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A stochastic approach for assessing the chronic environmental risk generated by wet-weather events from integrated urban wastewater systems†

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Wet-weather discharges from urban areas with a combined wastewater system represent a threat for surface waters. In fact, when the system capacity is reached during medium/big rain events, a mixture of stormwater and untreated wastewater is discharged through combined sewer overflows (CSOs) or bypass (BP) of wastewater treatment plants (WWTP). The discharged pollutant loads are highly variable in time and space, making it difficult to correctly monitor and assess the environmental risks for a specific catchment. The present work proposes a methodology to assess the chronic impact of wet-weather discharges from integrated urban wastewater systems (IUWS) by using a stochastic approach. Monitoring data from the literature were used to characterize the discharges and to predict the risk posed by (micro-)pollutants on a yearly basis in an archetype IUWS. Calculated risks from wet-weather discharges are compared against those posed by WWTP effluent. The results show that CSOs pose a higher risk to surface waters compared to WWTP effluent and bypass, with polycyclic aromatic hydrocarbons being the category of micro-pollutants of major concern for CSOs. Conversely, WWTP effluent discharges are responsible for most of the risk associated with pharmaceuticals. A sensitivity and uncertainty analysis highlighted the importance of performing an accurate estimation of the recipient flow rate, which can provide a better risk estimation than focusing only on the characterization of the discharged concentrations. In climate change scenarios, where recipient flow rate reduction and overflow volume increment is expected, the risk caused by wet-weather discharges may increase for all micropollutant categories, including pharmaceuticals.

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Water impact

To reduce impacts from urban areas on natural water, holistic approaches are needed. We propose a stochastic methodology for chronic environmental risk assessment posed by different urban wastewater discharges, both in dry- and wet-weather. Our method can be applied to several (micro-)pollutants, helping to identify the most critical discharges and to prioritize mitigation actions, also from a climate change perspective.

1. Introduction

Growing urbanization worldwide is increasing the environmental impacts caused by wastewater discharges.¹ Wastewa-

ter from urban areas is collected through sewer systems and conveyed to wastewater treatment plants (WWTP), before discharging the treated effluent (EFF) to the surface water recipient. Most cities around the world are served by combined sewer systems, collecting both domestic and industrial wastewater as well as rainwater runoff.² In Europe, for example, 70% of the 2.2 million km of existing sewers is combined.³ In the case of medium to large rainfall or snowmelt events, the hydraulic capacity of the sewer system or of the WWTP might be exceeded, causing the discharge of untreated (or only partially treated) wastewater into the environment, through combined sewer overflows (CSOs) along the sewer system, or through bypass at the WWTP (BP). These wet-

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weather discharges represent one of the major water pollution impacts from urban areas, in particular for non-persistent substances removable in WWTP⁴ and for runoff pollutants.⁵

The number of CSO structures in urban areas can be very high, easily reaching >50 discharge points across a catchment,⁶ depending on multiple factors, such as the historical development of the sewer system, regulation, and physical factors (drainage area, imperviousness, slope). However, the distribution of discharged volumes is often uneven, with a small number of the CSO structures responsible for the greatest fraction of the discharged volume.^{7,8}

The WWTP bypass is located at the plant, downstream the catchment. It is designed to completely bypass the whole plant and/or only some treatment units. The discharged water has thus different pollution levels (ranging from untreated wastewater to wastewater that has undergone primary treatment),⁹ and it can also be mixed with the plant effluent before the discharge to the recipient.

Climate change is going to exacerbate the impacts of wet-weather discharges. In some areas the increase of high intensity rain events will result in more frequent wet-weather discharges.^{10,11} Tavakol-Davani *et al.*¹² estimated an increase in wet-weather discharge frequency (18%), volume (12%), and duration (17%) in Toledo (Ohio, USA). Salerno *et al.*¹³ estimated an increase of 40% in phosphorus load in a river in northern Italy. Gogien *et al.*¹⁴ reported for the city of Valence (France) an increase in CSO volumes for five climate models between 13% and 52% at the end of the century. In some climatic regions (such as Western and Southern Europe), the expected increase in CSO volume will be aggravated by the concurrent decrease in river annual average flow rates,¹⁵ which will lead to lower dilution and thereby greater impacts.

In Europe, the Water Framework Directive (WFD – 2000/60/EC – European Commission, 2000)¹⁶ requires the achievement of a “good” ecological and chemical status in natural waters by 2027. To achieve this goal, it is thus important to map and quantify the threats and environmental risks posed by continuous (effluent) and intermittent (CSOs and bypass) discharges. Wet-weather discharges are considered to be the major cause of the degradation of surface water quality compared to WWTP effluent,¹⁷ for both short-term (acute) and long-term (chronic) impacts. The acute risk related to wet-weather discharges has already been addressed by several authors.^{18,19} In these studies, however, only single CSO discharge points were monitored, and the impact of recipient dilution (a relevant factor when assessing the environmental risk) was not always considered. Other authors assessed the long-term impacts through the pollutant yearly loads released into the environment by specific CSO structures,^{8,20,21} but a chronic risk assessment was never performed. The major impact of micropollutants is however on the long-term scale: Gooré Bi *et al.*²² showed the potential impact of wet-weather discharges in chronic ecotoxicity tests, but did not detect any effect in acute ecotoxicity tests. Thus, it is important to further understand the long-term impact of wet-weather dis-

charges, especially related to micropollutant release, and to identify adequate treatments if needed.

A thorough risk assessment of wet-weather discharges is currently hampered by the lack of measurements for both their quantity and quality. Indeed, the highly intermittent and unpredictable nature of wet-weather discharges^{23–25} and the technical constraints in accessing CSO structures²⁶ are an obstacle to extensive monitoring campaigns.

Some studies report a wide range of (micro-)pollutants detected in wet-weather discharges,^{5,18,27–29} but the number of articles is still limited compared to the availability of studies on effluents. Also, the type and number of analyzed (micro-)pollutants is highly variable between studies and scarce when referred to emerging contaminants. All these factors reduce the chance to compare and generalize results.³⁰

Various studies and reviews^{2,18,30} have highlighted the high variability in concentration of micropollutants among the available data. These are often gathered from monitoring campaigns carried out only on very few CSO structures,^{17,27,31} limiting the possibility to estimate the loads discharged by the whole sewer system. However, recent modelling studies³² have tried to quantify the wet-weather overflow volumes at the regional scale. The scarcity of measurements is even more critical when looking at the bypass, since few monitoring data can be found in the literature.³³ Therefore, a stochastic approach is suggested to cope with this general lack of data and with the inherent intra- and inter-events' high variability of wet-weather discharges.^{21,34}

This work aims at assessing and apportioning the chronic environmental risk posed by the different discharges of urban wastewater (CSOs, bypass, effluent) to the surface water recipient (river). This assessment was performed on an archetype integrated urban wastewater system (IUWS, *i.e.* an integration of sewer, treatment plant, and receiving waters),³⁵ representing a typical urban catchment. A stochastic approach was then applied, using available monitoring data present in the literature. Different scenarios were identified to assess the influence on the estimated risk of i) the pollution level of selected (micro-)pollutants (expressed as concentration percentiles) and ii) the dilution in the surface water recipient (expressed as dilution factor). The latter allows the assessment of the impact of climate change and consideration of geographical variability of hydraulic regimes. The pollutant loads released by each discharge over a one-year period were estimated and used for the assessment of the chronic environmental risk, which was expressed as: i) risk quotient (RQ) for micropollutants (12 compounds belonging to heavy metals, pharmaceuticals, pesticides and polycyclic aromatic hydrocarbons); ii) ecological status using a quality level index, calculated combining standard indicators. The impact of the high variability in quantity and quality data on the estimated risk was assessed with an uncertainty and sensitivity. The proposed approach can be adapted to a specific IUWS to (i) assess the chronic risk related to annual loads released, (ii) apportion the risk between continuous (effluent) and intermittent discharges (CSOs and bypass), (iii) identify



actions to reduce the risk, and (iv) comply with new or more stringent environmental regulations.

2. Materials and methods

The structure of the archetype IUWS was defined by taking inspiration from other ideal not deterministic systems found in the literature.^{36–38} The structure of this ideal system is schematized in Fig. 1 and it includes three discharge types: several CSO discharges, a WWTP bypass (BP), and a WWTP effluent (EFF); all discharging to the same river. All these i -th elements of the IUWS system were characterized both in

terms of water quantity (volume (V_i) for the three types of discharges, and flow rate (Q_R) for the recipient) and quality (concentrations of j -th (micro-)pollutants for the i -th discharge type – $C_{i,j}$). Data gathered from the literature were used to estimate probability distributions for each of the considered IUWS variables (V_i , Q_R and $C_{i,j}$). All the references were treated with the same level of confidence, although it could be expected that a smaller number of available references is linked to higher uncertainty.

