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**Modelling micropollutant fate in sewer systems – A new systematic
approach to support conceptual model construction based on in-sewer
hydraulic retention time**

Riccardo Delli Compagni¹, Fabio Polesel^{2,3}, Kerstin J.F. von Borries², Zhen Zhang², Andrea
Turolla¹, Manuela Antonelli^{1*} and Luca Vezzaro^{2*}

¹Department of Civil and Environment Engineering (DICA), Politecnico di Milano, Piazza
Leonardo da Vinci 32, 20129 Milan, Italy

²DTU Environment, Technical University of Denmark, Bygningstorvet, Building 115, 2800
Kongens Lyngby, Denmark

³DHI A/S, Agern Allé, 2970 Hørsholm, Denmark

*Corresponding author: manuela.antonelli@polimi.it

Co-corresponding author: luve@env.dtu.dk

18 **Abstract**

19 Conceptual sewer models are useful tools to assess the fate of micropollutants (MPs) in integrated
20 wastewater systems. However, the definition of their model structure is highly subjective, and
21 obtaining a realistic simulation of the in-sewer hydraulic retention time (*HRT*) is a major challenge
22 without detailed hydrodynamic information or with limited measurements from the sewer network.
23 This study presents an objective approach for defining the structure of conceptual sewer models in
24 view of modelling MP fate in large urban catchments. The proposed approach relies on GIS-based
25 information and a Gaussian mixture model to identify the model optimal structure, providing a
26 multi-catchment conceptual model that accounts for *HRT* variability across urban catchment. This
27 approach was tested in a catchment located in a highly urbanized Italian city and it was compared
28 against a traditional single-catchment conceptual model (using a single average *HRT*) for the fate
29 assessment of reactive MPs. Results showed that the multi-catchment model allows for a successful
30 simulation of dry weather flow patterns and for an improved simulation of MP fate compared to the
31 classical single-catchment model. Specifically, results suggested that a multi-catchment model
32 should be preferred for (i) degradable MPs with half-life lower than the average *HRT* of the
33 catchment and (ii) MPs undergoing formation from other compounds (e.g. human metabolites); or
34 (iii) assessing MP loads entering the wastewater treatment plant from point sources, depending on
35 their location in the catchment. Overall, the proposed approach is expected to ease the building of
36 conceptual sewer models, allowing to properly account for *HRT* distribution and consequently
37 improving MP fate estimation.

38

39 **Keywords:** geographical information system, cluster analysis, sewer system modelling,
40 wastewater-based epidemiology, emerging contaminants

41

42 1. Introduction

43 Organic micropollutants (MPs) have been recognized as a concern for the environment and human
44 health due to the detrimental effects (e.g. toxicity, estrogenicity) they can pose even at low
45 concentrations (ng L^{-1} to $\mu\text{g L}^{-1}$) (Galus et al., 2013; Fent et al., 2006; Daughton and Ternes, 1999).
46 Several MPs (e.g. pharmaceuticals and personal care products) enter the water cycle through
47 wastewater discharges flowing along sewer systems to wastewater treatment plants (WWTPs),
48 where they are not entirely removed and consequently discharged into environmental recipients
49 (Petrie et al., 2015). In sewer systems, MPs can undergo degradation (biotic and abiotic), adsorption
50 and retransformation – from other excreted metabolites (Bahlmann et al., 2014), remobilisation of
51 sewer deposit (Launay et al., 2016), abiotic formation from other MPs (Sengeløv et al., 2003). The
52 importance of these processes depends on the MP properties, environmental and hydraulic
53 conditions (D’Ascenzo et al., 2003; Gomes et al., 2009; Plósz et al., 2012; Thai et al., 2014; Ramin
54 et al., 2016; McCall et al., 2016; Menzies et al., 2017). Combining the abovementioned processes
55 with the hydrodynamics of the sewer itself is a challenging modelling task. Nevertheless, MP fate
56 models can be highly beneficial for (i) providing high-frequency input data to assess performances
57 of WWTP models (i.e. to assess MP discharge into the environment) when full-scale measurements
58 are scarce (e.g. Snip et al., 2014); (ii) evaluating possible mitigation strategies within the urban
59 drainage system taking into account interactions with the WWTP system (e.g. Eriksson et al.,
60 2011); and (iii) back-calculating consumption of chemicals in upstream catchments using
61 wastewater-based epidemiology approaches while considering in-sewer losses (e.g. McCall et al.,
62 2017).

63 In sewer systems, water transport is usually modelled by using distributed hydrodynamic or
64 conceptual models (Obropta and Kardos, 2007; Zoppou, 2001). Hydrodynamic models are
65 computationally demanding and require detailed information about the network (number of pipes,
66 slopes, diameters, etc.) to explicitly describe the hydraulic conditions (e.g. water level, flow
67 velocity, etc.) in each part of the system. On the other hand, conceptual models lump parts of the

68 system into simple units, while flow routing is described by using continuously stirred tank reactors
69 (CSTRs) in series (Saagi et al., 2016). These models use general information such as the average
70 hydraulic residence time (*HRT*) to describe water dynamics at specific points of the system (e.g. the
71 sewer outlet, overflow structure). The loss of details is balanced by the increase of computational
72 speed, making conceptual models ideal for simulating water quality, both for traditional water
73 quality indicators (Flores-Alsina et al., 2014; Martin and Vanrolleghem, 2014) and MPs (De Keyser
74 et al., 2010; Snip et al., 2016; Mannina et al., 2017). Although alternative approaches have been
75 also tested to simulate the stochastic behaviour of specific MP sources (Ort et al., 2005; Pouzol et
76 al., 2018), conceptual models are often applied in a deterministic manner (i.e. MP sources are
77 modelled as deterministic).

