

1 Modelling the fate of organic micropollutants in stormwater ponds

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13

14 **Abstract**

15 Urban water managers need to estimate the potential removal of organic micropollutants
16 (MP) in stormwater treatment systems to support MP pollution control strategies. This study
17 documents how the potential removal of organic MP in stormwater treatment systems can be
18 quantified by using multimedia models. The fate of four different MP in a stormwater
19 retention pond was simulated by applying two steady-state multimedia fate models (EPI Suite
20 and SimpleBox) commonly applied in chemical risk assessment and a dynamic multimedia
21 fate model (Stormwater Treatment Unit Model for Micro Pollutants - STUMP). The four
22 simulated organic stormwater MP (iodopropynyl butylcarbamate - IPBC, benzene,
23 glyphosate and pyrene) were selected according to their different urban sources and
24 environmental fate. This ensures that the results can be extended to other relevant stormwater
25 pollutants. All three models use substance inherent properties to calculate MP fate but differ
26 in their ability to represent the small physical scale and high temporal variability of
27 stormwater treatment systems. Therefore the three models generate different results. A
28 Global Sensitivity Analysis (GSA) highlighted that settling/resuspension of particulate matter
29 was the most sensitive process for the dynamic model. The uncertainty of the estimated MP
30 fluxes can be reduced by calibrating the dynamic model against total suspended solids data.
31 This reduction in uncertainty was more significant for the substances with strong tendency to
32 sorb, i.e. glyphosate and pyrene and less significant for substances with a smaller tendency to
33 sorb, i.e. IPBC and benzene. The results provide support to the elaboration of MP pollution
34 control strategies by limiting the need for extensive and complex monitoring campaigns
35 targeting the wide range of specific organic MP found in stormwater runoff.

36

37

38 **Keywords:** Stormwater, stormwater treatment; organic micropollutants; multimedia
39 modelling; dynamic modelling; model calibration.

40 **1. Introduction**

41 Stormwater treatment facilities are becoming an essential option in current strategies to
42 reduce urban water pollution (e.g. Nordeidet et al., 2004; Bedan and Clausen, 2009).
43 Identification of environmental risks posed by stormwater discharge (Eriksson et al., 2007;
44 Kayhanian et al., 2008; Karlaviciene et al., 2009; Naito et al., 2010; Brix et al., 2010) and
45 recent regulations (e.g. European Union (EU) Water Framework Directive (Directive
46 2000/60/CE) and EU Environmental Quality Standards Directive (Directive 2008/105/EC))
47 have furthermore increased the number of substances that should be considered. In addition
48 to “traditional” macropollutants (i.e. total suspended solids (TSS), organic matter and
49 nutrients), these include a large number of micropollutants (MP) such as metals and organic
50 compounds which differ in terms of their sources, release patterns, inherent properties and
51 fate in the environment. Urban water managers should be able to assess, compare and select
52 the most appropriate treatment option (also called structural Best Management Practice -
53 BMP) according to local water quality targets. However when dealing with MP, this
54 assessment is affected by a general lack of information regarding the performance of
55 stormwater BMPs (examples provided in DiBlasi et al., 2009; Hatt et al., 2009).

56
57 Scholes et al. (2008) and Revitt et al. (2008) proposed a method to assess the relative
58 treatment efficiency of a specific BMP based on the inherent properties of a substance, which
59 are usually among the sparse data available for several MP. This approach provides
60 qualitative results as to which BMP is the most appropriate to remove a specific substance,
61 although the potential removal efficiency is not quantified. These qualitative results can be
62 obtained without field measurements and they can thus represent a useful surrogate for
63 stormwater management while waiting for more detailed results provided by future field
64 monitoring campaigns.

65
66 Mathematical models can improve this qualitative assessment with a quantitative estimation
67 of MP fate within a specific BMP. Multimedia fate models are commonly applied in
68 chemical risk assessment to calculate the distribution of substances between different
69 compartments. Hence they can also estimate MP fate between compartments of a stormwater
70 BMP (e.g. water, sediments, and atmosphere) based on a substance’s inherent properties.
71 Several state-of-the-art multimedia fate models with user-friendly interfaces are currently
72 available including EPI Suite (USEPA, 2008) and SimpleBox (den Hollander and van de
73 Meent, 2004). Results from multimedia models can corroborate the qualitative assessment

74 outcomes mentioned above, although they encounter difficulties in representing the small
75 spatial scale and dynamic behaviour of real stormwater treatment systems.
76 The Stormwater Treatment Unit model for MicroPollutants (STUMP -Vezzaro et al. (2010))
77 is a dynamic multimedia model that estimates MP fluxes in BMPs based on MP inherent
78 properties. This model expands upon existing stormwater treatment models, which are
79 flexible enough to simulate a wide range of BMPs (Wong et al., 2006) but only target
80 traditional macropollutants. The expansion yields the possibility of simulating various
81 fate/removal processes for MP (volatilization, biodegradation, adsorption/desorption,
82 hydrolysis, and photolysis) using MP inherent properties.
83 The structure, the spatial and temporal scale of these models, as well as the financial and
84 technical difficulties in monitoring MP (e.g. Ledin et al., in press) limits the application of
85 complex statistical methods for assessing model performance. Advanced methods for
86 uncertainty analysis have been applied in stormwater quality modelling: for example,
87 Bayesian methodologies were investigated by e.g. Kanso et al. (2006), Kleidorfer et al.
88 (2009), Dotto et al. (2010); pseudo-Bayesian methods were investigated by e.g. Lindblom et
89 al. (2007a), Mannina and Viviani (2010), Rodriguez et al. (2010); while Lindblom et al.
90 (2007b) presented a comparison of the latter with grey-box modelling. Freni et al. (2009a)
91 suggested that pseudo-Bayesian methods (namely the Generalized Likelihood Uncertainty
92 Estimation (GLUE) methodology (Beven and Binley, 1992)) can be appropriate for
93 stormwater quality models, i.e. in condition where only a limited number of prior
94 assumptions can be proved. However, these examples mainly deal with runoff quality models
95 or integrated urban water systems, and they focus on traditional macropollutants and MP with
96 fate strongly related to TSS (heavy metals). Stormwater treatment models are seldom
97 analyzed, with examples limited to traditional macropollutants (e.g. Kutzner et al. (2007))
98 and MP with fate that is strongly related to TSS (as the metals and total hydrocarbons
99 assessed for a sand filter by Avellaneda et al. (2010)). The substances and the model
100 typologies investigated in this study are seldom addressed: when dealing with MP and
101 multimedia models, in fact, evaluations of model performance are limited to simple
102 regression methods, as shown e.g. by Pederson et al. (2001) and Hollander et al. (2007).

