Supporting Information

Model-based evaluation of reduction strategies for micropollutants from wastewater treatment plants in complex river networks

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SI 1 Calculation example

The following example illustrates how the topology matrix is being calculated with the directed graph (no loops, the wastewater is assumed to always flow downstream of a WWTP and does not return).

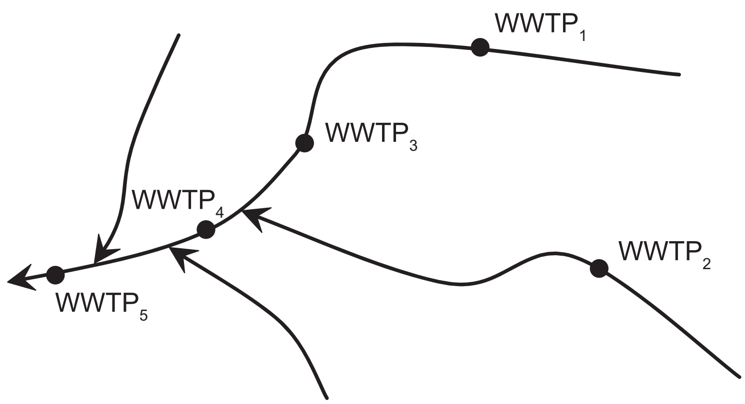


FIGURE SI 1. Theoretical example of a small river network with 5 WWTPs. Arrows indicate flow direction.

$$\text{adjacency-matrix } W = \begin{array}{c|c} \text{WWTP} & \begin{array}{ccccc} 1 & 2 & 3 & 4 & 5 \end{array} \\ \begin{array}{c} 1 \\ 2 \\ 3 \\ 4 \\ 5 \end{array} & \begin{pmatrix} 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 \end{pmatrix} \end{array} \Rightarrow \text{topology-matrix } T = (I - W)^{-1} = \begin{pmatrix} 1 & 0 & 1 & 1 & 1 \\ 0 & 1 & 0 & 1 & 1 \\ 0 & 0 & 1 & 1 & 1 \\ 0 & 0 & 0 & 1 & 1 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

Parameters for a theoretical calculation example:

$$C_{\mathrm{CH}} = 7000,\ P_{\mathrm{CH}} = 7459000,\ \ p = 0.2,\ \ m = 0,\ \ \overline{P}_{WWTP} = \begin{pmatrix} 5000 \\ 3000 \\ 6000 \\ 10000 \\ 100000 \end{pmatrix},\ \ \overline{e} = \begin{pmatrix} 0.25 \\ 0.25 \\ 0.95 \\ 0.25 \\ 0.25 \end{pmatrix}$$

with: C_{CH} national consumption [kg a^{-1}];

P_{CH} total population [inhabitants];

p fraction of parent compound excreted and discharged to sewer [-];

m fraction of known metabolites (as toxicity equivalents for parent compound) [-];

$\overline{P}_{WWTP}$ population in the catchment of each WWTP [inhabitants];

$\overline{e}$ fraction substance S eliminated in WWTP [-] (one value if all elimination rates are equal, a vector if different elimination rates for different WWTP apply)

The load that results downstream of the catchments taken into account that $WWTP_3$ was upgraded and exhibits a larger removal rate calculates as follows:

$$L(S)_{river\ catchment\ WWTP_{\mathrm{j}}} = \frac{1000}{365} \cdot \sum_i \left[\frac{C_{\mathrm{CH}}}{P_{\mathrm{CH}}} \times (p+m) \right] \cdot \overline{P}_{\mathrm{WWTP}} \cdot (1-\overline{e}) \cdot (T_{\mathrm{ij}})$$

$$L(S)_{river\ catchment\ WWTP_{\mathrm{j}}} = \frac{1000}{365} \cdot \sum_i \left[\frac{7000}{7459000} \times (0.2+0) \right] \cdot \begin{pmatrix} 5000 \\ 3000 \\ 6000 \\ 10000 \\ 100000 \end{pmatrix} \cdot \left(1 - \begin{pmatrix} 0.25 \\ 0.25 \\ 0.95 \\ 0.25 \\ 0.25 \end{pmatrix} \right) \cdot \begin{pmatrix} 1 & 0 & 1 & 1 & 1 \\ 0 & 1 & 0 & 1 & 1 \\ 0 & 0 & 1 & 1 & 1 \\ 0 & 0 & 0 & 1 & 1 \\ 0 & 0 & 0 & 0 & 1 \end{pmatrix}$$

Particularly, the calculation is carried out for the river section downstream of WWTP j=4:

$$L(S)_{river\ catchment\ WWTP_4} = \frac{1000}{365} \cdot \sum_i \left[\frac{7000}{7459000} \times (0.2+0) \right] \cdot \begin{pmatrix} 3750 \\ 2250 \\ 300 \\ 7500 \\ 0 \end{pmatrix} = 7.1\mathrm{g\ d}^{-1}$$

SI 2 Sampling and chemical analysis

This study. Sampling was carried out under dry weather conditions in August and September 2007. The number of inhabitants in the selected, independent river catchments ranged from 14’000 to 187’000. Samples from rivers are grab samples, because none of the river sections we selected was equipped with a gauging station including a well maintained composite sampler. WWTP samples were 24h-composite samples collected routinely by the WWTP personnel without time shift between influent and effluent. Local authorities regularly check the sampling procedure (volume-proportional, only one WWTP time-proportional every 15 minutes; samples from effluent primary clarifier, effluent secondary clarifier and, where applicable, effluent sand filter were collected simultaneously).

