct discharges and transport through stormwater drains [8]. Rivers, canals, and groundwater often become repositories for various micropollutants [9], posing significant threats to both aquatic ecosystems and human health, causing disruptions in aquatic life and contaminating drinking water sources [9]. Further complexity is added by the influence of multiple physical factors and chemical reactions on the fate and transport of micropollutants within urban water systems [10]. Among the released micropollutants, per- and polyfluoroalkyl substances (PFAS) and polycyclic aromatic hydrocarbons (PAHs) are of paramount importance, since they pose significant risks to both the environment and human health due to their widespread sources of emission, their persistence and toxicity, potentially affecting organisms at the top of the food chain [11,12]. PFAS stem from various industrial and commercial uses, such as firefighting foams, waterproof fabrics, packaging, electronics, and cosmetics [12]. PAHs originate from industrial processes, vehicle parts and emissions, combustion processes, paved and buildings surfaces [7]. Water quality management in urban areas can rely on both monitoring and modeling strategies. However, strategies based solely on monitoring require important financial resources and logistical investments in e.g. monitoring equipment and personnel, to cope with the peculiar characteristics of micropollutant release and transport. Micropollutant sources show high temporal and spatial variations, being influenced by seasonal changes, weather conditions, and/or the timing of industrial and municipal discharges. Covering all these aspects with monitoring only would require extensive monitoring activities over long time periods. Further, monitoring cannot be utilized to predict the impacts and feasibility of new water management strategies, which are essential to support a robust shift from a linear to a circular approach.

Modeling has thus emerged as a fundamental tool [9] to integrate and supplement monitoring in the assessment of water quality in urban systems, as it can fill temporal and spatial gaps between measurements, allowing for a more comprehensive understanding of the system dynamics. Further, it enables the impact assessment of future water management strategies, even in climate change scenarios.

In this context, it is fundamental to be able to model and assess the possible impacts of the transition towards a water-wise approach, in terms of environmental risk posed by micropollutants and evaluating the possible effects of climate change, aspects that are currently lacking adequate attention in the existing literature.

The objective of this work is to show how it is possible to account for new micropollutant release pathways, potential impacts, and possible mitigation actions in the context of the transition to a water-wise city by using an integrated modelling approach. Specifically, micropollutants (PFAS and PAHs) released from a complex urban water system were modeled to predict their concentrations and the related environmental risk in the receiving surface water, under different scenarios of water management strategies and climate change.

The case study of the city of Milan (Italy) was investigated, where future transition plans include the re-opening an important historical waterway, that would re-connect the upstream canal with the southernmost agricultural peri-urban area. This will allow the restoration (daylighting) of an important historical waterway, the use of rising groundwater table for sustainable energy supply, the requalification of an agricultural reserve, combined with the present issues linked to emissions from the city drainage infrastructure. This implies a complex interplay of current and future urban water management strategies. Further, the area will be affected by climate change, with consequent uncertainties on the planning horizon. We demonstrated how an integrated dynamic model allows to assess the feasibility and impacts (expressed as chronic and acute effects) of these transition plans, also quantifying the uncertainties related to climate change projections.

2. Materials and methods

2.1. Modeling framework for micropollutants fate and transport

The Integrated Urban Wastewater and Stormwater system model library (IUWS_MP) [11,12], implemented in WEST (DHI A/S, Denmark), was used to model micropollutants fate in urban (waste)water systems [10,13]. The IUWS_MP library [13] adopts a conceptual approach, simulating water transport across all the elements of the urban water system (including urban rivers) with a series of continuously stirred tanks reactors (CSTRs). Specifically for river stretches, each CSTR, consists of two compartments (bulk water and sediments), in which fate processes (abiotic and biotic degradation, sorption to suspended solids and colloids) occur and mass exchange between the two are also considered, through sedimentation–resuspension and pore water–bulk water diffusion. The model library considers the micropollutants to be partitioned into three fractions: dissolved (S_MP), sorbed to particulate organic carbon (X_MP), sorbed to the dissolved, colloidal, organic carbon (S_MP_DOC) [13], assuming an instantaneous equilibrium among the three fractions. When referring to total concentration we mean the sum of the three fractions (S_MP + X_MP + S_MP_DOC).

2.2. System conceptualization

The selected case study of Milan (Italy) is presented in Fig. 1a. An upstream canal, derived from the Adda river, enters the system with a constant flow from the north (INLET point in Fig. 1a). In the current situation, this canal does not cross the city, and the historical waterway present in the city center is currently covered and unused. In this study we investigate the possibility of daylighting and hydraulic reconnecting the upstream canal with the historical waterway and the downstream natural canal, which receives the discharge of a large wastewater treatment plant (WWTP, 1'250'000 IE). The upstream canal, after reconnecting with the historical waterway, is diverted to a secondary canal, with flow equivalent to the inlet. The exceeding water volume (equivalent to the flows added along the canal) continues its southbound flow along the natural path. South of the city, the canal receives the treated effluent from a WWTP. The water in the natural canal downstream the WWTP is used for agricultural purposes, before ending in the Lambro River. In the area crossed by the canal there is a problem of rising groundwater table, with plans to pump the shallow groundwater to use it in groundwater heat pumps (GHP), generating heat in a greener way. The extracted groundwater will be discharged to the canal through 8 different outlets located between INLET and the WWTP outlet (represented as houses in Fig. 1a). It is also planned to convert part of the current combined sewer system into a separate stormwater system, in order to reduce the load to the WWTP and thereby the unwanted discharges of untreated wastewater. The separate storm sewer would discharge to the canal in the stretch between the SECONDARY CANAL and WWTP outlet.

The canal downstream the WWTP outlet discharge was already modeled by Delli Compagni et al. [10]. This model was (i) modified to take into account daily and seasonal variations of the effluent flowrate and quality, and (ii) extended to include the upstream hydraulic reconnection system related to the historical waterway daylighting. A total of 27 km of waterway, divided in 38 river units, were considered in the model. Fig. 1b represents the overall system as it has been implemented in the software WEST.