103

104 The primary aim of this study is to document how the potential fate of organic MP in
105 stormwater treatment systems can be quantified using multimedia fate models. The dynamic
106 STUMP model and the two steady-state models EPI Suite and SimpleBox are compared
107 focusing on the quantification of fate for selected substances representing a wide range of
108 inherent properties (and uses/releases) in order to ensure that the results can be extended to
109 other relevant stormwater pollutants. The secondary aim of the study is to identify the major
110 model factors affecting the results of the dynamic model and to use this information to reduce
111 the result uncertainty. This is obtained by performing a Global Sensitivity Analysis (GSA) on

112 the dynamic model, which was preferred to steady-state models for its flexibility, the
113 possibility of simulating the highly dynamic processes taking place in stormwater treatment
114 systems, and the possibility of using non-MP measurements (flow, TSS) for uncertainty
115 assessment. The GSA results provide the basis for the reduction of the uncertainty in MP fate.
116
117

118 **2. Material and methods**

119 **2.1 The Lilla Essingen case study.**

120 MP fate was calculated for a stormwater retention pond located in Lilla Essingen, Stockholm
121 (Sweden). The pond is the first part of a treatment train used to treat highway runoff from a
122 1.2 ha catchment before secondary treatment by filtering with several sorbent materials and
123 discharge to a receiving water body. The pond has a permanent volume of about 150 m³, a
124 maximum storage volume of 200 m³ with an emptying time needed to restore dry-period
125 conditions of about 69 h (see Stockholm Vatten (2006) for more details).

126 The available flow and water quality measurements covered the period between March 2004
127 and May 2005. Composite samples were taken with a flow-proportional sampler at the pond
128 inlet (9 samples) and outlet (28 samples). The time interval covered by the each composite
129 sample varied from 2.7 to 16 days for the inlet and 0.8 to 17 days for the outlet. A wide range
130 of water quality parameters was quantified (TSS, organic matter, selected polycyclic aromatic
131 hydrocarbons and metals), with measured TSS ranging between 15 and 13000 mg/l at the
132 inlet (with median 220 mg/l) and between 2 and 110 mg/l (with median 19 mg/l) at the outlet.
133 The Lilla Essingen system thus represents a typical situation where stormwater flow and
134 select, scarce water quality measurements are available, and hence where the potential
135 removal of most organic MP needs to be estimated through the application of a model.

136 **2.2. MP fate models**

137 Two widely used steady-state multimedia models, EPI Suite (USEPA, 2008) and SimpleBox
138 (den Hollander and van de Meent, 2004), and the dynamic STUMP model (Vezzano et al.,
139 2010) were applied. In all three models the MP fluxes and distributions were calculated from
140 the substances' inherent properties. In addition, they all simulate the environmental
141 compartments as fully mixed boxes, with fate processes expressed as pseudo-first order
142 processes (see the details provided in Table 1). The STUMP and SimpleBox models were set
143 to simulate the Lilla Essingen system, while the EPI Suite software was run in its default
144 configuration that could not be changed. No advection was included in the EPI suite model
145 (i.e. a closed system was simulated).

146

147 The EPI Suite software package (USEPA, 2008) includes an implementation of the
 148 “classical” Mackay models (Mackay, 2001). These models are based on the fugacity
 149 approach, i.e. the tendency of a chemical to “escape” from a compartment. EPI Suite features
 150 a Mackay level III model, which assumes steady state but not equilibrium conditions. As EPI
 151 Suite provides output regarding the mass distribution when steady state is reached and all the
 152 degradation processes are completed, it is not possible to “backtrack” the process and
 153 quantify the amount of degraded substance. Furthermore, the EPI Suite software does not
 154 allow the user to change the dimension of the environmental compartments (see Table 2), and
 155 thus the default values were applied to simulate the Lilla Essingen system. MP discharge into
 156 the pond was assumed to be constant and only in relation to the aqueous compartment.

157
 158 **Table 1.** Comparison of EPI Suite, SimpleBox and STUMP models used to estimate organic
 159 MP fate.

Compartments	EPI Suite	SimpleBox	STUMP
Air	X	X	-
Sediment	X	X	X
Soil	X	X	-
Water	X	X	X
Kinetics	Pseudo first order	Pseudo first order	Pseudo first order
State variable	Fugacity ^a	MP concentration ^b	MP mass
Possibility to define the size of the compartments	No	Yes	Yes (initial conditions)
Output	MP mass distribution at steady state	MP mass fluxes at steady state	TSS and MP mass fluxes under dynamic conditions

160 ^a calculated for each compartment as the product of the substance compartmental
 161 concentration *C* and a fugacity capacity constant *Z* (calculated from the substance’s inherent
 162 properties); ^b mass transfer coefficients between the environmental compartments are
 163 dimensionally consistent with the majority of measured values (e.g. as mol·s⁻¹ as opposed to
 164 mol·hr⁻¹Pa⁻¹ in the fugacity based model).

165
 166 The SimpleBox model (Brandes et al., 1996; den Hollander and van de Meent, 2004) is a
 167 nested model that resembles the structure of Mackay models with similar environmental
 168 compartments and fate processes at different scales (regional, continental and global) but uses
 169 the MP concentration as state variable. In this study only the regional scale submodel was
 170 applied. The dimensions of the environmental compartments were adjusted to represent the
 171 Lilla Essingen system (Table 2) and the model output consisted of the mass fluxes at steady

172 state. MP discharge into the pond was assumed to be constant and only in relation to the
173 aqueous compartment.

174

175 STUMP (Vezzaro et al., 2010) is a dynamic model specifically developed to estimate the
176 potential organic MP removal in stormwater BMPs. The conceptual model, extending the
177 approach presented in Wong et al. (2006), consists of a series of two-compartment (water and
178 sediment), fully mixed process reactors (Figure 1). The model estimates mass fluxes to other
179 environmental compartments that are not included in the model, including receiving waters,
180 groundwater and the atmosphere. Unlike the two multimedia models, the sizes of the STUMP
181 compartments vary during the simulation (e.g. water volume varies due to dynamic storage
182 and sediment thickness varies due to settling and resuspension) and the atmosphere is not
183 included in the model. Different stormwater treatment units can be simulated by changing the
184 number of serial tanks, which is defined to achieve a hydraulic efficiency λ (ratio between
185 actual and theoretical hydraulic retention time (Persson et al., 1999)) resembling that of the
186 real system under study.

187

188 **Table 2.** Dimensions of environmental compartments used in the simulations.