A side aspect of this sampling campaign was to collect further information on elimination rates of micropollutants for different types of conventionally operated WWTPs and the per capita load in WWTP effluents. To this end, samples from 14 WWTPs were analyzed. The number of inhabitants connected to these WWTPs ranged from 6’000 to 19’000. These results are presented in the table of SI 5. For most compounds the observed elimination agree with values from literature. However, the data base is too weak to meaningfully correlate the observed elimination with common parameters such as sludge age, hydraulic retention time, NH_4-N effluent concentrations or other generally available parameters.

Samples were filtered on the same day (glass fibre filter, pore size 1 µm) and stored refrigerated or partly frozen until analysis. After spiking of isotope labelled internal standards 100 mL of influent and effluent as well as 250 - 500 mL of surface water, respectively, was enriched using solid phase extraction with different materials and extraction conditions dependent on the different compound properties *(1,2)*. Subsequently, analyses were performed by HPLC-MS-MS in the selected reaction mode using one transition as quantifier and another as qualifier. Internal standards were used for quantification and limit of quantification was determined by signal-to noise ratio >10. Recoveries were determined for all matrices and were usually in the range of 80 - 120 %.

A detailed list of all chemical analyses can be found on http://pubs.acs.org in the file “si_paper_ort_et_al_data_monitoring_campaign.xls”.

Additional data. Additional data for carbamazepine and diclofenac was provided by the local authorities of the Cantons Zurich and St. Gallen *(3,4)*. These sampling campaigns took place in November 2004, April 2005 respectively. The number of inhabitants in all investigated river catchments ranged from 5’000 to 410’000. The measured concentrations (MEC) are reported as single values with exact date and location. Loads were determined using the discharge in the rivers at the time of sampling available from gauging stations operated by the Cantons. The catchments in these Cantonal investigations have a total population between 5’000 and 410’000 (sampling locations in Figure 1 of the main paper).

SI 3 List of substances

P	Acetylsulfamethoxazole	P	Indomethacin
P	Amidotrizoate	P	Iodipamid
P	Atenolol	P	Iohexol
Pe	Atrazine	P	Iomeprol
Pe	Atrazine-Desethyl	P	Iopamidol
Pe	Atrazine-Desisopropyl	P	Iopanoic acid
Pe	Atrazine-Hydroxy	P	Iopromide
P	Azithromycin	P	Ioxaglic acid
C	Benzotriazole	P	Ioxitalamic acid
P	Bezafibrate	M	Irgarol
I	Bisphenol-A	M	Irgarol-Descyclopropyl
P	Carbamazepine	M/PE	Isoproturon
PE/M	Carbendazim	P	Ketoprofen
P	Clarithromycin	Pe /R	Mecoprop
P	Clofibric acid	C	Methylbenzotriazole
P	Diazepam	P	Naproxen
IN	Diazinon	I	Nonylphenol
P	Diclofenac	P	Pentoxifyllin
M	Diuron	P	Phenacetin
M	Dimethylphenylsulfamide	P	Primidone
M	Dimethyltolylsulfamide	P	Roxithromycin
P	Erythromycin+Dehydrato-Erythromycin	P	Sotalol
P	Estradiol	PE	Sulcotrione
P	Estron	V	Sulfadiazine
P	Ethinylestradiol	V	Sulfadimethoxine
P	Etofibrate	V	Sulfamethazine
P	Fenofibrate	P	Sulfamethoxazole
P	Fenofibric acid	P	Sulfapyridine
P	Fenoprofen	M	Terbutryne
P	Gemfibrozil	Pe	Terbutylazine
P	Ibuprofen	P	Trimethoprim

C Anti-corrosive agents
I Industry
IN Insecticide
M Material protection
P Pharmaceutically active compound and hormones
R Material protection (roofs)
PE Pesticide
V Veterinary antibiotics

SI 4 Dilution factors and $Q_{95\%}$

Measured $Q_{95\%}$-values were taken from Aschwanden et al. *(5)*. When $Q_{95\%}$ was unknown for a river section downstream from a WWTP, values were interpolated by using the method of Staub et al. *(6)*. This procedure led to values for $Q_{95\%}$ for river sections downstream from 543 WWTPs out of the 660 that discharge to rivers. The evaluation of dilution at $Q_{95\%}$ reveals that river sections directly downstream of 150 WWTP provide a local dilution factor of 10 or less. This assumes that all water upstream from a WWTP does not contain any micropollutants. In fact the treated wastewater and, therewith, recalcitrant substances accumulate in the aqueous phase along the rivers and a dilution factor of “cumulated wastewater” may be a more appropriate indicator for dilution. This results in over 230 river sections directly downstream from WWTPs with dilution factors smaller than 10. Thus, a default value of 10 for dilution is often by far too optimistic *(7,8)* and site-specific investigations on the discharge in rivers are crucial.