For each monitored site found in the literature, various percentiles were extracted from the variables' probability distributions. These were used to define six scenarios

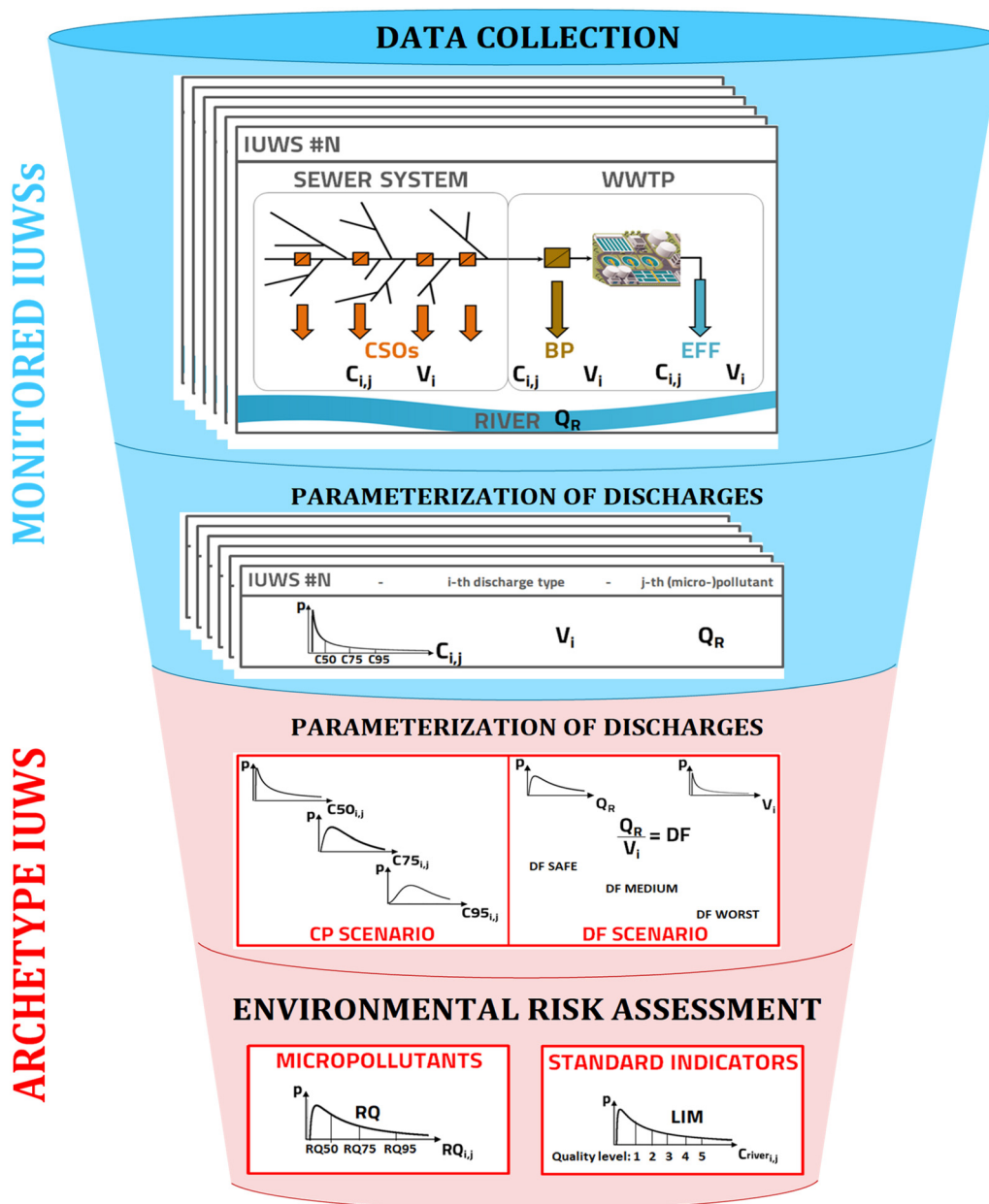


Fig. 1 Procedure used for the environmental risk assessment.



representing different pollution levels in the discharges (CP scenarios – accounting for urban areas with different land usages and pollutant sources) and different dilution levels in the receiving water body (DF scenarios – accounting for urban areas discharging to rivers of different sizes):

- CP scenarios were based on three pollution levels, corresponding to the 50th, 75th, 95th percentiles of the concentration distribution estimated from literature data;

- DF scenarios were based on three dilution levels (expressed as dilution factor), representing safe, medium, and worst cases (see section 2.3. for the definition of these cases).

Then, the chronic risk was assessed for each (micro-)pollutant in each scenario. Fig. 1 illustrates the steps of the implemented environmental risk assessment procedure, which are further described in the next sections.

2.1. Data collection

A total of 71 scientific articles were reviewed, dealing with CSOs (25), bypasses (17), effluents (38), and rivers (22). The data cover different geographical areas across the world, with a dominance of Europe and North America (see the ESI† in Fig. S1). All collected data were treated with the same level of confidence, although it could be expected that a smaller number of available references is linked to higher uncertainty.

Typically, quantity and quality data were not available for the same study, as detailed in Table S1†. The available dataset includes information on 52 CSOs, 29 bypasses, 232 effluent discharges and 65 rivers. Data on rivers were gathered from studies where a discharge of CSO/bypass/effluent was declared, while only 2.3% of the reviewed IUWSs monitored simultaneously more than one discharge type. Data on CSOs found in the literature were referred to single structures of the sewer system. Data describing effluent discharges refer to dry-weather conditions.

2.1.1. Water quantity data. The collected water quantity data for CSO and bypass were reported in the literature as (i) volumes discharged from multiple points during one event, and/or (ii) volumes discharged during multiple events at the same point. Data on effluent volumes and river flow rate were available as the annual average flow rate. The available data were aggregated at the annual level (Table S2†) as (i) volumes released during one-year period by each i -th discharge type (CSOs, bypass, effluent), and (ii) river annual average flow rate.

2.1.2. Water quality data. Available water quality data (see Table S2†) were classified into two categories. The first category includes standard indicators (pollutants): *E. coli*, BOD₅, COD, NH₄, NO₃, TP (total phosphorus). The second category includes 12 micropollutants (Table S3†), further grouped into 4 classes:

1. heavy metals (HM): cadmium (Cd), nickel (Ni), lead (Pb);
2. pharmaceuticals (PHARM): carbamazepine (CBZ), diclofenac (DCF), triclosan (TCS);

3. pesticides (PEST): carbendazim (CBD), diuron (DRN), terbutryn (TRB);

4. polycyclic aromatic hydrocarbons (PAHs): benzo(*a*)pyrene (BaP), chrysene (CHR), fluoranthene (FLU).

These classes of micropollutants were identified to provide a comprehensive analysis, covering a representative number of chemical properties. Single micropollutants were chosen based on: (i) availability of a reference value for chronic toxicity; (ii) availability of data in each discharge for at least 3 IUWSs; (iii) concentrations in discharges close to/above the toxic level.

Concentration data referred to (micro-)pollutants are available in the literature for one or more specific events at one or more discharge points of the same IUWS. However, raw data for published studies were not always available, as also reported by Mutzner *et al.*³⁰ Therefore, depending on how data were reported, gathered values for each event and discharge point included: (i) 25th, 50th, 75th percentiles (most frequent way of reporting); (ii) mean and standard deviation; (iii) 5th, 50th, 95th percentiles; (iv) single values (less frequent way). Data related to different events of the same discharge type or to different CSOs of the same IUWS were grouped together.

2.2. Parameterization of the monitored IUWSs

Statistical distributions were fitted to (micro-)pollutants' concentration data of each discharge type of a literature monitored IUWS, by testing: normal, Cauchy, logistic, exponential, chi-square, uniform, gamma, lognormal, Weibull, F , Student's T , and Gompertz. For each distribution the 50th, 75th, 95th percentiles were calculated (*cf.* the CP scenarios).

No distributions could be fitted to water quantity data of a single discharge type of a literature monitored IUWS, as these data are reported per single events during a period of up to 1.5 years or as an annual aggregated value. Aggregated values (annual discharged volumes, average annual river flow rate, *etc.*) were thus calculated and used for describing the hydraulics of each literature monitored IUWS.