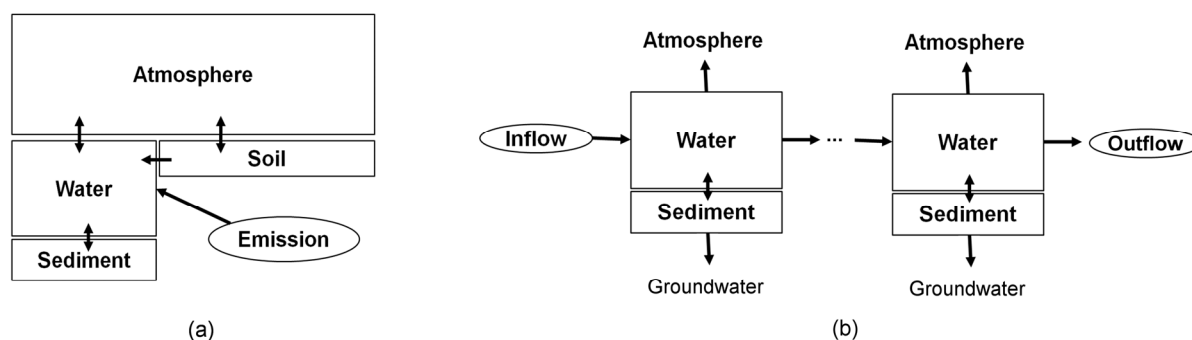
	Parameter	EPI Suite ^a	SimpleBox	STUMP
Air	Depth [m]	1000	100	-
	Volume [m ³]	10 ¹⁴	10 ⁶	-
Sediment	Depth [cm]	5	5	7 ^b
	Volume [m ³]	5·10 ⁸	22.5	10.5 ^b
Soil	Depth [m]	0.2	0.05	-
	Volume [m ³]	1.8·10 ¹⁰	477.5	-
Water	Depth [m]	20	1.5	1 ^c
	Residence time [hr]	-	69	-
	Volume [m ³]	2·10 ¹¹	300	150 ^c

189 ^a Default settings; ^b Average value during simulation period; ^c Conditions during dry weather.

190

191 The volume of the water compartment and the number of serial reactors were defined to
192 represent the measured hydraulic behaviour of the Lilla Essingen pond. Persson and Wittgren
193 (2003) and Jansons et al. (2005) estimated a λ value around 0.9 for a pond with similar
194 layout. The eight-reactor configuration which was adopted to simulate the Lilla Essingen
195 pond ensured a λ equal to 0.88. A constant MP concentration was used as model input, while
196 the observed output of the model was the mass of settled and degraded MP as well as the
197 mass fluxes to the atmosphere and recipient.

198



199

200 **Figure 1.** Environmental compartments in the three analysed models: EPI Suite and
 201 SimpleBox (a), and STUMP (b).

202 2.3. Modelled substances

203 To ensure general results not dependent on the properties of a single substance, the models
 204 were run for three “extreme” substances (with properties suggesting a dominance of one fate
 205 process over the others) and a “moderate” substance (with properties suggesting fate
 206 processes with similar magnitude).

207

208 **Table 3.** Substance data used in the simulations.

Parameter	Substance			
	IPBC ^a	Benzene ^b	Glyphosate ^c	Pyrene ^d
Boiling point [°C]	-	80	-	404
Melting point [°C]	66	5.5	189.5	151.2
Octanol water partition coefficient (Log K _{ow})	2.81	2.13	-4.00	4.88
Vapour pressure [mmHg]	2.57·10 ⁻⁵	94.8	2.89·10 ⁻¹⁰	4.5·10 ⁻⁶
Water solubility [mg/l]	168	1790	12000	0.135
Dimensionless Henry's law constant	1.2·10 ^{-7 e}	2.26·10 ⁻¹	8.6·10 ^{-11 e}	4.87·10 ^{-4 e}
Assumed inlet concentration [µg/l]	11 ^{f,g}	0.15 ^{h,i}	9 ^{j,c}	1 ^{h,i}
Main urban sources	Biocide (building materials)	Combustion processes	Biocide (gardening)	Combustion processes

209 ^a ESIS (2008); ^b Lützhøft et al. (2008); ^c HSDB (2006); ^d HSDB (2002); ^e Neglected in
 210 simulations; ^f Togerö (2004); ^g Szenasy (1998); ^h Borden et al. (2001); ⁱ Hwang and Foster
 211 (2006); ^j Botta et al. (2009)

212

213

Parameter	Description	Sampling Interval ^a				
Factors (not related to MP)	Background					
	C^*_{TSS}	concentration for TSS [g _{TSS} /l]	[3;20] ^b			
	E_0	erodability constant [g/m ² /d]	[294;648] ^c			
	K_m	Manning's constant [m ^{3/5} /s]	[5;5000] ^d			
	$\tau_{crit,set}$	critical shear stress for settling [Pa]	[0.02;0.10] ^e			
	$\tau_{crit,res}$	critical shear stress for resuspension [Pa]	[0.03;0.62] ^f			
v_{sed}	average settling velocity for particles [m/d]	[17;2600] ^g				
		IPBC ^h	Benzene ⁱ	Glyphosate ^j	Pyrene ^k	
MP factors	$DT_{50,aer}$	aerobic degradation half-life [d]	not degraded ₁	[2;28]	[1.85;130]	[238-630]
	$DT_{50,anor}$	anaerobic degradation half-life [d]	[0.063;1.25]	[56;270]	8.1	not degraded ^l
	$DT_{50,hydr}$	hydrolysis half-life [d]	[248;539]	not available ¹	not available ¹	not degraded ^l
	$DT_{50,pho}$	Photodegradation half-life [h]	not degraded ₁	405.6	[504;840]	[0.68-0.85]
	k_d	MP soil-water partition coefficient [l/kg]	[3.43;31.3]	[4;614]	24000	13060
	k_{sor}	MP sorption rate [l/d]	[0.05;1.5]	[0.05;1.5]	[0.05;1.5]	[0.05;1.5]

216 ^a expressed as [min; max]; ^b defined by the TSS measurement at the pond outlet; ^c Schaaf et
 217 al. (2006); ^d defined after calibrating the pond model outflow against measurements; ^e lower
 218 bound defined by the observing the minimum simulated shear stress in the pond (29 mPa),

219 higher bound defined from Van Der Ham and Winterwerp (2001); ^f lower bound defined by
220 the observing the range of simulated shear stress in the pond (29-31 mPa), higher bound
221 defined from Parchure and Mehta (1985); ^g Bentzen and Larsen (2009); ^h ESIS (2008); ⁱ
222 Lützhøft et al. (2008); ^j HSDB (2006); ^k HSDB (2002); ^l neglected in the simulations.

223

224 The four substances were selected among those identified in stormwater and with relevant
225 uses and release in urban areas (Shinya et al., 2000; Borden et al., 2001; Togerö,
226 2004; Schoknecht et al., 2009; Botta et al., 2009): iodopropynyl butylcarbamate (IPBC – CAS
227 number 85045-09-6) as a “moderate” substance, benzene (CAS no. 71-73-2) as a volatile
228 substance, glyphosate (CAS no. 1071-83-6) as a biodegradable substance and pyrene (CAS
229 no. 129-00-0) as a sorbing and photodegradable substance. The inherent properties that were
230 used to run the three models are listed in Table 3 and in Table 4. As no inflow MP
231 measurements were available at Lilla Essingen, average runoff concentrations extrapolated
232 from literature were used as input to the STUMP model.

