Supplementary material: **"Smarter sediment screening: Effect-based quality assessment, chemical profiling and risk identification"**

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SI 1 – Previously reported surface water and sediment contaminant concentrations at the investigated urban and agricultural locations.

Table S1. Exceedances of the intervention values (>I) for PAH and metal concentrations that were previously reported in the sediment of the investigated urban locations. Locations: WK = Wittenkade, WBV= Wittenburgervaart, WD= Westerdok, BG= Bickersgracht, OBV= Oosterburgervaart.

class	compound	intervention value (mg/kg)	location WK	WBV	WD	BG	OBV
PAHs		40	>I	>I	>I	>I	>I
metals	As	85	-	-	>I	-	-
	Cd	14	-	-	-	>I	>I
	Cr	380	-	-	-	>I	>I
	Cu	190	-	-	>I	>I	>I
	Ni	210	-	-	-	-	-
	Pb	580	>I	>I	>I	>I	>I
	Zn	2000	-	-	>I	>I	-

Table S2. Pesticide concentrations (in µg/L) that were previously reported in the surface waters of the investigated agricultural locations. Locations: BW = Balgweg, WL = Westland, SX = Sexbierum.

class	Compound	location BW	WL	SX
herbicides	2,4,5-trichlorophenoxy acetic acid	0.01	-	<0.06
	2,4- dichlorophenoxy acetic acid	0.01	-	<0.04
	4-(2,4-dichlorophenoxy)butyric acid	0.02	-	<0.05
	Dichlorprop	0.01	-	<0.04
	2,6-dichlorobenzamide	0.03	0.02	-
	MCPA	0.01	-	<0.05
	MCPB	0.01	-	<0.1
	dinitro-ortho-cresol	0.01	0.07	-
	Aclonifen	-	0.1	<0.03
	Alachlor	0.02	-	<0.02
	Atrazine	0.02	0.01	<0.02
	Bentazone	0.02	-	0.14
	Bifenox	0.05	0.02	<0.03
	Chlorbromuron	-	0.02	<0.05
	Chloroxuron	0.01	0.02	-
	Chlorpropham	0.03	0.01	<0.02
	Chlorotoluron	0.01	-	<0.03
	Chloridazon	0.01	0.06	0.038
	clomazone	0.01	0.01	<0.006

	cycloxydim	-	0.03	<0.003
	desethyl-atrazine	0.02	0.02	-
	desethylterbuthylazine	0.01	0.05	<0.05
	desmedipham	-	0.06	<0.02
	desmetryn	0.03	-	0.01
	dichlobenil	0.02	0.01	-
	diflufenican	-	0.08	<0.02
	dimethenamide	-	0.01	<0.007
	diuron	0.01	0.01	<0.04
	ethofumesate	0.01	0.01	<0.1
	phenmedipham	-	0.06	<0.04
	flufenacet	0.01	0.07	-
	fluroxypyr	0.01	-	<0.05
	irgarol	0.05	-	< 0.05
	isoproturon	0.01	0.01	<0.03
	linuron	0.01	0.02	0.034
	mesotrione	-	0.03	<0.005
	methabenzthiazuron	-	0.01	<0.03
	metamitron	0.02	0.05	<0.03
	metazachlor	0.02	0.01	<0.003
	metsulfuron methyl	-	0.01	<0.002
	metobromuron	-	0.03	<0.03
	metolachlor	0.01	0.02	<0.02
	metoxuron	0.02	0.01	<0.03
	metribuzin	0.02	0.01	<0.009
	monolinuron	-	0.01	0.026
	monuron	-	0.03	<0.03
	nicosulfuron	-	0.01	<0.004
	pendimethalin	-	0.01	<0.03
	propazine	0.02	0.01	-
	propyzamide	0.02	0.01	-
	prosulfocarb	0.01	-	<0.01
	simazine	0.02	0.02	<0.01
	sulcotrion	-	0.06	<0.007
	terbutrin	0.01	0.01	<0.04
	terbuthylazine	0.02	0.01	<0.02
	tri-allate	-	0.01	<0.02
	trifluralin	0.02	0.02	<0.02
	triflusulfuron methyl	-	0.01	<0.008
insecticides	avermectin	0.07	0.07	-
	acetamiprid	-	0.01	<0.003
	aldicarb	0.01	0.05	-
	aldoxycarb	0.05	0.05	-
	chlorfenvinphos	0.02	0.02	<0.02
	coumaphos	0.08	-	<0.004
	cypermethrin	0.05	-	<0.04

