Electronic Supplementary Information

Biocidal substances in the Seine River: Contribution from urban sources in the Paris megacity

Claudia Paijens[a,b], Damien Tedoldi[a,c], Bertrand Frère[b], Romain Mailler[d], Vincent Rocher[d], Régis Moilleron[a], Adèle Bressy*[a]

[a] Leesu, Ecole des Ponts, Univ Paris Est Creteil, Marne-la-Vallee, France
[b] LCPP, Laboratoire Central de la Préfecture de Police, Paris, France
[c] Univ Lyon, INSA Lyon, DEEP, EA7429, 69621 Villeurbanne, France
[d] SIAAP, Direction de l'Innovation, Colombes, France
*Corresponding author: adele.bressy@enpc.fr

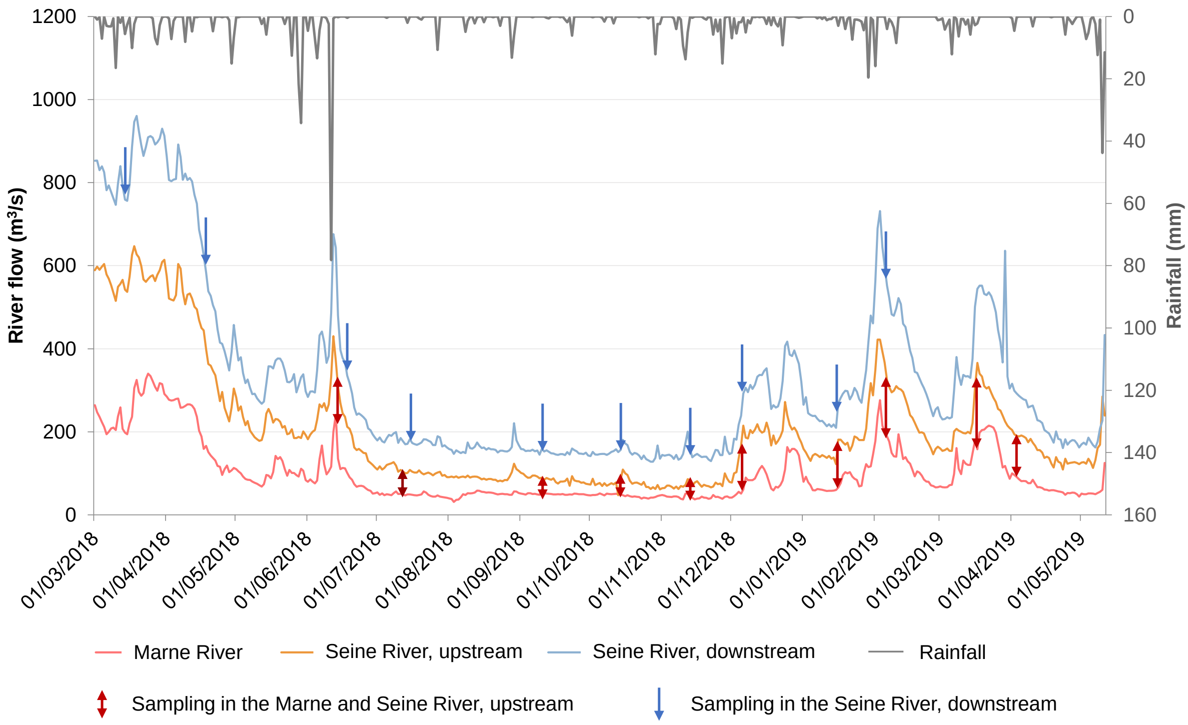

Fig. S1. Flow rate in the Marne and Seine Rivers, rainfall and sampling campaigns

Table S1. Information on sampling campaigns (TSS: total suspended solids; DOC: dissolved organic carbon; POC: particulate organic carbon)