233 **2.4. Identification of sensitive factors in the dynamic model**

234 All the assessed models can be affected by various sources of uncertainty (model structure,
235 inputs, and parameters) which needs to be identified to evaluate the models’ performance and
236 to reduce the model results uncertainty. The application of methods to assess and eventually
237 reduce uncertainty is however limited by the scarcity of MP measurements in stormwater
238 treatment systems. Among the three models, only the dynamic STUMP model provides flow
239 and TSS fluxes as output in addition to MP mass fluxes (Table 1). STUMP thus includes
240 parameters and processes other than MP fate related processes (see Vezzaro et al. (2010) and
241 Table 4) which can be assessed without requiring MP data (i.e. flow and TSS measurements
242 are sufficient to partially evaluate STUMP uncertainty).

243 The identification of the most sensitive model factors (input and, parameters) is therefore
244 important to recognise the most important processes, understand the behaviour of the
245 STUMP model, and assess the possibility of reducing the uncertainty of its results. Among
246 other advantages, model sensitivity analysis can facilitate the process of removing any non-
247 relevant factors and therefore better focus the available resources on the factors that are
248 responsible for producing reliable results.

249

250 Traditional methods to assess each factor’s sensitivity are based on the “One-At-a-Time”
251 (OAT) approach, i.e. the impact of changing the value of each factor is calculated
252 independently. These methods are not able to identify possible interactions between factors,
253 and therefore more advanced Global Sensitivity Analysis (GSA) approaches are suggested.
254 GSA methods evaluate the influence of model factors on the model output variance (such as
255 the methods described in e.g. Chan et al., 2004, Saltelli et al. (2006), Gatelli et al., (2009) and

256 Saltelli and Annoni (2010)) or on the sensitivity function (relating the output changes with
257 the variation in the factors), as described in the examples provided for example by Reichert
258 and Vanrolleghem (2001), Brun et al. (2002) and Freni et al. (2009b). While the variance
259 based approaches ranks the model factors according to their influence on the output without
260 requiring any field observations, the latter approaches (also defined as identifiability analysis)
261 extends the sensitivity analysis by identifying the factors that can be estimated by using the
262 available measurements (as in the example presented by Freni et al., 2011). All these GSA
263 approaches thus provides a deep insight about the importance of each factor, including
264 potential interactions between factors, but can be computationally demanding.

265
266 In this analysis, it was considered that the detailed information provided by these methods
267 was excessive and unnecessary and therefore a more simple yet effective screening method
268 was preferred. This provides only a qualitative assessment of interactions between model
269 factors, rather than the quantitative measures provided by advanced methods (which can be
270 applied on a second stage). Furthermore, the limited data availability discouraged a detailed
271 identifiability analysis. The elementary effect method proposed by Morris (1991) and further
272 improved by Campolongo et al. (2007) is a compromise between a simple OAT approach and
273 the more complex GSA methods. In fact, it can be considered as an OAT method that is
274 randomly applied in a defined number of R regions of the parameter space Ω which was
275 defined by the intervals listed in Table 4. Campolongo et al. (2007) also showed that the
276 modified Morris method approximates the results provided by variance-based methods with
277 significantly lower computational requirements. The elementary effects are estimated by
278 comparing the variation of the model's output with the variation of a given parameter. Two
279 statistical measures μ^* and σ^* , based on the average and standard deviation of the elementary
280 effect respectively, are computed and used to identify factors with effects that are negligible,
281 linear and additive, non-linear or interacting with other factors.

282
283 When inherent data were found to be scarce (e.g. a single value found for photodegradation
284 rate for benzene) in literature, a $\pm 100\%$ "safety factor" was used to define the sampling
285 interval, with an approach similar to that applied in chemical risk assessment (European
286 Commission, 2003). The screening of the model factors was performed by generating 20
287 Morris trajectories (Campolongo et al., 2007) through applying the simplex-based method
288 described in Pujol (2009).

289
290

291 **3. Results and discussion**

292 **3.1. STUMP hydraulic submodel**

293 The eight serial tank model has a general tendency to overestimate the peaks in the outflow
294 from the pond (up to 20%): the modelled hydraulic residence time is thus shorter than for the
295 real system, and the calculated removal efficiency is thus expected to be slightly lower than
296 in reality.

297 **3.2. Estimation of MP fluxes**

298 The mass distribution estimated by the three models is presented in Figure 2 (see Table A1 in
299 the Appendix for details). It is not possible to evaluate the importance of the degradation
300 process in EPI Suite, as the estimated equilibrium fate distribution assumes the complete
301 transformation of the degradable fraction which is not listed in the model outputs.

302
303 The agreement between the models depends on the substance. A “moderate” substance such
304 as IPBC is not expected to be significantly removed in the pond, which is confirmed by all
305 the three models (Figure 2a). The results for benzene highlight the importance of the physical
306 dimensions of the modelled system. The greater fraction of benzene is expected to volatilize,
307 and this result is confirmed by all the three models although to varying degrees (Figure 2b),
308 i.e. for benzene how the atmospheric compartment is modelled plays the major role. Because
309 the STUMP model does not account for the substance concentration in the atmosphere,
310 volatilization is not constrained and STUMP provides a higher removal rate for benzene than
311 the other two models. To investigate this aspect, the STUMP model could be connected to a
312 multimedia model as presented by De Keyser et al. (in press) which includes an
313 implementation of SimpleBox in the same simulation platform used by STUMP (WEST[®]
314 (Vanhooren et al., 2003)). On the other extreme, EPI Suite shows a lower removal by
315 volatilization: in the closed system the atmosphere reaches equilibrium and a greater fraction
316 of the substance remains in the water compartment. Given the small physical scale of the
317 modelled system, it can be assumed that not the size of the atmosphere compartment but the
318 water-atmosphere boundary conditions control the flux, and hence STUMP provides a more
319 realistic representation of the system.

320
321 The difference between the complex and dynamic settling/resuspension processes (also
322 dependent on the inlet TSS concentration and sorption/desorption) in STUMP and the
323 constant water-sediment fluxes in EPI Suite and SimpleBox explains the different results
324 obtained in the estimation of the settled fraction of MP. In STUMP, settling is in fact reduced
325 during high flow conditions and a part of the settleable fraction can be discharged to the
326 receiving waters. Another cause of disagreement between the models (e.g. on the degradation

327 of pyrene) is the degradation rates used by EPI Suite and SimpleBox that are estimated by
328 QSAR relationships while STUMP uses measured rates.