2.3. Parameterization of the archetype IUWS

The variables (V_i , Q_R , C_{ij}) defining the archetype IUWS were described by probability distributions. For each i -th discharge type (CSOs, bypass or effluent) and for the river, the distributions of the water quantity parameters were estimated as follows:

- Step 1: grouping all the available data for each discharge type (annual discharged volumes V_i , river annual average flow rate Q_R), described in section 2.1.1.

- Step 2: finding the best probability distributions fitting these values (Table S4†).

To assess the impact of dilution, a dilution factor (DF), defined as the ratio of Q_R and V_i , was defined. Three DF scenarios were built, by using the distribution estimated at step 2 (Fig. S2, Table S5†):

(i) Safe scenario (high dilution): ranges between 25 ± 10 percentiles of V_i and 75 ± 10 percentiles of Q_R .



(ii) Medium scenario (medium dilution): ranges between 50 ± 10 percentiles of V_i and Q_R .

(iii) Worst scenario (low dilution): ranges between 75 ± 10 percentiles of V_i and 25 ± 10 percentiles of Q_R .

An additional “all-DF scenario” was considered in the sensitivity analysis (section 2.4.1), and it was obtained considering all the values of V_i and Q_R simultaneously (range of values between 5th and 95th percentiles).

Climate change will impact the dilution factor differently based on the regions and the climate models considered.³⁹ However, it is largely reported that, even under high uncertainty, wet-weather discharge volume will increase (increments between 11% and 148% based on the region).⁷ Furthermore, Abily *et al.*¹⁵ showed that the river flow rate will decrease in Western and Southern Europe up to 17%, with the strongest reduction in the Mediterranean regions. Northern and Eastern Europe will have a slight increase in river flow rate up to 8.2%, an effect that diminishes for more severe scenarios and for more distant periods in time. Coupling these two pieces of information, we can assume a general decrease of DF for wet-weather discharges in Europe. The situation could be different in specific areas of the world, however the most critical effect of climate change for surface water quality is the one related to the reduction of DF that causes a quality degradation. For this reason, the impact of climate change was considered in this study by assuming a decrease of DF for wet-weather discharges compared to the current situation.

The distributions of the water quality parameters of the archetype IUWS were defined through the following steps, which were repeated for each i -th discharge type (CSOs, bypass or effluent) and for each j -th (micro-)pollutant:

- Step 3: extraction of the 50th, 75th, 95th percentile values from the concentration probability distributions of each literature monitored IUWS (section 2.2.).
- Step 4: grouping of the same percentiles.
- Step 5: finding the best probability distributions fitting these percentiles values.

Step 5 resulted in a probability distribution for each of the considered percentile groups (50th, 75th, 95th percentile), hereafter referred to as $C50_{ij}$, $C75_{ij}$, and $C95_{ij}$, or in general as $C_{X_{ij}}$. These three percentile groups were defined to consider different pollution levels, *i.e.*, three CP scenarios were analyzed: (i) C50; (ii) C75; (iii) C95.

2.4. Environmental risk assessment: micropollutants

The environmental risk posed by micropollutants was calculated as risk quotient (RQ), considering the loads discharged to a clean surface water recipient (simple dilution was considered) during the chosen one-year reference period. This period is in line with approaches presented in previous studies^{7,27,40,41} and it facilitates the comparison with the chronic environmental quality standards (expressed as annual average, *i.e.*, AA-EQS). The RQ distribution was calculated as:

$$RQ_{ij} = \frac{C_{X_{ij}} \cdot V_i \cdot n_i}{TL_j \cdot Q_R \cdot t} \quad (1)$$

where i is the discharge type (CSOs, bypass or effluent); j is one of the 12 investigated micropollutants; $C_{X_{ij}}$ is the distribution of the values corresponding to the X -th percentile of the literature monitored IUWS concentration distributions (step 5 in section 2.3.); V_i is the distribution of the annual volume released by the i -th discharge type (step 2 in section 2.3), n_i is the number of structures per discharge type (set to 1 for bypass and effluent, while for CSOs this value was sampled from a uniform distribution between 2 and 20); Q_R is the distribution of the river annual average flow rate (step 2 in section 2.3); t is the reference time (1 year); TL_j is the toxic level for the j -th micropollutant. The latter was defined as AA-EQS, described in the EU legislation (Directive 2013/11/EU).⁴² The lowest chronic predicted no-effect concentration ($PNEC_{\text{chronic}}$), found in public databases (NORMAN Network, 2022),⁴³ was used when AA-EQS for the specific micropollutant was not available (CBZ, CBD, DCF, TCS), or was higher than $PNEC_{\text{chronic}}$ (DRN). Transport and fate processes were neglected, assuming that contaminant loads released during wet-weather events remain in the water compartment.

To assess the uncertainties in the estimated risk, a Monte Carlo approach was applied, propagating the input uncertainty in eqn (1) into the output distribution.⁴⁴ A total of 10 000 parameter combinations were sampled from the estimated input distributions, resulting in 10 000 values of RQ_{ij} . A distribution was then fitted to these risk values (hereafter defined as RQ distributions). TL and t were kept fixed. This procedure was applied to each of the 12 micropollutants released into the river by each of the 3 discharge types, in the 9 combinations of the DF and CP scenarios, obtaining 324 RQ distributions. The resulting RQ_{ij} were evaluated in correspondence of three percentiles (RQP): 50th, 75th, 95th, hereafter referred to as RQ50, RQ75, RQ95, respectively. Using these 972 RQ values, it was possible to evaluate the risk quotient for: (i) each j -th micropollutant in the river due to all discharges, as RQ_j calculated by eqn (2), (ii) all the micropollutants in the river due to a single i -th discharge type, as RQ_i calculated by eqn (3), (iii) all the micropollutants due to all discharges in the river, as RQ_R calculated by eqn (4):

$$RQ_j = \sum_{i=1}^3 RQP_{ij} \quad (2)$$

$$RQ_i = \sum_{j=1}^{12} RQP_{ij} \quad (3)$$

$$RQ_R = \sum_{i=1}^3 \sum_{j=1}^{12} RQP_{ij} \quad (4)$$

RQ_i allows apportionment of the risk among different discharges (CSOs, bypass and effluent); in turn, RQ_j permits apportionment of the risk among different micropollutants



downstream all discharges (CSOs + bypass + effluent), while RQ_R represents the impact of all micropollutants on the river posed by all the discharges from the archetype IUWS.

2.4.1. Sensitivity analysis. The influence of four factors ($I = C, V, Q, n_{CSO}$) on the $RQ_{i,j}$ estimation was assessed by performing a global sensitivity analysis (GSA), which allows consideration of interaction effects between parameters.⁴⁴ The analysis was performed for each CP and DF scenario, and also for the all-DF scenario. Among the available GSA methods, Sobol's method⁴⁵ was chosen as it allows quantification of the influence of each I -th parameter on the output variance, and it also accounts for interactions among parameters.

Sobol's method provides the first order index (S_I) and the total-effect index (S_{T_i}). The first-order index S_I measures the effect of varying a I -th parameter alone on the model output, but averaged over variations in other input parameters⁴⁴ and it is computed as:

$$S_I = \frac{V_{X_I}(E_{X_{-I}}(Y|X_I))}{V(Y)} \quad (5)$$

where X_I is the I -th factor; X_{-I} is the matrix of all factors but X_I ; $E_{X_{-I}}(Y|X_I)$ is the mean of $Y(X_I)$ taken over all possible values of X_{-I} while keeping X_I fixed; $V_{X_I}(E_{X_{-I}}(Y|X_I))$ is the output variance when all the factors except I are modified; $V(Y)$ is the total variance of the model output.

The total effect index S_{T_i} gives the total effect of a factor, inclusive of all its interactions with other factors⁴⁴ and it is computed as:

$$S_{T_i} = 1 - \frac{V_{X_{-I}}(E_{X_I}(Y|X_{-I}))}{V(Y)} \quad (6)$$

where X_{-I} is the matrix of all factors but X_I ; $E_{X_I}(Y|X_{-I})$ is the mean of $Y|X_{-I}$ taken over all possible values of X_I while varying the other inputs X_{-I} ; $V_{X_{-I}}(E_{X_I}(Y|X_{-I}))$ is the output variance when the factor I is modified; $V(Y)$ is the total variance of the model output.

Sobol's method is computationally demanding, as it requires $(2 \cdot p + 1)n$ simulations, with p the number of investigated parameters (in this study: $p = 4$) and n the number of samples (in this study: $n = 1000$), which should be sufficiently large to obtain a good estimate of the output variance. Furthermore, all indices were calculated for different combinations of DF scenarios and micropollutants.