The model considers multiple dynamics in boundary conditions and forcing functions (temporal dynamic of energy demand, rainy days, water withdrawals, different types of contaminants, and change in yearly rain pattern due to climate change) over a 1-year period. It evaluates micropollutants concentrations at five monitoring points along the waterway (Fig. 1a): (i) INLET, representing the water quality of the upstream canal entering the system; (ii) POST_GHP, located after the last discharge into the waterway of groundwater from GHPs; (iii)

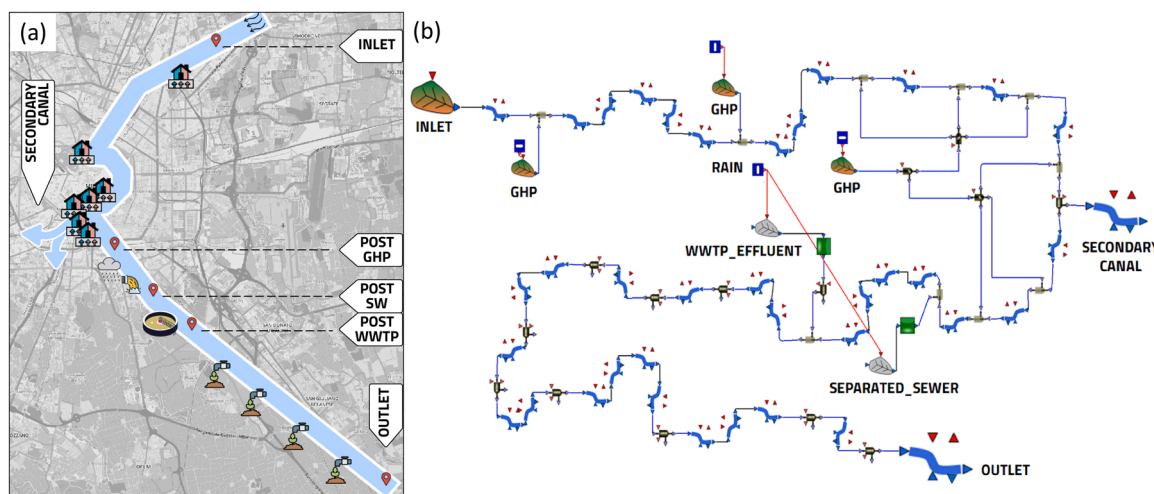


Fig. 1. (a) System conceptualization: map of the waterway flowing from the north to the south of Milan, input sources (GHPs discharging groundwater, stormwater runoff from separated sewer, WWTP effluent, agricultural withdrawals) and monitoring points set for the model (INLET, POST_GHP, POST_SW, POST_WWTP, OUTLET); (b) implemented layout of the physical model in WEST.

POST_SW, located positioned in the waterway after the discharge from the separate sewer; (iv) POST_WWTP, located downstream the WWTP effluent discharge; (v) OUTLET positioned at the end of the natural canal, before it enters the Lambro river. The model solves ordinary differential equations at variable timesteps, with an output generated at 1-hour steps.

2.2.1. Micropollutants selection

The micropollutants considered in this study belong to the class of PFAS and PAHs. PFAS have become pervasive in the environment [12], being found also in more than 70% of groundwaters in Europe [14], raising awareness about potential health risks and the need for strict regulatory limits [15]. In Milan, PFAS are found in groundwater, surface water and wastewater effluent as reported by Castiglioni et al. [16], with groundwater showing the highest concentrations, and PFOA and PFOS displaying the highest PFOA-equivalent concentration (assessed with the Relative Potency Factors (RPFs) [14]) across all water sources. For this reason, PFOA and PFOS were selected. PAHs are released by several human activities in urban environments, they can easily accumulate on particulates and be washed off with runoff, interfering with photosynthetic processes in aquatic plants, resulting in reduced primary productivity and altered community dynamics [17]. To represent the contamination from urban stormwater runoff, pyrene was chosen as representative of PAHs, due to the highest concentration and frequency of detection reported in previous studies [17,18], the large availability of monitoring data for the different water streams considered in the case study, and the low EQS (Environmental Quality Standard) compared to the detected concentrations.

2.2.2. Characterization of the input sources

The water input sources considered in the model were: (i) upstream canal; (ii) groundwater discharged by GHPs; (iii) stormwater runoff discharged by separate sewer system; (iv) WWTP effluent.

For the upstream canal and GHP discharges, measurements of conventional pollutants (ammonia, nitrite, nitrate, organic nitrogen, phosphorus, total suspended solids, BOD₅, COD, dissolved oxygen) and micropollutants (PFOA, PFOS, pyrene) were obtained from a 6-year monitoring dataset (2015–2020, 5–26 measurements available per parameter, see Table S1), provided by the Regional Agency for Environmental Protection (ARPA Lombardia) [19]. Considering the slow dynamics of concentrations in surface water bodies and groundwater (see Table S1), and the very low concentrations with respect to other sources (Fig. 2), for each parameter the mean value was chosen as

constant input to the model throughout the year. Moreover, we assumed that the water discharged by GHPs had the same quality as the withdrawn groundwater. The upstream canal is derived from the Adda river with a constant flow of 2 m³/s [20]. The water flowrate discharged by GHPs varies along the year, with daily and seasonal fluctuations following the energy demand, with peaks during winter and summer, and no flow in spring and autumn (see Figure S1).

The contribution from the WWTP was included by extending the model developed by Delli Compagni et al. [10] (simulating only a constant dry-weather flow) adding the temporal dynamics, simulating also wet-weather days. The WWTP effluent in dry-weather was represented by using a daily pattern of flowrate and pollution loads, based on data provided by the water utility (year 2021, Table S1) and gathered from Castiglioni et al. [21]. These measured data are thus representative of both the micropollutants from wastewater and groundwater that infiltrate in the sewer system and enters the WWTP. Wet-weather contribution was included by using data from a rain gauge in the catchment, providing data with a 10-minutes resolution [22]. The average daily flowrate of the WWTP effluent was calibrated over a year, in order to properly predict the increment of flowrate in wet-weather, but seasonal variation in dry-weather was neglected (i.e. reduction in flowrate during holidays), obtaining errors < 30% (see Figure S2).

Wet-weather micropollutants concentrations were not available for the case study, thus, representative values were gathered from Mutzner et al. [23] assuming no removal for PFAS in WWTP [16] and 90% removal for pyrene as reported by Wu et al. [24]. Micropollutants concentrations used as inputs to the model for all water sources are summarized in Table S2. The annual trend of total withdrawals of water used for crop irrigation is reported in Figure S3.

2.3. Modeling objectives

The water management strategies enabled by the historical waterway re-opening include (i) the discharge of groundwater from GHPs, and (ii) stormwater from a separate sewer system; and (iii) crop irrigation using a mix of the WWTP effluent and the previous discharges. Climate change can have an impact on the effects of the implementation of these strategies. Their impacts on micropollutants concentrations at the monitoring points identified in Fig. 1a were assessed with long-term simulations (1 year) with 1-hour output resolution.

2.3.1. Assessment of model performance on fate prediction

Model performance was assessed by comparing predicted daily

concentrations against the available measurements [19] at the OUTLET monitoring point, with 4 values provided for PFAS (year 2021), and 28 for pyrene (2015–2021).

2.3.2. Risk assessment of future water management strategies

The simulated concentrations were used to assess the environmental risk associated to the selected micropollutants along the waterway. Both chronic and acute risks were assessed in terms of Risk Quotient (RQ), i.e. the ratio between Predicted Environmental Concentration and (i) EQS (when available) or (ii) Predicted No-Effect Concentrations (PNEC) (see Table S3). The RQs were evaluated at the five monitoring points identified in Fig. 1a. For PFOA and PFOS, the chronic risk was assessed using the RPFs to convert each compound concentration in PFOA-equivalent concentration.