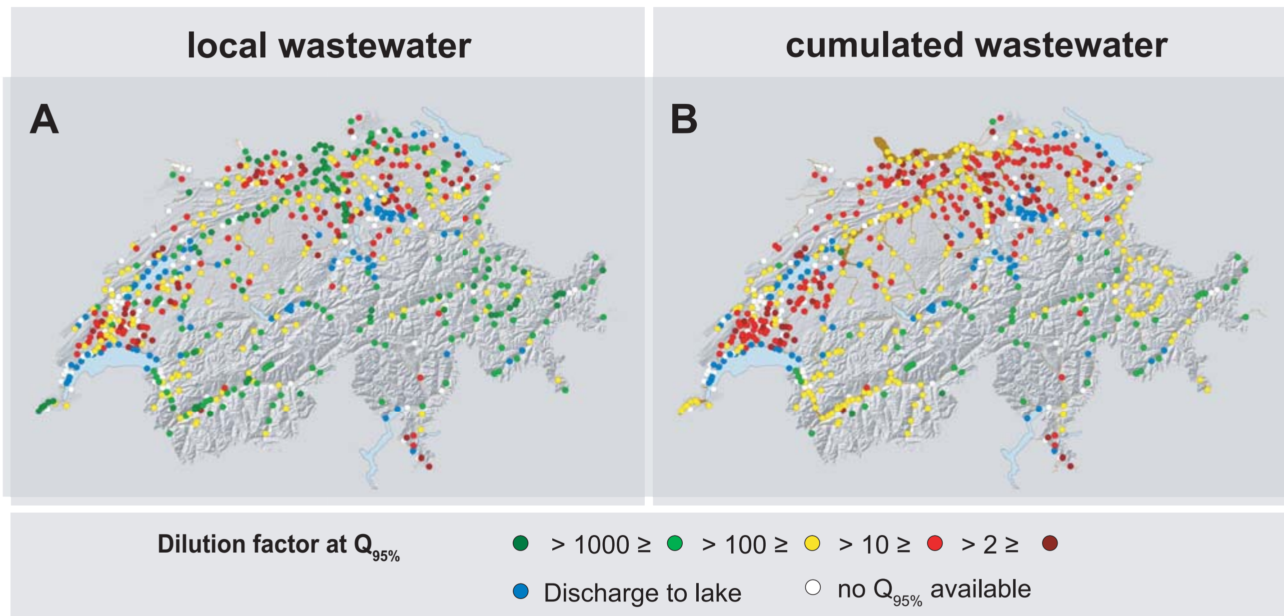


Figure SI 4.1 A: Dilution factors at base flow $Q_{95\%}$, as traditionally determined (local) and B: when wastewater is accumulated along rivers and lakes (cumulated). Discharge from WWTP in Switzerland during dry weather normally around 400L c^{-1} d^{-1} (c=capita).