78 The realistic description of in-sewer *HRT* represents a major challenge for the development of
79 conceptual models for large urban catchment. Moreover, *HRT* can strongly influence the extent of
80 in-sewer MP processes and their overall attenuation, and it should therefore be carefully considered
81 during model construction (Jelic et al., 2015; Polesel et al., 2016; Ramin et al., 2016, McCall et al.,
82 2017; Li et al., 2018). Typically, one of the first steps during model construction consists of
83 subdividing the urban catchment into smaller sub-catchments in a heuristic or empirical manner,
84 where *HRTs* are defined based on the available information of the area (e.g. geographical maps,
85 topography, distances). However, this step is highly subjective and requires several trial-and-error
86 iterations. To make this step objective, automatic algorithms have been proposed for hydrological
87 models (Davidsen et al., 2017; Wolfs et al., 2013), while tools supporting the building of conceptual
88 models focusing on water quality are still missing. Alternative approaches have been developed to
89 define *HRT* as a probability density distribution, which was derived using road network as proxy
90 variable for sewer network (Kapo et al., 2017) or by running complex hydrodynamic models
91 (McCall et al., 2017). To date, however, an automated procedure for constructing a conceptual
92 model is still lacking.

93 This study aimed at developing a new, systematic and fast approach to support the construction of
94 conceptual models for predicting in-sewer MP fate in large urban catchments. The method relies on
95 GIS information (e.g. consumer locations and sewer network), quantitative data (e.g. water
96 consumption and WWTP inflow data) and advanced statistical techniques (cluster analysis) in order
97 to cluster areas of the urban catchment based on similar *HRT*. As a result, a multi-catchment
98 conceptual model (i.e. with a discrete *HRT* distribution) is obtained. The approach was tested for a
99 large urban catchment and its performance was compared against a traditional single-catchment
100 model (i.e. one *HRT*) for three scenarios: (i) MP undergoing biodegradation; (ii) MP undergoing
101 biodegradation and retransformation; (iii) MP emissions from a point source at different locations in
102 the catchment, i.e. with different distance and transport time to the receiving WWTP.

103

104 **2. Materials and methods**

105 **2.1. Case study**

106 The modelling approach was developed for a large urban catchment in Northern Italy (total area of
107 69 km² with approximately 1.250.000 inhabitants with a negligible industrial contribution. The
108 catchment is relatively flat (maximum elevation change of 40 meters over about 10 km) and all the
109 wastewater flow is gravity driven, without pumps along the sewer network. No detailed
110 hydrodynamic model of the catchment was available during the study. Relevant data for the area
111 were provided by the local water utility, and they included shape files of the gravity sewer network,
112 boundaries of the catchment area, geographical location of potable water consumption points along
113 the distribution system (around 28,000 points), and the potable water consumption for each point
114 over a reference period (1 year, from January to December 2016). WWTP influent flow data (at 5-
115 minute resolution) were also available for the study period. The average potable water consumption
116 in the study area is 0.22 m³ inh⁻¹ d⁻¹ (ISTAT, 2018).

117

118 **2.2. The approach**

119 *2.2.1. Identification of sub-catchments*

120 The wastewater discharge points (assumed to coincide with the GIS location of potable water
121 consumption points) were grouped into sub-catchments based on three steps:

- 122 i) the shortest in-sewer distance between each point and the WWTP was calculated using
123 the Dijkstra's algorithm (Cormen, 2001; see Supplementary Information for more
124 information on the algorithm), available in ArcGIS 10.3 (ESRI);
- 125 ii) distances were input to the iterative Expectation-Maximization (EM) algorithm to fit a
126 Gaussian mixture model (Reynolds, 2015), optimizing the likelihood function of a
127 number of probability density functions (we called them as virtual sub-catchments due
128 to their mathematical nature). The number n of virtual sub-catchments was varied from 1

to 30 (considered as the highest number feasibly described by a conceptual model), and the number that minimised the Bayesian Information Criterion (BIC) was selected;

- iii) each wastewater discharge point was assigned to the virtual sub-catchment that maximised its probability density function, providing a geographical representation.

Step ii and iii were coded in Matlab R2016a (Mathworks).

2.2.2. Estimation of dry-weather flow parameters

Two dry-weather parameters were estimated, namely the in-sewer flow velocity v and the total infiltration flow $Q_{inf,tot}$. The in-sewer flow velocity v [$m\ s^{-1}$], assumed constant in the catchment due

$$HRT_i = \frac{d_i}{v} \quad \text{Eq. 1}$$

to the flat characteristic of the urban area, is linked to the HRT in each sub-catchment (Eq. 1):

where d_i [m] is the average in-sewer distance of the i^{th} sub-catchment.