2.5. Environmental risk assessment: standard indicators

The environmental risk associated with the standard indicators was calculated according to the approach described in the WFD, *i.e.*, by using an ecological status quality level index. Specifically, the macro-descriptor pollution level (LIM), as defined in the Italian implementation of the WFD (D. Lgs.152/2006), was utilized. Although the LIM index was replaced in the Italian legislation by a more synthetic index (macro-descriptor pollution level for the ecological status, LIM_{eco} D.M. 260/10), the LIM index is still in use in order to

ensure a long-period evaluation of surface water status. Therefore, it was also adopted in this study to evaluate the general quality status of the river.

The LIM was estimated for the river downstream all discharges of the archetype IUWS (Fig. 1) through the following steps:

1. The annual average concentration in the river downstream all discharges was calculated for each j -th standard indicator as the median value of:

$$C_{riverj} = \sum_{i=1}^3 C75_{i,j} \frac{V_i}{Q_R \cdot t} \quad (7)$$

where all the input parameters except t (equal to 1 year) are described by probability distributions.

2. A specific score was assigned for each j -th standard indicator (see Table S6†) according to the calculated C_{riverj} .

3. The scores for all the standard indicators were summed together to get a single value.

4. The single value was compared against the range of values belonging to a specific quality level class, to get the LIM value (Table S6,† 1 = excellent, 2 = good, 3 = sufficient, 4 = poor, 5 = bad).

This procedure was repeated considering only one or all discharge type(s) and for the three DF scenarios. Among the required standard indicators, only the value of dissolved oxygen (DO) was not found largely in the literature, so it was kept fixed for each DF scenario assigning a score equivalent to: (i) class 1 for the safe scenario; (ii) class 3 for the medium scenario; (iii) class 5 for the worst scenario.

2.6. Analysis of inter-event and spatial variability

Inter-event and spatial variabilities were assessed by the coefficient of variation (CV), calculated as the ratio between the interquartile range (IQR) and the median of the concentration probability distributions (IQR/C50). Inter-event variability addresses the variability among different events of the same IUWS, while spatial variability addresses the variability among different IUWS. Inter-event variability was calculated using the statistics of the distributions of literature monitored IUWSs (section 2.2.), leading to a CV value for each IUWS and (micro-)pollutant. Spatial variability was calculated using the statistics of the distributions derived for the median concentrations (C50) of the archetype IUWS (section 2.3.), resulting in only one CV value for each (micro-)pollutant.

3. Results and discussion

3.1. Discharges' volumes released

The reviewed data showed great variability, with values spread across 3 orders of magnitude. In fact, these values are strongly site-specific, and the discharged volumes depend on several catchment-specific characteristics (*e.g.*, catchment area, impervious fraction, pipe dimensions, rainfall patterns, groundwater infiltration, storage capacity^{12,46}). Furthermore,



the CSO structures are more than one and the actual number of them varies from site to site. In the reviewed data, the total yearly volumes discharged by single CSO structures is almost comparable to the one discharged by WWTP bypass (median values equal to $6.3 \times 10^4 \text{ m}^3$ per year and $9.1 \times 10^4 \text{ m}^3$ per year, respectively). Therefore, in the analyzed literature data, CSOs appear to be the major wet-weather contributor in terms of released volumes compared to bypass.

3.2. Discharges' median concentrations

Fig. 2 shows the boxplot of the median concentrations (C50) found across all literature monitored IUWSs. These are reported for each (micro-)pollutant and for each discharge type.

CSOs are characterized by significantly higher concentrations than effluents for standard indicators (except for NO_3 and TP), for 2 out of 3 heavy metals, for PAHs, and by slightly higher concentrations for pesticides. Instead, lower concentrations are shown for NO_3 , TP, Ni, and pharmaceuticals. NO_3 is not present in the sewer system, contrary to effluents where NO_3 derives from the nitrification process. As for TP and pharmaceuticals, during wet-weather they are only diluted inside the sewer systems, leading to lower concentrations in wet-weather discharges while the majority of WWTPs are not planned to remove TP⁴⁷ or pharmaceuticals.⁴⁸ Surface runoff is the major source of PAHs and some heavy metals,²⁸ which are effectively removed by WWTP. Therefore, these substances are present with higher concentrations in wet-weather discharges than in the effluent. One exception is observed for Ni, with slightly higher concentrations in the effluent. This was also observed previously in other studies.^{27,49}

Bypass has comparable concentrations than CSOs for all the (micro-)pollutants, except for pesticides, showing higher

concentrations in CSOs. This exception may be related to point sources, localized only in some sub-catchments close to the CSOs, while bypass receives a more mixed flow, where pollution from local point sources is diluted. Fig. 2 confirms the well-known high spatial variability in pollution levels of wet-weather discharges, with ranges of median values of concentration spread over one to two orders of magnitude.

3.3. Inter-event and spatial variability of discharges' concentrations

Inter-event and spatial variabilities of (micro-)pollutant concentrations were calculated to evaluate respectively (i) the magnitude of the fluctuation of concentrations across different events in the same IUWS, (ii) whether the concentration identified in one literature monitored IUWS can be informative for other IUWS. Inter-event CV higher than 1 suggests high inter-event variability inside the same IUWS, while high spatial variability describes micropollutants with concentrations very different from IUWS to IUWS, leading to $\frac{\text{Inter-event CV}}{\text{Spatial CV}}$ ratio lower than 1.

For each (micro-pollutant) and discharge type of all literature monitored IUWS, inter-event variability and spatial variability are shown in Fig. 3a, while the ratio between inter-event and spatial variability is shown in Fig. 3b.

By observing the median inter-event CV in Fig. 3a, micro-pollutants in wet-weather discharges show higher CV values compared to effluents, and CV values higher than 1, confirming that CSOs and WWTP bypass are affected by high inter-event variability, as previously demonstrated in the literature.³⁴ The opposite is observed for standard indicators, where median CV values are more frequently lower for CSOs and bypass than for the effluent and always smaller than 1,

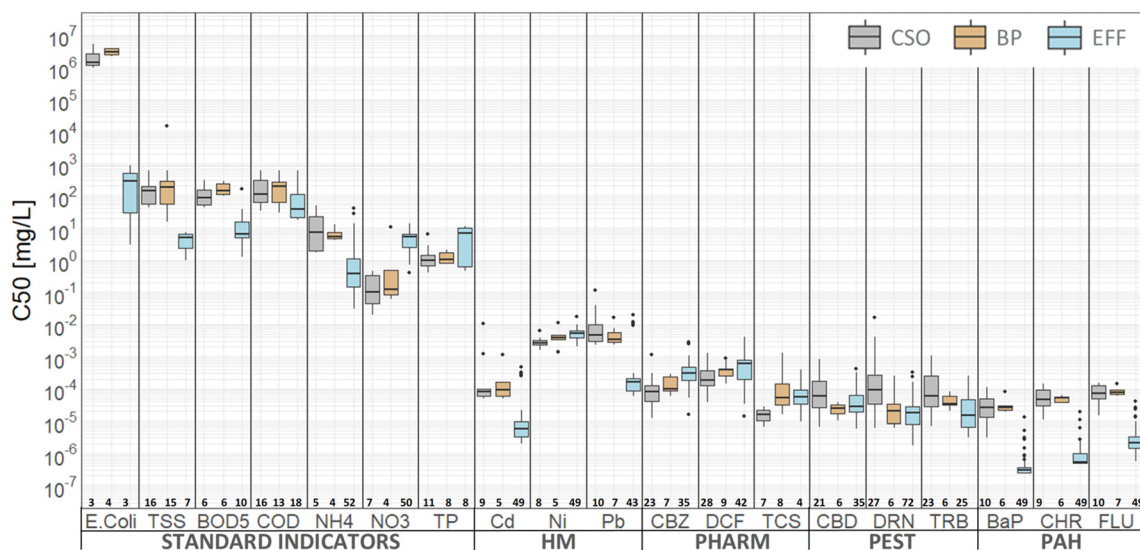


Fig. 2 Boxplots of median concentrations detected in each monitored IUWS per discharge type. The number of available data (*i.e.*, number of IUWS) for each combination of discharge type and (micro-)pollutant is reported at the bottom of the graph. *E. coli* values refer to CFU/100 mL.