	deltamethrin	0.03	0.02	<0.02
	diazinon	0.04	0.01	<0.02
	dichlorvos	0.05	0.02	<0.01
	dimethoate	0.04	0.03	<0.02
	disulfoton	-	0.02	<0.02
	esfenvalerate	0.02	0.01	<0.03
	ethoprophos	0.02	-	<0.02
	azinphos-ethyl	0.01	-	<0.04
	bromophos-ethyl	0.02	0.01	-
	chlorpyrifos	-	0.01	<0.02
	parathion	0.03	0.06	<0.02
	fenamiphos	0.01	0.02	-
	fenitrothion	0.03	0.1	<0.03
	fenoxycarb	0.02	0.02	-
	fenthion	0.02	0.01	<0.02
	fipronil	0.01	0.02	<0.03
	flonicamid	-	0.09	<0.09
	phosalone	0.05	0.01	-
	phosphamidon	0.05	0.02	-
	heptenophos	0.02	0.01	<0.01
	hexythiazox	0.01	0.01	-
	imidacloprid	0.02	0.006	<0.006
	lambda-cyhalothrin	-	0.01	<0.03
	malathion	0.02	0.01	<0.02
	methiocarb	0.02	0.01	<0.01
	methoxyfenozide	0.01	0.04	-
	azinphos-methyl	0.03	0.02	<0.06
	bromophos-methyl	0.02	0.01	-
	pirimiphos-methyl	-	0.01	< 0.0006
	mevinphos	0.04	0.01	< 0.02
	pentachlorophenol	0.06	-	< 0.2
	pirimicarb	0.01	0.03	< 0.005
	propoxur	0.03	0.01	< 0.006
	tetrachlorvinphos	0.02	0.01	-
	thiacloprid	0.01	-	< 0.006
	thiamethoxam	-	0.28	0.013
	triazophos	0.03	0.01	< 0.02
fungicides	azoxystrobin	0.01	0.2	0.23
	bitertanol	0.02	0.01	-
	boscalid	0.01	0.03	0.08
	carbendazim	0.09	0.23	< 0.02
	chlorothalonil	-	0.03	< 0.02
	cymoxanil	-	0.06	< 0.03
	cyproconazole	-	0.07	< 0.03
	cyprodinil	0.01	0.1	-
	dichlofluanid	-	0.02	< 0.02

difenoconazole	-	0.04	< 0.03
dimethomorph	0.02	0.04	< 0.04
dodemorph	0.04	0.06	-
epoxiconazole	0.02	-	0.018
etridiazole	0.08	0.01	-
fenpropidin	-	0.02	< 0.02
fenpropimorph	-	0.01	< 0.05
fluazinam	0.02	0.12	< 0.02
flutolanil	-	0.01	0.015
furalaxyl	0.02	0.01	-
imazalil	0.01	0.03	< 0.04
iprodione	-	0.03	< 0.05
kresoxim-methyl	0.01	0.02	< 0.02
metalaxyl	0.02	0.03	< 0.006
pencycuron	0.02	0.01	0.14
prochloraz	0.05	-	< 0.02
procymidone	0.01	0.02	-
propamocarb	-	0.03	< 0.04
propiconazole	0.02	-	< 0.02
pyraclostrobin	0.01	0.05	< 0.005
pyrazophos	0.03	0.01	-
pyrimethanil	0.01	0.02	-
tebuconazole	0.03	0.02	< 0.06
thiabendazole	0.02	-	< 0.06
tolclofos-methyl	0.01	0.01	< 0.08
tolylfluanid	-	0.01	< 0.02
triadimenol	-	0.02	< 0.03
trifloxystrobin	0.02	0.02	< 0.005
vinclozolin	-	0.01	0.02

SI 2 - Sampling locations.

Table S3. Overview of the investigated study sites, with grouping based on their main pollution source.

land use	location	name code	GPS coordinates	sampling day (dd/mm/yy)
Reference	Science Park	SP	52.356795, 4.955046	03/04/17
Urban	Wittenkade	WK	52.380458, 4.873499	23/03/17
	Wittenburgervaart	WBV	52.371604, 4.924437	21/03/17
	Westerdok	WD	52.387007, 4.891236	22/03/17
	Bickersgracht	BG	52.386725, 4.888277	20/03/17
	Oostenburgervaart	OBV	52.369790, 4.926579	17/03/17
WWTP	Hilversum	HI	52.252807, 5.243704	24/03/17
	Eindhoven	EI	51.463189, 5.508095	30/03/17
	Utrecht	UT	52.109390, 5.104465	31/03/17
Agriculture	Balgweg	BW	52.886506, 4.870424	27/03/17
	Westland	WL	51.961299, 4.192689	28/03/17
	Sexbierum	SX	53.227556, 5.497638	29/03/17

