Table S1. Yearly volume (in million cubic meters) of water flowing through the selected stations/points for the years 2007-2010.

Year	Brussels Entry	Brussels Exit	Total CSO	Eppegem
2007	107	231	10	375
2008	129	239	8	390
2009	121	237	9	375
2010	144	283	18	460

Table S2. Increment on total metal concentration (µg/l) at Eppegem in response to a given percentage increment on the total metal concentrations at possible CSO outlets.

Increment	CuT	CdT	PbT	ZnT	% change CuT	% change CdT	% changePbT	% change ZnT
Original	14.44	0.20	16.40	99.93	-	-	-	-
20%	15.29	0.21	17.12	104.67	6	5	4	5
50%	16.57	0.22	18.20	111.77	15	11	11	12

Table S3. Performance evaluation of MLR- and PCR- derived equations on representing the total metal concentration (MeT) and partitioning coefficient (Log based: LogKd) at rural catchment runoff discharging points.

Variable	Station	Period	Time Span	Sample Size	RMSE	MAE	PBIAS (%)	RSR	NSE	Performance
MLR Results										
MeT-Cd		Calibration	2009-2010	113	0.12	0.06	-29.25	0.99	0.02	Satisfactory
		Validation		39	0.60	0.340	-34.43	0.94	0.11	Unsatisfactory
MeT-Cu	GESZ	Calibration	2009-2010	113	4.57	2.58	-22.76	0.92	0.14	Satisfactory
	Stations*	Validation		39	10.08	12.11	-26.53	0.56	0.69	Good
MeT-Pb		Calibration	2009-2010	113	7.27	3.94	-30.69	0.93	0.14	Satisfactory
		Validation		39	35.83	12.70	7.58	1.67	-1.78	Satisfactory
MeT-Zn		Calibration	2009-2010	113	31.07	15.87	-16.22	0.92	0.16	Satisfactory
		Validation		39	52.95	57.94	-11.56	0.66	0.56	Good
LogKd-Cd		Calibration	2009-2010	113	0.40	0.30	1.56	0.68	0.53	Good
		Validation		39	1.13	0.85	14.17	1.59	-1.54	Satisfactory
LogKd-Cu	GESZ	Calibration	2009-2010	113	0.33	0.24	0.00	0.69	0.53	Good
	Stations*	Validation		39	0.75	0.56	-0.12	2.07	-3.28	Satisfactory
LogKd-Pb		Calibration	2009-2010	113	0.31	0.25	0.00	0.71	0.49	Satisfactory
		Validation		39	0.66	0.55	3.51	1.36	-0.85	Satisfactory
LogKd-Zn		Calibration	2009-2010	113	0.41	0.34	-0.84	0.90	0.19	Satisfactory
		Validation		39	0.46	0.35	2.61	1.37	-0.87	Satisfactory
PCR Results										
MeT-Cd		Calibration	2009-2010	113	0.12	0.06	-29.29	0.99	0.02	Satisfactory
		Validation		39	0.62	0.34	-29.75	1.01	-0.03	Satisfactory
MeT-Cu	GESZ	Calibration	2009-2010	113	3.70	2.03	-18.64	0.75	0.44	Satisfactory
	Stations*	Validation		39	10.59	12.11	-11.47	0.51	0.74	Good
MeT-Pb		Calibration	2009-2010	113	6.56	3.39	-20.8	0.84	0.3	Satisfactory
		Validation		39	119.82	12.70	157.49	6.39	-39.8	Unsatisfactory
MeT-Zn		Calibration	2009-2010	113	30.75	15.68	-15.31	0.91	0.17	Satisfactory
		Validation		39	39.73	57.94	18.46	0.42	0.82	Very Good
LogKd-Cd		Calibration	2009-2010	113	0.34	0.25	0.00	0.59	0.65	Very Good
		Validation		39	0.92	0.60	8.79	1.40	-0.96	Satisfactory
LogKd-Cu	GESZ	Calibration	2009-2010	113	0.28	0.20	0.00	0.69	0.53	Good
		Validation		39	1.38	0.76	-3.06	1.68	-14.4	Satisfactory
LogKd-Pb	Stations*	Calibration	2009-2010	113	0.35	0.26	0.00	0.70	0.51	Good
		Validation		39	0.62	0.46	3.96	1.42	-1.02	Satisfactory
LogKd-Zn		Calibration	2009-2010	113	0.35	0.27	2.83	1.27	-0.62	Satisfactory
		Validation		39	1.52	0.81	0.67	1.96	-2.84	Satisfactory