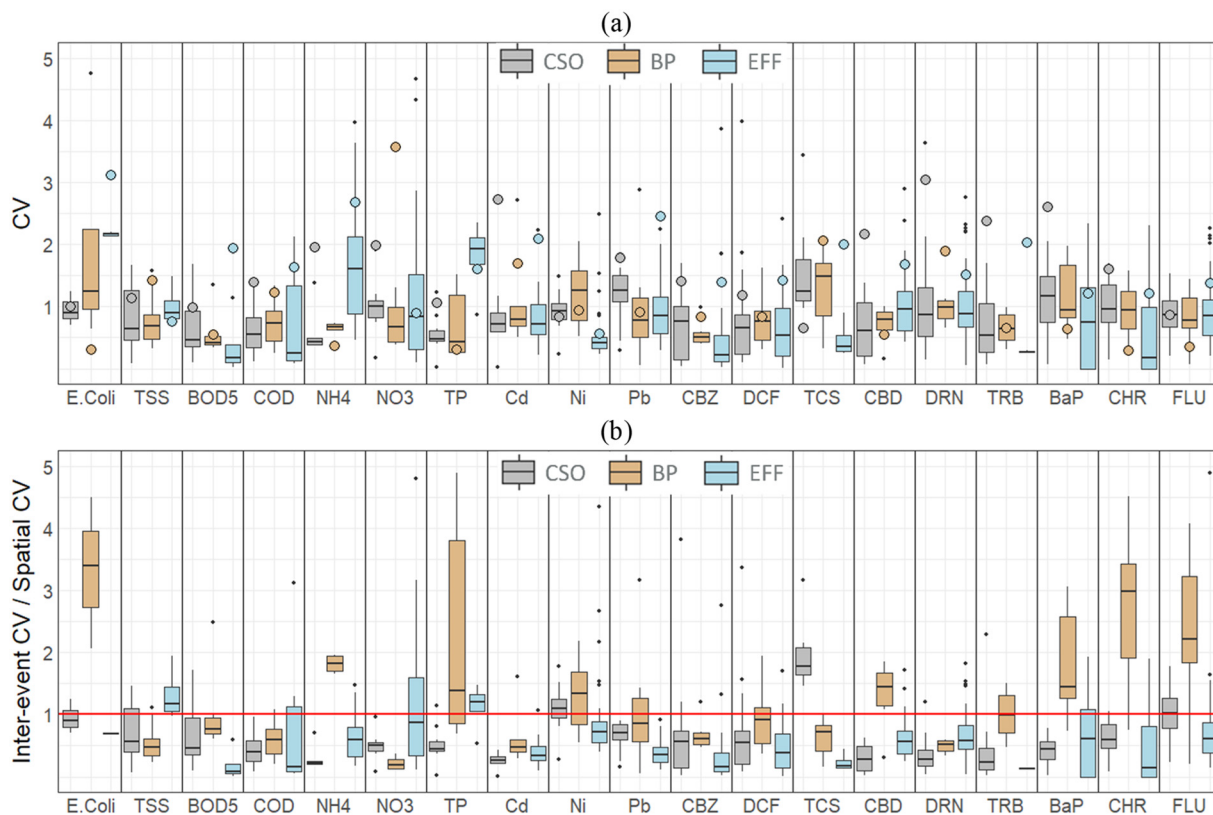


Fig. 3 (a) Boxplots show inter-event CV (interquartile range/median) of each (micro-)pollutant in each discharge type across different events of the same IUWS. For each IUWS one inter-event CV was calculated. Colored points represent spatial variability across different IUWSs of each (micro-)pollutant in each discharge type. (b) Ratio between inter-event CV and spatial CV. The black dots in the graphs represent the outliers. The red line identifies when inter-event and spatial variability are equal.

except for *E. coli*. The highest inter-event variability is observed in wet-weather discharges for *E. coli*, Ni, Pb, TCS, and BaP. This means that these contaminants are highly variable during the overflow event, probably with the highest concentrations in the first part of the event, due to the resuspension of sewer sediments, as previously reported by Madoux-Humery *et al.*⁵⁰ Consequently, heavy metals and PAHs, which are known to be particle-bound,²³ are more influenced by this phenomenon, but also this can be applied to contaminants with high sorption affinity, such as TCS. For contaminants showing this behavior, this could require a higher number of samples collected during the same event in order to correctly assess the discharged loads.

Looking at the ratio between inter-event and spatial variability (Fig. 3b), when the spatial CV is smaller than the inter-event CV ($\frac{\text{Inter-event CV}}{\text{Spatial CV}} > 1$) a monitoring campaign performed in a specific IUWS can be representative of other IUWS. This is the case of the bypass displaying higher ratios with respect to CSOs and effluent. Only for NO₃, Cd, and DRN literature data might be not a good indication for the bypass, since the respective ratios are much smaller than 1 (median value <0.6). For CSOs, the ratio between inter-event and spatial CV is close to 1 for *E. coli*, TSS, BOD₅, Ni, Pb, pharmaceuticals, CHR, FLU; thus concentration data on

these contaminants can be drawn from other studies. Instead, a low ratio is obtained for NH₄, Cd and pesticides in CSOs, due to the high spatial variability. This may be due to the fact that CSOs is impacted by the discharge source, that is respectively domestic (NH₄), industrial-agricultural (Cd), and agricultural (pesticides), more than what occurs for bypass. For the effluent, the ratio is below 1 for most of the micropollutants, while for some standard indicators (TSS, COD, NO₃, TP) the ratio is close to 1. This means that the spatial variability is higher than the inter-event variability for micropollutants, while for those standard indicators the spatial variability is smaller or comparable to inter-event variability. Wastewater composition in terms of standard indicators (especially for domestic wastewater) tends to be less variable at the WWTP inlet, with WWTP processes bringing their level below discharge limits and further decreasing variability. Conversely, micropollutant levels are strongly dependent on the sources and usage in the upstream catchment, and their levels are less affected by the processes in the WWTP, resulting in the observed high spatial variability.

3.4. Distributions fitted to data

Data collected and described in section 3.1. and 3.2. were fitted to probability distributions. Four probability



distributions were defined to describe yearly volumes discharged by CSOs, bypass, effluent, and river annual flow rate. For each of the 18 (micro-)pollutants three distributions were defined to describe C50, C75, and C95. When referring to wet-weather discharges and WWTP effluent, concentration and volume data are known to be skewed within the same discharge and the lognormal distribution is the most used to describe these data.^{27,30,51} In this study several distributions were tested, and we found that the lognormal distribution is the best for describing water quantity data across different IUWSs (*i.e.*, annual volumes discharged and average river flow rate), while different types of probability distributions were found to best fitting concentration data.

Distributions fitted to the concentration datasets of each literature monitored IUWS were found to be lognormal for CSOs, bypass, and effluent in 69%, 64%, and 61% of all cases respectively, while the remaining best fitting distributions were normal. Deviations from the lognormal distribution can be found when the size of the analyzed dataset is limited.⁵¹

Distributions fitted for the archetype IUWS to the groups of concentration percentiles were found to be lognormal for CSOs, bypass, and effluent in 89%, 58%, and 84% of all cases respectively, while the remaining best fitting distributions followed a left-skewed Weibull distribution.

This means that quantity and quality data are not only skewed when referred to the same discharge point, but also the same concentration percentiles are skewed across different IUWSs.

3.5. Micropollutant environmental risk assessment

In the literature, *C* and *RQ* percentile values are arbitrarily chosen for risk assessment procedures, varying from study to study, leading to different results based on the selected percentiles. Instead, different choices of *DF* not only represent different hydraulic conditions present across different IUWS, but it also allows evaluation of the climate change impact that may result in lower dilution of the discharges and then in a worse *DF* scenario. In the following sections the impact of choosing different values of *DF*, percentiles of *C* and *RQ* is analyzed.

