Model-based screening for critical wet-weather discharges related to micropollutants from urban areas

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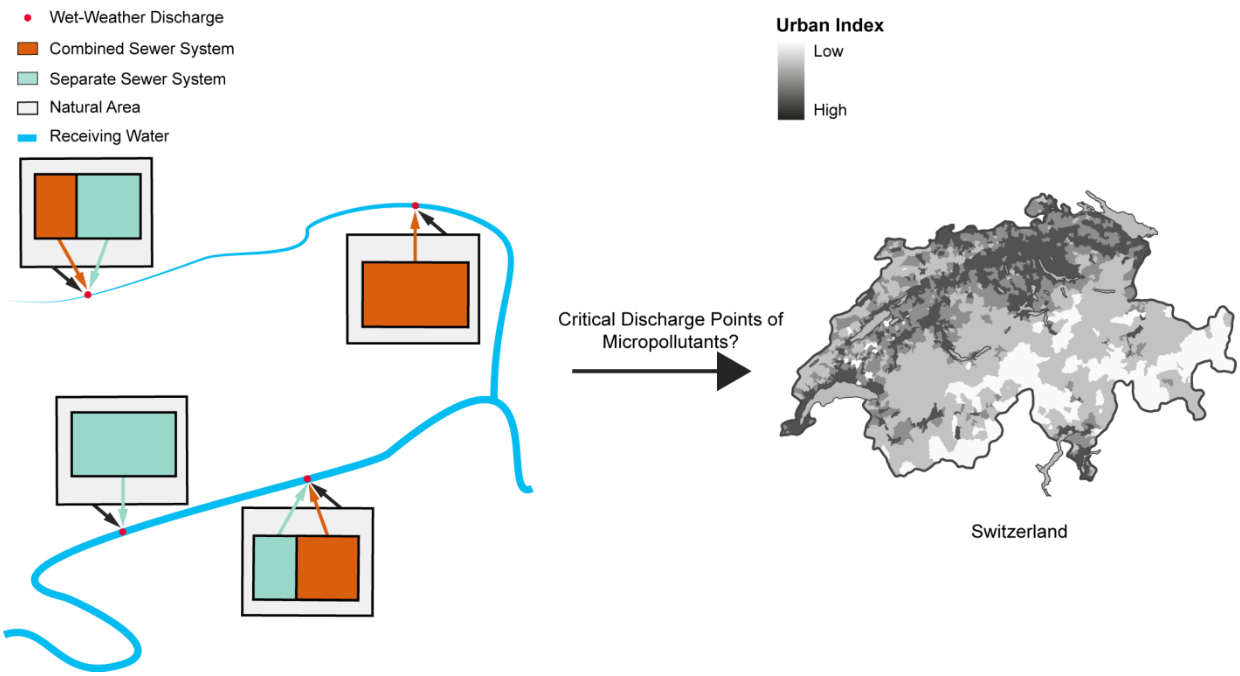
Graphical Abstract



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Abstract

Wet-weather discharges contribute to anthropogenic micropollutant loads entering the aquatic environment. Thousands of wet-weather discharges exist in Swiss sewer systems, and we do not have the capacity to monitor them all. We consequently propose a model-based approach designed to identify critical discharge points in order to support effective monitoring. We applied a dynamic substance flow model to four substances representing different entry routes: indoor (Triclosan, Mecoprop, Copper) as well as rainfall-mobilized (Glyphosate, Mecoprop, Copper) inputs. The accumulation on different urban land-use surfaces in dry weather and subsequent substance-specific wash-off is taken into account. For evaluation, we use a conservative screening approach to detect critical discharge points. This approach considers only local dilution generated onsite from natural unpolluted areas, i.e. excluding upstream dilution. Despite our conservative assumptions, we find that the environmental quality standards for Glyphosate and Mecoprop are not exceeded during any 10-minute time interval over a representative one-year simulation period for all 2,500 Swiss municipalities. In contrast, the environmental quality standard is exceeded during at least 20% of the discharge time at 83% of all modelled discharge points for Copper and at 71% for Triclosan. For Copper, this corresponds to a total median duration of approximately two weeks per year. In general, stormwater outlets contribute more to the calculated effect than combined sewer overflows for rainfall-mobilized substances. We further evaluate the Urban Index ($A_{urban,impervious}/A_{natural}$) as a proxy for critical discharge points: catchments where Triclosan and Copper exceed the corresponding environmental quality standard often have an Urban Index >0.03. A dynamic substance flow analysis allows us to identify the most critical discharge points to be prioritized for more detailed analyses and monitoring. This forms a basis for the efficient mitigation of pollution.

Keywords

Combined system; effect assessment; runoff quality modelling; separate system; Toxic Units; urban catchment

Abbreviations

CSO	Combined Sewer Overflow
dSFA	dynamic Substance Flow Analysis
EQS	Environmental Quality Standard
ha	hectare of impervious surface
STP	Sewage Treatment Plant
SWO	Stormwater Outlet
TU	Toxic Unit

1 Introduction

A variety of substances such as pharmaceuticals, personal care products and pesticides are used daily in urban areas. They are discharged into the environment via sewage treatment plants (STP), stormwater outlets (SWO) in separate stormwater systems and combined sewer overflows (CSO) in combined sewer systems. The occurrence of these anthropogenic substances was reported in concentration ranges of µg/l or ng/l – hence subsequently referred to as micropollutants – in rivers during or after rainfall events (e.g. Gasperi et al. 2014, Madoux-Humery et al. 2013, Musolff et al. 2010, Weyrauch et al. 2010). Urban sources of these micropollutants can be divided into two main groups: substances contained in dry-weather flow, subsequently referred to as *indoor* substances, and *rainfall-mobilized* substances from outdoor surfaces. Indoor substances are found in dry weather flows and are mainly discharged via STP (Phillips et al. 2012), whereas rainfall-mobilized substances are washed-off during rain events and can therefore make a greater contribution to wet-weather discharges (WWD, i.e. CSO and SWO). For example, concentrations of three pesticides (Diuron, Isoproturon and Glyphosate) were 5 – 20 times higher in CSO discharges compared to dry weather flows in the city of Paris (Gasperi et al. 2012a). Overall, wet-weather discharges can be important contributors to the micropollutant loads found in the aquatic environment (e.g. Brix et al. 2010, Gasperi et al. 2008, 2011, Meyer et al. 2011).

Pesticides (for plant protection purposes) and biocides (for non-plant protection use) (SR-813.12 2005) may be particularly harmful to the aquatic environment. Some of these substances originate solely from urban areas, e.g. Terbutryn used as a biocide in building materials to prevent growth of unwanted organisms (Burkhardt et al. 2007, Coutu et al. 2012). Other substances such as Glyphosate occur in the runoff from agricultural fields as well as in urban gardening (Burkhardt et al. 2007, Hanke et al. 2010, Wittmer et al. 2010). Glyphosate was implicated as being ‘probably carcinogenic’ to humans (WHO 2015), and a study by Hanke et al. (2010) showed that as much as 60% of the Glyphosate of a catchment can originate from urban systems. In addition, pesticide emission loads from urban areas were found to be in the same range as emissions from agriculture (Blanchoud et al. 2007, Wittmer 2010).