Figure S1. Sediment sampling locations in The Netherlands.
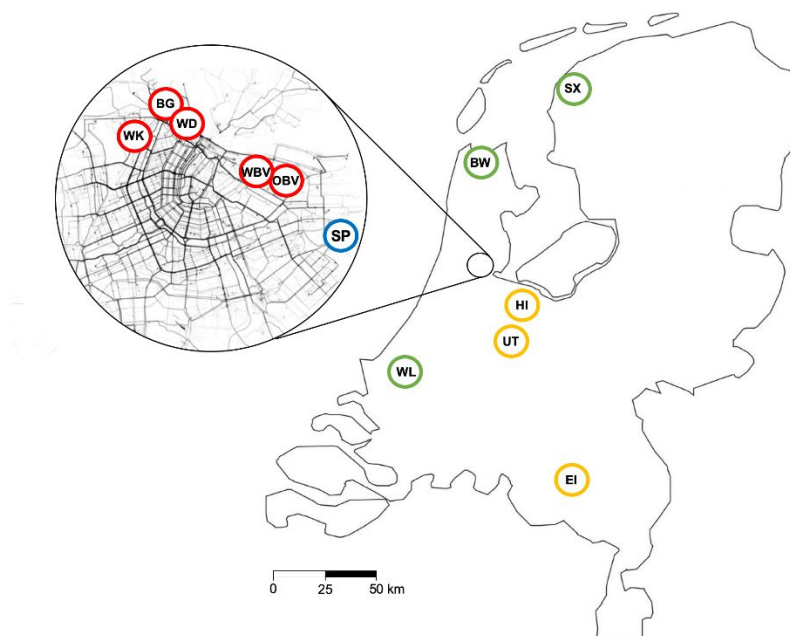
SI 3 - Chemical target analysis of sediment associated contaminants.

Additional details on total extraction of metals from sediment samples

For each location in duplicate, approximately 250 mg sample was used to extract metals. Sediment with 4 mL HNO_3 65% and 2 mL of HCl 37% was added to a destruction tube. After 60 minutes, 1 mL of ultra-pure water was added and the tubes were placed in a microwave (Multiwave; Perkin Elmer, Groningen, The Netherlands) for destruction. After the extraction, the sample (approx. 5 mL) was transferred to a 50 mL volumetric flask and supplemented with ultra-pure water to 50 mL. Per sample, 1 mL was diluted with 8 mL ultra-pure water and 0.5 ml cesium chloride and 0.5 ml yttrium internal standards to a final volume of 10 mL.

Table S4. Compounds targeted in chemical profiling of the investigated sediments and their respective limits of quantification (LOQ). In fiber and freely dissolved LOQs are calculated based on $logK_{ow}$, $logK_{fw}$ and analytical LOQ using the equations presented in the main body of the article.

compound group inorganic	target compound	pollutant type	remark	detector	LOQ	unit
metals	Al	legacy		ICP-OES	24	µg/L
	As	legacy		ICP-OES	37	µg/L
	Ag	legacy		ICP-OES	1	µg/L
	Cd	legacy		ICP-OES	1	µg/L
	Cr	legacy		ICP-OES	2	µg/L
	Cu	legacy		ICP-OES	1	µg/L
	Fe	legacy		ICP-OES	1	µg/L
	Mn	legacy		ICP-OES	3	µg/L
	Ni	legacy		ICP-OES	4	µg/L
	Pb	legacy		ICP-OES	15	µg/L

| | Se | legacy | | ICP-OES | | | 16 | | | µg/L |
| | Zn | legacy | | ICP-OES | | | 4 | | | µg/L |

| compound group | | | | | | | | | LOQ | |
organic	target compound	pollutant type	remark	detector	$\log K_{ow}$	$\log K_{fw}$	analytical	in fiber	freely dissolved	unit
PAHs	phenanthrene	legacy		LC-FLU	4.46	4.29	12	3908.1	0.200	µg/L
	Pyrene	legacy		LC-FLU	4.88	4.99	2	651.4	0.007	µg/L
WWTP markers	HHCB	musk fragrance		GC-MS	5.9	6.19	100	24450.6	0.016	µg/L
	bisphenol A	plastic precursor		LC-MS	3.3	3.30	2	651.4	0.326	µg/L
	Nonylphenol	surfactant precursor	isomer mixture	GC-MS	5.15	5.36	100	24450.6	0.108	µg/L
	Triclosan	antimicrobial agent		GC-MS	4.3	4.41	100	24450.6	0.949	µg/L
	mehtyl-triclosan	metabolite		GC-MS	5	5.19	100	24450.6	0.158	µg/L
pesticides	2,4,5-trichlorophenoxyacetic acid	herbicides	dissociated	LC-MS	4	4.08	6	1954.1	0.163	µg/L
	2,4-dichlorophenoxyacetic acid	herbicides	dissociated	LC-MS	2.81	2.76	4	1302.7	2.287	µg/L
	dichlorprop	herbicides	dissociated	LC-MS	3.43	3.44	4	1302.7	0.468	µg/L
	2,6-di-tert-butyl-4-methylphenol	n.a.		GC-MS	5.1	5.30	250	81418.8	0.408	µg/L
	4-(2,4-dichlorophenoxy)butyric acid	herbicides	dissociated	LC-MS	3.53	3.56	5	1628.4	0.453	µg/L
	4-chloroaniline	n.a.		GC-MS	1.83	1.67	50	16283.8	350.823	µg/L
	4-chlorophenoxyacetic acid	herbicides	dissociated	LC-MS	2.25	2.13	4	1302.7	9.583	µg/L
	4-nonylphenol	n.a.		GC-MS	5.76	6.03	10	3256.8	0.003	µg/L
	4-tert-octylphenol	n.a.		GC-MS	5.25	5.47	25	8141.9	0.028	µg/L
	acetamiprid	insecticides		LC-MS	0.8	0.52	0.3	97.7	29.355	µg/L
	aclonifen	herbicides		GC-MS	4.04	4.12	500	162837.7	12.289	ng/L
	alachlor	herbicides		GC-MS	3.52	3.54	150	48851.3	13.945	ng/L
	atrazine	herbicides		GC-MS	2.61	2.53	100	32567.5	95.379	ng/L
	azinphos-ethyl	insecticides		GC-MS	3.18	3.17	250	81418.8	55.470	ng/L
	azinphos-methyl	insecticides		GC-MS	2.75	2.69	750	244256.5	499.985	ng/L
	azoxystrobin	fungicides		LC-MS	2.5	2.41	0.9	293.1	1.137	µg/L
	bentazon	herbicides		LC-MS	2.8	2.74	3	977.0	1.760	µg/L
	bifenox	herbicides		GC-MS	4.48	4.61	1.25	407.1	0.010	µg/L
	bixafen	fungicides		LC-MS	3.3	3.30	0.8	260.5	0.131	µg/L
	boscalid	fungicides		LC-MS	2.96	2.92	2	651.4	0.779	µg/L