Sampling date dd/mm/yy hh:mm	Flow rate (m^3/s)	$H_{rainfall}$ over the last 4 days[c] (mm)	TSS (mg/L)	DOC (mgC/L)	POC (mgC/L)
Marne River					
13/06/18 14:35	241[a]	81.2	200	3.2	6.6
12/07/18 11:00	41[a]	0	18	1.9	0.92
11/09/18 11:00	52[a]	0	18	2.6	0.86
16/10/18 10:30	45[a]	0	10	3.1	5.8
13/11/18 11:00	42[a]	28.2	5.4	4.2	10
06/12/18 11:00	59[a]	9.2	7.1	3.7	6.8
14/01/19 11:00	58[a]	2.8	7.9	3.2	6.1
06/02/19 11:00	189[a]	4	89	2.6	4.2
18/03/19 11:00	201[a]	5.2	55	3.2	4.3
05/04/19 11:00	81[a]	4.8	12	2.0	8.2
Seine River at Alfortville					
13/06/18	372[a]	81.2	34.1	3.93	2.0
14:5512/07/18 11:30	105[a]	0	6.77	2.07	0.76
11/09/18 11:30	84[a]	0	9.68	2.58	0.94
16/10/18 11:00	100[a]	0	4.89	3.04	12
13/11/18 11:30	84[a]	28.2	5.63	3.65	20
06/12/18 11:30	215[a]	9.2	14.88	3.53	9.8
14/01/19 11:30	138[a]	2.8	5.13	3.41	8.9
06/02/19 11:30	324[a]	4	47.7	5.52	5.8
18/03/19 11:30	340[a]	5.2	24.8	2.64	7.1
05/04/19 11:30	191[a]	4.8	8.87	2.36	6.2
Seine River at Conflans-Sainte-Honorine					
14/03/1810:00	762[b]	7.7	20.1	-	-
17/04/18 10:00	635[b]	0.2	10.2	2.64	0.79
19/06/18 10:00	318[b]	0.4	15.5	3.69	0.98
17/07/18 10:00	171[b]	2	5.09	2.62	0.71
11/09/18 09:00	150[b]	0	7.28	3.49	0.82
16/10/18 09:50	174[b]	0	6.66	3.57	12.7
13/11/18 09:00	160[b]	28.2	3.92	5.60	25.0
06/12/18 09:00	289[b]	9.2	5.89	4.30	12.5
15/01/19 09:00	210[b]	1.6	5.26	4.41	14.3
06/02/19 09:00	552[b]	4	71.9	3.27	5.03

[a] data from “Hydro” database
[b] calculated flow rate from “Hydro” database and data from SIAAP
[c] data from Infoclimat, Paris Montsouris station