3.5.1. *RQ* distributions across different scenarios. To exemplify the results obtained by the 10 000 Monte Carlo simulations for each $RQ_{i,j}$, Fig. 4a–c illustrate the calculated *RQ* for chrysene (CHR) in the case of the medium *DF* scenario and different *CP* scenarios. Similarly, Fig. 4d–f illustrate the *RQ* distribution for C50 and different *DF* scenarios. The following observations presented for CHR are valid also for the other 11 micropollutants,

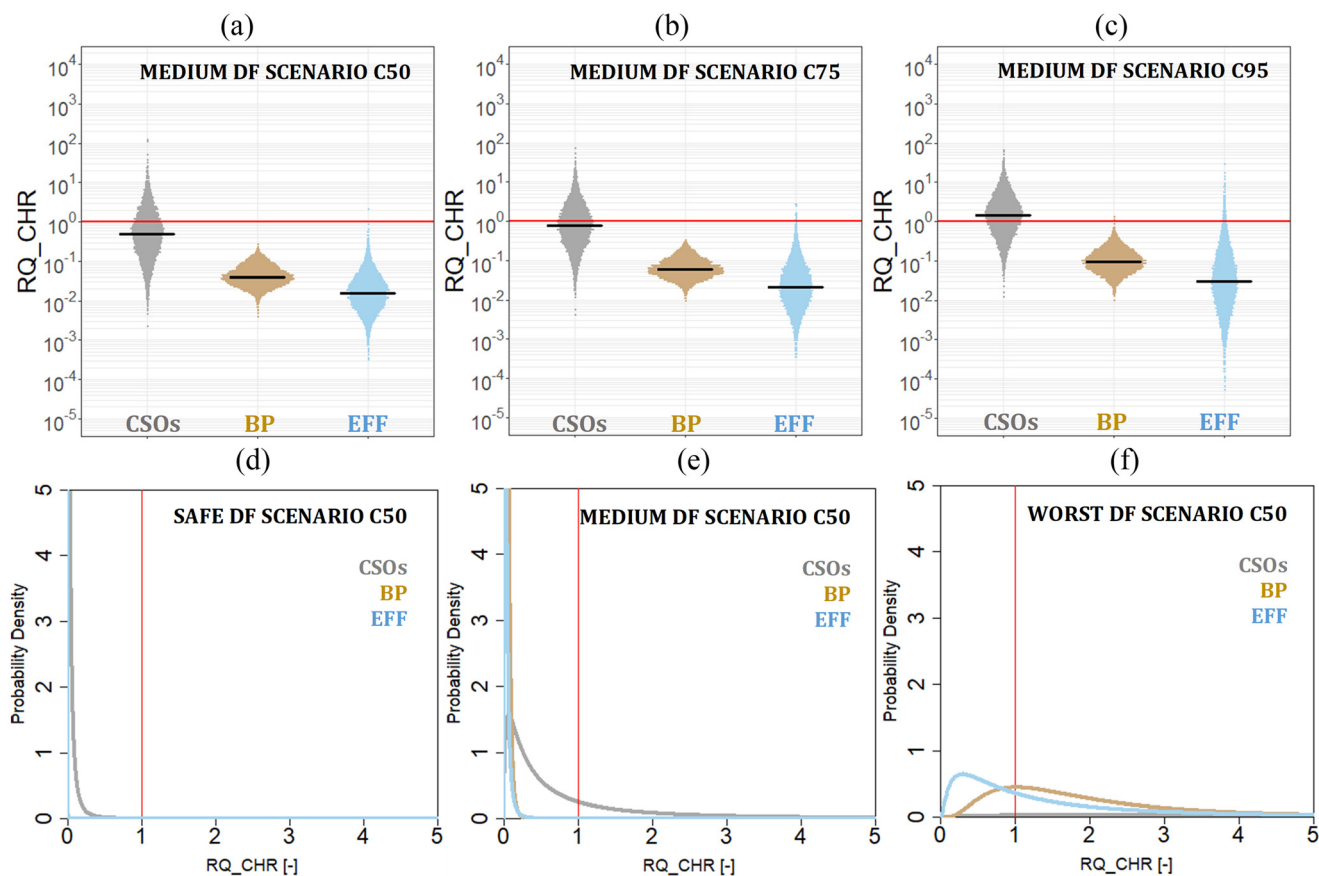


Fig. 4 *RQ* values for CHR in the medium *DF* scenario using (a) C50 distribution, (b) C75 distribution, and (c) C95 distribution. *RQ* distributions of CHR using the C50 distribution in safe (d), medium (e) and worst (f) *DF* scenarios. Red lines correspond to *RQ* = 1.



for which the resulting RQ_{ij} using C50 and C95 in safe and worst DF scenarios are shown in Fig. S3.†

Similar results were obtained when using different percentiles of concentrations (CP scenarios) in a fixed DF scenario (Fig. 4a–c); however, a slight RQ increment is observed when increasing the percentile (*i.e.*, from C50 to C95). There is also an increase of RQ variability, related to the increase of variability of the distributions of higher percentiles of concentrations.

The effect of dilution (DF scenario) can be observed in Fig. 4d–f, showing how the RQ distributions are heavily affected by the chosen DF. For the safe scenario, the distributions of $RQ_{i,CHR}$ for each discharge type are below the thresh-

old $RQ = 1$, while for the worst scenario, most of the area under the distributions is above the threshold. This shows how the choice of different percentiles of the pollutant concentration does not determine high differences in the RQ values, while the choice of DF can completely change the risk assessment. In fact, RQ median values are up to 2 times higher from C50 to C95, while values are up to 10 000 times higher from the safe to worst scenario. Therefore, an accurate risk assessment requires correct quantification of the hydraulic variables of the IUWS (and specifically the dilution factor), because neglecting dilution and looking only at the discharged concentrations might lead to significant overestimation of the environmental risk.

SCENARIOS		RQ _j												RQ _i			RQ _g					
		BaP	CHR	DCF	CBZ	FLN	Pb	TCS	Cd	DRN	Ni	TRB	CBD	CSOs	BP	EFF	RIVER					
DF	CP	PAH	PAH	PHARM	PHARM	PAH	HM	PHARM	HM	PEST	HM	PEST	PEST									
SAFE	C50	RQ50																0.2				
		RQ75																0.5				
		RQ95	2.2														2.5	2.7				
	C75	RQ50																	0.3			
		RQ75																	0.8			
		RQ95	3.1															3.5	3.8			
	C95	RQ50																	0.5			
		RQ75	1.1																1.4			
		RQ95	6															6.2	6.8			
MEDIUM	C50	RQ50	5															5	1.4	7		
		RQ75	15	1.3	1.4													17	3	21		
		RQ95	85	5	3	3	1.9	1.7	1.8	1.0								94	1.8	9	104	
	C75	RQ50	8																8	1.6	11	
		RQ75	23	1.9	1.7														25	1.5	4	31
		RQ95	116	6	4	3.4	2.9	2.7	2.7	1.2	1.4							128	3.1	11	142	
	C95	RQ50	15	1.5															15	1.6	2	18
		RQ75	44	3.3	2	1.5	1.7	1.4											44	3	5	52
		RQ95	213	10	7	6	5	6	3.4	1.7	2.5			1.2				220	8	19	247	
WORST	C50	RQ50	214	25	40	24	15	7	12	2.6	2.5	5	2.3	1.4				242	22	88	352	
		RQ75	711	64	91	54	32	20	32	32	9	8	10	7	4			803	38	201	1042	
		RQ95	4158	254	236	175	99	88	134	52	51	23	35	16				4621	84	616	5321	
	C75	RQ50	347	38	48	27	22	12	15	4	4	7	2.8	2				387	36	105	528	
		RQ75	1092	92	108	65	48	32	41	12	13	13	8	5				1216	63	250	1529	
		RQ95	5865	329	286	228	150	134	180	65	78	30	40	21				6449	142	815	7406	
	C95	RQ50	680	70	54	34	36	24	20	6	6	10	4	3				747	69	132	947	
		RQ75	2122	159	122	93	84	66	54	18	21	20	12	8				2309	137	334	2780	
		RQ95	11136	532	414	404	290	283	218	89	123	52	65	33				11935	372	1332	13640	

Fig. 5 RQ values are reported for: a) each micropollutant (RQ_j) calculated with eqn (2); b) each discharge type (RQ_i) calculated with eqn (3); c) for all micropollutants and discharges (RQ_g) calculated with eqn (4). RQ values are reported only when the threshold $RQ = 1$ is exceeded. The discharge type(s) that causes RQ_j exceeding the threshold is displayed below the respective RQ value and colored differently based on the discharge(s). Also different background colors are used to define the ranking of RQ for each row, with dark blue being used for higher RQ values.



3.5.2. Risk at specific percentiles of the RQ distributions.

To allow the evaluation and comparison of risks, $RQ_{i,j}$ was evaluated in correspondence of the 3 percentiles of the RQ distributions, as explained in section 2.4. This was done for each of the 12 micropollutants in each of the 3 discharge types under 9 different combinations of DF and CP scenarios, resulting in 972 values of $RQ_{i,j}$. These values were used to assess RQ_j , RQ_i , and RQ_R . Results are summarized in Fig. 5, where only the values above $RQ = 1$ (threshold) are reported.

Based on the aggregated values of RQ (RQ_j , RQ_i and RQ_R), the ranking of micropollutants and discharges was performed for each combination of DF, CP, and RQP, identifying the ones most contributing to the environmental risk, which require specific mitigation actions.