carbendazim	fungicides	LC-MS	1.48	1.28	2	651.4	34.359	µg/L
carfentrazone-ethyl	herbicides	GC-MS	n.a.	n.a.	150	48851.3	n.a.	ng/L
chlorbromuron	herbicides	LC-MS	3.09	3.07	5	1628.4	1.397	µg/L
chlorfenvinphos	insecticides	GC-MS	3.81	3.87	500	162837.7	22.135	ng/L
chloridazon	herbicides	LC-MS	1.14	0.90	0.5	162.8	20.500	µg/L
chlorothalonil	fungicides	GC-MS	2.94	2.90	125	40709.4	51.250	µg/L
chlorotoluron	herbicides	LC-MS	2.41	2.31	3	977.0	4.773	µg/L
chlorpropham	herbicides	LC-MS	2.96	2.92	2	651.4	0.779	µg/L
chlorpyrifos	insecticides	GC-MS	4.96	5.14	750	244256.5	1.751	ng/L
cis-1,2,3,6-tetrahydrophthalimide	n.a.	GC-MS	0.3	-0.03	12.5	4070.9	4395.702	µg/L
clomazone	herbicides	LC-MS	2.5	2.41	0.6	195.4	0.758	µg/L
clothianidin	insecticides	LC-MS	0.905	0.64	10	3256.8	747.990	µg/L
coumaphos	insecticides	LC-MS	4.13	4.22	0.4	130.3	0.008	µg/L
cyazofamid	fungicides	LC-MS	3.2	3.19	4	1302.7	0.843	µg/L
cycloxydim	herbicides	LC-MS	3.31	3.31	0.3	97.7	0.048	µg/L
cymoxanil	fungicides	LC-MS	0.67	0.38	3	977.0	409.382	µg/L
cypermethrin	insecticides	GC-MS	6.6	6.97	225	73276.9	0.008	ng/L
cyproconazole	fungicides	LC-MS	3.09	3.07	3	977.0	0.838	µg/L
DEHP	n.a.	GC-MS	7.6	8.08	250	81418.8	0.001	µg/L
deltamethrin	insecticides	GC-MS	6.2	6.52	250	81418.8	0.024	ng/L
desethylterbuthylazine	herbicides	GC-MS	2.23	2.11	500	162837.7	1260.793	ng/L
desmedipham	herbicides	LC-MS	3.39	3.40	2	651.4	0.259	µg/L
diazinon	insecticides	GC-MS	3.81	3.87	50	16283.8	2.214	ng/L
dichlofluanid	fungicides	GC-MS	3.7	3.74	200	65135.1	11.732	ng/L
dichlorvos	insecticides	GC-MS	1.43	1.22	50	16283.8	976.186	ng/L
dicofol	insecticides	GC-MS	4.3	4.41	50	16283.8	0.632	ng/L
DEET	insect repellant	GC-MS	2.18	2.06	500	162837.7	1432.845	ng/L
difenoconazole	fungicides	GC-MS	4.36	4.48	1.25	407.1	0.014	µg/L
diflufenican	herbicides	GC-MS	4.9	5.08	500	162837.7	1.361	ng/L
dimethanamid	herbicides	LC-MS	1.89	1.73	0.7	228.0	4.213	µg/L
dimethoate	insecticides	GC-MS	0.78	0.50	125	40709.4	12873.448	ng/L