Concentration measurements are the most important information for assessing the effects of wet-weather discharges on receiving waters. However, in the absence of flow (load) and specific land-use data, the transferability of concentrations to other sites is low. In view of the high land-use diversity on small scales, it is challenging, if not impossible, to identify and describe a single typical, representative discharge. Furthermore, as for example in Switzerland, there is often a vast number of uncounted wet-weather discharge points, with very limited or no systematically collected information available on location and operation characteristics. In addition, it is resource and time-consuming to measure wet-weather discharges accurately, since emission concentrations vary temporally with rainfall intensity and spatially with land use (e.g. Gasperi et al. 2014, Madoux-Humery et al. 2013). A model-based screening tool designed to facilitate the comparison of different sewer systems, catchments and pollutants of wet-weather discharge points is consequently crucial for decision-makers.

A substance flow analysis (SFA) based on the concept of mass balances within defined system boundaries is an effective method to calculate loads entering the water cycle (Bader and Scheidegger 2012). An SFA was applied in Lausanne to determine Copper and pharmaceutical loads discharged into a lake (Chèvre et al. 2013, Chèvre et al. 2011). We apply the SFA concept to all Swiss municipalities and additionally consider the dynamic accumulation and wash-off behaviour of the rainfall-mobilized substances, as was done for micropollutants from facades, for example (Coutu et al. 2012, Wittmer et al. 2011). This dynamic substance flow analysis (dSFA) allows us to calculate discharge concentrations at high temporal resolution.

In this study, we aim to answer the following three questions:

i. How can we screen for potentially critical wet-weather discharge points?
ii. How do SWO and CSO compare with regard to discharged micropollutants?
iii. Can we find a proxy – available area-wide on a national/regional scale – to highlight critical wet-weather discharges?

2 Methods

2.1 System description and boundaries

The dSFA was carried out for entire Switzerland (41,285km^2) at municipal level, i.e. 2,500 administrative regions (median area 748ha, 95%-interquantile range 138 to 5,889ha; median number of inhabitants 1,170, 95%-interquantile range 106 to 10,5950 inhabitants). Wet-weather discharge points were aggregated to one location (for CSO and SWO individually) per municipality. Municipalities were selected as catchment boundaries in order to have a realistic data set representing the variability of urban areas and their sewer systems. Aggregation at municipal level was found to be suitable because most urban sewer systems, corresponding STPs and wet-weather discharges are autonomous within a municipality. Ten-minute intervals were chosen as a temporal resolution for modelling, corresponding to the potentially short duration of wet-weather discharges. In order to quantify the effect of wet-weather discharges in a conservative way, the following two conditions were set:

i. The maximum tolerable discharge load is limited to the environmental quality standard (EQS) at the corresponding flow in the receiving water during wet-weather discharges. This requirement is in line with the Clean Water Act (EPA 1972) of the United States as well as the relevant Swiss regulations (WPO 1998).

ii. Unused "capacity" from upstream must not be filled up. Thus, unpolluted runoff from lightly populated areas upstream should not compensate local emission hotspots further downstream.

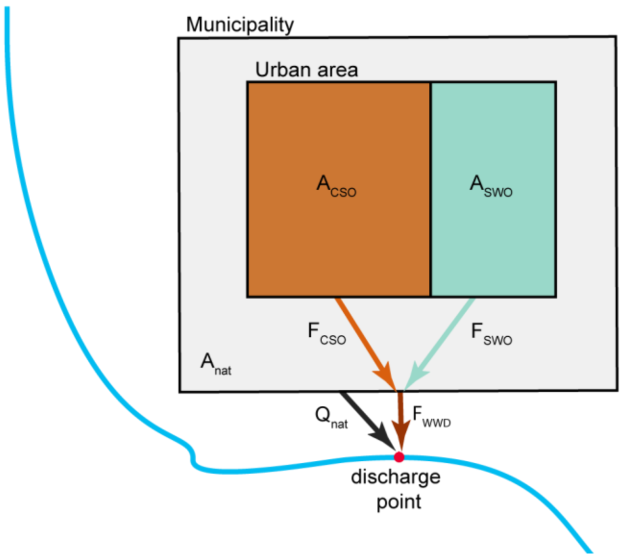

Figure 1. Schematic representation of the mass fluxes in one municipality. The wet-weather discharge from the municipality FWWD(t) (= FCSO(t) + FSWO(t)) is locally diluted by the natural flow Qnat (= qnat · Anat). The flow in the receiving upstream water is not taken into account in order not to use upstream capacity (local dilution potential).

In order to meet these two conditions, each municipality is considered to be "self-sustaining". This means that the clean runoff from natural areas (A_{nat}), generated locally within each municipality, must be sufficient so that urban wet-weather discharges do not lead to the EQS being exceeded (Figure 1). As long as this condition is fulfilled locally, wet-weather discharges are not anticipated to cause any detrimental effects in all water bodies. Subsequently, the ratio of locally generated clean runoff (q_{nat}) and wet-weather discharge flow (q_{WWD}) is referred to as the *local dilution potential*, and the effect assessment (exceeding the EQS) as the *local effect potential*. The implications of considering only the local dilution potential for the effect assessment are further discussed in Section 2.3.7.

Consequently, the maximum tolerable load (F_{EQS}) needs to be greater than the total load from all wet-weather discharges draining a municipality (F_{WWD}) as shown in Eq. 1. F_{EQS} is calculated as the sum of the flow from the local natural catchment and the flow from wet-weather discharges multiplied with a concentration equal to the EQS. In this study, the local contribution to river flows q_{nat} is set to 0.32 L/s/ha, which is the average specific natural runoff in Switzerland (Hades 1990). This average was used because urban runoff potentially reacts much faster to rainfall than rivers sourced from natural surfaces and groundwater.

$$\sum F_{WWD,i}(t) < F_{EQS}(t) \quad (1)$$

$$\sum A_{urb,imp,i} \cdot q_{WWD,i}(t) \cdot c_{\mathrm{WWD},i}(t) < \left(A_{urb,imp} \cdot q_{WWD}(t) + A_{nat} \cdot q_{nat}\right) \cdot EQS \quad (2)$$

with

F_{EQS}	M/T	Maximum tolerable load meeting conditions i and ii
F_{WWD}	M/T	Load from wet-weather discharges
A_{nat}	(ha)	Natural, non-urbanized area
$A_{urb,imp}$	(ha)	Impervious urban area
q_{WWD}	(L/s/ha)	Wet-weather discharge from urban catchment
q_{nat}	(L/s/ha)	Average specific flow from natural (non-urbanized) areas (= 0.32 average for Switzerland (Hades 1990))
EQS	(µg/L)	Environmental Quality Standard
c_{WWD}	(µg/L)	Concentration in the stormwater / combined sewage matrix
i		Index over all wet-weather discharge points in the area (here i = 1)

2.2 Dynamic substance flow analysis

Model structure

The dSFA model consists of two modules: (i) the flow compartment which calculates runoff formation, overland and pipe flow. This part is based on REBEKA (Rossi et al. 2005) implemented in the R software (R Core Team 2010) by Daebel and Gujer (2005). (ii) the pollutant transport module which considers wastewater loads (households, minor industry) and the release of pollutant loads from surfaces. Additional effects, e.g. sedimentation of particulate matter in the modelled storage tanks, were not included. Details of the equations are enclosed in the supporting information (SI). In summary, the pollutant transport module exhibits the following properties:

i. compound-specific release rates (seasonal or constant application)
ii. pollutant accumulation and wash-off for each source, land-use and substance

As measured data about loads and concentrations of micropollutants is scarce, parameterization and input loads were taken from the literature. Parameter sets are included in the SI (Table C4-C6). Input data, i.e. description of the catchment and sewer systems, rainfall and the pollutant sources used to run the model is also listed in the SI. The dSFA was set up in the software R (R Core Team 2010). The discharge point into the receiving water body was calculated on the basis of a digital elevation model and located either at a STP or at a surface water body at the lowest point of the municipality.

