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Modelling the fate of organic micropollutants in stormwater ponds

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

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

1. Introduction

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

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

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

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

The primary aim of this study is to document how the potential fate of organic MP in stormwater treatment systems can be quantified using multimedia fate models. The dynamic STUMP model and the two steady-state models EPI Suite and SimpleBox are compared focusing on the quantification of fate for selected substances representing a wide range of inherent properties (and uses/releases) in order to ensure that the results can be extended to other relevant stormwater pollutants. The secondary aim of the study is to identify the major model factors affecting the results of the dynamic model and to use this information to reduce the result uncertainty. This is obtained by performing a Global Sensitivity Analysis (GSA) on the dynamic model, which was preferred to steady-state models for its flexibility, the possibility of simulating the highly dynamic processes taking place in stormwater treatment systems, and the possibility of using non-MP measurements (flow, TSS) for uncertainty assessment. The GSA results provide the basis for the reduction of the uncertainty in MP fate.

2. Material and methods

2.1 The Lilla Essingen case study.

MP fate was calculated for a stormwater retention pond located in Lilla Essingen, Stockholm (Sweden). The pond is the first part of a treatment train used to treat highway runoff from a 1.2 ha catchment before secondary treatment by filtering with several sorbent materials and discharge to a receiving water body. The pond has a permanent volume of about 150 m^3, a maximum storage volume of 200 m^3 with an emptying time needed to restore dry-period conditions of about 69 h (see Stockholm Vatten (2006) for more details).
The available flow and water quality measurements covered the period between March 2004 and May 2005. Composite samples were taken with a flow-proportional sampler at the pond inlet (9 samples) and outlet (28 samples). The time interval covered by the each composite sample varied from 2.7 to 16 days for the inlet and 0.8 to 17 days for the outlet. A wide range of water quality parameters was quantified (TSS, organic matter, selected polycyclic aromatic hydrocarbons and metals), with measured TSS ranging between 15 and 13000 mg/l at the inlet (with median 220 mg/l) and between 2 and 110 mg/l (with median 19 mg/l) at the outlet. The Lilla Essingen system thus represents a typical situation where stormwater flow and select, scarce water quality measurements are available, and hence where the potential removal of most organic MP needs to be estimated through the application of a model.

2.2. MP fate models

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

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

Table 1. Comparison of EPI Suite, SimpleBox and STUMP models used to estimate organic 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

[a] calculated for each compartment as the product of the substance compartmental concentration *C* and a fugacity capacity constant *Z* (calculated from the substance's inherent properties); [b] mass transfer coefficients between the environmental compartments are dimensionally consistent with the majority of measured values (e.g. as $mol \cdot s^{-1}$ as opposed to $mol \cdot hr^{-1} Pa^{-1}$ in the fugacity based model).

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

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

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

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]	$5 \cdot 10^8$	22.5	10.5 [b]
Soil	Depth [m]	0.2	0.05	-
	Volume [m^3]	$1.8 \cdot 10^{10}$	477.5	-
Water	Depth [m]	20	1.5	1 [c]
	Residence time [hr]	-	69	-
	Volume [m^3]	$2 \cdot 10^{11}$	300	150 [c]

[a] Default settings; [b] Average value during simulation period; [c] Conditions during dry weather.

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

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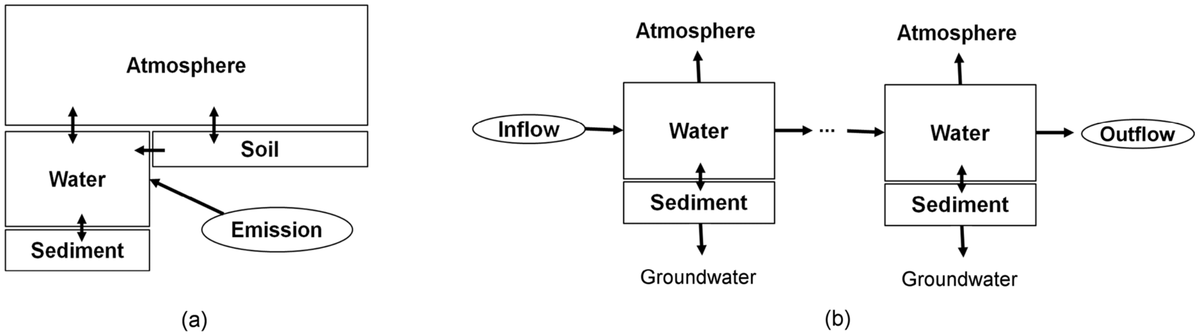

Figure 1. Environmental compartments in the three analysed models: EPI Suite and SimpleBox (a), and STUMP (b).