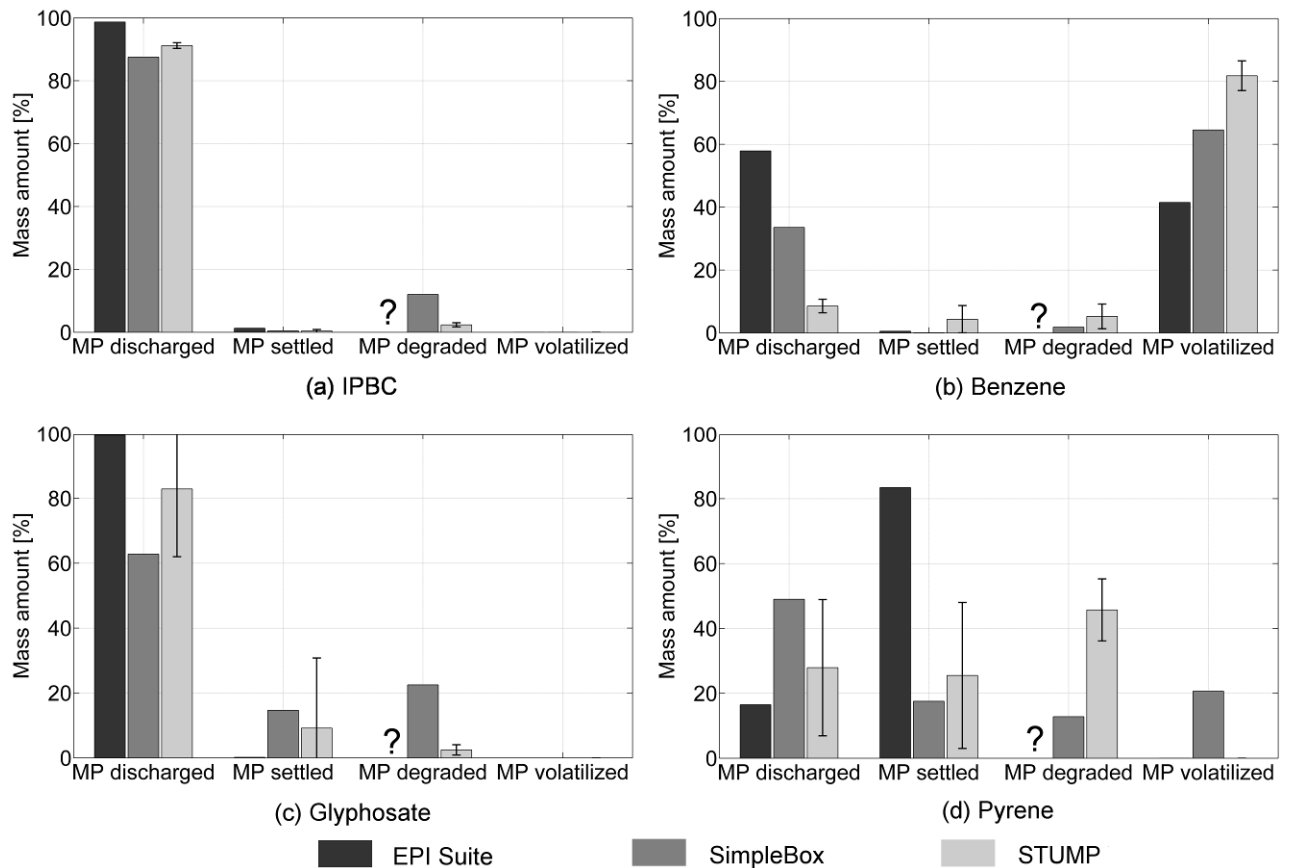
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330 Similarly, SimpleBox calculates a greater MP fraction degraded in the system than STUMP
331 for IPBC and glyphosate (Figure 2a and 2c). SimpleBox uses a constant hydraulic residence
332 time in the system while this varies during the STUMP simulation. The residence time in the
333 pond is lower during peak flow conditions, decreasing the overall removal by degradation
334 processes as shown by the increased glyphosate discharge estimated by STUMP. STUMP can
335 thus handle the reduction of the removal efficiency during high flow condition which is
336 commonly seen for traditional pollutants and expressed in STUMP by the hydraulic
337 efficiency. The results for glyphosate and pyrene highlight the importance of a dynamic
338 representation of the fate processes for the mass balance of the system. The greater
339 degradation of pyrene estimated by STUMP can be explained by the high photodegradation
340 rate found in the literature and used in the simulations.

341

342 Generally, there is a greater agreement between SimpleBox and STUMP, which can be
343 explained by the dimensions of the simulated system and the nature of the models which do
344 not represent a system in equilibrium. The size of the environmental compartment in those
345 two models for example is significantly smaller (10^7 - 10^8 times) than in EPI Suite and the
346 ratio between the compartments is different (the ratio between the sediment and water
347 volume is 1:400 in EPI suite compared to 1:13 in SimpleBox and 1:14 in STUMP). When the
348 SimpleBox results are not included within the standard deviation interval calculated for the
349 STUMP results (represented by error bars in Figure 2), this is explained by the different
350 model structure (absence of the atmospheric compartment and settling depending on flow
351 conditions in STUMP) or by the different degradation rates (estimated in SimpleBox and
352 measured in STUMP). Although the assessed multimedia models generally confirm the
353 assumptions made in the selection of the simulated substances, the results of these models
354 represent a static system which is unlike actual stormwater systems during rain events.
355 Settling and degradation processes are strongly affected by the hydraulic conditions in the
356 system (e.g. variation in the hydraulic residence time, poor settling conditions, resuspension)
357 as shown by the results for glyphosate. SimpleBox, in fact, calculates a higher fraction that is
358 settled and degraded than STUMP, as it estimates the mass distribution at equilibrium.
359 Dynamic models are thus necessary to achieve a realistic overview of the BMP performances,
360 especially during extreme conditions (i.e. when mass and concentration peaks in the
361 discharge are expected).