3.5.2.1. Micropollutant impacts due to all discharges. The risk quotients of each micropollutant (RQ_j , Fig. 5a) show that in the safe scenario the only exceedance was observed for BaP, due to CSOs when higher RQP are used. In the medium scenario, more micropollutants exceed the threshold, due to CSOs for PAHs and heavy metals (with the exclusion of Ni), and to effluent for pharmaceuticals. Much lower exceedances and lower RQ were observed for pesticides in the medium scenario (caused by CSOs), while in the worst scenario they always exceed the threshold, with higher risks for DRN. In the worst scenario all micropollutants exceed the threshold due to exceedances for all discharges, except for bypass that never causes exceedances ($RQ_{BP,j} < 1$) for pesticides and Cd.

To summarize, the micropollutants that pose a major risk in all cases are PAHs with BaP as the worst. Pharmaceuticals represent the second class posing a threat to the river, where the main source is represented by the effluent, while wet-weather discharges contribute substantially to pharmaceuticals risk only in the worst scenario. The third class posing a risk is heavy metals, which is a problem mainly in the worst scenario, while in the medium scenario only when considering RQ95, except for Ni that is the least problematic. Pesticides pose the smallest risk to the river both in the medium and worst scenario, with DRN being the most critical compound.

Wet-weather discharges pose a considerable high risk to the river for pharmaceuticals and heavy metals only in the worst scenario. However, these two classes of contaminants should not be fully neglected. From a climate change perspective, their impact will increase, requiring additional research and appropriate interventions, to limit their release to the environment.

3.5.2.2. Discharge impacts due to all micropollutants. The risk quotients for each discharge type (RQ_i , Fig. 5b) show that CSOs are the major cause of exceedances, followed by effluent and bypass. CSOs not only cause a greater number of exceedances, but also result in higher RQ_i values than the respective values for bypass and effluent.

For each discharge type the number of micropollutants released, causing the exceedance of the risk threshold in the river ($n_{RQ_{i,j}} > 1$), was calculated. Results are summarized in Fig. S4.† As expected, $n_{RQ_{i,j}} > 1$ increases moving from the

safe scenario (1 for CSOs) to the medium scenario (up to 9 for CSOs, 1 for bypass and 4 for effluent) to the worst scenario (12 for CSOs, 8 for bypass and 12 for effluent). In total, considering the 27 combinations of DF, CP, and RQP, the risk threshold is exceeded by at least 1 micropollutant for CSOs 22 times, 15 for bypass and 15 for effluent.

3.5.2.3. Impacts due to all discharges and all micropollutants. When looking at the risk posed by all micropollutants and all discharges downstream the archetype IUWS (RQ_R , Fig. 5c), the threshold is never exceeded in the safe scenario (except when looking at RQ95), while it is always exceeded in the medium and worst scenarios. It is fundamental to note the differences in RQ values obtained when considering only effluent discharge to the river (Fig. 5b, $RQ_i - \text{EFF}$) with respect to when considering also wet-weather discharges (Fig. 5c, RQ_R). When considering also wet-weather discharges, the estimated risk is 10 times higher on average than the one caused by effluent alone; besides, the value of the risk caused by CSOs alone is directly comparable with the risk values obtained when all the discharge types are considered. Therefore, on an annual basis, the major source of risk is related to CSOs. This is in line with the study by Weyrauch *et al.*,⁴ who showed theoretically that, when WWTP are upgraded with tertiary treatments, the majority of contaminant loads released to the river are due to wet-weather discharges. It should be noticed that removing PAHs from discharges would lower the risk on average of 77%. As a consequence, interventions are needed also on wet-weather discharges, in order to reduce the risk for rivers at acceptable levels. This might be exacerbated in the case of urban areas discharging to multiple river bodies with different dilution factors. For example, CSOs can discharge to small creeks (with lower DF), while WWTP are typically placed along large water bodies (with greater DF).

As reported by Müller *et al.*,⁵² sources of PAHs are widely spread on urban areas since they are largely found in many urban sources: paved surfaces, exhaust gases and particles, tires, brakes, and rubber mulch of playgrounds. Furthermore, PAHs can easily adsorb on solids, that can be generated by road maintenance and construction activities. Moreover, PAHs can also be released by industrial activities, with direct discharge in sewer, runoff of industrial land, or by emissions into the atmosphere and subsequent atmospheric deposition.

3.5.2.4. Effect of the choice of percentile of the RQ distribution. Risk assessment present in the literature studies uses different percentiles of the RQ distribution and/or the concentration distribution, leading to different results based on this choice. From Fig. 5, it emerges that exceeding the risk threshold of 1 depends on the percentile selected to assess the risk when a probabilistic approach is adopted. This section analyzes in detail the impact of different choices that can be made by different operators during a risk assessment. In Fig. 6 it is possible to compare and find a relationship between different common choices of RQ and concentration percentiles (median and 95th percentile).⁵³ Values displayed in Fig. 6 represent $RQ_{i,j}$, calculated for all



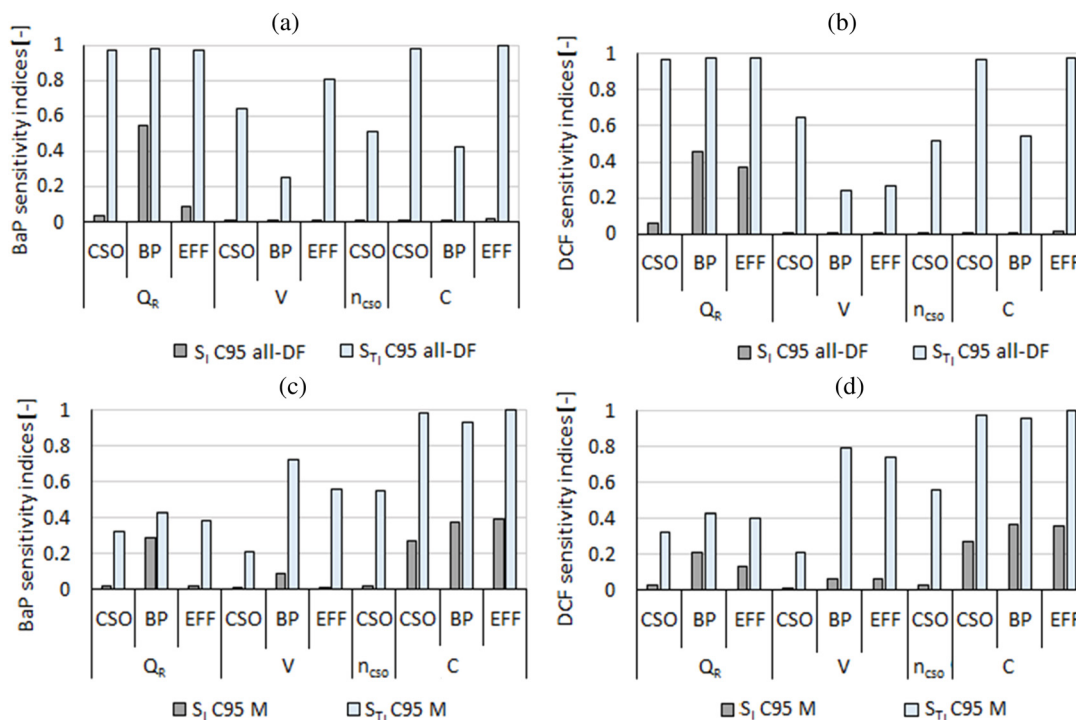


Fig. 7 S_1 (in grey) and S_{T_1} (in light blue) values for (a) BaP and (b) DCF in the all-DF scenario; in the medium scenario for (c) BaP and (d) DCF. Results refer to the scenario using the C95 distribution.