The impact of each strategy was assessed through four scenarios:

- B (Baseline): upstream canal ($2 \text{ m}^3/\text{s}$) completely flowing to the diversion canal out of the model (no hydraulic reconnection), presence of WWTP effluent ($4 \text{ m}^3/\text{s}$ in dry-weather), agricultural withdrawals (up to $3.2 \text{ m}^3/\text{s}$).
- B+GHP: hydraulic reconnection with additional flow of groundwater coming from the discharges of GHPs into the waterway, with seasonal fluctuations up to $5.8 \text{ m}^3/\text{s}$.
- B+GHP+SS08: hydraulic reconnection with GHPs discharge and additional flow from separate sewer system conveying stormwater from a district of 8 km^2 (12% of the total catchment), subtracted from the combined sewer system served by the WWTP.
- B+GHP+SS24: hydraulic reconnection with GHPs discharge and additional flow from separate sewer system conveying stormwater from 24 km^2 (35% of the total catchment), subtracted from the combined sewer system served by the WWTP.

2.3.3. Assessment of the influence of climate change

Climate change scenarios were derived modifying rain patterns, upstream canal flowrate and concentrations detected in urban stormwater runoff. These scenarios were implemented for the case when all water strategies were considered and 24 km^2 of sewer system were separated (B+GHP+SS24). The effect of climate change was investigated only on pyrene, since it is found in surface water bodies almost entirely due to stormwater runoff (Table S2), differently from PFAS, that are mainly released by groundwater and WWTP effluent. Rain patterns were modified adopting the predicted rain in the Lombardy region by the World Bank Climate Change Portal [25] (SSP2–4.5, reference period: 2040–2059). To consider the large uncertainty related to this projection, different scenarios using the 10th, 50th, 90th percentiles of monthly predicted rainfall were realized. Moreover, the upstream canal flowrate was reduced by 5%, as reported for the same SSP2–4.5 scenario and the specific canal of the case study by Abily et al. [26]. Finally, the pyrene concentrations in stormwater runoff were assumed to change based on the accumulation-wash-off hypothesis: longer dry-weather periods increase the amount of micropollutants build-up and consequently washed off by stormwater (as shown by e.g. Lee et al. [27]). Thus, we realized different scenarios by using the 10th, 50th, 90th percentiles of pyrene, total suspended solids and COD concentrations gathered from Mutzner et al. [23] and Wicke et al. [28], respectively. As a result, 9 climate change (CC) scenarios were identified, by combining the 3 percentiles of rain (10 R, 50 R, 90 R) with the 3 percentiles of pyrene concentration (10 C, 50 C, 90 C): CC_10R_10C, CC_10R_50C, CC_10R_90C, CC_50R_10C, CC_50R_50C, CC_50R_90C, CC_90R_10C, CC_90R_50C, CC_90R_90C.

3. Results and discussion

3.1. Model performance on fate prediction

The model performance in predicting the micropollutants total

concentration ($S_{MP}+S_{MP_DOC}+X_{MP}$) at the OUTLET monitoring point is shown in Figure S4. The comparison considers the statistics of measured (2015–2020) and simulated (1-year dynamics) concentrations. A good match was observed, with the model predicting an average concentration of $13.2 \pm 1.3 \text{ ng/L}$ for PFOA, $3.6 \pm 1.0 \text{ ng/L}$ for PFOS, and $2.2 \pm 1.7 \text{ ng/L}$ for pyrene, while the measurements are equal to $15.0 \pm 6.2 \text{ ng/L}$ of PFOA, $6.3 \pm 3.2 \text{ ng/L}$ of PFOS, and $4.0 \pm 5.9 \text{ ng/L}$ of pyrene.

However, differences in the variability ranges of measured and simulated concentrations can be observed. In fact, measured data represent a snapshot information of river concentrations for few days and might not be fully representative of the variations in contaminants concentrations [29]: measured data are available only for 4 and 28 days for PFAS and pyrene, respectively, while the predicted concentrations are based on 24-hour average concentrations over an entire year. Therefore, the latter exhibit a lower variability compared to the measured data. However, considering the sampling analytical uncertainty affecting the measurements, and the parameter and structural uncertainty affecting the model, the overall results can be judged as satisfactory.

These results underline the robustness of the chosen modelling approach: the model library described by Vezzaro et al. [13], further extended and validated by Delli Compagni et al. [30], relies on the micropollutants inherent properties, limiting the impact of scarce data. Indeed, despite the limited number of available measurements (5–26) and the multiple sources of uncertainty, the simulated concentrations were consistent.

3.2. Impact of water management strategies: concentrations along the waterway

3.2.1. PFAS

In all analyzed scenarios, PFAS total concentrations were almost entirely represented by the soluble fraction, while only 0.01–1% of the total concentrations were represented by the sum of fractions sorbed on particulates and sorbed on colloids ($X_{MP}+S_{DOC_MP}$). In the Baseline scenario, PFOA is present at higher concentrations (2.5 ng/L in the upstream canal and 11.7 ng/L at POST_WWTP) than PFOS (0.5 ng/L in the upstream canal and 2.7 ng/L at POST_WWTP) (Fig. 2). Considerably lower concentrations of PFOS compared to PFOA at POST_WWTP are due to the coexistence of two reasons: a lower concentration of PFOS in the upstream canal with respect to PFOA, and a different behavior of PFOS in the WWTP with respect to PFOA. PFOS has a higher adsorption tendency ($\log D_{OW} = 3.05$) compared to PFOA ($\log D_{OW}=1.58$) [31], resulting in a higher removal, due to sorption on activated sludge, and thereby lower effluent concentrations, as observed by Castiglioni et al. [16]. This increases the possibility for PFOS of being sorbed on activated sludge flocs and being removed by sedimentation with sludge. During wet-weather, there is a notable increase in the concentrations of PFOS at POST_WWTP, reaching up to 9.9 ng/L , whereas PFOA experiences dilution, decreasing to 4.8 ng/L .