362



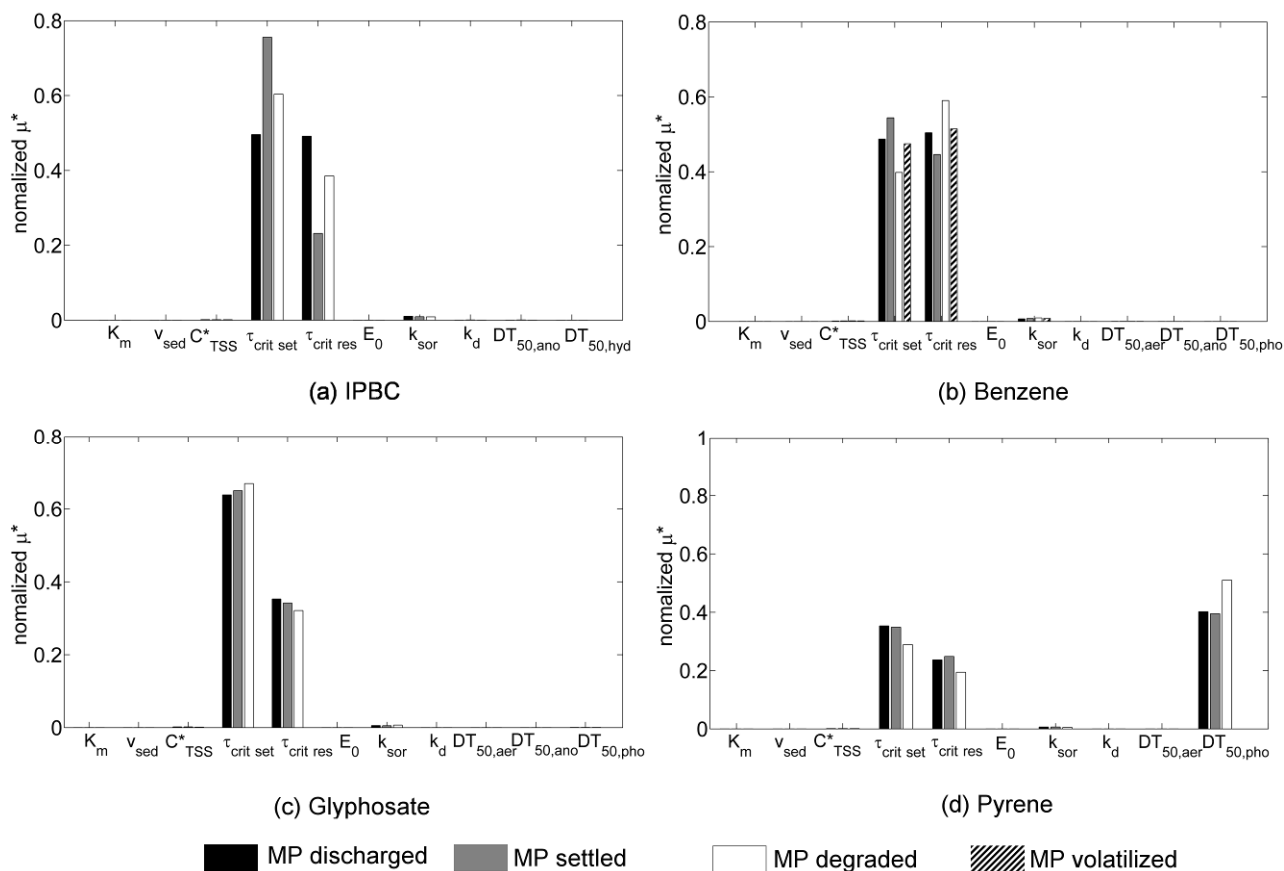
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365

Figure 2. Mass distribution calculated by using the three models. STUMP results are expressed as mean \pm standard deviation (calculated as part of the GSA).

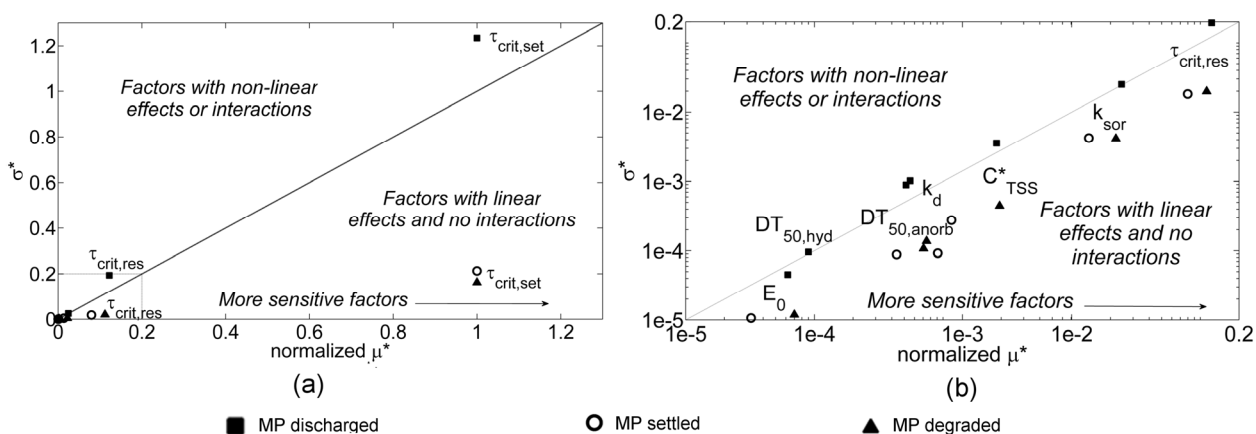
366 3.3. Identification of sensitive factors in the dynamic model

367 The analysis of the model factors focuses on their effect on the following model outputs for
 368 MP: mass accumulation in sediment, mass degraded by biotic and abiotic processes, mass
 369 transferred to atmosphere (if substance is volatile) and overall MP removal (i.e. difference
 370 between the MP mass entering the pond and the MP discharged to the receiving waters). For
 371 all four simulated MP, the settling/resuspension process parameters (i.e. the critical shear
 372 stress for settling $\tau_{crit,set}$ and the critical shear stress for resuspension $\tau_{crit,res}$) represent the most
 373 sensitive factors for defining the mass balance of the system (Figure 3). All the other MP fate
 374 process parameters show low sensitivity for calculating MP fluxes with the exception of
 375 photodegradation rate ($DT_{50,pho}$) for pyrene. The high sensitivity of the photodegradation rate
 376 for pyrene is explained by the very low half-life found in the literature and used in the
 377 simulation (Table 4). The analysis of the two statistical measures μ^* and σ^* (Figure 4)
 378 suggests also that the critical stress $\tau_{crit,res}$ has a non-linear influence or strong interactions
 379 with other factors when investigating the total mass removed in the pond, i.e. in the simulated
 380 system the settling process interacts with other fate processes. In fact a reduction of the
 381 settling process as defined by the critical shear stress $\tau_{crit,set}$ affects both the particulate and
 382 (through the sorption/desorption process) the dissolved MP fractions when varying the

383 importance of other fate process parameters. The other parameters do not show significant
 384 interactions or non-linear effects on the model outputs.
 385



386 **Figure 3.** Normalised elementary effects for STUMP fate process parameters (the parameters
 387 are described in Table 4 and in Vezzaro et al. (2010)).
 388
 389



390 **Figure 4.** Estimated mean and standard deviation for elementary effects of IPBC (a) and an
 391 enlargement of the factors (b). The parameters are described in Table 4 and in Vezzaro et al.
 392 (2010).
 393
 394

395 A hydraulic residence time of 69 hr and the use of settling velocities listed in Table 4 suggest
 396 that all the settleable particles entering the pond would settle. The two critical shear stress
 397 parameters $\tau_{crit,set}$ and $\tau_{crit,res}$ can however reduce the effect of the settling process and/or
 398 enhance resuspension, enabling particles to reach the pond outlet and significantly modifying
 399 the mass balance of the pond model. For instance, settling is partially inhibited when the
 400 actual shear stress τ (ranging from 29 to 31 mPa during the simulation period) is close to the
 401 critical shear stress for settling $\tau_{crit,set}$ and the whole particulate fraction is discharged in the
 402 outlet when τ is above $\tau_{crit,set}$. When τ is higher than the critical shear stress for resuspension
 403 $\tau_{crit,res}$, the water turbulence furthermore removes sediments from the bottom of the pond
 404 (accumulated during previous minor rain events), which may lead to TSS outlet
 405 concentrations that are higher than the inlet concentrations. These variations in TSS outlet
 406 concentrations directly affect the behaviour of the particulate MP fraction (X_{MP}) and
 407 indirectly the dissolved fraction (S_{MP}) through the sorption/desorption process.