Substances

Four micropollutants were selected to exemplify different pathways from urban settlements towards wet-weather discharges and the environment. Each substance combines a distinct set of sources (Table 1): (i) Triclosan, an antibacterial agent used in personal care products, (ii) Glyphosate, a pesticide used for plant protection, (iii) Mecoprop, used for both plant and material protection purposes, and (iv) total Copper, a heavy metal originating from all the urban sources considered. The potential sedimentation and remobilization of particulate fractions of these substances was not taken into account in the screening procedure.

Table 1. Urban sources of selected micropollutants. The reported $LogK_{ow}$ and $LogK_{oc}$ for organic compounds are given as a reference only. Total concentrations (dissolved and particulate) were used in the dSFA for comparison with the EQS irrespective of speciation.

Substance	Log Kow[1]	Log Koc[1]	Household	Building	Street	Garden
Triclosan	4.76	4.26	●			
Glyphosate	-4.00	1.27				●
Mecoprop	3.20	1.69	●	●		●
Copper	-	-	●	●	●	●

[1]www.chemspider.com

Table C.3 in the SI summarizes the approaches used to determine the emission potential (EP), accumulation and wash-off behaviour for each of the four substances. The selected set of parameters is detailed in the SI (Table C.4 to Table C.6).

Loss via wet-weather discharges

We express the loss via wet-weather discharges into the environment as the ratio of the substance load via wet-weather discharges to the total substance load entering the sewer system. For separate stormwater systems in Switzerland, this ratio corresponds to the fraction of a sub-area which is drained by stormwater sewers because treatment systems or storage tanks are rarely found in separate stormwater systems.

2.3 Effect assessment

With the dSFA described above, the concentration $c_{WWD}(t)$ in the stormwater in the combined sewage matrix and the wet-weather discharge $q_{WWD}(t)$ are determined for each time step (Δt=10min) for all 2,500 municipalities. Rearranging Eq. 2 leads to Eq. 3.

$$\frac{c_{WWD}(t)}{EQS} < \frac{A_{nat}}{A_{urb,imp}} \cdot \frac{q_{nat}}{q_{WWD}(t)} + 1 \qquad (3)$$

Based on Eq. 3, we define $\omega(t)$ as a single indicator variable (Eq. 4). Thus a value of $\omega \leq 1$ is of particular interest, indicating that the local dilution potential is sufficient to prevent the EQS being exceeded without the need to rely on (unpolluted) flows from upstream (condition Eq. 1). An $\omega > 1$ implies that the local dilution is insufficient. Whether the EQS is violated in reality depends on upstream pollutants loads ($\omega \leq 1$) and unused upstream capacity ($\omega > 1$).

$$\omega(t) \equiv \frac{\frac{c_{WWD}(t)}{EQS}}{\frac{A_{nat}}{A_{urb,imp}} \cdot \frac{q_{nat}}{q_{WWD}(t)} + 1} \qquad (4)$$

This is particularly applicable to small creeks, where additional water sources are rarely available. Based on a one-year time series of discharge and concentration, we calculate $\omega(t)$ according to Eq. 4 for each municipality *i* (Figure 2A) and the corresponding cumulative frequency distribution of ω (Figure 2B). From the latter, we derive the cumulative frequency distribution $p(\omega < 1)$ over all 2,500 municipalities (=100% on the y-axis), which describes the fraction of discharge time without the EQS being exceeded (Figure 2C).

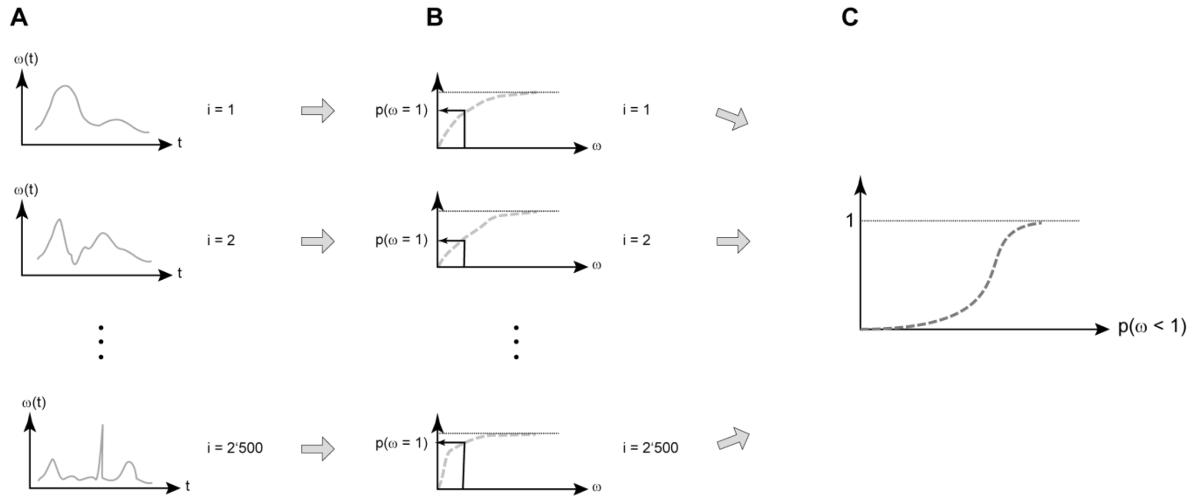

Figure 2. Schematic representation of evaluation procedure. A) Time series ω(t) for each municipality i (simulation period one year). B) Cumulative frequency distribution of ω per municipality. C) Cumulative frequency distribution which shows on the y-axis fraction of municipalities (all municipalities = 100%) and on the x-axis the fraction of discharge time with no EQS exceedance p(ω<1).

To appropriately incorporate the extended periods of sub-lethal concentrations and the concentration dynamics obtained with the dSFA model, the concept of Toxic Units (Liess and von der Ohe 2005) was modified towards:

$$TU_{mun} = \sum_t \omega(t) \cdot \Delta t = \sum_t \frac{c_j(t)}{EQS} \cdot \Delta t \tag{5}$$

Where

TU_{mun}	-	Toxic Unit per municipality
cj	(µg/L)	Substance concentration in recipient after wet-weather discharge and local dilution with qnat
t		Time

The concentration c_j in the recipient is then determined, taking into account the wet-weather discharge load and subsequent local dilution. Since the time step is constant, Eq. 5 can be simplified without changing the effect ranking within the screening procedure. To facilitate the comparison between different sewer systems (CSO and SWO) as well as among different pollutants and thus pollutant sources, a national sum of TU_{mun} is used:

$$TU_{CH} = \sum_{mun} \sum_t \frac{c_j(t)}{EQS} \tag{6}$$

2.4 Urban Index

The idea of the Urban Index is to define and evaluate a simple proxy to assess the local dilution potential and critical locations for wet-weather discharges with minimal data requirements. For each time-step, the maximum tolerable load is reached when F_{EQS} and F_{WWD} are equal. Equation 2 then leads to the definition of the Urban Index θ as presented in Eq. 7.

$$\frac{\frac{q_{nat}}{q_{WWD}}}{\left(\frac{c_{WWD}}{EQS}-1\right)} = \frac{A_{urb,imp}}{A_{nat}} = \theta \qquad (7)$$

The Urban Index θ describes the fraction of urban, impervious area in the natural area of a municipal catchment. A high Urban Index indicates a high percentage of urban area and, consequently, a small local dilution potential. Hence, θ is a proxy for the local dilution potential, which is easily calculated for a catchment because data on impervious and natural areas is available on a national scale.