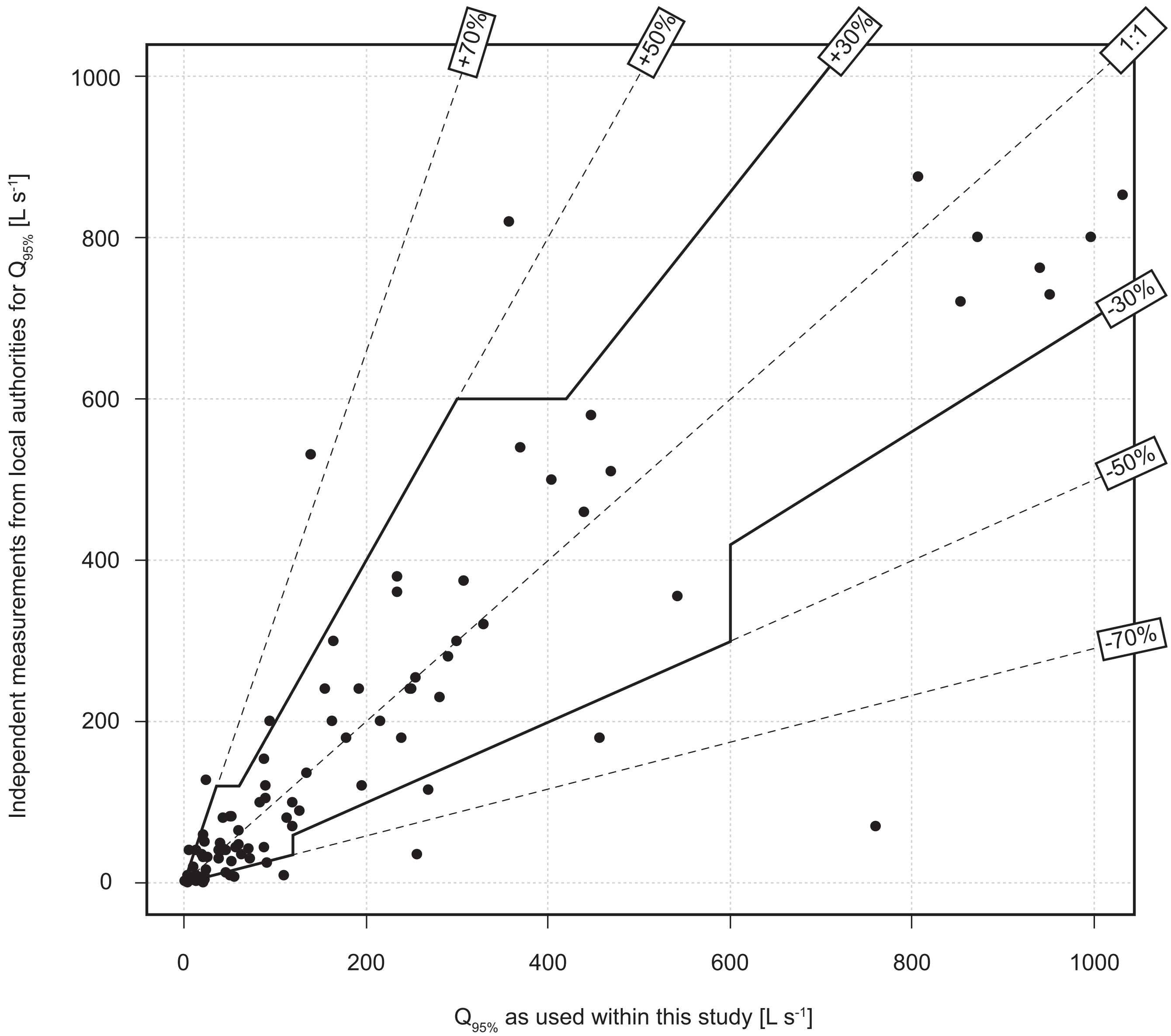


Figure SI 4.2 Comparison of $Q_{95\%}$.for uncertainty estimation, x-axis: values as used in this study, y-axis: independent measurements from local authorities for comparison.

SI 5 Monte Carlo simulation: sampling values to account for uncertainty

To calculate pollutant loads including uncertainty factors downstream of WWTPs (see also the didactical example in SI 1), equation SI 5.1 is used for the Monte Carlo simulations. As stated in the main paper the individual uncertainty factors are independent for each WWTP within one model run, and also from model run to model run (see Table SI 5 on next page). The loads obtained in each Monte Carlo run are divided by a $Q_{95\%}$ to obtain pollutant concentrations at base flow. While the uncertainty factors related to the load calculations are independent, the one for $Q_{95\%}$ is not: a lower value upstream also implies a lower value downstream to ensure consistency within catchments. This is achieved by sampling only one uncertainty value for Q95% in one run from a uniform distribution U(-1,1). This value is then scaled according to the uncertainty range derived for different rivers categories according to their flows (see main paper for explanation, Figure SI 4.2 and Figure SI 5). Furthermore, this procedure can be followed by understanding Table SI 5. In the next model run the procedure is repeated by sampling first sampling again from U(-1,1) and then scaling this value.

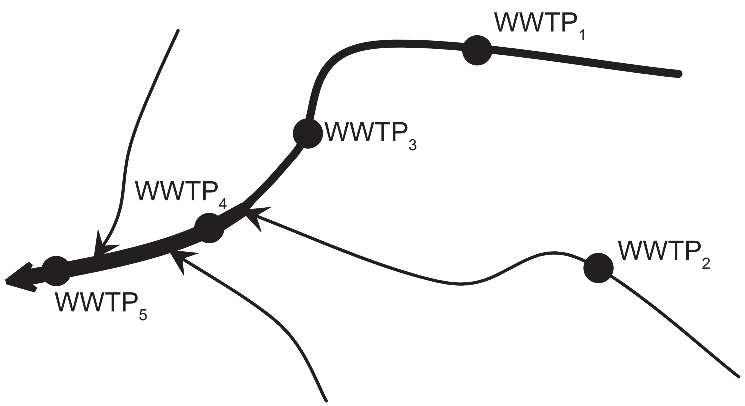


FIGURE SI 5. Theoretical example of a small river network with 5 WWTPs. Arrows indicate flow direction and the line width stands for the river category (small: $Q_{95\%} < 60\text{L s}^{-1}$, medium-sized: $60\text{L s}^{-1} < Q_{95\%} < 600 \text{ L s}^{-1}$ and large $Q_{95\%} > 600\text{L s}^{-1}$).