This discrepancy is attributed to the higher prevalence of PFOS in stormwater compared to PFOA (see Table S2). The accumulation of solids on urban surfaces, which are then washed off during wet-weather events, determines elevated concentrations of suspended solids and the associated sorbed micropollutants at the influent of the WWTP. Thus, due to PFOS's greater sorption affinity compared to PFOA, stormwater represents a significant source of PFOS through the transport of particles, while causes a dilution for PFOA, resulting then in higher concentrations of PFOS in the WWTP effluent. In B+GHP scenario, PFAS concentrations increase in the waterway downstream the POST_GHP monitoring point due to the contribution of the discharged groundwater, approaching concentrations up to 14 and 16 ng/L for PFOA and PFOS, respectively. Seasonal fluctuations are present, following the energy demand profile (Figure S1), and reaching concentrations similar to those in the Baseline scenario when GHPs are not in use (spring and fall), while the highest peaks are reached in winter. In the sewer separation

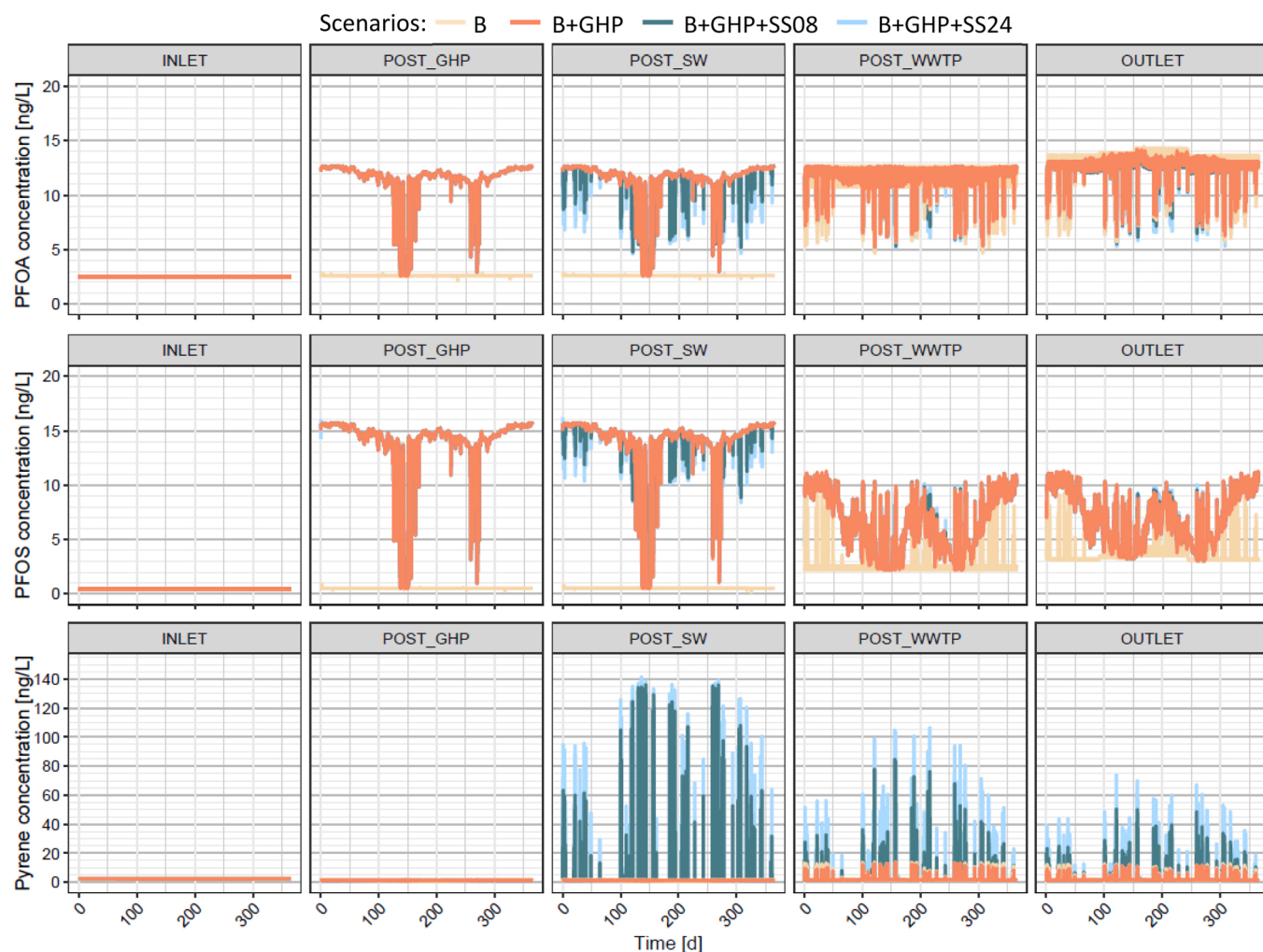


Fig. 2. 1-hour resolution concentration at each monitoring point (INLET, POST_GHP, POST_SW, POST_WWTP, OUTLET) in different scenarios (B, B+GHP, B+GHP+SS08, B+GHP+SS24), showed with different colors, for PFOA (top), PFOS (center), and pyrene (bottom).

scenarios (B+GHP+SS08 and B+GHP+SS24), a dilution effect is observed in all locations downstream the stormwater discharge, due to the lower concentrations of PFAS in stormwater than in groundwater. A higher dilution is observed when a larger area adopts a separate sewer system (B+GHP+SS24). In all scenarios a slightly higher concentration of PFAS is observed at the OUTLET with respect to the POST_WWTP. This is due to the equilibrium between water and sediment compartments, influenced by the withdrawals of water for crop irrigation.

3.2.2. Pyrene

Unlike PFOA and PFOS, which can be considered ubiquitous micropollutants, the main source of pyrene is urban stormwater runoff. Hence, its concentration does not change after the GHP discharges (Fig. 2), but it is affected almost completely by the discharge of stormwater and the WWTP effluent. High pyrene concentrations are present in surface water during wet-weather only at the locations POST_SW (in B+GHP+SS08 up to 136 ng/L and B+GHP+SS24 up to 141 ng/L) and POST_WWTP (in all scenarios, up to 14 ng/L in Baseline and B+GHP, and up to 106 ng/L in B+GHP+SS24), where stormwater is discharged, and subsequently at the OUTLET (in all scenarios, up to 74 ng/L in B+GHP+SS24). An attenuation of the pyrene concentration is shown from POST_SW towards the OUTLET due to sedimentation. The use of GHPs (B+GHP) slightly leads to a reduction of the concentration at POST_WWTP, due to the dilution with water containing lower levels of pyrene (up to 3 ng/L depending on the GHPs flowrate). In general, the highest concentrations (up to 142 ng/L) are observed when a larger area

is converted to separate sewers (B+GHP+SS24). Regarding the fractionation of pyrene, differently from PFAS, it is found largely in the sorbed fraction during rain events. Across all scenarios and locations, during dry-weather the soluble fraction (S_MP) represents the 65%-85% of the total concentration, the sorbed on colloids (S_MP.DOC) represents the 9%-12%, and the sorbed on particulates (X_MP) represents the 4%-26%. During wet-weather, the X_MP fraction reaches up to 63% and the S_MP.DOC up to 24% in the B+GHP+SS24 scenario at the POST_SW monitoring point.