2.5 Environmental quality standards

Environmental quality standards are used to preclude negative effects of substances in the environment. Table 2 summarizes the prescriptive limits for the four substances used in this study and compares them to the EQS recently suggested in the literature. In this study, we use the annual average to assess the degree of exceeding the EQS in order to assure a sufficient safety margin in our conservative screening approach. Effects on speciation of the substances were not taken into account in the dSFA, since the total substance load was considered. Copper for example is transported up to 55% in particulate form in the sewer system (Houhou et al. 2009).

Table 2. Environmental Quality Standards (EQS) and prescriptive limits for receiving waters [in µg L^{-1}].

Substance	This study	AA-EQS[d)]	MAC-EQS [d)]	WPO[b)]	Literature
Triclosan	0.02	0.02[a)]	0.02[a)]	-	
Glyphosate	108	108 [a)]	300 [a)]	0.1	11-196 [c)]
Mecoprop	3.6	3.6 [a)]	187 [a)]	0.1	0.1-11 [c)]
Copper (total)	5 [b)]			5	

[a)] Oekotoxzentrum (2014) [b)] Waters Protection Ordinance WPO (1998), [c)] Junghans and Kase (2012) [d)] AA: annual average, MAC: maximum allowable concentration

3 Results and discussion

3.1 Emission Loads: Substance comparison

In the following section, the discharged emission loads of the dSFA model are compared for the four substances.

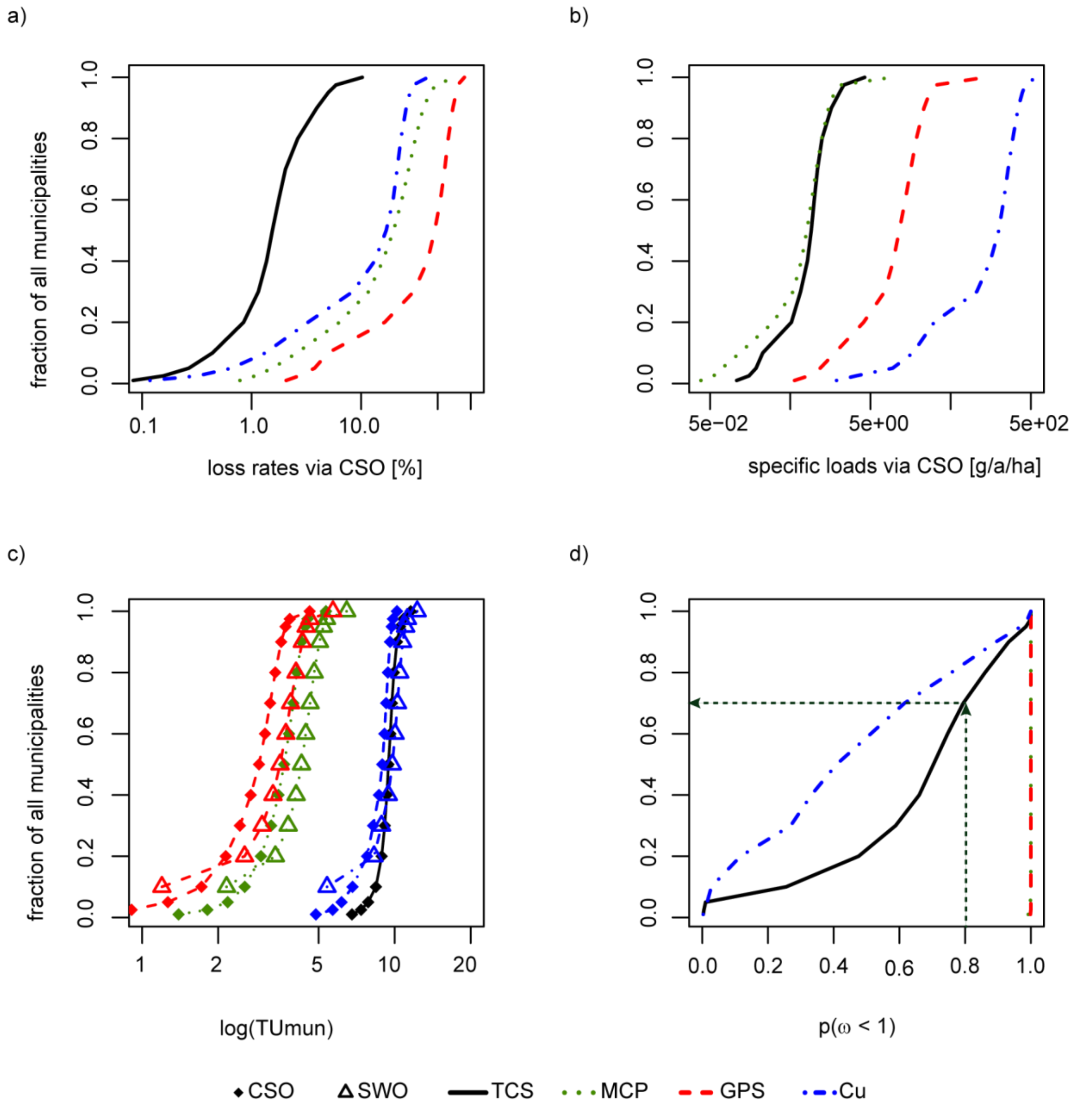

Figure 3. Cumulative probability distributions of all Swiss municipalities for Triclosan (TCS), Mecoprop (MCP), Glyphosate (GPS) and Copper (Cu) for combined sewer overflows (CSO) and stormwater outlets (SWO) with respect to a) loss via CSO [%], b) specific loads via CSO [kg/ha/a], c) logTU_{mun}, d) the fraction p(ω<1) of the time during which a discharge point meets the EQS criteria. Reading example (dashed arrows) for Triclosan: 71% of the municipal CSO exceed the EQS in at least 20% of the discharge time.

Our model calculations show that CSO are active 2.7% (median) of the year and SWO in 8.9% (median) of the year. Triclosan (only CSO), Mecoprop and Copper show a similar pattern to the discharged flow: this means that if there is a discharge, the substance is present. This is due to the underlying processes, with substance loads occurring in dry-weather flow or being washed-off depending on the rain intensity. Glyphosate, on the other hand, is modelled as source-limited. Source-limited substances show distinctive first flush behaviour (e.g. Cristina and Sansalone 2003). If a substantial part of the load is transported at the beginning of the runoff event, storage units in combined systems become more effective. Thus, Glyphosate is discharged via CSO in 0.9% (median) of the year and via SWO in 2.1% (median).