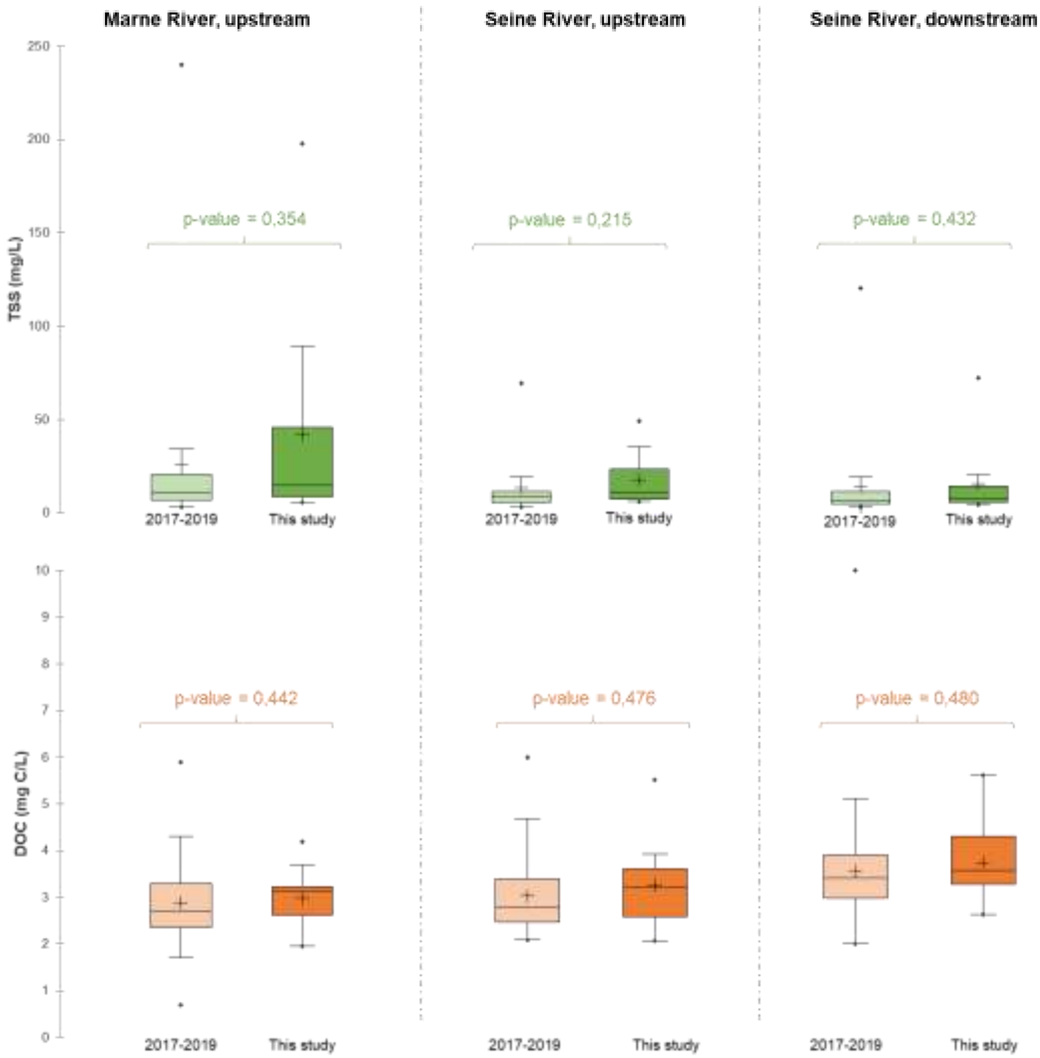

Fig. S2. Representativeness of the sampling campaigns: comparison of water quality parameters (TSS and DOC). The bottom of the box represents the 1st quartile and the top the 3rd quartile. The horizontal line represents the median value and the cross the mean value. The two data sets were compared using a Mann-Whitney test. The resulting p-values are indicated on the figure.