$$L(S)_{river\ catchment\ WWTP_j} = \frac{1000}{365} \cdot \sum_i \left[\frac{C_{\mathrm{CH}}}{P_{\mathrm{CH}}} \times (p+m) \right] \cdot \overline{u}_{\text{infl. load}} \cdot \overline{P}_{\mathrm{WWTP}} \cdot \left(1 - \overline{e} \cdot \overline{u}_{\text{elim.}}\right) \cdot \left(T_{\mathrm{ij}}\right) \cdot \overline{u}_{\text{chem.anal.}} \tag{SI 5.1}$$

Table SI 5. Sampled uncertainty values for two runs of the Monte Carlo simulation to estimate prediction uncertainty (see also main paper for further explanations).

Example for a first Monte Carlo run											
Location	Uncertainty factors for load calculation						Uncertainty factor for dilution at base flow $Q_{95\%}$				
							Unity	scaled to range derived from Fig. SI 2.2			
	U(-0.5,0.5)	$\overline{u}_{\text{infl. load}}$	U(-0.2,0.2)	$\overline{u}_{\text{elim.}}$	U(-0.2,0.2)	$\overline{u}_{\text{chem.anal.}}$	U(-1.0,1.0)	small river U(-0.7,0.7)	medium river U(-0.5,0.5)	large river U(-0.3,0.3)	$\overline{u}_{Q_{95\%}}$
$WWTP_1$	0.32	1.32	-0.06	0.94	-0.19	0.81	-0.80	NA*	-0.40	NA	0.60
$WWTP_2$	-0.15	0.85	0.03	1.03	-0.13	0.87	-0.80	-0.56	NA	NA	0.44
$WWTP_3$	-0.47	0.53	-0.17	0.83	-0.16	0.84	-0.80	NA	-0.40	NA	0.60
$WWTP_4$	0.08	1.08	0.16	1.16	0.17	1.17	-0.80	NA	NA	-0.24	0.76
$WWTP_5$	0.21	1.21	0.05	1.05	-0.18	0.82	-0.80	NA	NA	-0.24	0.76

Example for a second Monte Carlo run											
Location	Uncertainty factors for load calculation						Uncertainty factor for dilution at base flow $Q_{95\%}$				
							Unity	scaled to range derived from Fig. SI 2.2			
	U(-0.5,0.5)	$\overline{u}_{\text{infl. load}}$	U(-0.2,0.2)	$\overline{u}_{\text{elim.}}$	U(-0.2,0.2)	$\overline{u}_{\text{chem.anal.}}$	U(-1.0,1.0)	small river U(-0.7,0.7)	medium river U(-0.5,0.5)	large river U(-0.3,0.3)	$\overline{u}_{Q_{95\%}}$
$WWTP_1$	-0.47	0.53	0.17	1.17	-0.09	0.91	0.31	NA	0.16	NA	1.16
$WWTP_2$	-0.39	0.61	-0.08	0.92	-0.19	0.81	0.31	0.22	NA	NA	1.22
$WWTP_3$	0.42	1.42	0.14	1.14	0.08	1.08	0.31	NA	0.16	NA	1.16
$WWTP_4$	0.13	1.13	-0.14	0.86	-0.04	0.96	0.31	NA	NA	0.09	1.09
$WWTP_5$	0.38	1.38	-0.07	0.93	-0.02	0.98	0.31	NA	NA	0.09	1.09