2.3. Modelled substances

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

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]	$2.57 \cdot 10^{-5}$	94.8	$2.89 \cdot 10^{-10}$	$4.5 \cdot 10^{-6}$
Water solubility [mg/l]	168	1790	12000	0.135
Dimensionless Henry's law constant	$1.2 \cdot 10^{-7}$ [e]	$2.26 \cdot 10^{-1}$	$8.6 \cdot 10^{-11}$ [e]	$4.87 \cdot 10^{-4}$ [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

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

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Table 4. Intervals for relevant model factors used in the simulations.

	Parameter	Description	Sampling Interval [a]			
Factors (not related to MP)	C^*_{TSS}	Background 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 [l]	[2;28]	[1.85;130]	[238-630]
	$DT_{50,anorb}$	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 [l]	not available [l]	not degraded [l]
	$DT_{50,pho}$	Photodegradation half-life [h]	not degraded [l]	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]

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

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

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

2.4. Identification of sensitive factors in the dynamic model

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

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

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

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

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

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

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3. Results and discussion

3.1. STUMP hydraulic submodel

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

3.2. Estimation of MP fluxes

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

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

The difference between the complex and dynamic settling/resuspension processes (also dependent on the inlet TSS concentration and sorption/desorption) in STUMP and the constant water-sediment fluxes in EPI Suite and SimpleBox explains the different results obtained in the estimation of the settled fraction of MP. In STUMP, settling is in fact reduced during high flow conditions and a part of the settleable fraction can be discharged to the receiving waters. Another cause of disagreement between the models (e.g. on the degradation of pyrene) is the degradation rates used by EPI Suite and SimpleBox that are estimated by QSAR relationships while STUMP uses measured rates.

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

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

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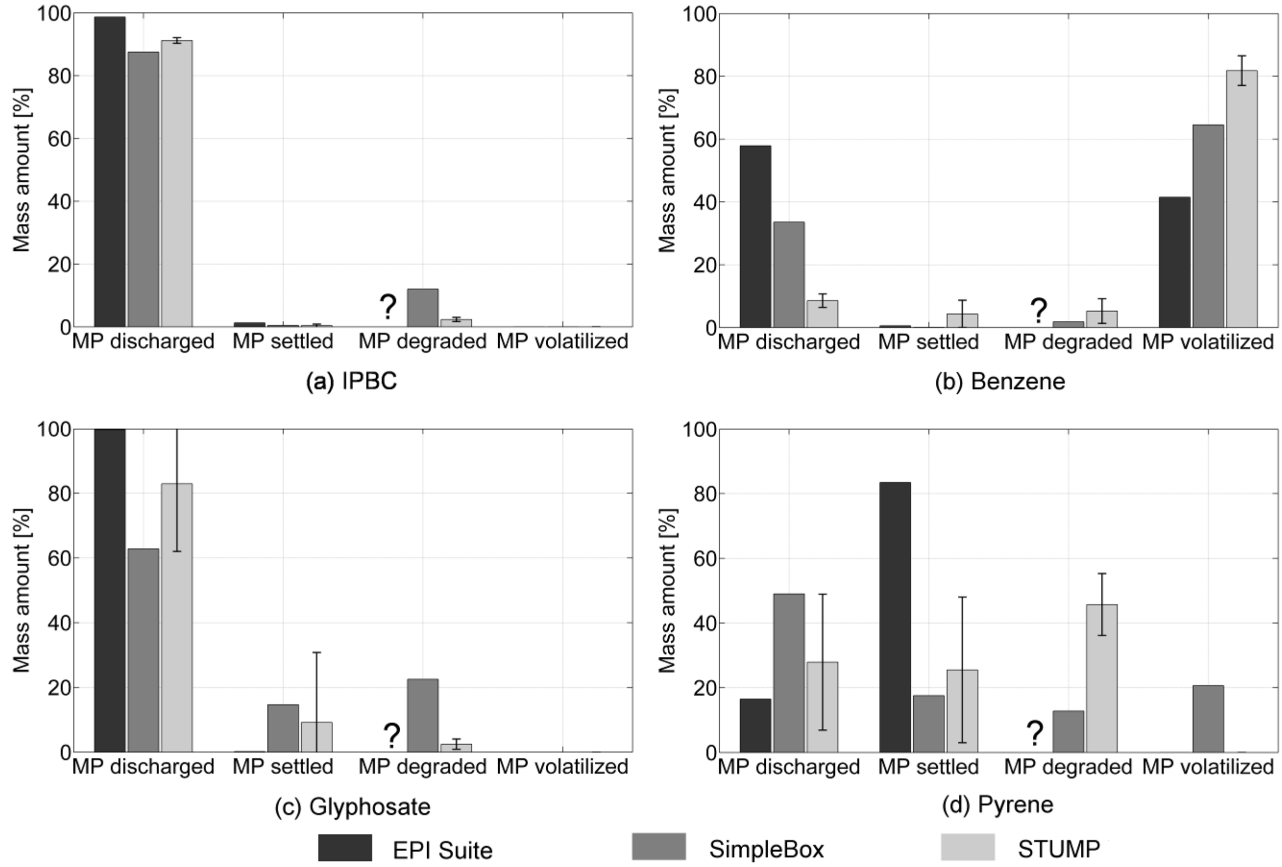