The optimization relied on a simple simplex search algorithm (Nelder et al., 1964) and minimized the root mean square error (RMSE) between the Measured Flow Pattern (MFP) and the calculated wastewater flow at the inlet of the WWTP (eq. 2):

$$\min_{v, Q_{inf,tot}} RMSE \left(\sum_{i=1}^n Q_{PW,i}(t + HRT_i)(1 - \alpha) + Q_{inf,tot}, MFP(t) \right) \quad \text{Eq. 2}$$

where $Q_{PW,i}(t)$ [$m^3\ s^{-1}$] is the potable water consumption of the i^{th} sub-catchment (n in total), calculated as the sum of the potable water consumed by all points within the i^{th} sub-catchment and normalized by a typical daily consumption profile (Candelieri and Archetti, 2014), α [-] is the water loss factor (due to e.g. gardening), assumed equal to 0.02 (Butler et al., 2004), and $Q_{inf,tot}$ [$m^3\ s^{-1}$] is the total infiltration flow considering the entire catchment. $MFP(t)$ was obtained by aggregating dry-weather flow data (excluding weekends and holiday periods) on an hourly basis to generate a daily flow pattern with its confidence interval (5th and 95th percentile).

151

152 2.2.3. *Building the conceptual model*

153 The conceptual model was built by combining elements of the IUWS_MP library (Vezzaro et al.,
154 2014), implemented in WEST 2014® (DHI A/S, Denmark). The elements allow simulating
155 wastewater/MPs generation at the household level (source), wastewater transport and MP
156 transformation processes (e.g. volatilization, sorption, aerobic biodegradation, etc.) in different
157 parts of the urban drainage system (e.g. sewer, WWTP, river). For our case study, each sub-
158 catchment was modelled as a wastewater source and a sewer system. Wastewater generation is
159 simulated by considering the main characteristics of the systems (population density, capita daily
160 wastewater production, groundwater infiltration, etc. – see Supplementary Information).
161 The sewer system was modelled as a series of CSTRs, whose number was iteratively adjusted to
162 match the HRT_i obtained from section 2.2.2 (see Supplementary Information). Verification of the
163 multi-catchment model was performed by comparing the simulated dry weather flow (sum of the
164 contributions of each sub-catchment) at the WWTP location with flow measurements (the $MFP(t)$
165 pattern obtained in section 2.2.2 was used).

166

167 2.3. *Scenario analysis*

168 2.3.1. *Comparison of conceptual model structures*

169 The performance of the multi-catchment model in simulating in-sewer MP fate was compared
170 against a classical single-catchment model. The latter was built using a single series of CSTRs,
171 whose number was adjusted to simulate an average HRT^* defined as the flow-weighted average of
172 the HRT_i of each sub-catchment. Model verification was also performed with flow measurements at
173 the WWTP as for the multi-catchment model (see section 2.2.2).
174 The fate of an ideal reactive non-sorptive MP, which can undergo biodegradation and
175 retransformation, was simulated with both models for two types of inputs:

- i) a pulse input (less than 1 hour), which refers to a compound with a relative small usage and/or discharged predominantly from few points (e.g. hospital or manufacturing facility);
- ii) a continuous input (over 24 hours following the same flow pattern), which refers to a substance with a relatively high consumption. An average concentration of $\sim 2.5 \mu\text{g L}^{-1}$ was selected as representative (Galus et al., 2013; Fent et al., 2006; Daughton and Ternes, 1999) to be emitted (where the sum of the individual contributions of each sub-catchment, proportionally to its size, was equal to the total contribution from discharge in the single-catchment).

The model output was calculated for the inlet of the WWTP. Five performance indicators, four for the pulse input (eq. 3, 4, 5 and 6) and one for the continuous input (eq. 7) were derived in Matlab 2016a: 1) the *cumulative load* [g] entering the WWTP (eq. 3); 2) the *removal efficiency* [%] during in-sewer transport (eq. 4); 3) the *peak delay* [min] (eq. 5); the *pulse duration* [min] (eq. 6); and the *average concentration* $\bar{C}$ [$\mu\text{g L}^{-1}$] derived to mimic a 24-hour flow-proportional composite sampler with 10-minute sampling frequency (eq. 7).

$$\text{Cumulative load} = \int_{t_{start}}^{t_{end}} C(t)Q(t) dt \quad \text{Eq. 3}$$

$$\text{Removal efficiency} = \frac{\text{pulse input} - \text{cumulative load}}{\text{pulse input}} \quad \text{Eq. 4}$$

$$\text{Peak delay} = t(C_{\max}) - t_{\text{release}} \quad \text{Eq. 5}$$

$$\text{Pulse duration} = t(C_{99}) - t(C_1) \quad \text{Eq. 6}$$

$$\bar{C} = \frac{\sum C(t)Q(t)}{\sum Q(t)} \quad \text{Eq. 7}$$

where C [$\mu\text{g L}^{-1}$] stands for the MP concentration and $C_{\max}$, C_1 and C_{99} are the maximum, 1st and 99th percentile concentrations, respectively; Q [$\text{m}^3 \text{d}^{-1}$] is the wastewater flow; t_{start} and t_{end} [min] are

the initial and final time of the simulation, respectively and, $t_{release}$ [min] is the releasing time of the pulse.