*Five GESZ sampling campaigns were conducted from September 2009 to October 2010

[#]Based on Moriasi et al. (2007) cosindering the PBIAS, RSR and NSE (see below)

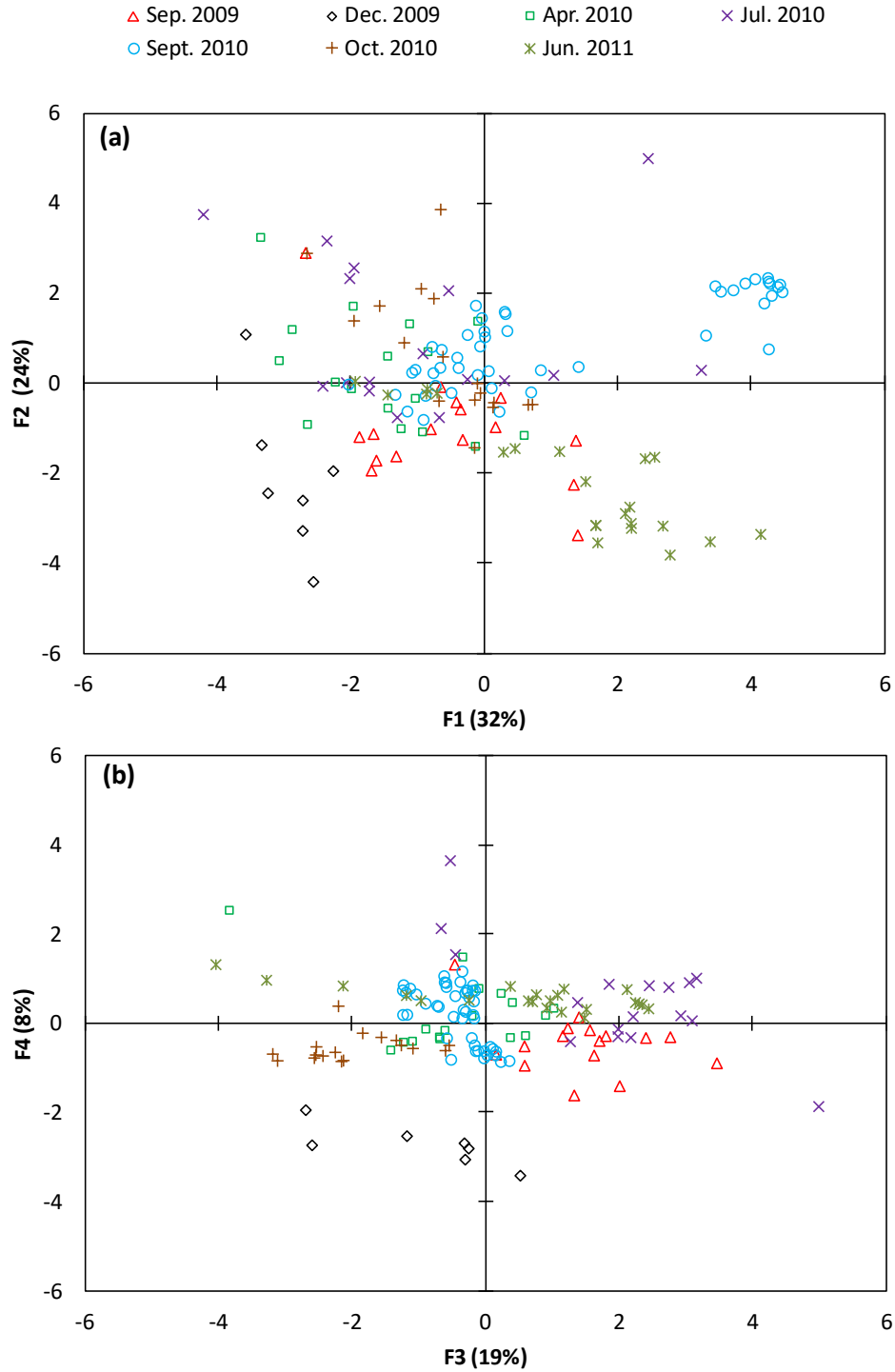| Performance rating	PBIAS (%) (Stream flow)	PBIAS (%) (Metal)	RSR	NSE	Color Scheme
Very good	< ±10	< ±15	0 to 0.5	0.75 to 1	
Good	±10 to ±15	±15 to ±30	0.5 to 0.6	0.65 to 0.75	
Satisfactory	±15 to ±25	±30 to ±55	0.6 to 0.7	0.5 to 0.65	
Unsatisfactory	> ±25	> ±55	> 0.7	< 0.5	