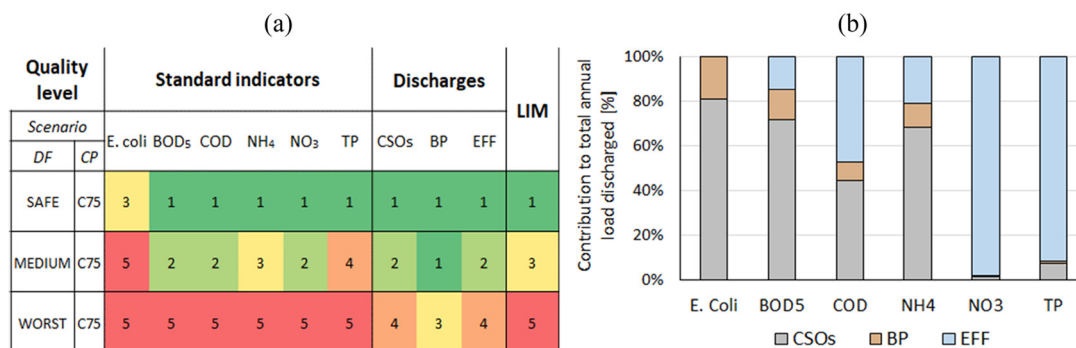


Fig. 8 (a) Quality level for single standard indicators in the river and due to single discharge types, with the resulting LIM in the last column. (b) Apportionment of the total annual load of standard indicators discharged to the river in the medium scenario.

in terms of percentages was obtained for each discharge across all DF scenarios, with a slight increase for effluent contribution when worsening the scenario (Fig. S6[†]). Higher loads are associated with CSOs with respect to bypass and effluent, except for COD (comparable loads between CSOs and effluent), NO₃, and TP (higher loads for effluent). These findings suggest that considering only the effluent for evaluating the ecological quality level of a river can significantly underestimate the actual impact of discharges from an IUWS.

3.8. Implications for IUWS risk assessment

This study, based on an archetype IUWS, suggests that an accurate risk assessment, which considers not only WWTP effluent discharge during dry-weather but also the wet-weather

discharges from combined sewers and WWTP, requires increased focus on hydraulics. Specifically, when adapting the proposed methodology to a specific case study, it is necessary to: (i) correctly quantify the river annual average flow rate, and (ii) accurately evaluate the relative contribution of volumes discharged by each discharge type. This is especially relevant for urban areas discharging to multiple water bodies, with different flow rates (see for example the case of the St. Charles river in Quebec City).⁵⁴

Once the hydraulics is defined within a realistic range, the variability of contaminant concentrations represents the residual higher uncertainty related to risk estimation. When applying the proposed methodology to a specific case study, it is therefore important to perform monitoring campaigns which take into account different contaminant characteristics, that require



different sample collection strategies. Since monitoring of contaminants' concentration during highly dispersed and uncertain events is challenging, in the case of lack of measurements, additional information can be retrieved from the literature. In fact, probability distributions were found to be skewed not only when referring to the same discharge point, but also when focusing on data deriving from different IUWSs. Furthermore, concentration data of CSOs and bypass show high inter-event variability, but median concentration values for bypass show smaller spatial variability, so literature data referred to bypass can more easily be extended to different case studies. However, specific attention should be given to the source of the literature data, as some regions of the world (North America and Europe) are overrepresented in the available literature,³⁰ adding uncertainty in the risk estimation for a specific case study.

When a probabilistic approach is adopted, the selection of the RQ percentile for risk description is crucial. In fact, we found that the impact of choosing different percentiles of RQ is higher than the influence of choosing different percentiles of the contaminant concentration. Notably, a correction factor was established in this study to allow switching from selected percentiles of *C* and RQ.

In this study we assumed that contaminant loads released during wet-weather events accumulate in the surface water recipient without considering transport and fate processes. Under this assumption, the class posing the highest environmental risk is PAHs (with BaP being the most critical compound), which are known to have a high sorption affinity. Therefore, the concentration found in water samples is expected to be lower when increasing the distance from the discharge point, due to sorption in sediments of the surface water recipient, resulting in lower risk. However, when the flow rate increases, resuspension of sediments occurs, becoming a source of (micro-)pollutants.

Considering the different discharges here studied, future efforts should focus on CSOs to reduce the environmental risk by reducing or treating the discharged volumes. Since CSOs derive from several overflow structures, the ones with the worst DF should be therefore prioritized. A sedimentation/filtration step should be considered to remove TSS carrying particle-bound micropollutants, *i.e.* PAHs and heavy metals, and fractions of some standard indicators. A disinfection step could be useful to reduce *E. coli* concentration, even if attention should be paid to disinfection by-product formation, especially in the case of recreational or aquaculture use of the recipient. With respect to pharmaceuticals, efforts should be focused at the WWTP level, adopting advanced treatments, such as adsorption on activated carbon (most effective for hydrophobic compounds) and ozonation or advanced oxidation processes, which are less selective and more effective in a wider range of micropollutants, but they can produce different unknown by-products that can be even more toxic than their parent compound.⁵⁵

From a climate change perspective (with increasing critical hydraulic conditions characterized by lower DF values), CSO contribution will increase, worsening their negative effect on

the ecological status of the surface waters and on the environmental risk associated with micropollutants. In detail, pharmaceuticals loads discharged with CSOs will become significant with respect to loads related to the effluent, as well as heavy metal loads. From this perspective, additional CSO managing strategies should be implemented to control (micro-)pollutants discharged to surface water recipients, for instance considering a more extensive adoption of nature-based solutions after a sedimentation/filtration step.

4. Conclusions

In this study we developed a comprehensive environmental chronic risk assessment of an archetype integrated urban wastewater system, considering both wet-weather discharges and dry-weather WWTP effluent. The variability of the most common parameters used was evaluated and the contaminants most contributing to the estimated risk were identified. The evaluation was based on detailed assessment of the existing literature and probabilistic modelling, using a simple dilution approach (*i.e.* neglecting transport and fate processes). The reviewed data showed how a single CSO structure can release annual volumes that are comparable to those from a bypass. Measured concentrations were generally found to be higher in wet-weather discharges than in the effluent, with some exceptions (NO₃, TP, Ni, pharmaceuticals). CSOs thus pose a major risk to rivers, with respect both to bypass and effluent.

The choice of the pollution level in the discharges (expressed as percentile of the concentrations) is less relevant than the correct definition of the dilution factor. An extensive monitoring of (micro-)pollutant concentrations in the discharged flows, which affects mostly the residual uncertainty, is the most challenging, expensive and time-consuming task. Smaller spatial concentration variability of micropollutants was found in bypass with respect to CSOs, meaning that bypass might be less sensitive to local uses (*i.e.* to specific sources located in one or few sub-catchments). Micropollutant classes that pose a major risk are in the following descending order: PAHs, pharmaceuticals, heavy metals, and pesticides. To accurately assess the risk, a wider range of micropollutants should be considered for PAHs and pharmaceuticals (in this study, BaP, CHR, FLU and CBZ, DCF, TCS were considered, respectively), since these classes encompass compounds with different chemical characteristics and environmental mobility. As for standard indicators, the impact caused by wet-weather discharges on the ecological quality level is mainly related to *E. coli*. This impact could be reduced by introducing a disinfection step, but only after a sedimentation/filtration step and a thorough assessment of the potential generation of toxic by-products. The second higher impact is related to the discharge of NH₄ that will promote eutrophication problems. TSS are also highly released by wet-weather discharges, but their impact is mainly related to the fact they are carrier of sorptive (micro-)pollutants.



This study provides a useful tool to assess impacts from different wastewater discharges through the assessment of both chronic risk and impact on the ecological quality level, and to identify the most critical (micro-)pollutants. The presented results were obtained on an ideal archetype IUWS. When adapted to the specific characteristics of a real catchment, our approach will allow for the prioritization of discharges and (micro-)pollutants both in the current situation and from a climate change perspective. This allows decision makers to evaluate the best mitigation actions which should be implemented to maintain the risk and the impact at acceptable levels.

Abbreviations

BP	Bypass
C	Concentration
CP	Concentration percentile
CSO	Combined sewer overflow
CV	Coefficient of variation
DF	Dilution factor
EFF	Effluent
AA-EQS	Annual average environmental quality standard
HM	Heavy metals
GSA	Global sensitivity analysis
IQR	Interquartile range
IUWS	Integrated urban wastewater system
LIM	Macro-indicators pollution level
LOQ	Limit of quantification
PAHs	Polycyclic aromatic hydrocarbons
PHARM	Pharmaceuticals
PEST	Pesticides
Q _R	River annual average flowrate
RQ	Risk quotient
RQP	Risk quotient percentile
TL	Toxic level
V	Volume
WFD	Water framework directive
WWTP	Wastewater treatment plant

Author contributions

Jessica Ianes: methodology, formal analysis, investigation, visualization, writing – original draft, writing – review & editing. Beatrice Cantoni: conceptualization, methodology, writing – review & editing. Enrico Ulisse Remigi: conceptualization, writing – review & editing. Fabio Polesel: validation, writing – review & editing. Luca Vezzaro: validation, writing – review & editing. Manuela Antonelli: conceptualization, writing – review & editing, supervision, project administration.

Conflicts of 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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