The comparison between the two conceptual models was based on the percentage *deviation* [%] between values of the above indicators derived for the single-catchment and the multi-catchment model (eq. 8):

$$Deviation = \frac{indicator_{multi-catchment} - indicator_{single-catchment}}{indicator_{single-catchment}} \quad \text{Eq. 8}$$

2.3.2. Simulated scenarios

Three scenarios were investigated, focusing on the effect of biodegradation kinetics (Scenario 1), simultaneous biodegradation and retransformation kinetics (Scenario 2) and geographical location of point sources of emission (Scenario 3):

- *Scenario 1: Effect of biodegradation.* Six biodegradation half-life values of 12 min, 20 min, 2.5 h, 4.5 h, 40 h and 1000 h were chosen to mimic the behaviour of a broad range of easily (e.g. ibuprofen), moderately (e.g. furosemide) and not biodegradable/recalcitrant (e.g. carbamazepine) substances. The selected half-life values lump the biodegradation by suspended microorganisms and biofilms in sewer, which have found to be both active in the biodegradation of MPs (Thai et al., 2014; Ramin et al., 2016, 2017; McCall et al., 2016; O'Brien et al., 2017).

- *Scenario 2: Effect of complex retransformation pathways.* We evaluated the impact of retransformation processes on model predictions for MPs that simultaneously undergo biodegradation. In the IUWS_MP library, we implemented retransformation as reported in Equations 9 and 10, similarly to the approach used by Plósz et al. (2010, 2012):

$$\frac{dS_{MP_{ret}}}{dt} = -k_{ret}S_{MP_{ret}} \quad \text{Eq. 9}$$

$$\frac{dS_{MP}}{dt} = -kS_{MP} + k_{ret}S_{MPret} \quad \text{Eq. 10}$$

where k_{ret} [d^{-1}] and k [d^{-1}] are the first-order rate of retransformation and biodegradation, respectively; S_{MP} [$g\ m^{-3}$] and S_{MPret} [$g\ m^{-3}$] are the concentrations of the parent and retransformable fractions, respectively. Three half-life values for retransformation (20 min, 2.5 h and 40 h, were selected to mimic retransformable fractions that can quickly transform back to their respective parent compounds (e.g. glucuronide conjugates) or are relatively stable (e.g. sulphate conjugates) (Gomes et al., 2009). Two types of proportions (1 and 10) between the released concentration of the parent MP and its retransformable fractions were selected, based on typical values found in raw wastewater (Khan and Ongerth, 2003; Bahlmann et al., 2014). All the possible combinations between the above-mentioned parameters were tested (see Table S3 in SI).

- *Scenario 3: Effect of location of point sources.* Two sub-catchments (A and F) were chosen as location of a point source discharging an easily (half-life = 12 min), moderately (half-life = 2.5 h) and hardly biodegradable (half-life = 40 h) MP.

3. Results and discussion

3.1. Conceptual model structure

3.1.1. Identification of sub-catchments

The cluster analysis resulted in the identification of six virtual sub-catchments (Figure 1a), for a minimum BIC value of $3.10 \cdot 10^5$ (ranging from $3.13 \cdot 10^5$ to $3.11 \cdot 10^5$ for 1 and 30 catchments, respectively). Figure 1b shows the geographical representation of the sub-catchments based on the location of the wastewater discharge points. The usefulness of an objective over a heuristic approach can be appreciated when considering sub-catchments C and D. While their geographical location (Figure 1b) would suggest considering them as unique catchment, the cluster analysis clearly highlighted two distinct *HRT* peaks of 150 and 180 min (Figure 1a). This 30-minute difference may influence fate estimations for degradable MPs (half-life ≤ 1 h).

Figure 1. (a) Results of the cluster analysis with identification of the virtual sub-catchments. (b) Geographical representation of the virtual sub-catchments based on the location of the wastewater discharge points.

3.1.2. Dry weather flow parameters

249 The calibration of dry-weather *MFP* (RMSE value of $0.16 \text{ m}^3 \text{ s}^{-1}$) resulted in a total infiltration flow
 250 $Q_{inf,tot}$ and in-sewer flow velocity v of $1.0 \text{ m}^3 \text{ s}^{-1}$ and 0.8 m s^{-1} , respectively. $Q_{inf,tot}$ corresponded to
 251 24% of the dry-weather flow and v fell within typical ranges for gravity sewer systems (Butler et
 252 al., 2004). The estimated *HRT* distribution had a flow-weighted average of 150 min (equal to
 253 HRT^*) and HRT_i values were placed at seemingly rather regular intervals (on average 40 min),
 254 ranging from 78 to 278 min (Figure 1a). These intervals depend on the shape of the *HRT*
 255 distribution (unique for every urban catchment) and should not be extrapolated for sub-catchment
 256 identification in other urban catchments.