408
409

Table 5. Statistics of the elementary effects for IPBC discharged in the pond outlet.

	Sampling interval listed in Table 1		Sampling interval for $\tau_{crit,set}$ and $\tau_{crit,res}$ reduced to 29-50 mPa	
	μ^*	σ^*	μ^*	σ^*
K_m	$2.33 \cdot 10^{-5}$	$6.36 \cdot 10^{-6}$	$2.38 \cdot 10^{-5}$	$6.66 \cdot 10^{-6}$
V_{sed}	$3.37 \cdot 10^{-5}$	$9.85 \cdot 10^{-6}$	$4.58 \cdot 10^{-5}$	$1.34 \cdot 10^{-5}$
C^*_{TSS}	$1.77 \cdot 10^{-2}$	$4.53 \cdot 10^{-3}$	$2.31 \cdot 10^{-2}$	$5.79 \cdot 10^{-3}$
$\tau_{crit,set}$	5.73	1.15	8.55	1.72
$\tau_{crit,res}$	5.68	$9.71 \cdot 10^{-1}$	5.89	1.28
E_0	$4.26 \cdot 10^{-4}$	$1.00 \cdot 10^{-4}$	$2.97 \cdot 10^{-4}$	$7.27 \cdot 10^{-5}$
k_{sor}	$1.20 \cdot 10^{-1}$	$3.35 \cdot 10^{-2}$	$1.12 \cdot 10^{-1}$	$3.18 \cdot 10^{-2}$
k_d	$3.66 \cdot 10^{-3}$	$1.12 \cdot 10^{-3}$	$3.97 \cdot 10^{-3}$	$1.26 \cdot 10^{-3}$
$DT_{50,anorb}$	$3.12 \cdot 10^{-3}$	$6.94 \cdot 10^{-4}$	$2.66 \cdot 10^{-3}$	$6.04 \cdot 10^{-4}$
$DT_{50,hydr}$	$4.98 \cdot 10^{-4}$	$8.80 \cdot 10^{-5}$	$4.87 \cdot 10^{-4}$	$1.06 \cdot 10^{-4}$

410

411 Similar values for the μ^* and σ^* measures were obtained again by running the Morris'
 412 analysis after narrowing the sampling interval for $\tau_{crit,set}$ and $\tau_{crit,res}$ to the values simulated
 413 during the study period (see Table 5). Thus the results of the Morris' analysis are not
 414 depending on the sampling interval and the two critical shear stress parameters are confirmed
 415 as the most sensitive parameters considered. Further research is needed to analyse the model

416 parameters' behaviour in different stormwater treatment units such as biofilters and
417 infiltration basins.
418

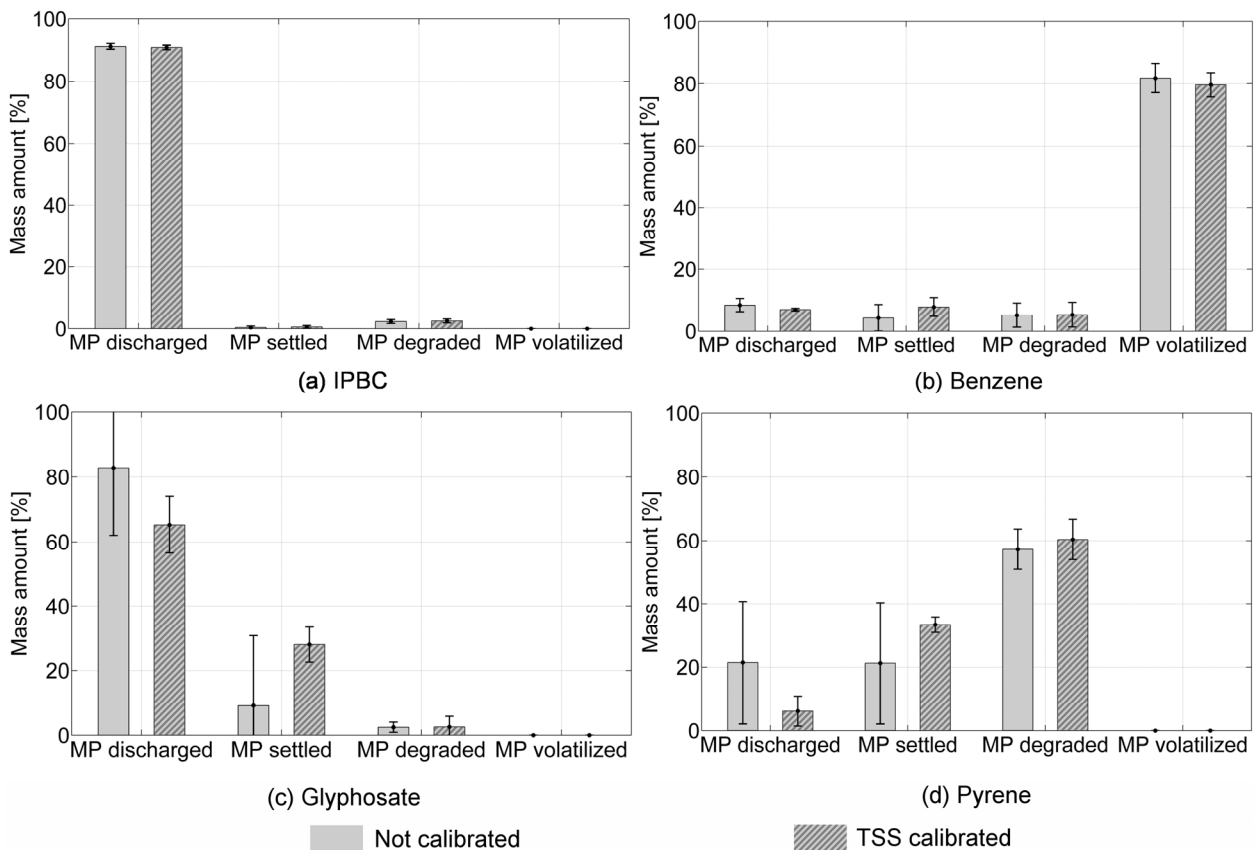
419 **3.4. Reduction of output uncertainty for the dynamic model**

420 The GSA results suggest that the calibration of the parameters related to TSS using
421 commonly available TSS measurements can result in a significant reduction of the variance
422 of calculated MP fluxes. Once the STUMP model is capable of simulating the TSS behaviour
423 in the system to a satisfactory degree, the uncertainty in the estimated MP fluxes is thus
424 reduced. This was tested by optimising the STUMP settling/resuspension parameters by
425 applying the pseudo-Bayesian GLUE methodology (Beven and Binley, 1992), which is
426 suitable for stormwater quality models (Freni et al., 2009a), i.e. for models where the level of
427 available information justifies a limited number of prior assumptions. The parameter sets
428 giving the best simulation of the available TSS data, with a root mean square error of 7.2
429 mg_{TSS}/l, were used to recalculate the fluxes for the four investigated MP. The resulting fluxes
430 are shown in Figure 5.