3.3. Environmental risk assessment along the waterway

3.3.1. PFAS

In all scenarios and monitoring points, PFAS are largely below the acute environmental risk threshold (290 ng_{PFOA}/L and 290 ng_{PFOS}/L [32]). However, the chronic environmental risk, RQ, is always greater than 1 (Fig. 3) in the Baseline scenario in all monitoring points downstream the discharge of the WWTP effluent (POST_WWTP and OUTLET).

These points have a high chronic risk also in all other scenarios. In the Baseline scenario the main contribution of PFAS is given by the WWTP effluent. When GHPs are considered (B+GHP), their contribution significantly increases the risk at the POST_GHP location (RQ values from <1 up to 10), which is lowered downstream by the dilution effect of the WWTP effluent. The strong variability in the locations POST_GHP and POST_SW refers to the period when GHPs are less/not in use (spring and fall) and when stormwater is released in the waterway. At these

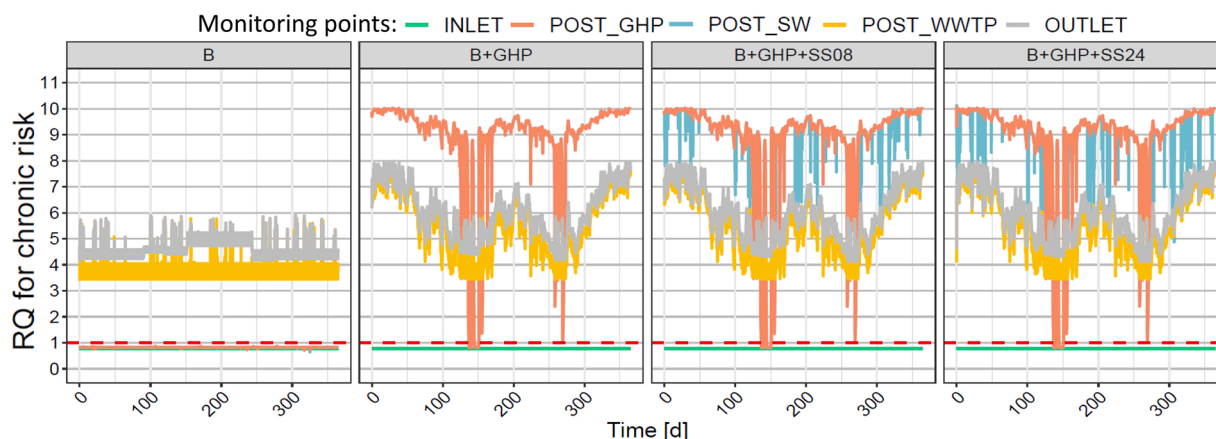


Fig. 3. 1-hour resolution RQ for chronic risk for the sum of PFAS, in each scenario (B, B+GHP, B+GHP+SS08, B+GHP+SS24) at the different monitoring points (INLET, POST_GHP, POST_SW, POST_WWTP, OUTLET) reported with different colors.

locations, when GHPs are not in use, the risk decreases to an acceptable level ($RQ < 1$) only for 9 days in a year. Stormwater discharges determine a reduction in the risk due to the dilution of the water inside the waterway with less polluted water. This effect is greater when the area covered by separate sewer is larger (B+GHP+SS24).

The chronic risk assessment was performed using as a reference the suggested value of the Annual Average Environmental Quality Standard (AA-EQS), reported in the revision of the European Water Framework Directive for the sum of 24 PFAS (4.4 ngPFOAeq/L , [14]). Nonetheless, a significant knowledge gap persists regarding these compounds and the impact they have on the ecosystem, resulting in inconsistencies among reference values reported in legislation of different water sources. For instance, the limit for the sum of 20 PFAS in drinking water is 100 ng/L [33], i.e. more than 20 times greater than the limit for surface water. Moreover, the two limits refer to different sets of PFAS (24 versus 20) and to a different way of calculating the sum of the concentration (PFOA-equivalent vs simple sum).

However, if the limit value for drinking water is used also for surface water, PFOA and PFOS would never exceed the threshold (concentration up to 29 ng/L) and no risk would be present for PFAS, assuming that in first place we can neglect other PFAS contribution, since PFOA and PFOS are those found at the highest concentrations. Moreover, no limits are present in the legislation for PFAS in WWTP effluent, and even the proposal of the European Commission for the revision of the Urban Wastewater Treatment Directive [34], that introduced a regulation for a set of micropollutants, does not include PFAS. Drinking water is transported to the WWTP, where PFAS are currently poorly/not removed [16], and subsequently discharged to surface water. In this context, it is clear that the limit set for surface water cannot be complied with, unless a (lower) limit is set for the contaminated water sources (i.e. groundwater and wastewater) that will be eventually discharged to surface water, or a higher limit is set for surface water.

3.3.2. Pyrene

As to the acute risk (Fig. 2), no exceedances are present in the Baseline and B+GHP scenarios, and no exceedances were found at the INLET and POST_GHP monitoring points in all scenarios, while after the discharge of the separate sewer, from POST_SW downstream, exceedances are present in the scenarios that include the separation of the sewer system (B+GHP+SS08 and B+GHP+SS24).

The chronic risk for pyrene in the Baseline and B+GHP scenarios (Table S4) is below the threshold of $RQ=1$ at all the monitoring points, being the Maximum Annual Concentration (MAC) EQS equal to 23 ng/L . In the scenarios with the separate sewer system, the POST_SW point is the only critical one, only when the separate sewer serves a larger area (B+GHP+SS24) with a RQ equal to 1.1 on an annual basis.

To understand in detail the exceedances of the AA-EQS and MAC-EQS values when sewer separation is implemented, Fig. 4 shows the number of months (for chronic risk) and days (for acute risk) exceeding the threshold at each monitoring point and scenario, based on 24-h concentration.

When only 8 km^2 of sewer network is separated (B+GHP+SS08), the acute risk is above the threshold ($RQ=1$) only immediately after the discharge of stormwater (POST_SW) for 12 days in a year, while the chronic risk is not exceeded as annual average, but it is above the threshold for 3 months in a year. When 24 km^2 are separated (B+GHP+SS24), the acute risk is above the threshold for 20 days in a year at POST_SW, for 7 days at POST_WWTP, and for 1 day at the OUTLET. The chronic risk as annual average is exceeded only at POST_SW, with exceedances of the threshold for 7 months in a year, while only for 2 months at POST_WWTP. However, the number of these exceedances do not pose a significant concern, and a mitigation strategy on the discharge of POST_SW could lower the risk below the acceptable level.

3.4. Impact of climate change

In the implemented climate change scenarios for pyrene, applied on the case with GHP and larger area of separate sewer system, we addressed all possible uncertainties that could be present, combining different intensities of rain patterns and levels of concentrations. Fig. 4 shows that climate change exacerbated the impacts of the stormwater concentrations. When pyrene concentrations in stormwater runoff are low (CC_10R_10C, CC_50 R_10C, CC_90R_10C), all monitored points comply with the limits for chronic and acute risk, regardless the considered climate change scenario. When stormwater concentrations are higher, the number of exceedances increases with more extreme rain patterns. In fact, the top three scenarios for number of exceedances are those with 90th percentile of concentration (90 C) ranked by rainfall pattern (90R, 50R, 10 R), followed by those with 50th percentile of concentrations (50 C), similarly ranked by the rainfall pattern.