257

258 3.1.3. Development of the conceptual model

259 A multi-catchment model (Figure 2a) was developed based on the results of the previous two steps.
 260 Model parameters were set as described in section 2.2.3 and reported in Table 1 where population
 261 density ρ ($18816 \text{ inh km}^{-2}$), wastewater production *WWP* ($0.218 \text{ m}^3 \text{ inh}^{-1} \text{ d}^{-1}$) and infiltration flow *I_{fl}*
 262 ($0.145 \text{ m}^3 \text{ s}^{-1} \text{ km}^{-2}$) were equal in each sub-catchment. The relative deviation between simulated and
 263 estimated HRT_i was small ($< 6\%$) for each sub-catchment, indicating a proper fit (see Table S2). As
 264 for the single-catchment model, model parameters are also reported in Table 1, and the relative
 265 deviation between simulated and estimated HRT^* and the relative deviation was also small (3%).
 266 Model verification using measured and simulated flow data can be seen in Figure 2b. The simulated
 267 dry-weather flow was within the confidence interval of the measured flow data, indicating an
 268 adequate description of the influent flow by both models.

269

270 **Table 1.** Conceptual model parameters

	Multi-catchment						Single-catchment
Sub-catchment	A	B	C	D	E	F	-
A (km^2)	13.1	16.4	17.5	6.6	13.8	2.2	69
Number of tanks	5	8	9	10	12	12	12

271

272

273 **Figure 2.** (a) Conceptual model in WEST®. (b) Model verification: measurements median and 5th and 95th
274 percentiles (dashed orange line), and model simulations (solid and dash black line).

275

276 **3.2. Scenario analysis**

277 **3.2.1. Scenario 1 – Effect of degradation**

278 Pulse source. The results from the simulations of a moderately biodegradable MP (half-life = 2.5 h)
279 are shown in Figure 3a. The pulse input resulted in bell-shaped curves, where the simulation of
280 advection and biodegradation led to a reduction of the area below the curves. The estimated
281 cumulative load and removal efficiency, and the corresponding deviation, for the whole range of
282 tested biodegradation half-lives is shown in Figure 3c and 3e, respectively. The cumulative load
283 deviation ranged from 0% to 312% (Figure 3c), being larger than 10% for MPs with half-lives ≤ 2.5
284 h and negligible or null value (5%, 1% and 0%) for the more recalcitrant MPs. Hence, the predicted
285 loads entering the WWTP were overall higher for the multi-catchment model. As to in-sewer
286 removal efficiency, deviations ranged from -15% to 0% (Figure 3e), showing that the multi-
287 catchment model predicted lower removal efficiencies than the single-catchment model, especially
288 for MPs with half-lives = 2.5 h and 4.5 h. The analysis of the peak delay indicator (Figure S1)
289 showed that the multi-catchment model predicts the peak load entering the WWTP earlier than the
290 single-catchment model (deviation ranging from -9% to -6%, corresponding to a difference between

the models of 70 to 50 minutes). This is mainly due to the contribution of the closest sub-catchment to the WWTP (indicated in blue in Figure 1b), for which MP release occurs sooner than the other sub-catchments due to its short *HRT* (78 min). Deviations for the pulse duration (see Figure S1) indicated that the a pulse takes longer to be completely release for the multi-catchment model (deviation ranging from 6% to 21%, corresponding to 20 to 90 minutes differences between the models).

Continuous source. The model results for a continuous input of a moderately biodegradable MP (half-life equal to 2.5 h) are shown in Figure 3b. The 24-h composite concentration and the deviation for all the whole range of substances (from easily biodegradable to recalcitrant) are shown in Figure 3d. The models predicted different concentrations for half-life lower than 2.5 h (deviation equal to ~ 10%), with a maximum deviation of 350% for half-life of 0.2 h. In these cases, the percentage deviation between the two models was higher than the uncertainty typically associated to analytics, quantifiable in 20–30% (Ort et al., 2009; Castiglioni et al., 2012), thus indicating a considerably lower estimated concentrations at the WWTP inlet with the single-catchment model. Notably, a high deviation (e.g., 350%) corresponded to small concentration differences (e.g. < 0.2 $\mu\text{g L}^{-1}$) due to the low input concentrations (~ 2.5 $\mu\text{g L}^{-1}$) that were used for simulations. On the other hand, higher input concentrations (e.g. ~ 100 $\mu\text{g L}^{-1}$) would lead, for the same deviation, to higher concentration differences (e.g. < 8 $\mu\text{g L}^{-1}$).

Predicted removal efficiencies were generally in good agreement with measurements from pilot- and full-scale sewer studies with degradable and persistent MPs (Table S4). Findings of both scenarios highlighted how the proposed approach supported the development of an appropriate model structure for predictions of biodegradable MPs with half-life close to or below the average *HRT* of the catchment (150 min).

314

315 **Figure 3.** Model response for a moderately biodegradable MP (half-life of 2.5 h) for (a) pulse input and (b)

316 continuous input. Calculated (c) cumulative load, (d) average concentration and (e and f) removal efficiency

for the single catchment model (black bar) and multi-catchment model (grey bar) with the corresponding percentage deviation (solid triangle) for different half-life.