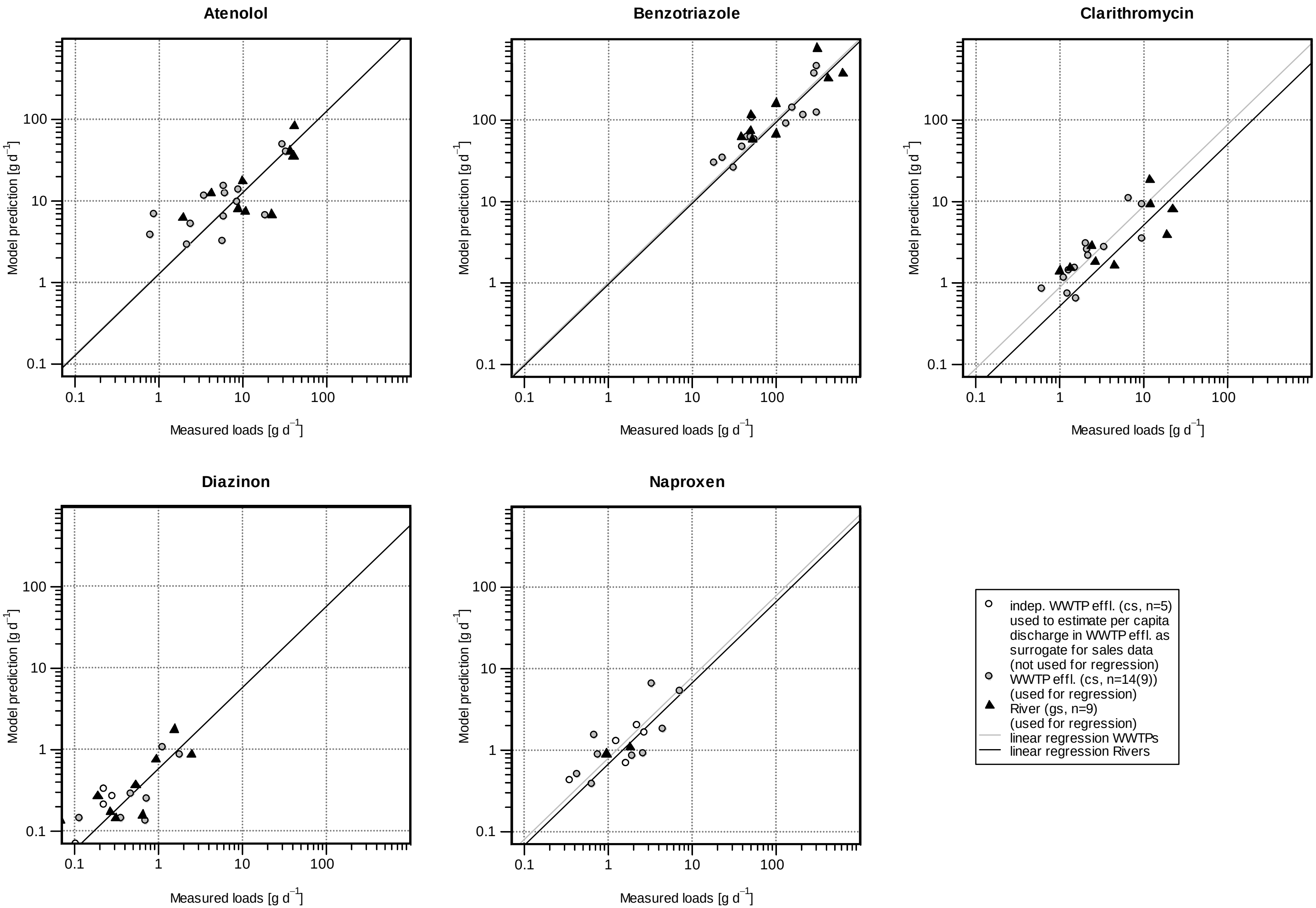
*NA: Not applicable.

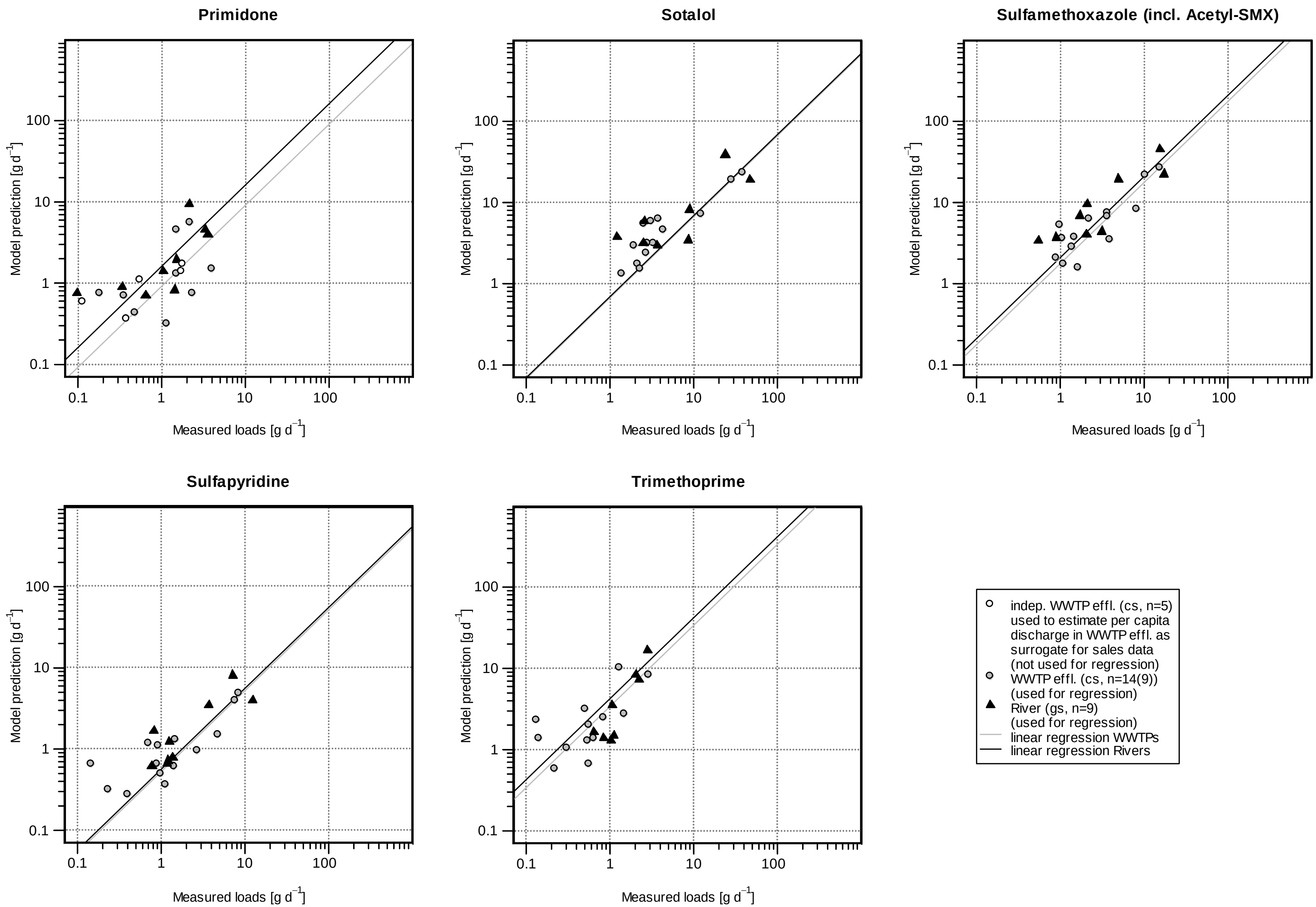
SI 6 Substances (model input data)