When evaluating all 2,500 municipalities, the distribution of loss rates via CSO reveals the following: Triclosan, contained in dry-weather flow, shows a median loss rate of 1.5% (Figure 3a). In contrast, a median loss of 47% via CSO was calculated for Glyphosate, a rainfall-mobilized substance. For Copper and Mecoprop, originating from indoor and rainfall-mobilized sources, the median loss via CSO was found to be 16.9% and 19.8% respectively.

Triclosan. We compared the calculated loss rates for Triclosan with a median of 1.5% (95%-interquantile range of 0.4% to 3.9%) with the loss rates for Caffeine found in the literature, as both substances originate solely from indoor sources. A mass balance for Caffeine in a specific municipality revealed that 4.4% of the annual load in sewer systems is emitted by CSO (Buerge et al. (2006)). Similar calculations were carried out for Caffeine loads measured in the Rhine at Basel, draining about two thirds of entire Switzerland, showing a median loss rate of 3.2% (95%-interquantile range of 1.1 to 5.4%; Staufer and Ort (2011)).

Mecoprop. Just 42% of the total Mecoprop load enters the sewer system due to rainfall mobilization (Table D.7 in SI). Hence, SWO and CSO are relevant Mecoprop sources during wet weather. The total sum of 104kg a^{-1} emitted via wet-weather discharges consists of 55kg a^{-1} from CSO (Table 3). Our modelled Mecoprop emission loads can be compared for a specific municipality (Grueningen), where monitoring data for the period April – November 2007 was available (Wittmer 2010). This study estimated that a total Mecoprop load of 49g a^{-1} is emitted via CSO in the monitoring period; this is of a similar order to our result of 30g a^{-1}.

Glyphosate. The comparison with the results of Wittmer et al. (2010) for Glyphosate shows an overestimation of the discharged load by a factor of five. Wittmer et al. (2010) estimated a discharge load of 84.5g a^{-1}, whereas the dSFA indicated a value of 427g a^{-1}. Glyphosate is modelled as a substance originating almost exclusively from gardens. Of the total flux of 110,000kg a^{-1} used by households and public entities as a herbicide (Wittwer and Gubser 2010), 2,081kg a^{-1} (2%) is estimated to enter a sewer system (Table 3). This is the same magnitude as for agricultural herbicides, for which loss rates in the range of 0.4 to 3.5% were reported from pervious areas (Singer et al. 2005).

Table 3. National load balance for input into sewer system, load to sewage treatment plant (STP), discharge via CSO and SWO

		Triclosan	**Glyphosate**	**Mecoprop**	**Copper**
Loads [kg a^{-1}]	Sewer input	5,113	2,081	347	117,309
	CSO	77.5	786	55	15,422
	SWO	-	718	49	19,136
	STP [a)]	5,035	577	243	83,748
Load CSO/Load SWO [-]		-	1.1	1.1	0.8

[a)] Load towards STP not treated effluent

Copper. Chèvre et al. (2011) applied a linear input-output SFA model to determine the annual Copper load entering the water cycle at Lausanne in Switzerland, and found it a suitable tool for the purpose of highlighting problems such as detecting the main pollution sources or analyzing different scenarios in order to plan specific measures. The overall Copper inputs from the sewers in our dSFA are in good agreement with the SFA for Lausanne. However, the distribution of the Copper load is quite different, indicating the high uncertainty of this input data set. That study found a Copper load entering the urban water cycle of 2,000kg a^{-1} considering the following main categories: drinking water 19.3kg a^{-1}, roofs 837kg a^{-1}, house sides 56kg a^{-1}, cars 144kg a^{-1}, trolleybuses 670kg a^{-1}, trains 240kg a^{-1}, dry deposition 30.7kg a^{-1} and rain 18.5kg a^{-1}. We estimated a total Copper load entering the sewer system of 1,928kg a^{-1} for Lausanne, taking into account the following inputs: household usage 1,033kg a^{-1}, roofs 840kg a^{-1}, garden application 1.02kg a^{-1}, cars and trolleybuses 47.3kg a^{-1}. In Chèvre et al. (2011), 12.6% of the Copper load entering the sewer system is released via CSO and 44% via SWO. Our dSFA results for Lausanne show a loss of 0.6% via CSO and of 40.2% via SWO. The difference in loss rates via CSO can be explained by the differences in input loads. We estimated that 53.6% of the total Copper load in the sewer system is contained in the dry weather flow (Table D.7 in SI). The proportion treated at the STP is therefore higher, as CSO are only active during heavy or long rain events.

3.2 Emission Loads: system comparison

In the following section, the discharged emission loads of the dSFA model are compared for the two types of sewer systems (CSO and SWO).

These two types of drainage systems are compared only for rainfall-mobilized pollutants (Glyphosate, Mecoprop, and Copper), but not for Triclosan. The latter load is discharged entirely to STP in separate stormwater systems during dry and wet weather. On a national scale, total wet-weather discharge loads from CSO are expected to be higher than discharges from SWO because combined systems predominate in Switzerland. However, SWO contribute disproportionally more to the fluxes emitted to urban streams for rainfall-mobilized substances (Table 3). The ratio between the annual fluxes from CSO to those of SWO are 1.1 (Glyphosate), 1.1 (Mecoprop) and 0.8 (Copper). These ratios are considerably lower than the ratio of surface drained by CSO to surface drained by SWO ($A_{red,CS}/A_{red,SS} = 2.3$), which shows that SWO are important emitters of rainfall-mobilized substances.

Glyphosate and part of Mecoprop are modelled as substances with a seasonal input during summer, when heavy convective rain events are frequent. These events activate CSO and carry higher Glyphosate and Mecoprop loads than small events. This leads to a higher proportion of Glyphosate and Mecoprop discharged via CSO in comparison to Copper. Additionally, the wash-off of Mecoprop in building materials is modelled so that higher rainfall intensities, and therefore larger runoffs, lead to higher mobilization.

In contrast to Glyphosate and Mecoprop, the loads of Copper from SWO exceed those from the CSO. Most events during the year are small (by number and by total volume). In combined systems, these small, frequent events are mainly treated by STPs. Small events particularly add to the emissions from SWO because every single runoff event contributes to direct discharges via SWO. The wastewater originating from households and small industries contributes to almost half the total Copper load entering the sewer system (Table 3). None of this indoor Copper load enters the separate stormwater system. Nevertheless, the annual Copper load discharged via SWO exceeds the load from CSO.

The same result for Copper was found by Brombach et al. (2011), who compared combined and separate stormwater systems with a mass balance and found different performances depending on the pollutant characteristics. For heavy metals, the analysis showed that combined systems perform better in terms of the total load emitted to the environment. This is because most heavy metals are found on outdoor surfaces, thus leading to a direct discharge in separate stormwater systems.

3.3 Local effect assessment: substance comparison

In this section, the substances are compared in terms of their local effect potential – as defined in 2.3 – of the wet-weather discharges.

Just 6.5% of the municipalities are estimated to never exceed the EQS for Triclosan during the whole discharge time (Figure 3d). The emissions of Mecoprop and Glyphosate from all municipalities do not exceed the EQS. Many municipalities miss the regulated EQS standard for Triclosan and Copper in more than 20% of the discharge time, which is 71% and 83% respectively. Over the whole simulation time of one year, this means that the EQS for Triclosan is exceeded in 2.4% (median) of the period and for Copper in 4.3% of the time. The EQS for Mecoprop and Glyphosate are not exceeded.