Figure 2. Mass distribution calculated by using the three models. STUMP results are expressed as mean ± standard deviation (calculated as part of the GSA).

3.3. Identification of sensitive factors in the dynamic model

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

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

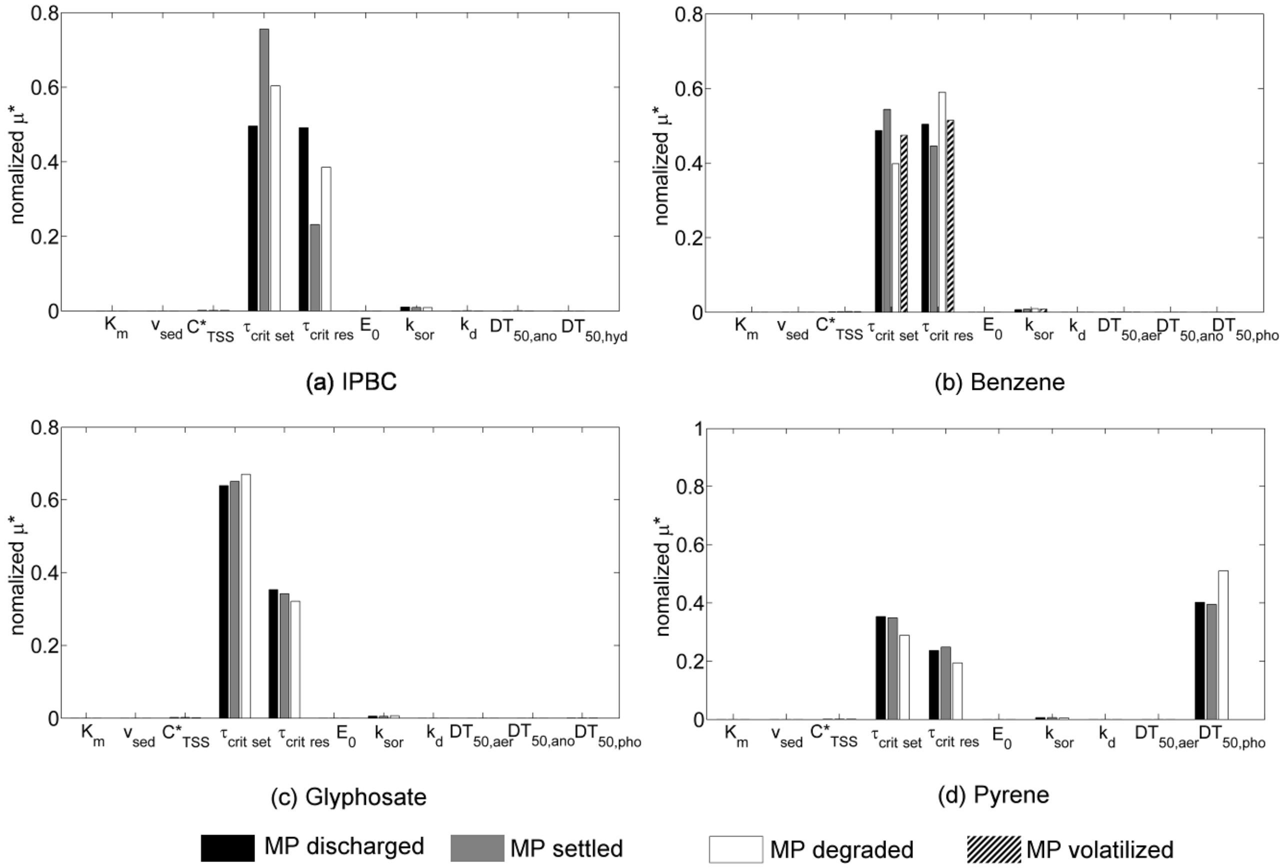

Figure 3. Normalised elementary effects for STUMP fate process parameters (the parameters are described in Table 4 and in Vezzaro et al. (2010)).

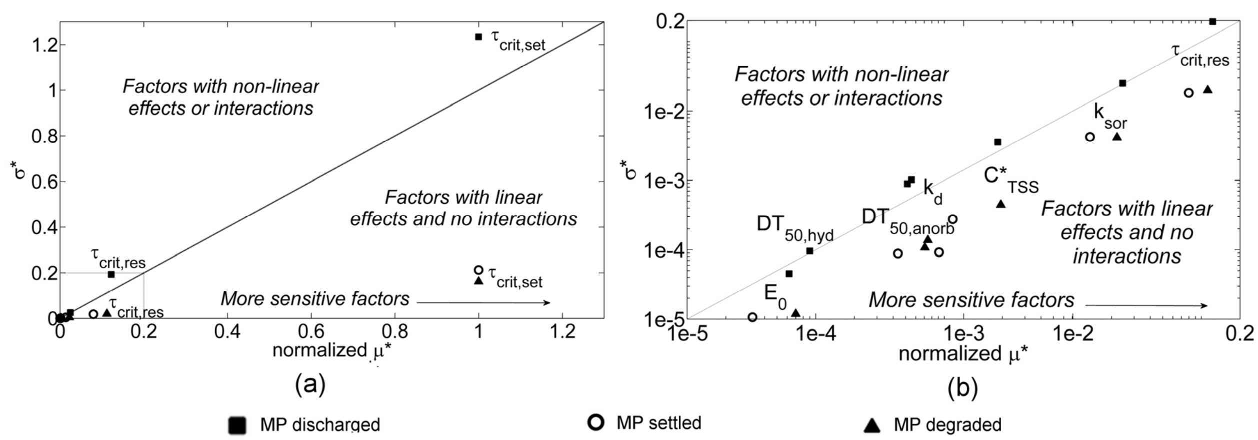

Figure 4. Estimated mean and standard deviation for elementary effects of IPBC (a) and an enlargement of the factors (b). The parameters are described in Table 4 and in Vezzaro et al. (2010).

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

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	$3.66 \cdot 10^{-3}$	$1.12 \cdot 10^{-3}$	$3.97 \cdot 10^{-3}$	$1.26 \cdot 10^{-3}$
$DT_{50,anorb}$	$3.12 \cdot 10^{-3}$	$6.94 \cdot 10^{-4}$	$2.66 \cdot 10^{-3}$	$6.04 \cdot 10^{-4}$
$DT_{50,hydr}$	$4.98 \cdot 10^{-4}$	$8.80 \cdot 10^{-5}$	$4.87 \cdot 10^{-4}$	$1.06 \cdot 10^{-4}$

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

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

3.4. Reduction of output uncertainty for the dynamic model

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

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

Compared to the general process description implemented in EPI Suite and SimpleBox, the STUMP model has a more flexible structure that can be adapted to represent the physical attributes and dynamic behaviour of the investigated pond or other stormwater treatment systems and BMPs. This is important when the fate processes do not have sufficient time to reach equilibrium conditions, as the process time scale is greater than the MP residence time in the treatment system. As a lack of data often represents an obstacle in the simulation of MP, STUMP only requires information that is commonly available such as BMP dimensions and MP inherent properties, although it can also benefit from additional data such as flow data and TSS measurements which can be used to reduce the uncertainty of the model predictions. The STUMP model is thus a useful compromise between lumped multimedia models used in chemical risk assessment and physically distributed deterministic models commonly used in urban drainage engineering. Combined with the integrated urban water cycle models, STUMP can be used to quantify the potential MP removal in stormwater BMPs as a basis for assessing strategies for reducing stormwater MP discharges from urban areas.