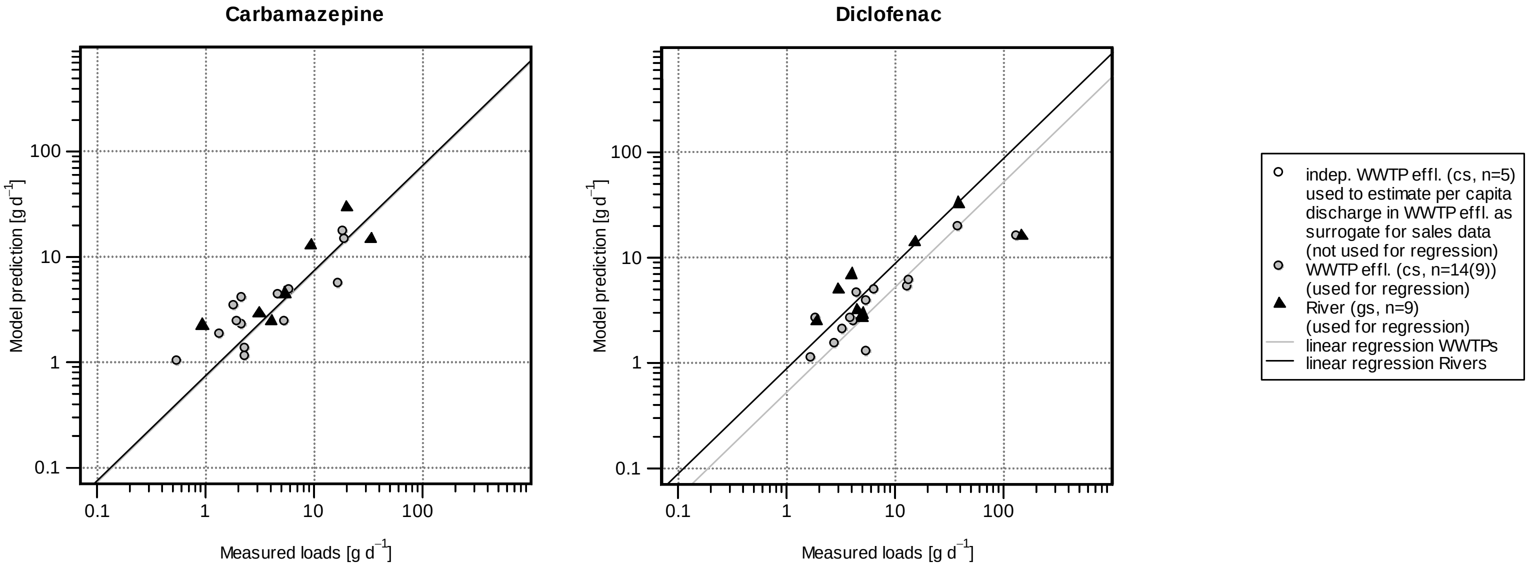
Substance	Sales data [kg a^{-1}]	Fraction parent compound [%] mean (min to max)	Elimination in WWTP [%] mean (min to max)	Mean calculated load in WWTP effluent [µg c^{-1} d^{-1}]
atenolol	3’071 [a]	73 (69 to 96) [d]	45 [i]	452
		50 (11 to 240) [*2]	52 (-48 to 84) [*]	287 (58-1447) [*]
benzotriazole	16’000 [b]	100 [e]	30 (0 to 60) [j]	4113
		- [*3]	- [*3]	3211 (1585-9427) [*]
clarithromycin	1’700 [c]	16 (4 to 30) [f]	0 (-45 to 20) [k]	100
		35 (4 to 316) [*2]	- [*3]	100 (59-2584) [*]
diazinon	n.a.	n.a.	n.a.	13 [l]
		-	-	13 (5-49) [*]
naproxen	n.a.	n.a.	n.a.	68 [l]
		-	62 (38 to 92) [*]	68 (25-162) [*]
primidone	n.a.	n.a.	n.a.	38 [l]
		-	68 (-56 to 79) [*]	38 (6-179) [*]
sotalol	877 [a]	106 (85 to 125) [d]	35 [i]	222
		71 (33 to 110) [*2]	8 (-25 to 35) [*]	207 (65-503) [*]
sulfamethoxazole (including Acetyl-SMX)	2’300 [a]	60 [g]	53 (-1 to 76) [k]	243
		45 (22 to 72) [*2]	65 (41 to 89) [*]	111 (38-270) [*]
sulfapyridine	840 [c]	15 [g]	2 (-107 to 074) [k]	46
		-	32 (-19 to 71) [*]	61 (9-134) [*]
trimethoprim	520 [c]	50 [h]	2 (-40 to 20) [k]	95
		- [*3]	- [*3]	8 (4-73) [*]