The local effect assessment with ω is based on the conservative approach which only takes the local dilution potential into account. This implies the following: (i) if ω of all municipalities is below 1, i.e. the local dilution potential is sufficient, there would be no problem due to substance accumulation in the recipient; (ii) if ω < 1 for a subarea, there could still be a problem in the recipient resulting from other sources (e.g. agriculture) or from upstream urban areas; (iii) if ω > 1, the upstream capacity may still be sufficient to further dilute concentrations calculated only with the local dilution. Therefore, ω must be <1, especially for small recipients, to ensure sufficient local dilution.

3.4 Sensitivity of environmental quality standards (EQS)

The required local dilution depends on the substance-specific EQS, so their value has a great influence on the model results. Figure 4 shows the sensitivity as a percentage of municipalities which exceed the EQS in 20% of the discharge time. Singer et al. (2002), for example, suggested an EQS for Triclosan of 0.05μg L^{-1}, which is 2.5 times greater than the EQS of 0.02μg L^{-1} used in this study. As a result, the fraction of municipalities exceeding the EQS in 20% of the discharge time would decrease from 71% to only 60% (non-linear).

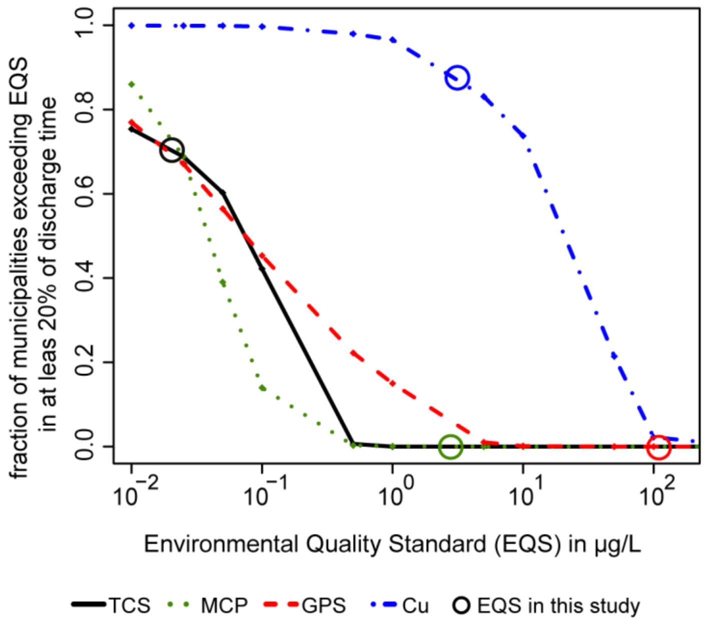

Figure 4. Sensitivity to a change in EQS as fraction of municipalities that exceed the EQS in at least 20% of the discharge time.

The four substances represent all possible urban input pathways: certain conclusions can therefore be drawn from the comparison between rainfall-mobilized and indoor substances. However, the violation of the EQS depends greatly on substance characteristics such as wash-off behaviour and toxicity (evaluated with EQS). As substances have different ways of impacting an organism, however, it is impossible to draw general conclusions for the effect of a substance group on the receiving water.

3.5 Toxic units to account for sub-lethal effects

In order to also account for the sub-lethal effects of the discharged substances, the substance concentration in the recipient after local dilution was used to determine the sum of ω(t) at municipal level (TU_{mun}, Figure 3c) as well as at national level TU_{CH} (Table 4).

Table 4. National sum of Toxic Units TU_{CH}, 95 % interval of the municipal Toxic Units TU_{mun}.

		Triclosan	**Glyphosate**	**Mecoprop**	**Copper**
National sum as	CSO	17.5	10.8	11.5	16.7
$logTU_{CH}$	SWO	-	11.5	12.2	17.8
95% interval of	CSO	7.3– 10.8	0.9 – 3.8	1.8 – 4.5	5.7 – 9.8
$logTU_{mun}$	SWO	-	0 [a)] – 4.6	0 [a)] – 5.4	0 [a)] – 11.2

[a)] Not logarithmized

While Mecoprop and Glyphosate show $logTU_{CH}$ values between 10.8 and 12.2, the values of the other two substances are higher by a factor of 10^4 – 10^7. On a national scale, the highest $logTU_{CH}$ was calculated for Copper from SWO as well as Triclosan from CSO. Mecoprop and Glyphosate from both systems do not reach the TU_{CH} level found for Triclosan.

Over the course of one year, TU_{mun} represents not only the lethal but also the sub-lethal effects of the locally diluted substance concentration. This can be shown by comparing the percentage of municipalities exceeding the EQS of Copper in 50% of the discharge time: the figures are 83% for CSO and 71% for SWO. However, the $TU_{CH,}$ of Copper for SWO is higher by a factor of 12. Ashauer et al. (2011) conducted a risk assessment of a time-varying exposure for Diuron in a Swiss catchment and showed that negative effects cannot be captured by a fixed concentration quality criteria because the sub-lethal toxicity effects over time are neglected. This is taken into account by TU_{mun}, thus facilitating a comparison of different sewer systems or substances. In addition, the sum of the Toxic Units assesses the effect of a combination of multiple substances by the addition of TU_{mun} as long as these substances have the same mode of action.

3.6 Local effect assessment: system comparison

The comparison of the spatial variability of municipalities represented by the spread (95%-interval) of $logTU_{mun}$ yields differences between the two sewer systems (Figure 3c). The spread of $logTU_{mun}$ (95%-interval) ranges from 11.2 for Copper from SWO to 2.7 for Mecoprop from CSO. Taking the variability of Triclosan from CSO as a benchmark with a spread of 3.5, the other compounds show similar spreads in the CSO of 2.9 (Glyphosate), 2.7 (Mecoprop), and 4.1 (Copper). In case of the separate stormwater system, the spreads increase from 4.6 for Glyphosate, 5.4 Mecoprop and 11.2 for Copper.

In addition to the loads discharged annually, the national TU_{CH} provides an indicator for evaluating the environmental effect of both types of wet-weather discharges. When comparing the TU_{CH} for CSO and SWO, it should be taken into account that SWO represent only 30% of all sewer systems. For the rainfall-mobilized substances Mecoprop, Glyphosate and Copper the TU_{CH} of SWO exceed those of CSO: the TU_{CH} are higher by a factor of 6 to 12 for SWO. CSO are only active during heavy rainfall, so that rainfall-mobilized compounds are more diluted during CSO events. This causes smaller TU_{CH} values for CSO in comparison with SWO. Interestingly, CSO emit greater annual loads than SWO in the case of Glyphosate and Mecoprop, but the corresponding TU_{CH} values are smaller by a factor of six. The SWO consequently seem to be more critical than the CSO on a national scale.

3.7 Urban index

In this section, we discuss the use of the Urban Index as a proxy for screening for critical wet-weather discharges and compare it with the dSFA model results.