Moreover, it is worth noting that the chronic risk is always exceeded in all months for any rain pattern when using the highest value of concentration (90 C, representative of long dry-weather periods), while acute risk exceedances are affected by the rainfall pattern, with a decrease of exceedances for less extreme scenarios (in decreasing order: CC_90R_90C, CC_50R_90C, CC_10R_90C). Given the predominant influence of the stormwater concentration to the risk calculation, the major action to lower the risk in any climate change scenario is thus to lower the pollution levels in stormwater, by e.g. introducing stormwater treatment options.

When considering all climate change scenarios, a wide range of

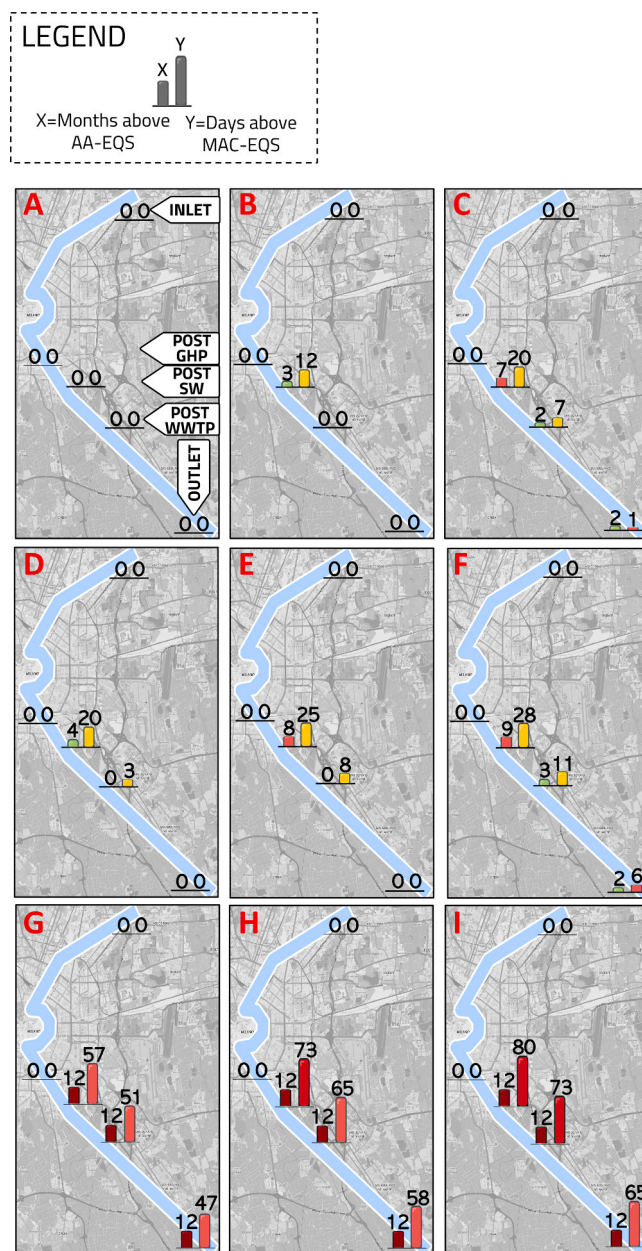


Fig. 4. Chronic and acute risk exceedances for pyrene in each simulated scenario. Exceedances of AA-EQS are reported on the left bar in month/year, exceedances of MAC-EQS are reported on the right bar in days/year. Both evaluations are based on 24-hours concentrations. (A) All scenarios with no exceedances (B, B+GHP, CC_10R_10C, CC_50R_10C, CC_90R_10C); (B,C) scenarios with separation of combined sewers (B+GHP+SS08, B+GHP+SS24); (D, E, F) scenarios with increasing climate-change rain intensity and medium stormwater concentration (50th percentiles, CC_10R_50C, CC_50R_50C, CC_90R_50C); (G, H, I) scenarios with increasing climate-change rain intensity and highly polluted stormwater (90th percentiles, CC_10R_90C, CC_50R_90C, CC_90R_90C).

exceedances is evident across the various scenarios. In a climate change perspective, this means that high uncertainty is present on the possible environmental risks, with a higher influence of concentration levels compared to rain patterns. Climate change can also indirectly influence the discharged concentrations. Indeed, stormwater concentrations can be dependent on the dry-weather periods, with seasonal effect found for Mediterranean/Semi-arid climates, i.e. where higher event-mean concentrations are observed for rainfall events following long dry periods [27]. Thus, the scenario CC_90R_90C is more likely if climate change in the study area moves towards longer dry periods followed by intense rainfall events. Conversely, the opposite can happen in case of a decrease in rainfall, leading to CC_10R_10C as more likely.

Micropollutant sources in urban areas can also change: for example, transition to electric vehicles can decrease pyrene emissions (a similar

effect was estimated for tire particles [35]). Furthermore, concentrations in stormwater runoff are currently highly unpredictable and are known to vary largely both temporally and spatially [23,36]. To include all these sources of uncertainty, we thus considered the CC_10R_10C, CC_50R_50C, CC_90R_90C as representative of the best-, medium-, and worst-case climate change scenarios. For these scenarios we investigated in detail the exceedances of the EQS at the monitoring points after the discharge of stormwater (POST_SW, POST_WWTP, OUTLET).

Fig. 5 shows the simulated concentrations against their frequency, along with the thresholds for acute (MAC-EQS) and chronic (AA-EQS) risk. It can be observed that in the best-case scenario (CC_10R_10C) even though the chronic risk is below the threshold, 2% of the time in the 1-year period is above the threshold at the POST_SW monitoring point, with values up to 8 ng/L. For the same scenario, the acute risk is below

the threshold. When looking at the medium-case scenario, the monitoring point with the highest concentration (75 ng/L) is the POST_SW, followed by POST_WWTP, with lower concentrations (up to 28 ng/L). In the worst-case scenario all monitoring points are characterized by significantly higher concentrations (above 100 ng/L) with the POST_SW monitoring point reaching 955 ng/L. This value lowers along the waterway reaching at the OUTLET monitoring point a maximum of 203 ng/L.