Figure S1. The score plot (a) for the first two components (F1 and F2) and (b) for the third and fourth components (F3 and F4), showing with distinction of data between seven GESZ sampling campaigns.
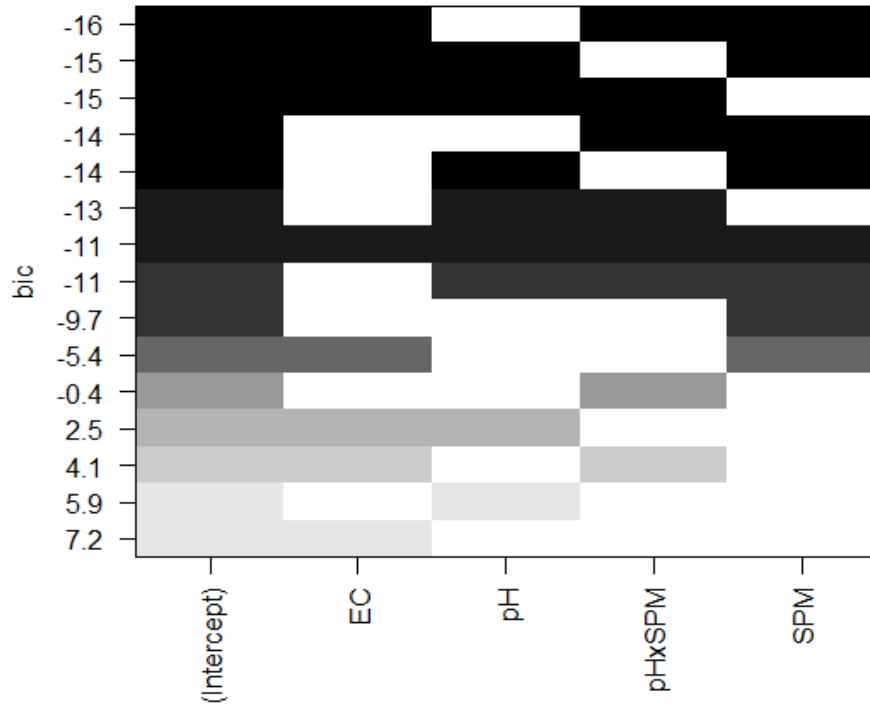
Figure S2. The Bayesian information criterion (BIC) scores corresponding to different independent variables used to derive the MLR based regression equation for total cadmium (MeT-Cd)
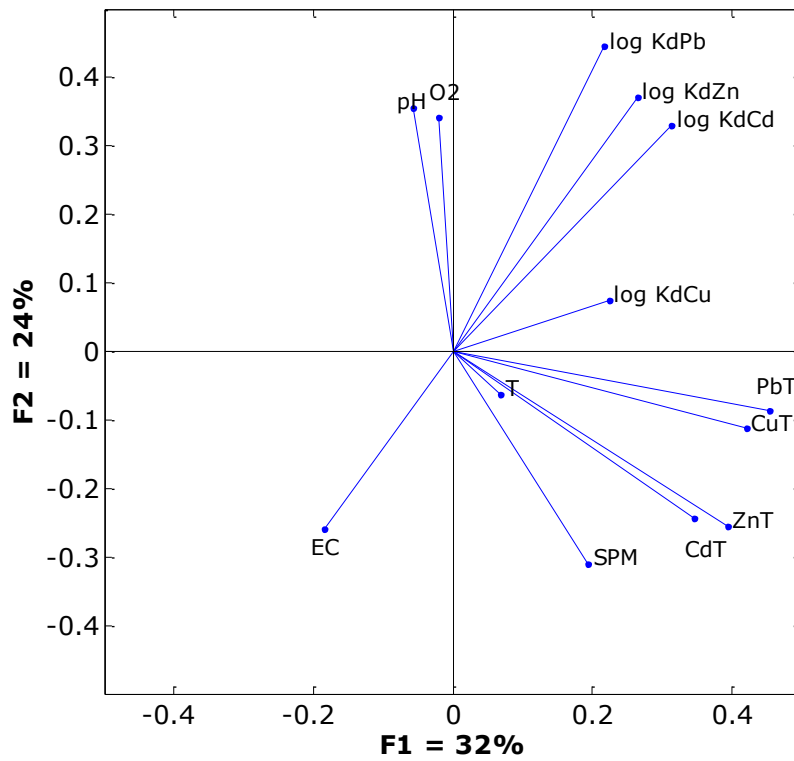