dimethomorph	fungicides		GC-MS	2.68	2.61	150	48851.3	119.609	ng/L
disulfoton	insecticides		GC-MS	4.02	4.10	1	325.7	0.026	µg/L
diuron	herbicides		LC-MS	2.68	2.61	4	1302.7	3.190	µg/L
epoxiconazole	fungicides		LC-MS	3.3	3.30	1	325.7	0.163	µg/L
esfenvalerate	insecticides		GC-MS	6.22	6.54	500	162837.7	0.046	ng/L
ethofumesate	herbicides		LC-MS	2.7	2.63	10	3256.8	7.576	µg/L
ethoprophos	insecticides		GC-MS	3.59	3.62	50	16283.8	3.886	ng/L
fenamiphos	insecticides		GC-MS	3.23	3.22	750	244256.5	146.428	ng/L
fenitrothion	insecticides		GC-MS	3.3	3.30	75	24425.6	12.242	ng/L
fenoxycarb	insecticides		GC-MS	4.3	4.41	1.25	407.1	0.016	µg/L
fenpropidin	fungicides	protonated	LC-MS	2.6	2.52	2	651.4	1.957	µg/L
fenpropimorph	fungicides		GC-MS	4.5	4.63	100	32567.5	0.758	ng/L
fenthion	insecticides		GC-MS	4.091	4.18	75	24425.6	1.618	ng/L
fipronil	insecticides		LC-MS	4	4.08	3	977.0	0.082	µg/L
flonicamid	insecticides		LC-MS	-0.24	-0.63	9	2931.1	12599.714	µg/L
florasulam	herbicides		LC-MS	-1.22	-1.72	0.3	97.7	5153.809	µg/L
fluazifop-p-butyl	herbicides		GC-MS	4.5	4.63	125	40709.4	0.947	ng/L
fluazinam	fungicides		LC-MS	4.03	4.11	2	651.4	0.050	µg/L
fluopicolide	fungicides		LC-MS	2.9	2.86	0.4	130.3	0.182	µg/L
fluoxastrobin	fungicides		LC-MS	2.86	2.81	0.4	130.3	0.201	µg/L
fluroxypyr	herbicides	dissociated	LC-MS	2.2	2.08	5	1628.4	13.614	µg/L
flutolanil	fungicides		LC-MS	3.17	3.16	0.4	130.3	0.091	µg/L
heptenophos	insecticides		GC-MS	2.32	2.21	50	16283.8	100.148	ng/L
imazalil	fungicides		LC-MS	2.56	2.48	4	1302.7	4.336	µg/L
imidacloprid	insecticides		LC-MS	0.57	0.27	0.6	195.4	105.747	µg/L
iodosulfuron-methyl-sodium	herbicides	dissociated	LC-MS	-0.7	-1.14	0.5	162.8	2270.907	µg/L
ioxynil	herbicides	dissociated	LC-MS	0.9	0.63	3	977.0	227.286	µg/L
iprodione	fungicides		GC-MS	3	2.97	500	162837.7	175.828	ng/L
irgarol	herbicides		GC-MS	4.07	4.16	500	162837.7	11.381	ng/L
isoproturon	herbicides		LC-MS	2.84	2.79	3	977.0	1.589	µg/L
kresoxim-methyl	fungicides		GC-MS	3.4	3.41	75	24425.6	9.478	ng/L

lambda-cyhalothrin	insecticides		GC-MS	6.8	7.19	200	65135.1	0.004	ng/L
linuron	herbicides		LC-MS	3.2	3.19	2	651.4	0.422	µg/L
malathion	insecticides		GC-MS	2.36	2.26	17.5	5699.3	31.642	ng/L
mandipropamid	fungicides		LC-MS	3.2	3.19	0.6	195.4	0.126	µg/L
MCPA	herbicides	dissociated	LC-MS	3.25	3.24	5	1628.4	0.927	µg/L
MCPB	herbicides	dissociated	LC-MS	2.79	2.73	10	3256.8	6.018	µg/L
MCPP-p	herbicides	dissociated	LC-MS	3.2	3.19	3	977.0	0.632	µg/L
mesosulfuron-methyl	herbicides	dissociated	LC-MS	-0.48	-0.90	0.3	97.7	776.079	µg/L
mesotrione	herbicides		LC-MS	0.9	0.63	0.5	162.8	37.881	µg/L
metalaxyl-m	fungicides		LC-MS	1.75	1.58	0.6	195.4	5.166	µg/L
metamitron	herbicides		LC-MS	0.83	0.56	3	977.0	271.863	µg/L
metazachlor	herbicides		LC-MS	2.13	2.00	0.3	97.7	0.977	µg/L
metconazole	fungicides		GC-MS	3.85	3.91	750	244256.5	29.973	ng/L
methabenzthiazuron	herbicides		LC-MS	2.64	2.57	3	977.0	2.650	µg/L
methiocarb	insecticides		LC-MS	2.92	2.88	1	325.7	0.432	µg/L
metobromuron	herbicides		LC-MS	2.38	2.28	3	977.0	5.154	µg/L
metolachlor	herbicides		LC-MS	3.13	3.11	2	651.4	0.504	µg/L
metoxuron	herbicides		LC-MS	1.64	1.46	3	977.0	34.226	µg/L
metrafenone	fungicides		GC-MS	4.3	4.41	1.25	407.1	0.016	µg/L
metribuzin	herbicides		LC-MS	1.7	1.52	0.9	293.1	8.807	µg/L
metsulfuron-methyl	herbicides		LC-MS	2.2	2.08	0.2	65.1	0.545	µg/L
mevinphos	insecticides		GC-MS	0.13	-0.22	50	16283.8	27162.959	ng/L
monolinuron	herbicides		LC-MS	2.3	2.19	2	651.4	4.216	µg/L
monuron	herbicides		LC-MS	1.94	1.79	3	977.0	15.886	µg/L
nicosulfuron	herbicides	dissociated	LC-MS	0.35	0.02	0.4	130.3	123.772	µg/L
oxadiazon	herbicides		LC-MS	5.33	5.56	10	3256.8	0.009	µg/L
oxydemeton-methyl	insecticides		LC-MS	-0.74	-1.19	1	325.7	5031.225	µg/L
parathion-ethyl	insecticides		GC-MS	3.83	3.89	75	24425.6	3.155	ng/L
parathion-methyl	insecticides		GC-MS	3	2.97	75	24425.6	26.374	ng/L
pencycuron	fungicides		LC-MS	4.68	4.83	0.7	228.0	0.003	µg/L
pendimethalin	herbicides		GC-MS	5.2	5.41	150	48851.3	0.190	ng/L