[a] IMS Health Ltd. (average of the years 2000 and 2004 for Switzerland)
[b] Henkel *(9)*
[c] Goebel et al. *(10)*
[d] Lienert et al. *(11)*
[e] McArdell et al. *(12)*
[f] Bryskier et al. *(13)*
[g] Vree and Hekster *(14)*
[h] Schwartz and Rieder *(15)*
[i] Wick et al. *(16)*
[j] Voutsa et al. *(17)*
[k] Göbel et al. *(18)*
[l] Median estimated from 5 independent WWTP effluents which were not used for the regression to check model validity (see SI 6, white circles)
[*] Median observed in this study (min-max), the median was taken due to the small number of observed values
[*2] Median observed in this study (min-max), calculated from sales data and WWTP influent loads
[*3] Problem with analytics for matrix in the influent of the WWTP

SI 7 Prediction vs. measurements for ten additional substances




Primidone
Sotalol
Sulfamethoxazole (incl. Acetyl-SMX)
Sulfapyridine
Trimethoprime
Model prediction [g d^{-1}]
Measured loads [g d^{-1}]
0.1
1
10
100
indep. WWTP effl. (cs, n=5) used to estimate per capita discharge in WWTP effl. as surrogate for sales data (not used for regression)
WWTP effl. (cs, n=14(9)) (used for regression)
River (gs, n=9) (used for regression)
linear regression WWTPs
linear regression Rivers



Carbamazepine
Diclofenac
Model prediction [g d⁻¹]
Measured loads [g d⁻¹]
0.1
1
10
100
indep. WWTP effl. (cs, n=5) used to estimate per capita discharge in WWTP effl. as surrogate for sales data (not used for regression)
WWTP effl. (cs, n=14(9)) (used for regression)
River (gs, n=9) (used for regression)
linear regression WWTPs
linear regression Rivers

SI 8 Evaluation of results for all twelve substances

Substance \ Statistics	$R^2_{WWTP,effluent}$ [a]	R^2_{river} [a]	$MPAF_{WWTP,effluent}$ [b]	$MPAF_{river}$ [b]	Remark
atenolol	0.88	0.83	2.3	1.6	assumed excretion ratio from literature or sales data seem to be too high
benzotriazole	0.82	0.68	1.2	1.5	-
clarithromycin	0.78	0.59	1.0	0.9	high variation in rivers
diazinon	0.85	0.74	0.9	0.9	-
naproxen	0.73	- (n=2)	1.0	0.8	-
primidone	0.47	0.69	1.8	2.5	assumed excretion ratio from literature or sales data seem to be too high and elimination in WWTP too low
sotalol	0.95	0.65	1.2	1.4	high variation in rivers
sulfamethoxazole (SMX) (including Acetyl-SMX)	0.94	0.84	2.3	3.4	assumed excretion ratio seems to be too high and elimination in WWTP too low
sulfapyridine	0.93	0.71	1.1	0.9	-
trimethoprim	0.77	0.87	6.5	3.1	assumed excretion ratio seems to be too high
for comparison					
carbamazepine	-	0.66 (0.78) [c]	-	1.1 (1.0) [c]	-
diclofenac	-	0.98 (0.94) [c]	-	0.9 (1.1) [c]	-

[a] MPAF = Mean predictive accuracy factor=mean(prediciton/observation), [b] $R^2 = R^2$ from linear regression forced through 0, [c] the values in brackets are the ones derived for carbamazepine and diclofenac from the main paper (Figure 1) where more data points were available.

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