Figure S3. The loading plot, showing relationships amongst different physio-chemical variables taken into consideration, and the total metal concentrations with the corresponding distribution coefficients.
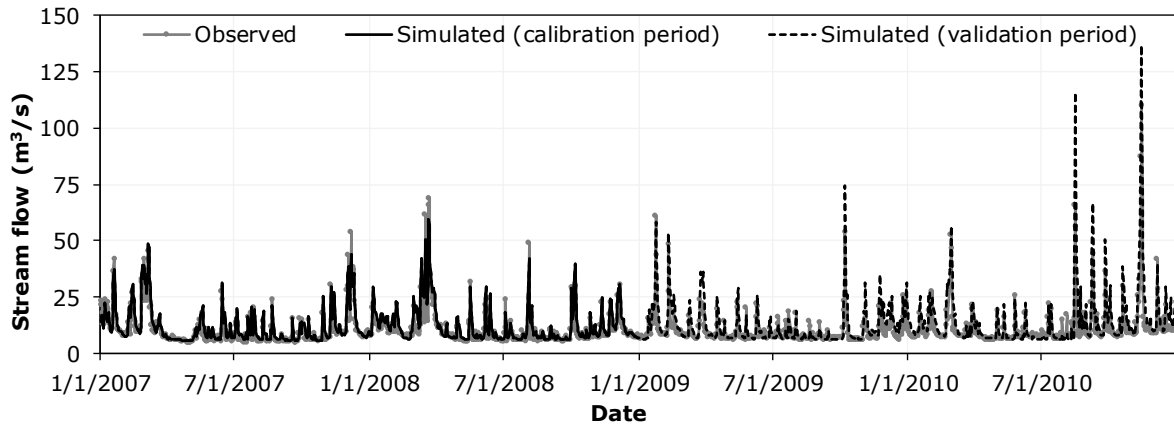
Figure S4. Streamflow results at Eppegem for calibration (2007-08) and validation (2009-10) at daily time scale.
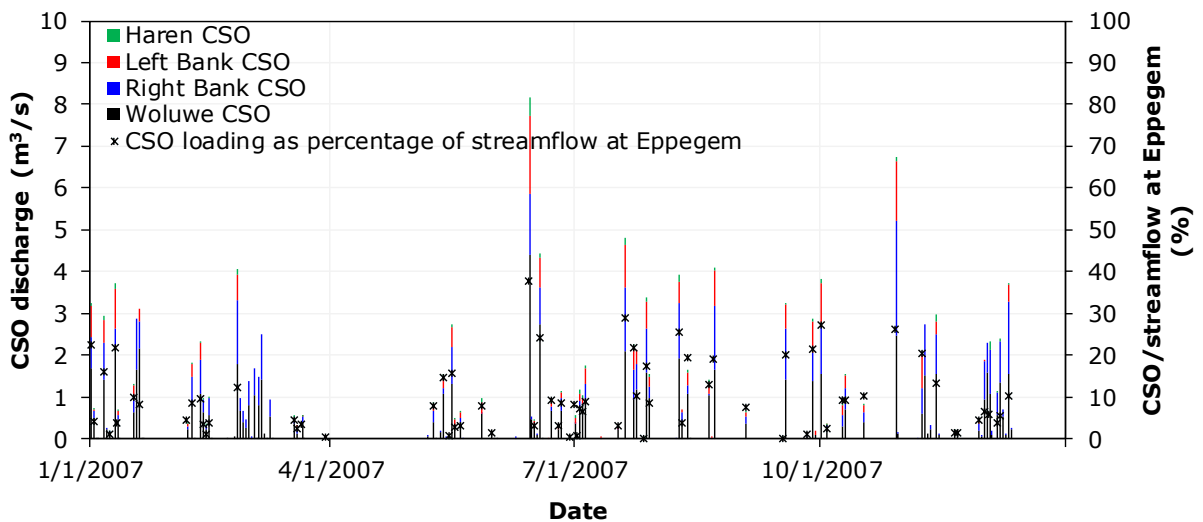