pentachlorophenol	insecticides	dissociated	LC-MS	5.12	5.32	20	6513.5	0.031	μg/L
phenmedipham	herbicides		LC-MS	3.59	3.62	4	1302.7	0.311	μg/L
phtalimide	fungicides		GC-MS	3.01	2.98	25	8141.9	8.569	μg/L
pirimicarb	insecticides		LC-MS	1.7	1.52	50	16283.8	489.252	ng/L
pirimiphos-methyl	insecticides		LC-MS	4.12	4.21	100	32567.5	2.003	ng/L
prochloraz	fungicides		LC-MS	3.5	3.52	2	651.4	0.196	μg/L
propamocarb	fungicides	protonated	LC-MS	-1.3	-1.81	4	1302.7	84324.924	μg/L
propiconazool	fungicides		GC-MS	3.72	3.77	150	48851.3	8.360	ng/L
propoxur	insecticides		LC-MS	1.52	1.32	0.6	195.4	9.305	μg/L
prosulfocarb	herbicides		GC-MS	4.65	4.80	50	16283.8	0.258	ng/L
prothioconazole	fungicides		LC-MS	2	1.86	30	9770.3	136.254	μg/L
pyraclostrobin	fungicides		LC-MS	3.99	4.07	0.5	162.8	0.014	μg/L
pyraflufen-ethyl	herbicides		GC-MS	3.49	3.51	750	244256.5	75.290	ng/L
pyridaben	insecticides		GC-MS	6.37	6.71	1	325.7	0.000	μg/L
pyroxsulam	herbicides		LC-MS	-1.01	-1.49	0.6	195.4	6023.168	μg/L
quinoxyfen	fungicides		GC-MS	5.1	5.30	75	24425.6	0.122	ng/L
quizalofop-p-ethyl	herbicides		GC-MS	4.61	4.76	500	162837.7	2.859	ng/L
rimsulfuron	herbicides	dissociated	LC-MS	-1.46	-1.99	0.6	195.4	19046.930	μg/L
simazine	herbicides		GC-MS	2.18	2.06	200	65135.1	573.138	ng/L
sulcotrione	herbicides		LC-MS	2.31	2.20	0.7	228.0	1.438	μg/L
tebuconazole	fungicides		GC-MS	3.7	3.74	125	40709.4	7.332	ng/L
tepraloxydim	herbicides		LC-MS	1.5	1.30	2	651.4	32.645	μg/L
terbuthylazine	herbicides		GC-MS	3.4	3.41	500	162837.7	63.189	ng/L
terbutryn	herbicides		GC-MS	3.74	3.79	75	24425.6	3.972	ng/L
thiabendazole	fungicides		LC-MS	2.39	2.29	6	1954.1	10.047	μg/L
thiacloprid	insecticides		LC-MS	1.26	1.03	0.6	195.4	18.097	μg/L
thiamethoxam	insecticides		LC-MS	-0.13	-0.51	0.3	97.7	316.969	μg/L
tolclofos-methyl	fungicides		LC-MS	3.8	3.86	8	2605.4	0.363	μg/L
Tolyfluanide	fungicides		GC-MS	3.9	3.97	500	162837.7	17.583	ng/L
Triadimenol	fungicides		LC-MS	3.18	3.17	3	977.0	0.666	μg/L
tri-allate	herbicides		GC-MS	4.6	4.74	50	16283.8	0.293	ng/L

Triazophos	insecticides		GC-MS	3.55	3.58	150	48851.3	12.915	ng/L
Trifloxystrobin	fungicides		LC-MS	4.5	4.63	0.5	162.8	0.004	μg/L
Trifluralin	herbicides		GC-MS	5.34	5.57	50	16283.8	0.044	ng/L
triflusulfuron-methyl	herbicides	dissociated	LC-MS	3.94	4.01	0.8	260.5	0.025	μg/L
trinexapac-ethyl	herbicides		LC-MS	-0.29	-0.69	0.8	260.5	1272.810	μg/L
Tritosulfuron	herbicides	dissociated	LC-MS	2.93	2.89	0.6	195.4	0.252	μg/L

Chromatographic details of target organic compound analysis in SPME extracts

Table S5: Chromatographic details of organic compound analysis.