3.2.2. Scenario 2 – Effect of complex transformation pathways

The impact of retransformation on single- and multi-catchment model predictions was assessed for parent MPs with biodegradation half-life equal to 2.5 h and 40 h. These two values were selected to describe easily-to-moderately biodegradable and recalcitrant, MPs, respectively. Furthermore, results from Scenario 1 showed that deviation between model predictions for these half-lives was $\leq 10\%$, hence retransformation may potentially increase such deviation.

Pulse source. The effect of simultaneous biodegradation and formation in the sewer on the fate of MPs was assessed by considering the removal efficiency as relevant indicator (Figure 4). Nearly all simulations predicted negative removal efficiency (Figure 4a), suggesting that retransformation can strongly affect MP fate during in-sewer transport. Very low values, ranging from -950% and -400%, were estimated for MPs which undergo retransformation rapidly (half-life ≤ 2.5 h) and when high retransformable fractions were present. When retransformation was slow (half-life = 40 h) or retransformable fractions were comparable to the one of parent compound, removal efficiencies ranged from -100 % to 35 %. This suggests a minor but not negligible effect of retransformable fractions on the parent compound estimation. Figure 4c presents the comparison between multi- and single-catchment predictions in terms of deviation of removal efficiency. For moderately biodegradable MPs (biodegradation half-life = 2.5 h) the deviation was around -7% on average (with a minimum of -35%), indicating that lower MP loads were estimated with the single-catchment model. Conversely, the deviation for hardly biodegradable MPs (biodegradation half-life = 40 h) was 16% on average (with a maximum of 50%), suggesting that the single-catchment model provided higher estimation of the MP loads entering the WWTP.

Continuous source. Predicted influent concentrations by multi-catchment and single-catchment models are presented in Figure 4b. A wide range of concentrations (3–26 $\mu\text{g L}^{-1}$) was obtained.

343 Specifically, the faster the retransformable fractions retransform, the more important is the effect of
344 the retransformation and retransformable fraction initial concentration on the parent compound
345 concentration. For example, when the retransformation half-life was 0.3 h, parent MP
346 concentrations differed significantly depending on biodegradable half-life and initial proportion,
347 while almost no differences in concentrations were observed for a retransformation half-life of 40 h.
348 Deviations between multi-catchment and single-catchment predictions (Figure 4d) ranged between
349 10% and -12%, exhibiting higher values than the ones reported for the continuous source in the
350 scenario 1 (section 3.2.1).

351 Notably, negative removal efficiencies (down to -66%) have been also measured in pilot- and full-
352 scale sewer studies (Table S4). The availability of empirical data is nevertheless limited as
353 compared to Scenario 1, as most studies have been relied on spiking of parent MPs alone.

354 Findings of both scenarios suggested that deviations between the models increased when
355 retransformation processes were considered. Specifically, the single-catchment model provided
356 either higher or lower estimation of removal efficiency/concentration without following any
357 particular trend, probably due to the non-linear interactions between the investigated parameters.

358

Figure 4. (a) Calculated removal efficiency and (b) average parent concentration by single-catchment (black triangle and black circle) and multi-catchment (white triangle and white circle) models for different initial conditions. Deviation for (c) removal efficiency and (d) average parent concentration.

3.2.3. Scenario 3 – Effect of point source location

Simulation results for easily (half-life = 12 min), moderately (half-life = 2.5 h) and hardly biodegradable (half-life = 40 h) MPs discharged from two different locations in the catchment are shown in Figure 5. Corresponding removal efficiencies, and their comparison with efficiencies derived from the single-catchment model, are reported in Table S5 (SI).

Results show that both location and MP biodegradability affected the MP loads entering the WWTP. The impact of point source location significantly affected the removal efficiency for easily and especially moderately biodegradable MPs (from 19% to 46% change), for which a considerable deviation was also shown from the single-catchment prediction (-49–24%). Conversely, discharge from different locations had a limited impact on in-sewer removal efficiencies for a hardly biodegradable compound (2%–5%). Overall, these results indicate that the extent of in-sewer attenuation processes for degradable MPs is associated with the spatial distribution of discharge sources. In this context, point sources of discharge require special consideration, and limited in-sewer attenuation may be decisive for the implementation of an *in situ* pre-treatment to minimize MP loads to WWTPs (Scott et al., 2018).

Figure 5. Estimated flux entering the WWTP of (a) a readily biodegradable, (b) moderately and (c) hardly biodegradable MP, based on point source location (sub-catchment A and F) and model conceptualization (multi-catchment and single-catchment).

3.3. Applicability, data requirements and future perspectives

This study presents a methodology for systematic construction of conceptual sewer models in large urban catchments with the intent of simulating the fate of reactive, non-sorptive MPs. The approach

388 can be held valid under dry-weather conditions and during small rain events, i.e. when *HRT* is not
389 significantly different. The applicability to medium events (resulting e.g. in combined sewer
390 overflows (CSO), or wastewater detention in storage basins) would require a model structure
391 including the addition of the most relevant points of the network. Moreover, the model can thus be
392 used as decision-support on whether pre-treatment at the point source is needed before discharge or
393 in-sewer attenuation is sufficient to reduce MP loads to WWTP.