Figure S5. Total CSO discharge sent to river in the year of 2007 through systems of four collector systems in/around Brussels. Also, shown is the CSO volume as percentage of streamflow at Eppegem at daily time scale
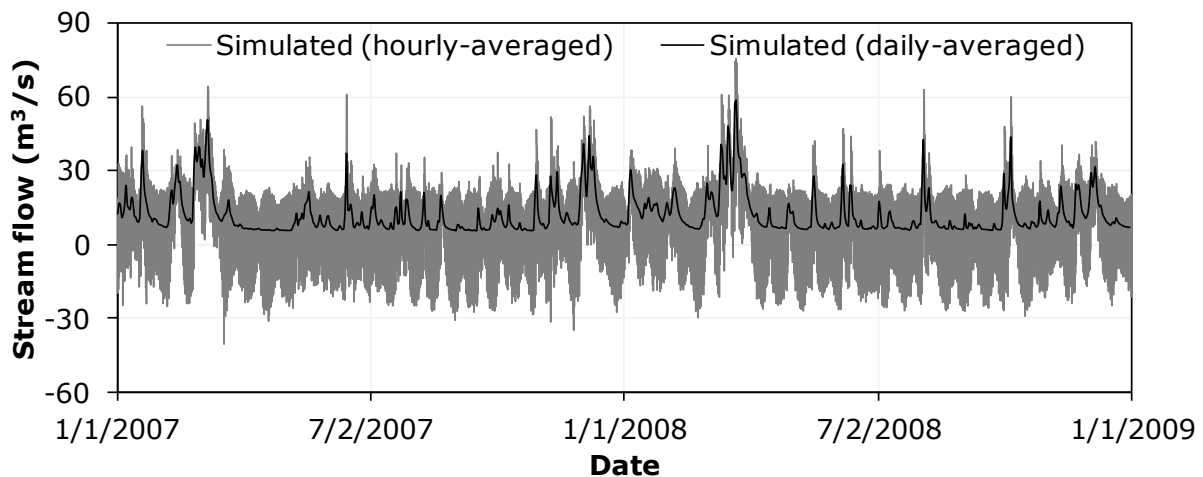

Figure S6. Hourly and daily (averaged) stream flow at GESZ sampling station Z12. From simulation, the tidal effects are observed up to 9 km upstream of the outlet of Zenne river.