Contaminant analysis (supplier of standard)	Chromatographic separation	Detection
• phenanthrene (J.T. Baker) • pyrene (J.T. Baker)	• **System:** Prominence, Shimadzu, Kyoto, Japan • **Column:** LiChrospher C18 column (5µm; 250 x 4 mm; Knauer, Berlin, Germany). • **Injection:** 20 µL injected of acetonitrile diluted two times in ultrapure water.	• **System:** Prominence Fluorescence detecter, Shimadzu, Kyoto, Japan • **Quantification:** PAH concentrations were quantified with external standard calibrations.
• HHCB (International Flavors & Fragrances, Hilversum, NL) • nonylphenol (Acros Organics, NJ, USA • triclosan (Sigma-Aldrich) • methyl-triclosan (Dr Ehrenstorfer GmbH, Augsburg, Germany)	• **System:** ThermoQuest Trace GC 2000 (Thermo Fisher Scientific) • **Column:** DB-5MS fused silica column (60 m × 0.25 mm, 0.25 µm film thickness; J&W Scientific, Folsom, CA, USA). • **Injection:** 1 µL of the extracts was directly injected cold on-column.	• **System:** Finnigan Trace MS quadrupole MS (Thermo Fisher Scientific) • **Quantification:** Selected ion monitoring (SIM), identification was based on retention time and three or four (nonylphenol) compound specific masses (Table S6). and external standard calibrations.
• BPA (Sigma-Aldrich)	• **System:** Prominence, Shimadzu, Kyoto, Japan • **Column:** Kinetex 5 µm (2.1 x 50 mm) • **Injection:** 20 µL injected of acetonitrile diluted three times in ultrapure water	• **System:** QTRAP 4000 MS system (AB SCIEX, MA, USA) • **Mode:** negative electrospray ionization (ESI) • **Quantification:** BPA concentrations were quantified with external standard calibrations.
• Pesticides via LC-MS/MS	• **System:** Accela 1250 HPLC system (Thermo Fisher Scientific) equipped with a CTC autosampler • **Column:** Hypersil GOLD aQTM SPE column (20 X 2.1 mm, 12 µm) + Hypersil GOLDTM HPLC column (50 X 2.1 mm, 3 µm), both Thermo Fisher Scientific) **Injection:** 1 µL	• **System:** TSQ Vantage triple quadrupole mass spectrometer • **Mode:** negative and positive mode with an electrospray ionization source (Thermo Fisher Scientific). • **Quantification:** selected reaction monitoring (SRM), and multiple external standards
• Pesticides via GC-MS	• **System:** Trace GC system (Thermo Fisher Scientific) • **Column:** DB-5MS fused silica column (30 m X 0.25 mm, 0.,25 µm film thickness, J&W Scientific).	• **System:** Dual stage quadrupole (DSQ) MS (Thermo Fisher Scientific) • **Quantification:** selected ion recording (SIR) mode, and multiple external standards

PAHs (HPLC)

For PAH detection in the acetonitrile SPME extracts, after 1 minute, the acetonitrile concentration was slowly increased to 80% at 8 minutes. From minute 8 to 11, the acetonitrile concentration was increased to 100%, after which the concentration was decreased to 45% at 15 minutes. Measurements started with a 45:55 acetonitrile:water (v:v) solution. Phenanthrene fluorescence was measured at 250/385 nm and pyrene fluorescence was measured at 335/383 nm.

WWTP markers (LC and GC)

BPA (HPLC). Retention of BPA was achieved on a Shimadzu Shim-pack XR-ODS III column (50 X 2.0 mm; 1.6 μm particle size) with the column oven set to 35 °C. The mobile phase consisted 0.1% acetic acid in ultrapure water (pump A) and methanol (pump B) with the following gradient at a flow rate of 0.3 mL/min: t=0: 20% B; t=3: 100% B; t=4.5: 100% B; t=5: 20% B, followed by 3 minutes equilibration before the next injection. External calibration standards prepared in 30/70 acetonitrile/water (v/v) had concentrations ranging from 0.07 – 200 μg/L. Using a log normalized linear calibration curve in the appropriate range ($R^2 > 0.9999$) showed a maximum deviation of 3% from the calculated concentrations for external calibration standards. Ionisation with negative ESI was used (400 ˚C, IS -4500V), and BPA was quantified with m/z 227/211.6 (CE -24 eV) with additional qualifying m/z 227/132.8 (CE -33 eV). Data acquisition and peak analysis were performed with AB SCIEX Analyst software (ver. 1.5.1).

HHCB, nonylphenol, triclosan and methyl-triclosan (GC). HHCB, nonylphenol, triclosan and methyl-triclosan analysis in the hexane SPME extracts was performed on a ThermoQuest Trace GC 2000 system (Thermo Fisher Scientific) fitted with a DB-5MS fused silica column (60 m × 0.25 mm, 0.25 μm film thickness; J&W Scientific, Folsom, CA, USA). Helium was used as a carrier gas at a constant flow of 1.6 mL/min. Mass spectrometric detection was performed using electron impact ionization (EI) carried out at 70 eV.