A high Urban Index indicates a high percentage of urban areas and consequently a small local dilution potential of the wet-weather discharges. Hence, θ is a proxy for the dilution potential, which is readily determined thanks to the availability of information on impervious and natural areas. In Switzerland, this dilution potential varies greatly. Figure 5 shows θ for Switzerland based on the borders of the 2,500 municipalities. The municipal catchments show a 95%-interquantile for θ of 0.008 to 0.82 with a median of 0.08. Despite local differences, the densely populated areas mostly show $\theta \geq 0.1$.

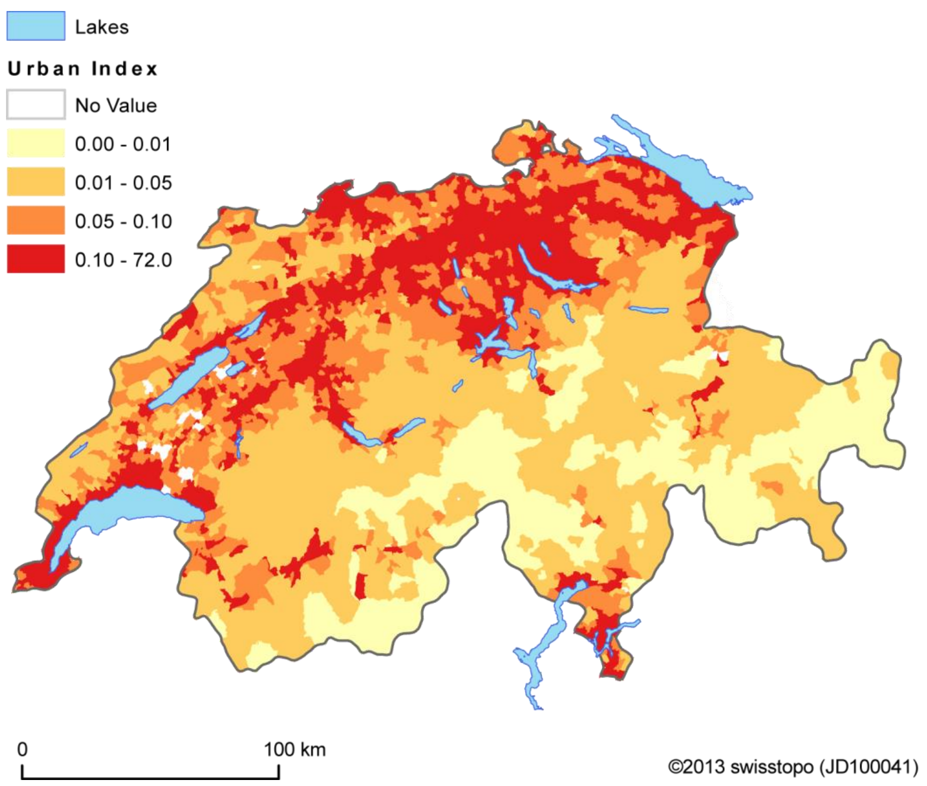

Figure 5. Urban index θ based on municipal boundaries (swisstopo (Art. 30 GeoIV): 5704 000 000 / vector25@2012, reproduced with permission of swisstopo / JA100119)

The minimal required dilution potential θ of a catchment depends on the substance-specific EQS as well as the land uses. This is illustrated by plotting the municipal θ against the total discharge time (SWO and CSO) in which the EQS is not exceeded ($p(\omega<1)$) in the dSFA model for Triclosan and Copper (Figure 6). The results show that a higher Urban Index θ also indicates a higher probability of exceeding the EQS. Glyphosate and Mecoprop are not shown, as no exceedance of the current EQS were found. When decreasing the EQS of Glyphosate and Mecoprop, a tendency for a higher probability of exceeding corresponding EQS can be seen with higher θ (SI Figure F.1 and F.2). To use θ as a conservative proxy for insufficient local dilution, false negatives need to be avoided (municipalities exceeding EQS despite a low θ). We, therefore, take a 10%-quantile, implying that ninety percent of municipalities with a θ greater than 0.035 for Copper and greater than 0.026 for Triclosan exceed the

EQS at least 20% of the discharge time. Based on the evaluation of these two substances a θ of around 0.03 indicates insufficient local dilution. Clearly, to further substantiate θ as a proxy, more substances need to be analysed, which would reveal how much lower θ needs to be in order to not exceed EQS for other, more critical substances.

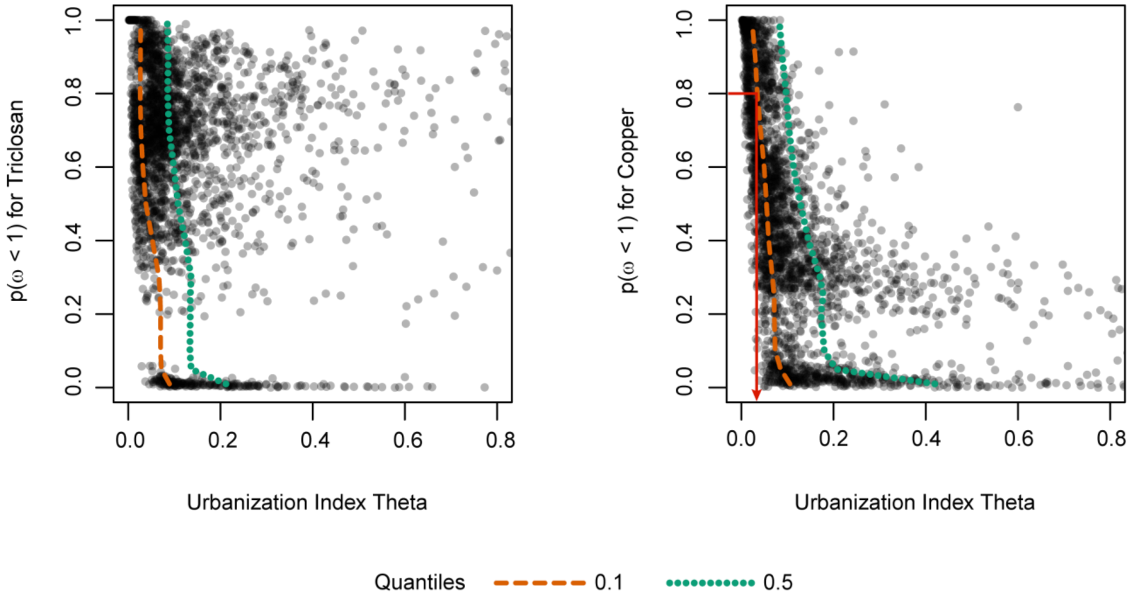

Figure 6. Urban Index vs. fraction of wet-weather discharge time in which the EQS is not exceeded for each municipality (transparent black dots). The dashed lines show the 10% and 50% quantile of all municipalities. Reading example for Copper (red arrow): 90% of all municipalities that exceed the EQS for Copper in at least 20% (80% non-exceedance of EQS on y-axis) of the discharge time have an Urban Index greater than 0.035.