Table S2. Information on the 18-targeted biocides

Biocide	Abbreviation	CAS number	Formula	MW (g/mol)	Log Kow	pKa	logD*	EQS[a] (µg/L)(average / max)	PNEC (µg/L)	DT50[b] in fresh waters (day)
Diuron		330-54-1	$C_9H_{10}Cl_2N_2O$	233.1	2.85		0.13	0.2 / 1.8	0.07[c]	113-2190
Isoproturon		34123-59-6	$C_{12}H_{18}N_2O$	206.3	2.5		2.45	0.3 / 1	0.32[d]	30-1560
Methylisothiazolinone	MIT	2682-20-4	C_4H_5NOS	115.2	-0.49		-0.23		3.39[e]	18-30
Benzisothiazolinone	BIT	2634-33-5	C_7H_5NOS	151.2	0.64		1.41		4.03[e]	>50
Chloro-methylisothiazolinone	CMIT	26172-55-4	C_4H_4ClNOS	149.6	0.4		1.12		0.049[e]	3-6.6
Octylisothiazolinone	OIT	26530-20-1	$C_{11}H_{19}NOS$	213.3	2.45		2.99		0.0071[e]	>30
Dichloro-octylisothiazolinone	DCOIT	64359-81-5	$C_{11}H_{17}Cl_2NOS$	282.2	3.59		4.43		0.034[e]	<1
Benzyldimethyldodecyl ammonium chloride	BZK C12	139-07-1	$C_{21}H_{38}ClN$	304.5	1.7				0.062[c]	30
Benzyldimethyltetradecyl ammonium chloride	BZK C14	139-08-2	$C_{23}H_{42}ClN$	346.6	2.5				0.043[c]	30
Benzyldimethylhexadecyl ammonium chloride	BZK C16	122-18-9	$C_{25}H_{47}ClN$	388.7	3.2				0.043[c]	30
Terbutryn		886-50-0	$C_{10}H_{19}N_5S$	241.4	3.7	4.3	1.38	0.065 / 0.34	0.065[c]	354
Cybutryn (Irgarol 1051)		28159-98-0	$C_{11}H_{19}N_5S$	253.4	3.7	4.1	3.21	0.0025 / 0.016	0.0025[c]	30
Terbuthylazine		5915-41-3	$C_9H_{16}ClN_5$	229.7	3.0	2	2.99		0.06[d]	77
Carbendazim		10605-21-7	$C_9H_9N_3O_2$	191.2	1.5	4.2	1.61		0.15[d]	42-350
Iodopropynyl butylcarbamate	IPBC	55406-53-6	$C_8H_{12}INO_2$	281.1	2.8		3.2		0.168[c]	7-139
Thiabendazole		148-79-8	$C_{10}H_7N_3S$	201.2	2.4	4.7 & 12	2.39		1.2[d]	203
Tebuconazole		107534-96-3	$C_{16}H_{22}ClN_3O$	307.8	3.7	5	3.74		0.24[c]	28
Mecoprop		93-65-2	$C_{10}H_{11}ClO_3$	214.6	0.1	3.7	-0.65		0.9[c]	31

MW: molecular weight / PNEC: predicted no effect concentration
*ChemSpider
[a] Environmental quality standards from ECHA; [b] Half-life in fresh waters from Paijens et al. (2020b); [c] Norman, 2022; [d]AA-EQS FW; [e] ECHA 2022

Table S3. Limits of detection (LOD_d) and quantification (LOQ_d) in the dissolved fraction of urban waters in ng/L

	River	
	LOD_d (ng/L)	LOQ_d (ng/L)
Diuron	0.27	0.66
Isoproturon	0.11	0.11
MIT	5	9.9
BIT	0.28	2.1
CMIT	1.6	8
OIT	0.21	0.52
DCOIT	0.04	0.45
BZK C12	5	17
BZK C14	4.7	16
BZK C16	3.6	12
Terbutryn	0.13	0.13
Cybutryn	0.14	0.14
Terbuthylazine	0.11	0.11
Carbendazim	0.17	0.17
IPBC	1.2	2.4
Thiabendazole	0.15	0.15
Tebuconazole	0.08	0.08
Mecoprop	1.5	2

Table S4. Limits of detection (LOD_p) and quantification (LOQ_p) (min-max) in the particulate fraction of waters in ng/g (dry weight)

	River	
	LOD_p (ng/g)	LOQ_p (ng/g)
Mass of particles (min-max in mg)	8.5 - 103	
Diuron	1.0-1.2	2.4-30
Isoproturon	0.5-5.9	0.5-5.9
MIT	2.4-30	4.9-59
BIT	1.0-12	7.3-89
CMIT	4.9-59	24-296
OIT	1.0-12	2.4-30
DCOIT	0.5-5.9	4.9-59
BZK C12	7.3-89	24-296
BZK C14	7.3-89	24-296
BZK C16	7.3-89	24-296
Terbutryn	1.0-12	1.0-12
Cybutryn	0.5-5.9	0.5-5.9
Terbuthylazine	0.5 5.9	0.5-5.9
Carbendazim	0.5-5.9	0.5-5.9
IPBC	4.9-59	9.7-118
Thiabendazole	0.5-5.9	0.5-5.9
Tebuconazole	1.0-12	1.0-12
Mecoprop	7.3-89	9.7-119