431
432 The substances with a higher tendency to sorb (i.e. glyphosate and pyrene) show a significant
433 reduction in the uncertainty of the simulated fluxes while the substances that are mostly
434 present in the soluble phase (i.e. benzene) or those that are not affected by important fate
435 process (i.e. IPBC) show a minor reduction, starting from a limited uncertainty in the original
436 results. A more realistic representation of TSS removal leads also to a modification of the
437 fraction of settled MP as calculated by EPI Suite and SimpleBox, and it consequently affects
438 the fraction discharged to the receiving waters (Figure 5c and 5d). These outcomes are a
439 consequence of the conceptual formulation of STUMP, as the majority of the MP fate process
440 is assumed to affect only the MP dissolved phase S_{MP} (Vezzaro et al., 2010). Consequently,
441 the optimisation of TSS predictions reduces the uncertainty in fate estimations for the
442 particulate fraction X_{MP} in the system without significantly affecting the uncertainty in the
443 fate of the dissolved fraction.

444
445 Compared to the general process description implemented in EPI Suite and SimpleBox, the
446 STUMP model has a more flexible structure that can be adapted to represent the physical
447 attributes and dynamic behaviour of the investigated pond or other stormwater treatment
448 systems and BMPs. This is important when the fate processes do not have sufficient time to
449 reach equilibrium conditions, as the process time scale is greater than the MP residence time
450 in the treatment system. As a lack of data often represents an obstacle in the simulation of
451 MP, STUMP only requires information that is commonly available such as BMP dimensions
452 and MP inherent properties, although it can also benefit from additional data such as flow

453 data and TSS measurements which can be used to reduce the uncertainty of the model
 454 predictions. The STUMP model is thus a useful compromise between lumped multimedia
 455 models used in chemical risk assessment and physically distributed deterministic models
 456 commonly used in urban drainage engineering. Combined with the integrated urban water
 457 cycle models, STUMP can be used to quantify the potential MP removal in stormwater BMPs
 458 as a basis for assessing strategies for reducing stormwater MP discharges from urban areas.
 459



460 **Figure 5.** Comparison of mass distributions by using the STUMP default parameter sets
 461 (light bars) and the parameters optimised for TSS predictions (dark bars). Values are
 462 expressed as mean \pm standard deviation.
 463
 464

465 4. Conclusions

466 This study shows how existing multimedia models can be used to estimate the potential fate
 467 and removal of organic MP in stormwater treatment systems. The three investigated models
 468 (EPI Suite, SimpleBox, and STUMP) were used to quantify the environmental distribution of
 469 four substances with different inherent properties (IPBC, benzene, glyphosate, and pyrene),
 470 showing how these models can be applied to simulate the fate of a broad range of organic
 471 stormwater MP with varying inherent properties. The use of multimedia models can provide a
 472 qualitative assessment to surrogate the information that would be provided by future field

473 observations regarding organic MP in stormwater treatment systems by employing existing or
474 easily obtainable data on system attributes and hydrology in combination with substance-
475 inherent properties about the MP in question.

476

477 The results suggest that conventional steady-state multimedia models (EPI Suite and
478 SimpleBox) do not appropriately represent the highly dynamic processes that take place in
479 stormwater treatment units. Dynamic models (like STUMP) can therefore yield a more
480 realistic estimation of MP distribution and fate in stormwater treatment systems than the
481 steady-state models typically employed in chemical risk assessment.

482

483 The Global Sensitivity Analysis performed on the dynamic model identified the parameters
484 linked to settling and resuspension of TSS as the most sensitive factors for the calculation of
485 the mass distribution in the simulated pond. This result stresses the importance of dynamic
486 processes (that are not implemented in steady-state models) on the estimation of MP fate in
487 stormwater treatment systems. The settling/resuspension parameters were then estimated
488 based on TSS measurements, leading to a reduction in the uncertainty of the results for the
489 organic MP with high tendency to sorb to particles (glyphosate and pyrene). A reduction of
490 uncertainty for TSS prediction can thus substitute the need for extensive on-site MP
491 measurements and contribute to reduce the uncertainty of MP fate estimation.

492

493 Generally, this study illustrates a favourable approach to realistically model the potential
494 removal of stormwater MP in stormwater BMPs by using dynamic multimedia models. These
495 can quantify the environmental distribution of MP based on substance-inherent properties.
496 They should also utilize the available field observations for typical macro pollutants for
497 calibration and reduction of model output uncertainty. This approach provides support to
498 urban water managers in the elaboration of MP pollution control strategies by integrating the
499 limited data that will be provided by future extensive and complex monitoring campaigns
500 targeting the wide range of specific organic MP found in stormwater runoff.

501

502

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513
514

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755

756 **A. Appendix**

757 Detailed results of the application of the three models

758 **Table A1.** Comparison of estimated environmental distribution of simulated substances.

Substance	Compartment	Mass distribution	Fluxes distribution (%)	
		(%)	SimpleBox	STUMP ^a
		EPI Suite		
IPBC	Air	$9.84 \cdot 10^{-10}$	$1.77 \cdot 10^{-4}$	-
	Water	98.7	87.5	91.2±0.90
	Soil	$4.41 \cdot 10^{-5}$	-	-
	Sediments	1.28	0.47	0.39±0.50
	Degraded	? ^b	12.0	2.36±0.66
Benzene	Air	41.5	64.6	81.8±4.72
	Water	57.9	33.6	8.54±2.15
	Soil	0.12	-	-
	Sediments	0.54	0.06	4.35±4.34
	Degraded	? ^b	1.83	5.25±3.93
Glyphosate	Air	$5.19 \cdot 10^{-24}$	-	-
	Water	99.8	62.81	82.9±20.9
	Soil	$2.16 \cdot 10^{-13}$	-	-
	Sediments	0.188	14.7	9.19±21.6
	Degraded	? ^b	22.5	2.47±1.59
Pyrene	Air	$1.3 \cdot 10^{-2}$	20.7	-
	Water	16.5	49.0	27.9±21.0
	Soil	$2.81 \cdot 10^{-2}$	-	-
	Sediments	83.4	17.6	25.5±22.5
	Degraded	? ^b	12.8	45.7±9.57

759 ^a Expressed as mean±standard deviation, ^b EPI Suite does not provide the fraction of
760 degraded substance during the simulation

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