The Urban Index gives an overview of the national distribution of settlements and the local dilution required in case of the anticipated wet-weather discharge loads. This provides a first estimate of the local dilution potential in cases where concentration measurements of wet-weather discharges are available but flow data is lacking. The Urban Index does not take into account the catchment-specific variability of land uses and pollutant sources. This variability can also be seen in the differences between the two pollutants Triclosan and Copper in Figure 6. Triclosan is only used in households and discharged pollutant loads do not directly depend on urban land use areas. This variability becomes apparent from the spread of the Toxic Unit of the municipalities in Figure 3c. Thus, a catchment has to be analyzed in more detail when $\theta > 0.03$ indicates a small local dilution potential. Both dSFA and θ are potential screening tools, at different levels of detail, for highlighting critical discharge points. The numbers of critical discharge points based on a threshold of a maximum tolerable exceedance of the EQS in 20% of the discharge time are therefore compared for dSFA and θ in Table 2.5.

Table 5. Number of potentially critical discharge points for dSFA and the Urban Index based on a defined threshold of a maximum tolerable exceedance of EQS in 20% of the discharge time. Total number of discharge points: 2,500.

Screening Tool	Threshold	Number of critical discharge points	
		Triclosan	Copper
dSFA	$p(\omega<1) \geq 0.8$: EQS exceedance in maximum 20% of discharge time	1,778	2,077
Urban Index	UI > 0.03	2,119	

Both screening tools (dSFA and the Urban Index) indicate up to 83% critical discharge points. On the other hand, at least 17% (Copper) or more of all discharge points are expected to be uncritical with the dSFA based on a threshold of not exceeding the EQS during 80% of the discharge time or more. Nevertheless, our results indicate that there could be many critical discharge points in reality when not relying on unpolluted dilution potential from upstream. This highlights the importance of further research on the effect of wet-weather discharges on receiving waters.

3.8 Model validation and transferability to other areas

The dSFA model framework provides a nationwide screening tool for wet-weather discharges of four selected substances and their effects on the environment. The dSFA CSO discharge concentration results for Copper show an interquartile of the median of all municipalities from 29 to 79µg L^{-1} (median 55µg L^{-1}). For Glyphosate an interquartile of the concentration median of all municipalities of 3.8 to 9.2µg L^{-1} results in the dSFA (median 6µg/L). In comparison Gasperi et al. (2012b) reported event mean concentration in the range 86-134µg L^{-1} for Copper and 0.13-0.46µg L^{-1} for Glyphosate in CSO. This indicates a good agreement between dSFA for Copper, whereas the Glyphosate concentration is overestimated in the dSFA. An overestimation for Glyphosate is also found when comparing with measured loads by Wittmer et al. (2010) for a specific Swiss municipality (Section 2.3.1 and Staufer et al. (2012)). In the dSFA fraction of substance washed-off garden areas was assumed 5% (combining wash-off from pervious and impervious surfaces; see SI C for details). This is higher than loss rates reported from agricultural application with pervious surfaces ranging from 0.1% to 1.4% (Leu et al. 2004). The comparison further shows an underestimation of the emitted Mecoprop loads (Section 2.3.1). Overall, the reported monitoring data is in appropriate agreement in view of the dSFA being a screen tool. In order to apply the dSFA model to other geographical areas, rain data in high resolution (e.g. 10 minutes), land use data and a characterization of the sewer system (percent of separate and combined system) is needed. Tank volumes and discharge amount treated by the STP can be estimated based on design standards. In addition to that, substance usage estimates (e.g. yearly substance load on national scale) are used as an input for the dSFA and can be country specific. Whereas, wash-off and accumulation behavior and parameters are found in literature and SI C.

3.9 Model structure and simplifications

The model produces a high-resolution time series which is important for predicting highly variable wet-weather discharges. Nevertheless, the model results have to be interpreted carefully and are suitable for the following purposes: (i) to detect emission hotspots on a national/regional scale; (ii) to compare pollutant emissions or sewage systems; (iii) to find catchments where the local dilution potential is insufficient based on conservative screening assumptions. The model cannot be used to return a high-resolution series of concentration times for one specific, real discharge point for a Swiss municipality without further analysis of the local characteristics. Once the fluxes on the surfaces are determined, they enter the combined sewer system of the respective municipality. The model then simplifies the drainage systems: while the transformation of the wave is considered, the model neglects a number of in-sewer processes to make the computation efficient: (i) the spatial dimensions of the system; (ii) in-sewer storage; (iii) pumping stations; or (iv) pressurized systems. In addition, a single SWO and a single CSO represent the wet-weather discharge points for each municipality; these tank locations and volumes are based on general assumptions. A detailed evaluation of 208 Swiss municipalities showed that in reality only one CSO tank was present in 70% of these sewer systems. Although this is an appropriate way to assess aggregated information, the individual location and number of discharge points may vary significantly. The GIS-based spatial analysis cannot represent each individual system. However, it provides a reasonable representation of the variability (2,500 municipalities studied) in the system with respect to (i) land-use, (ii) size of the system, and (iii) capacity of combined and separate sewage treatment consisting of the storage volume and the wet-weather treatment at the STP. A specific catchment should therefore be modelled with more precise parameterization of catchment-specific properties and further parameter identification techniques. The input substance quantification in particular is associated with high uncertainty: despite the high uncertainty for a single discharge point (CSO, SWO), the nationwide analysis decreases the uncertainty thanks to spatial compensation (Benedetti et al. 2006, Petrucci et al. 2014). There is currently a lack of data on catchment-specific substance usage, land-use distribution and locations of wet-weather discharge points. So we have two options: either to look at an isolated catchment in detail, which requires a lot of effort and may not be representative of other catchments, or to screen for potential hot spots in order to prioritize where to look in more detail in a next step.

4 Conclusions

We screened SWO and CSO in 2,500 municipalities with our dSFA model and estimate that 17% of all discharge points are uncritical on the basis of conservative screening assumptions and a maximum tolerable EQS exceedance in 20% of the discharge time.

i. How can we screen for potentially critical wet-weather discharge points?

Our results imply that the dSFA is a conservative screening tool, as the actual dilution potential in the receiving water is not considered, i.e. it excludes unpolluted water from upstream. It consequently provides an indication as to whether a local urban settlement causes the EQS to be exceeded and would thus warrant further analysis. The dSFA model results show that up to 83% of the discharge points can exceed the EQS for Copper in at least 20% of the discharge time. This clearly indicates the need for further research on the contribution of wet-weather discharges to receiving waters. The effect assessment depends strongly on the substance characteristics (application amount in urban catchments, wash-off behaviour and EQS). Potentially more or less critical substances should therefore be studied.

ii. How do SWO and CSO compare with regard to discharged micropollutants?

The dSFA model hints that emission loads from SWO are higher than CSO for source-limited substances such as Glyphosate. In addition, the local effect assessment suggests a higher effect potential (lower emission load, higher Toxic Units) for SWO than CSO for rainfall-mobilized substances (Mecoprop, Glyphosate, Copper). However, due to the low EQS, the effect of the wastewater-borne substance Triclosan from CSO is in the same range as the rainfall-mobilized substances.

iii. Can we find a proxy – available area-wide on a national/regional scale – to highlight catchments where the local dilution is insufficient to avoid the EQS being exceeded by wet-weather discharges?

The dSFA model indicates that urban areas where Triclosan and Copper exceed the EQS often have an Urban Index >0.03. We could therefore reduce the discharge points for further analysis - 15% of all discharge points are indicated as being uncritical by the Urban Index. However, the Urban index does not consider land uses, pollutant accumulation and wash-off processes. Nevertheless, it can be used as a first indicator for insufficient local dilution where more detailed data is not available.

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