Table S5. Management of < LOD or < LOQ values for data treatment

Data treatment	
Case 1: one fraction (1 - dissolved or particulate) was ≥ LOQ_1 and the other (2) was > LOD_2 and < LOQ_2, *i.e.*, the total concentration was between $C_{determined}$ + LOD_2 and $C_{determined}$ + LOQ_2.	The indeterminate term was approximated by max(LOD_2, LOQ_2/2).
Case 2: One fraction (1) was ≥ LOQ_1 and the other was < LOD_2, *i.e.*, the total concentration was between $C_{determined}$ and $C_{determined}$ + LOD_2.	The indeterminate term was considered equal to zero.
Case 3: Both fractions were < LOQ or < LOD.	Concentrations in these samples were reported as "< M", where M was calculated from the corresponding LOQ_i or LOD_i. When this applied to more than half of the dataset, the median value was reported as "< M", and no attempt was made to perform further statistics on the data.
Particulate proportion (f_{part}) calculation	
Case 1: the substance was quantified in both C_d and C_p fractions (both expressed in ng/L).	$$f_{part} = \frac{C_p}{C_d + C_p}$$
Case 2: the concentration in the particulate fraction C_p was lower than the limit of quantification LOQ_p (resp. of detection LOD_p).	An upper limit of the f_{part} proportion was estimated by replacing the unquantified (resp. detected) value with the LOQ_p (resp. LOD_p): $$C_p < LOQ_p \implies f_{part} < \frac{LOQ_p}{C_d + LOQ_p}$$
Case 3: the dissolved C_d concentration was below the limit of quantification LOQ_d (resp. of detection LOD_d).	A lower bound on the proportion f_{part} was estimated by replacing the unquantified (resp. non-detected) value by LOQ_d (resp. LOD_d) $$C_d < LQ_d \implies f_{part} > \frac{C_p}{LOQ_d + C_p}$$
Case 4: the substance was not quantified in any fraction.	f_{part} was not calculated.