394 As for the data requirement, the method required the location of the wastewater discharge points
395 along the sewer network. In this work, we used the location of potable water consumption points
396 (28,000) as proxy variable for the position of the wastewater discharge points. Alternatively, nodes
397 of the sewer network (McCall et al., 2017) or the centroids of the census block polygons (Kapo et
398 al., 2017) can be used. The sewer network structure is also required, although road networks are a
399 valid alternative as suggested by Kapo et al. (2017). As for the in-sewer flow velocity, an average
400 value was estimated, matching the simulated wastewater flow (derived from potable water
401 consumption) against measurements at the inlet of the WWTP. Alternatively, a design standard
402 velocity could be used (Kapo et al., 2017), although the topography of the area should be carefully
403 considered. In our study, given the flat characteristics of urban area, a unique value was assumed
404 across the catchment. However, different in-sewer flow velocities should be assigned (e.g. to each
405 sub-catchments) to account for different altitudes (resulting in different *HRTs*).

406 Overall, the above-mentioned assumptions can affect the sub-catchment identification and further
407 investigation should be done to assess their sensitivity. Further investigations should also include:

- 408 • *Wet-weather conditions.* Wet-weather conditions are not expected to be relevant when
409 assessing the overall MP loads to the WWTP over long time periods, since they typically
410 represent a minor (<10%) fraction of the total WWTP operating time. However, the
411 presence of wet-weather discharges (CSO, WWTP bypass) might require a redefinition of
412 the model structure in order to fully investigate the impacts on the receiving waters.

- *Complexity of the biochemical model.* A first-order kinetic for both biodegradation and retransformation process was assumed in the IUWS_MP library. It should be investigated if more complex process description can improve the estimation of the MP fate (e.g. biodegradation rates dependence on total suspended solids—TSS).
- *Integration with other elements of the wastewater system.* Since the proposed approach can be extended to predict MP fate across the whole integrated wastewater system (including WWTP and recipients), the scenarios investigated in this study (e.g. location of MP point sources) should possibly be replicated with an integrated model. The integrated assessment should mainly focus on moderately-to-hardly biodegradable MPs that are subjected to retransformation processes, for which poor removal in the WWTP or persistence in the environment can pose a risk to receiving water bodies.

425 **4. Conclusions**

426 In this study, we present a new systematic approach combining GIS-based information and
427 statistical analysis to identify the optimal structure of a conceptual model for simulating in-sewer
428 *HRT* in a large urban catchment, while keeping model complexity as simple as possible. The
429 approach was developed to improve fate predictions of down-the-drain MPs that undergo
430 degradation and/or formation during transport in sewers. Findings from the study allowed reaching
431 the following conclusions:

- 432 • The conceptual modelling approach allowed deriving a multi-catchment model, and the
433 large catchment was subdivided into sub-catchments, each characterized by a typical *HRT*.
434 The obtained model allowed for successful simulation of dry weather flow and is applicable
435 (i) in the absence of a complex hydrodynamic model and (ii) when a single-catchment
436 model (with one average *HRT*) is not representative of large urban areas.
- 437 • The multi-catchment model should be preferred over a single-catchment model for
438 simulating the fate of (i) biodegradable MPs with half-life lower than the average *HRT* of
439 the catchment and (ii) MPs that undergo rapid formation (half-life < 2.5 h) in the presence
440 of high concentrations of retransformable compounds (e.g., conjugated metabolites).
- 441 • The multi-catchment model allowed assessing the importance of point source location
442 within the catchment, providing decision-support on whether pre-treatment at the source is
443 needed before discharge or in-sewer attenuation is sufficient to reduce MP loads to WWTP.

444 Overall, the proposed approach is expected to ease the building of conceptual sewer water quality
445 models, allowing for a broader implementation of integrated models (sewer, WWTP, receiving
446

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450 The code for the conceptual model construction approach developed in this study is freely available
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452

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**Modelling micropollutant fate in sewer systems – A new
systematic approach to support conceptual model construction
based on in-sewer hydraulic retention time**

Riccardo Delli Compagni¹, Fabio Polese^{2,3}, Kerstin J.F. von Borries², Zhen Zhang², Andrea
Turolla¹, Manuela Antonelli^{1*} and Luca Vezzaro^{2*}

¹Department of Civil and Environment Engineering (DICA), Politecnico di Milano, Piazza Leonardo da Vinci
32, 20129 Milan, Italy

²DTU Environment, Technical University of Denmark, Bygningstorvet, Building 115, 2800 Kongens Lyngby,
Denmark

3DHI A/S, Agern Allé, 2970 Hørsholm, Denmark.

SUPPLEMENTARY MATERIAL

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Materials and methods

Identification of sub-catchments

The Dijkstra's algorithm (taking its name from the inventor, Edsger W. Dijkstra), is used to find the shortest path between nodes in a graph or a network by solving an optimization problem (Cormen, 2001). In the current study, we used the algorithm to identify the shortest in-sewer path from each discharge point to the wastewater treatment plant.

Building the conceptual model

Table S1 describes the calculations utilized to define the structure and the parameters of each sub-catchment. These values are utilized in the different blocks from the IUWS_MP library.

Table S1: Conceptual model parameters for each sub-catchment; n.d. stands for not defined.