To better understand the fate of pyrene across the different fractions in the water compartment (soluble, sorbed on colloids, sorbed on particulates), we assessed pyrene partition in the three best-, medium-, worst-case scenarios of climate change. In dry days, pyrene concentration at the POST_SW (Fig. 2) has an average value of 1.3 ng/L, with the majority in the dissolved fraction (81%), only 2% sorbed on colloids, and the 17% sorbed on particulates. A similar fractionation was also found downstream, with a higher fraction of pyrene sorbed on colloids (S_MP_DOC) and lower sorbed on particulates (X_MP). A different picture appears when the concentration is affected by rain events (concentration at least equal to 2 times the average dry-weather concentration), as shown by the fractionation in Fig. 6.

In the best-case scenario (CC_10R_10C), the fractionation is similar to dry-weather: 80% (average) of pyrene was in the dissolved phase (S_MP), with the highest value (84%) reached at the OUTLET monitoring point, where the fraction sorbed on particulates (X_MP) was the lowest. The location with the highest percentage of pyrene sorbed on particulates is the POST_SW monitoring point. In the medium-case scenario (CC_50R_50C), the amount of dissolved pyrene lowers in favor to the sorbed fraction, with a strong increase in variability. In the worst-case scenario (CC_90R_90C) the majority of pyrene is sorbed on particulates in the location POST_SW (78%) and at POST_WWTP (52%), while at the OUTLET it is mainly dissolved in water and sorbed on colloids (80%). This spatial decrement is due to the process of sedimentation along the waterway, that is more accentuated in location further downstream the discharge of POST_SW. Moreover, the increment of the concentration of pyrene in the X_MP fraction in the medium- and worst-case scenarios is related to the hypothesized increment of solids washed off from urban surfaces in those scenarios.

3.5. Risk mitigation strategies

The previous assessment has shown that PFAS and pyrene may exceed threshold values for acute and chronic risk under several of the simulated present and future scenarios. One option to effectively reduce

the risk is to remove PFAS and pyrene from the contaminated water sources discharged to the waterway. Since these micropollutants are released by different main sources, mitigation strategies need to be applied at different locations, accounting for the characteristics of the water source as well as the properties of the micropollutants to be removed.

3.5.1. PFAS

The risk associated to PFAS appears to be exclusively chronic. This risk is present only if we consider the AA-EQS proposed by the revision of the Water Framework Directive [14]. To lower the resulting chronic risk, the sum of PFAS should reach values below 4.4 ng/L of PFOA-equivalents.

The level of concentration in the waterway corresponding to the chronic risk threshold is already reached in the Baseline scenario due to WWTP effluent. Mitigation strategies should thus be prioritized at this location. The minimum removal required at OUTLET to ensure RQ=1 is 83% and 70% for PFOA and PFOS, respectively. To guarantee a safer concentration (RQ=0.1) removal of 98% and 97%, respectively, are required. However, the proposal for a revision of the Urban Wastewater Treatment Directive [34], does not include PFAS in the list of micropollutants that have to be removed from WWTP effluents. Subsequently, mitigation strategies could be implemented at the discharge of each GHP or right after the withdrawal of groundwater. The minimum removal in groundwater should be 83% and 92%, while a safe removal should be 98% and 99%.

Adsorption on activated carbon is among the most effective technologies tested for the removal of micropollutants from water. Compared to other treatment processes (e.g. electrochemical treatment, chemical oxidation, photodegradation, reduction mineralization [37]), it is economically sustainable, it does not result in transformation products, it is able to remove a wide range of micropollutants, and it is being used and tested largely in drinking water treatment plants [38]. Cantoni et al. [31] studied PFAS removal from the groundwater of Milan, by a full-scale monitoring of granular activated carbon fixed-bed adsorbers focusing on 8 PFAS, including PFOA and PFOS. According to this study, the removal extent required for the compliance with the regulatory limits in the waterway cannot be obtained using activated carbon, unless a very large number of adsorbers or a very frequent reactivation of the activated carbon is applied.

3.5.2. Pyrene

Pyrene poses both acute and chronic risk, mainly in climate change

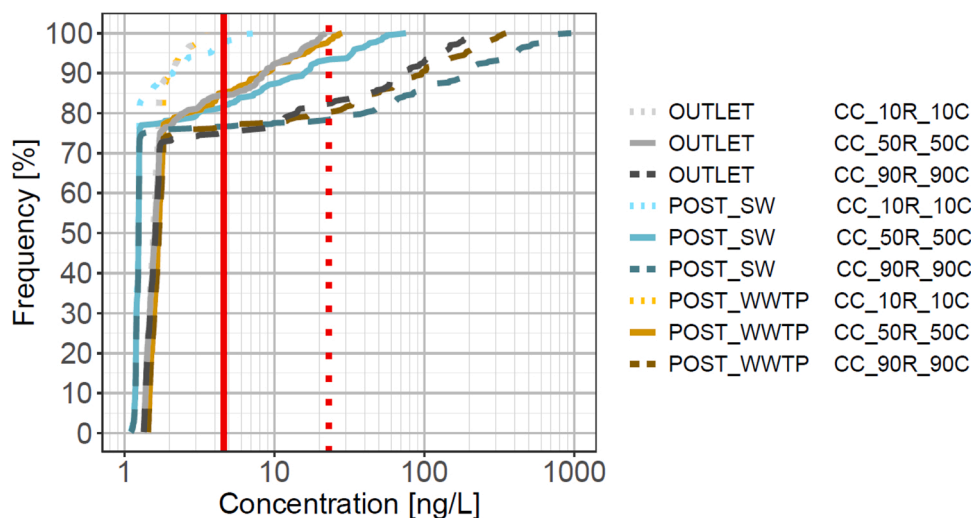


Fig. 5. Cumulated frequency of 24-h concentration in best-, medium-, worst-scenario of climate change (CC_10R_10C, CC_50R_50C, CC_90R_90C) at different monitoring points (POST_SW, POST_WWTP, OUTLET).

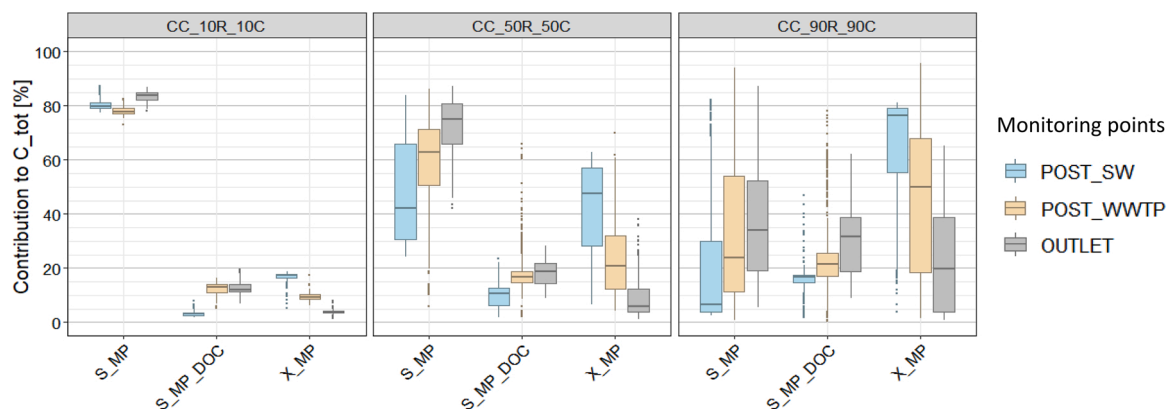


Fig. 6. Fractionation of 1-h resolution pyrene concentration among dissolved, sorbed on colloids, sorbed on particulate fraction (S_MP, S_MP_DOC, X_MP) at different monitoring points (POST_SW, POST_WWTP, OUTLET) and climate change scenarios (CC_10R_10C, CC_50R_50C, CC_90R_90C), when influenced by rain events.

scenarios and when the sewer system is separated for a large area (B+GHP+SS24). The most critical monitoring point is the POST_SW. The worst-case scenario is the CC_90R_90C. The main source of pyrene in our case study is stormwater runoff.