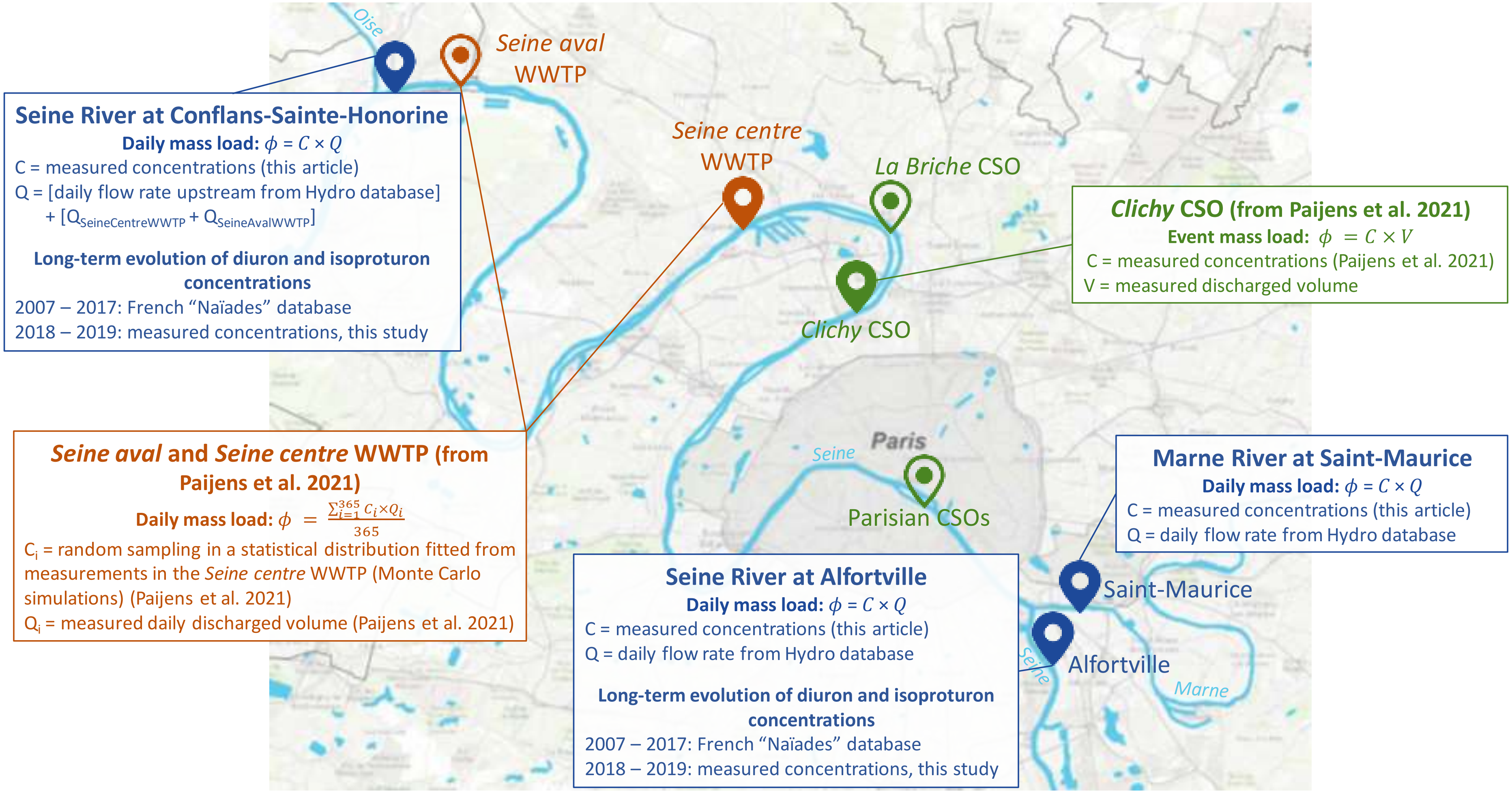

Fig. S3. Overview of the overall estimation approach to estimate daily mass loads and to study long-term evolutions of diuron and isoproturon concentrations

Table S6. Particulate contents measured in the Marne and the Seine Rivers up- and downstream the Paris conurbation (quantification frequencies, median contents (min-max))

Compound	Marne River (Saint-Maurice)		Seine River upstream (Alfortville)		Seine River downstream (Conflans-Ste-Honorine)	
	Number of quantification	Median content (ng/g) (min – max)	Number of quantification	Median content (ng/g) (min – max)	Number of quantification	Median content (ng/g) (min – max)
Diuron	0/10	-	1/10	<2.0 – 2.9	1/10	<3.0 – 51
Isoproturon	5/10	1.6 (<0.5 – 6.9)	4/10	<1.1 – 10	3/10	<1.7 – 44
MIT	9/10	78 (<6.6 – 1,100)	9/10	170 (<15 – 2,300)	8/10	140 (<13 – 3,600)
BIT	3/10	<7.3 – 12	3/10	<13 – 22	8/10	7.9 (<0.9 – 110)
CMIT	3/10	<13 - 270	3/10	<11 – 350	1/10	<6.0 – 1,900
OIT	0/10	-	1/10	<4.3 – 3.6	1/10	<3.0 – 63
DCOIT	0/10	-	0/10	-	0/10	-
BZK C12	10/10	83 (18 – 24,000)	10/10	630 (36 – 40,000)	9/10	2,200 (<90 – 11,000)
BZK C14	9/10	38 (<3.5 – 870)	10/10	770 (27 – 5,400)	9/10	170 (<42 – 2,000)
BZK C16	2/10	<2.4 – 9.0	3/10	<43 – 150	5/10	17 (<7.3 – 130)
Terbutryn	7/10	3.0 (<0.5 – 7.1)	7/10	3.8 (<1.1 – 100)	2/10	<1.7 – 5.8
Cybutryn	0/10	-	0/10	-	0/10	-
Terbuthylazine	8/10	2.6 (<0.5 – 5.7)	5/10	3.0 (<2.6 – 8.0)	4/10	<1.8 – 41
Carbendazim	7/10	1.9 (<1.3 – 9.0)	3/10	<1.1 – 4.2	3/10	<1.7 – 6.0
IPBC	7/10	37 (<11 – 150)	5/10	130 (<20 – 160)	9/10	76 (<31 – 170)
Thiabendazole	7/10	2.0 (<1.3 – 12)	5/10	3.6 (<1.1 – 16)	5/10	4.0 (<1.7 – 36)
Tebuconazole	10/10	11 (3.7 – 42)	9/10	7.9 (<3.4 – 34)	10/10	6.6 (1.9 – 63)
Mecoprop	0/10	-	0/10	-	0/10	-