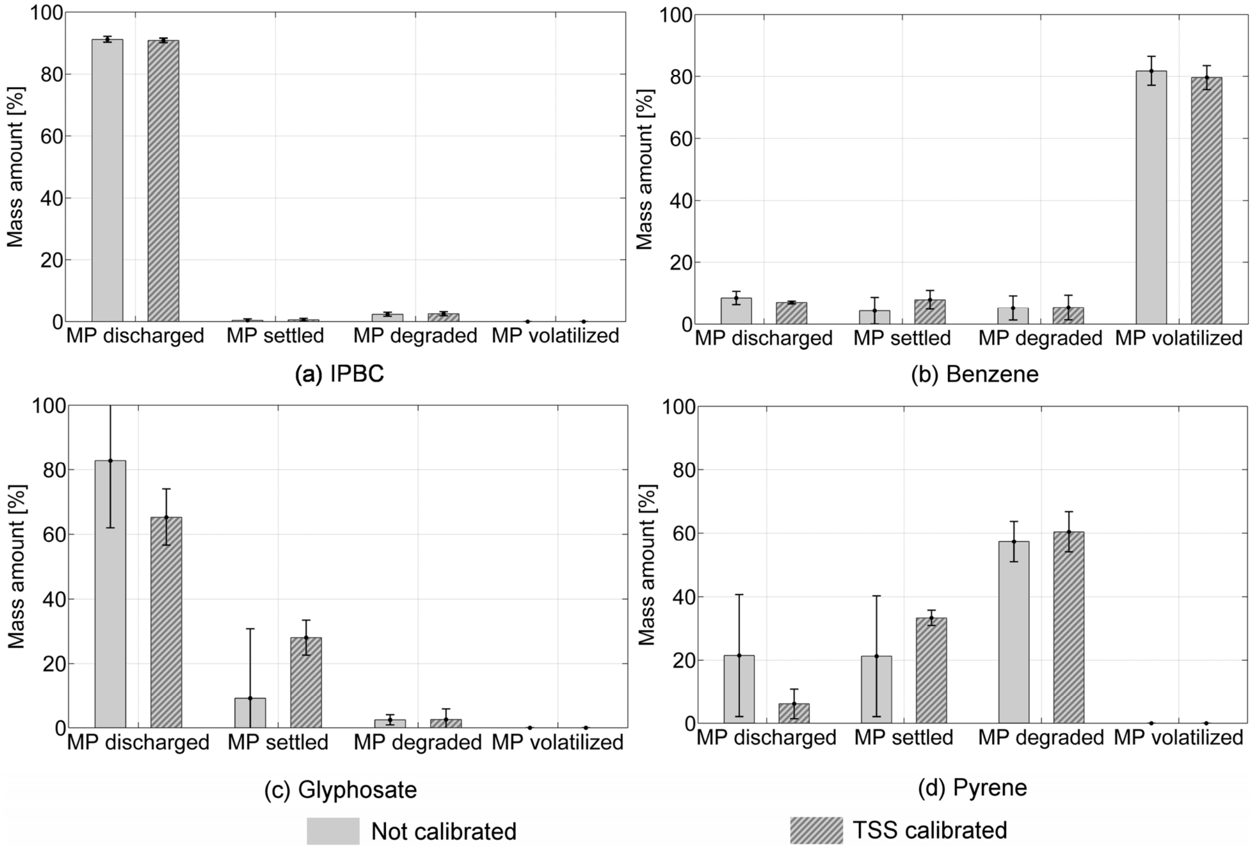

Figure 5. Comparison of mass distributions by using the STUMP default parameter sets (light bars) and the parameters optimised for TSS predictions (dark bars). Values are expressed as mean ± standard deviation.

4. Conclusions

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

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

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

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

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

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A. Appendix

Detailed results of the application of the three models

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

Substance	Compartment	Mass distribution (%)	Fluxes distribution (%)	
		EPI Suite	SimpleBox	STUMP [a]
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

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

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