	Population density ρ [inh km ⁻²]	Wastewater production WWP [m ³ inh ⁻¹ s ⁻¹]	Infiltration flow rate I_{fr} [m ³ s ⁻¹ km ⁻²]	Area A_i [km ²]	Hourly peak factors for WW release PF [-]	Number of in-series CSTR [-]
Source	$= \frac{1.250.000^a}{69^b}$	$= \frac{0.22^c * (1 - \alpha^d)}{Cf^e}$	$= \frac{Q_{inf,tot}^f}{69^b}$	$= \frac{Q_{PW,i}^g (1 - \alpha^d)}{\rho * WWP}$	$pattern^h$	n.d.
Sewer	n.d.	n.d.	n.d.	n.d.	n.d.	Iteratively adjusted to minimise $\frac{ HRT_i^f - HRT_{simulated} ^l}{HRT_{simulated}}$

^a Total number of inhabitants in the area

^b Total urban area in km²

^c Average potable water consumption in the study area in m³ inh⁻¹ d⁻¹ (ISTAT, 2018)

^d Water losses (Butler et al., 2004)

^e Conversion factor equals to 86400 s d⁻¹

^f Estimated from section 2.2.2; see equation 1-2

^g Sum of the potable water consumption of all the points within the ith sub-catchment, in m³ s⁻¹

^h Normalized daily potable water consumption pattern for workdays (Monday to Friday) reported by Candelieri and Archetti (2014)

^l Formula of the relative deviation

Equation S1 describes how the dry weather flow for each i^{th} catchment (sum of wastewater flow $Q_{ww,i}$ and infiltration flow $Q_{inf,i}$) is calculated by the WEST model.

$$Q_{dwf,i} = Q_{ww,i} + Q_{inf,i} = \rho * WWP * A_i * PF + Ifr * A_i \quad \text{Eq. S1}$$

where ρ [inh km⁻²] is the population density, WWP [m³ inh⁻¹ s⁻¹] the per capita wastewater production, A_i [km²] the area of the i^{th} sub-catchment and, PF the peak factors to introduce flow temporal variability; Ifr [m³ s⁻¹ km⁻²] is the groundwater infiltration rate.

Table S2 indicates the number of tanks (in the IUWS_MP library indicated as pipes) and the corresponding length after model calibration. The relative deviation was calculated according to the equation reported in Table S1. The volume of each pipe, obtained as product of the surface and length of the pipe, was initially fixed (~ 1750 m³) and slightly tuned for minor adjustments once the optimal number of CSTRs was found.

Table S2. Model parameters and performance indicator for each sub-catchment.

Sub-catchment	Number of tanks (-)	Length of each pipe (m)	Relative deviation (%)
A	5	600	3.1
B	8	600	5.3
C	9	650	0.2
D	10	500	2.5
E	12	650	2.5
F	12	475	0.8

Scenario 2: Effect of complex retransformation pathways.

Table S3 shows the parameters combinations (12 in total) that were tested in scenario 2. The third column indicates the proportion between the release concentration of the parent micropollutant and its retransformable fractions.

Table S3: parameter combination for each simulation for scenario 2.

Half-life biodegradation	Half-life retransformation	Retransformable fraction/parent	Simulation number
2.5 h	20 min	1	1
		10	2
2.5 h	2.5 h	1	3
		10	4
2.5 h	40 h	1	5
		10	6
40 h	20 min	1	7
		10	8
40 h	2.5 h	1	9
		10	10
40 h	40 h	1	11
		10	12

Results and discussion

Scenario analysis

Scenario 1 – Effect of degradation

Figure S1. Deviation for the peak delay and pulse duration between the multi-catchment model and the single-catchment model for different biodegradable half-lives.

Scenario 2 – Effect of complex transformation pathways

Table S4. Comparison between predicted and measured in-sewer removal efficiencies for MPs. Characteristics of investigated sewers are provided for literature studies.

		In-sewer removal efficiency (%)	
		Predicted (this study)	Measured (literature)
Scenario 1 (biodegradation)	1% to 32% (half-life > 2.5 h)		0 to 60% (Jelic et al., 2015: pressurized sewer, HRT = 21 h)
			0% to 35% (Gao et al., 2018: pilot gravity sewer, HRT = 2.5 h)
			20% to 60% [cocaine]; 25% to 70% [6-AM]; 20% to 80% [methadone] (Li et al., 2018: pressurized sewer, HRT > 3.5 h)
			25% [cocaine]; 15% [MDMA]; 20% [methadone] (Li et al., 2019: gravity sewer, HRT = 2-3 h)
Scenario 2 (biodegradation and retransformation)	-950% to 0%		-66% to 0% (Jelic et al., 2015: pressurized sewer, HRT = 21 h)
			-15% [benzoylecgonine] (Li et al., 2019: gravity sewer, HRT = 2-3 h)

Scenario 3 – Effect of point source location

Table S5. Simulated removal efficiencies by the multi-catchment model and the single-catchment model for different point source locations and biodegradable half-lives.

Half-life	Single-catchment	Sub-catchment F	Sub-catchment A
12 min	99	99	88
2.5 h	37	46	19
40 h	4	5	2

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