Table S7. Daily/event loads of biocides discharged by the sewer system through WWTP effluents and CSOs, and transiting in the river upstream (Marne + Seine Rivers) and downstream (Seine River) the Paris conurbation: data presented as min-max (median), except for WWTPs (95% confidence interval about the mean value). NC: not calculated.

	WWTP effluents (*Seine aval* + *Seine centre*) (Paijens et al. 2021)	***Clichy* CSO discharges)**	**Marne + Seine Rivers, upstream**	**Seine River, downstream**
	g/day	**g/event**	**g/day**	**g/day**
Diuron	32 ± 2	3 – 290 (20)	28 – 870 (100)	55 – 1020 (160)
Isoproturon	2.7 ± 0.2	<1 – 12 (1)	<1 – 200 (20)	<1 – 280 (32)
MIT	290 ± 20	1 – 240 (20)	<10 – 3200 (480)	<10 – 4800 (500)
BIT	47 ± 3	1 – 54 (7)	<10 – 200 (50)	<60 – 450 (140)
CMIT	NC	<1 – 30 (<5)	<20 – 240 (<70)	<50 – 820 (<80)
OIT	NC	1 – 38 (8)	<2 – 41 (15)	<2 – 120 (20)
DCOIT	3.9 ± 0.3	<1 – 8 (1)	<4 – 130 (17)	<1 – 620 (24)
BZK C12	1460 ± 130	63 – 3000 (700)	270 – 27000 (7100)	730 – 43000 (3700)
BZK C14	NC	26 – 2200 (230)	50 – 6300 (660)	170 – 3800 (980)
BZK C16	NC	<10 – 250 (40)	<70 – 2200 (<300)	<80 – 4000 (450)
Terbutryn	31 ± 2	1 – 66 (10)	5 – 160 (36)	30 – 200 (58)
Cybutryn	NC	<1 – 5 (<1)	<1 – 10 (<3)	<1 – 120 (<3)
Terbuthylazine	1.9 ± 0.2	<1 – 8 (1)	<3 - 2000 (23)	<1 – 630 (26)
Carbendazim	32 ± 3	2 – 190 (15)	28 – 740 (110)	<10 – 760 (150)
IPBC	7.6 ± 0.5	<1 – 9 (<1)	<15 – 330 (22)	<20 – 150 (25)
Thiabendazole	23 ± 2	<1 – 26 (3)	<3 – 65 (30)	25 – 250 (60)
Tebuconazole	14 ± 1	1 – 67 (10)	20 – 5100 (60)	30 – 1200 (100)
Mecoprop	56 ± 4	<10 – 140 (40)	<20 – 790 (60)	<25 – 340 (160)