However, it should be considered that urban drainage systems worldwide are transitioning towards decentralized systems, with a wider use of Stormwater Control Measures (SCM, [3]) for local treatment of stormwater. SCMs provide multifunctional benefits, including runoff attenuation (for flooding risk reduction), pollutant reduction and increasing livability. Several of the commonly applied SCM, such as biofilters, filter strips, infiltration basins have shown relatively good removal potential (above 90%) for pyrene [39]. Assuming SCM implementation in the study area with 90% removal rate, the exceedance of the acute threshold at POST_SW is reduced to 10 days for the worst-case scenario (CC_90R_90C), compared to 80 days with no treatment. Moreover, the SCM implementation leads to acute risk below 1 at POST_WWTP and OUTLET, and chronic risk below 1 for the entire waterway. However, large urban areas (17% of the impermeable area of the catchment [39]) are required to be converted into SCM.

3.5.3. Additional issues to be considered in the transition towards a water-wise city approach

For a comprehensive evaluation of the implications of the transition towards a water-wise city approach in urban areas, the proper identification of the boundary conditions of the considered system is of paramount importance, to properly assess the fate of micropollutants. With respect to the case study used here, the boundary conditions could be expanded to include transport to the groundwater under the urban area and to the peri-urban agriculture system. In fact, SCM implementation could create new pollutant propagation pathways and hence their mitigation role should be considered integrating various points of views. For example, several SCM are based on local infiltration of stormwater, with consequent risk of contaminating the shallow groundwater due to the percolation of contaminants [40]. We did not include this aspect in our study, since PFAS main contamination source is groundwater, and pyrene tends to accumulate on solids, being efficiently removed in infiltration basins. For this reason, the contamination of groundwater due to SCM could be negligible for these micropollutants. However, the impacts of SCM strategies on soil and groundwater, related to other micropollutants that could possibly pose a significant risk due to infiltration, should be carefully investigated extending our integrated modelling approach (as in De Keyser et al. [41]). For instance, pesticides and herbicides could pose a risk for groundwater, if used to manage vegetations related to SCM management. Moreover, when a peri-urban agricultural system is established, as well as a recreational use of the water is promoted, the risk receptors should be expanded and risk for human health should also be taken into account. Multiple exposure

pathways are present for humans, such as inhalation (relevant for highly volatile micropollutants), dermal contact, and food ingestion. In recreational areas, if bathing is not permitted, the main exposure pathways for micropollutants could be inhalation, that can be modelled with an air pollution model, such as the box model (as in Srivastava et al. [42]). Regarding food ingestion, this can be an important exposure pathway when water is reused for crop irrigation. This can be considered through the implementation of a plant-uptake model (as in Delli Compagni et al. [10]) and further assessment of the risk, based on the concentration of micropollutants in crops.

Finally, for more accuracy in the risk assessment, sources of uncertainty should be lowered or, at least, characterized. For this reason, a proper characterization of the input sources should be carried out. In some cases, for example, the surface water body entering the city could be affected by seasonal variations, thus it should be considered as an input varying in time.

4. Conclusions

In this study we used a novel and comprehensive modeling approach to assess the impacts on the surface water quality of complex water management strategies in urban areas, along with the expected effects of climate change. Our assessment focused on the chronic and acute environmental risk posed by PFOA, PFOS, and pyrene. Following an initial model verification with available data for the current situation, future scenarios were assessed, highlighting the following findings:

- Strategies aiming at lowering the groundwater table and generating heat with heat pumps can lead to an increase in the chronic risk posed by PFAS, while no acute risk was observed. These micropollutants are already posing a chronic risk in the Baseline scenario due to the WWTP effluent discharge. Implementation of GHP, with discharge of polluted groundwater can increase PFAS emission to surface water and increase risk exceedance. Current treatment technologies (adsorption on granular activated carbon) would not be able to lower PFAS emissions to a level that ensure no chronic risk in an economically sustainable manner. However, inconsistencies between limits proposed by regulations on different water sources were found (i.e. limits in drinking water higher than limits for surface water and currently there are no limits for WWTPs).
- Conversion of parts of the urban areas to separate sewer systems, directly discharging stormwater to the waterway, can increase pyrene emissions during wet-weather. However, a chronic risk exceedance (RQ=1.1) was observed only right after the discharge of stormwater when a large area of the catchment (35%) is converted to separate sewer systems.

- Uncertainty in the pollution levels from wet-weather discharges had a higher influence on the risk estimation than expected changes in rainfall patterns due to climate change. Scenarios with high risk were dominated by those where 90th percentile of the pyrene concentrations were used. In these scenarios, pyrene resulted mostly in the particulate fraction just after discharge, being removed along the waterbody due to settling. Nature-based solutions, such as SCM, could be used to treat stormwater, but attention should be paid to potential contamination of groundwater.

This study provides a useful tool to assess impacts from different water sources through the assessment of both chronic and acute risk, and to identify the most critical points along a waterway. The presented results were obtained on a specific case study, but the model can be adapted to the specific water sources discharging to a waterway of another urban area. It will allow for the identification of critical sources and points along a waterway, both in the current situation and in a climate change perspective. This allows decision makers to evaluate future water management practices and identify best mitigation actions, which should be implemented to maintain the risk and the impact at acceptable levels.

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CRediT authorship contribution statement

Jessica Ianes: Writing – original draft, Visualization, Methodology, Formal analysis. **Beatrice Cantoni:** Writing – review & editing, Validation. **Fabio Scana:** Formal analysis. **Riccardo Delli Compagni:** Methodology, Formal analysis. **Fabio Polesel:** Writing – review & editing, Methodology, Conceptualization. **Enrico Ulisse Remigi:** Writing – review & editing, Validation. **Luca Vezzaro:** Writing – review & editing, Methodology, Conceptualization. **Manuela Antonelli:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jece.2024.112676](https://doi.org/10.1016/j.jece.2024.112676).

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