Table S6. Temperature program applied in GC-method for chemical analysis of WWTP marker compound concentrations in hexane SPME extracts equilibrated in sediment slurries for 28 d.

rate (°C/min)	temperature (°C)	time (min)
	50	2
60	180	0
5	220	0
20	230	0
2	235	5
20	325	5

Table S7. Retention times and identification masses applied in GC-method for chemical analysis of WWTP marker compound concentrations in hexane SPME extracts equilibrated in sediment slurries for 28 d.

Compound	retention time (min)	identification masses
nonylphenol	10.00-12.25	107, 121, 135, 146
HHCB	12.25-14.80	213, 243, 258
Triclosan	14.80-16.88	218, 288, 290
methyl-tricolsan	16.88-20.00	252, 302, 304

Pesticides (LC-MS/MS and GC-MS)

Acetonitrile SPME extracts were subjected to chemical screening for 150 commonly used pesticides at the laboratory of the water authority of Fryslân using liquid chromatography coupled to tandem mass spectrometry (LC-MS/MS), as well as gas chromatography coupled to mass spectrometry (GC–MS). Liquid chromatography (LC) was performed on an Accela 1250 HPLC system (Thermo Fisher Scientific, Landsmeer, The Netherlands) equipped with a CTC autosampler. For LC analysis, 50 µL of the acetonitrile extracts was evaporated and reconstituted in 5 mL of artificial surface water. Chromatographic separation was performed on a Hypersil GOLD™ HPLC column (50×2.1 mm, 3 µm particle size, Thermo Fisher Scientific) preceded by a Hypersil GOLD aQ™ SPE column (20×2.1 mm, 12 µm particle size, Thermo Fisher Scientific) using a methanol/water system (Tables

S8-9). Detection of compounds was performed on a TSQ Vantage triple quadrupole mass spectrometer (MS) equipped with an electrospray ionization source (Thermo Fisher Scientific). Target compounds were identified based on selected reaction monitoring (SRM), and quantified by multiple external standard calibrations. For gas chromatography (GC), acetonitrile SPME extracts were directly analysed in duplicate on a Trace GC system (Thermo Fisher Scientific) fitted with a DB-5MS fused silica column (30 m × 0.25 mm, 0.25 µm film thickness; J&W Scientific, Folsom, CA, USA). Detection of compounds was performed on a dual stage quadrupole (DSQ) MS (Thermo Fisher Scientific) set to selected ion recording (SIR) mode. Identification of target compounds was based on retention time and three compound specific masses, one quantification mass and two masses for peak ratios, for confirmation of the compound. Identified compound concentrations in the extracts were quantified with a five-point calibration curve, applying a correction for internal standard recovery for each specific compound.

Table S8. Gradients of solvent A (MQ-water + 0.5% acetic acid) and B (MeOH + 0.5% acetic acid) applied in HPLC-method for chemical analysis of 150 pesticides.

time (min)	flow (mL/min)	% A	% B
method 1			
0.00	0.5	95.0	5.0
2.00	0.5	70.0	30.0
8.00	0.5	60.0	40.0
10.00	0.5	20.0	80.0
12.00	0.5	95.0	5.0
14.00	0.5	95.0	5.0
method 2			
0.00	0.5	95.0	5.0
1.00	0.5	95.0	5.0
4.50	0.5	40.0	60.0
6.50	0.5	40.0	60.0
10.00	0.5	2.0	98.0
14.00	0.5	2.0	98.0
15.00	0.5	95.0	5.0
19.00	0.5	95.0	5.0
method 3			
0.00	0.35	98.0	2.0
1.25	0.35	98.0	2.0
10.00	0.35	10.0	90.0
12.00	0.35	80.0	20.0

| 14.00 | 0.35 | 80.0 | 20.0 |

Table S9. Gradients of solvent C (MQ-water + 0.5% acetic acid) and D (MeOH) applied in SPE-method for chemical analysis of 150 pesticides.

time (min)	flow (mL/min)	% C	% D
method 1			
0.00	1.0	100.0	0.0
1.50	1.0	100.0	0.0
1.60	0.1	0.0	100.0
4.90	0.1	0.0	100.0
5.00	1.0	0.0	100.0
8.00	1.0	0.0	100.0
9.00	0.1	0.0	100.0
11.00	1.0	100.0	0.0
13.00	1.0	100.0	0.0
14.00	0.1	100.0	0.0
method 2			
0.00	1.0	100.0	0.0
1.50	1.0	100.0	0.0
1.60	0.1	0.0	100.0
4.90	0.1	0.0	100.0
5.00	1.0	0.0	100.0
7.00	1.0	0.0	100.0
7.10	0.1	100.0	0.0
15.00	1.0	100.0	0.0
17.00	1.0	100.0	0.0
17.01	0.2	100.0	0.0
method 3			
0.00	1.00	100.0	0.0
1.25	1.00	100.0	0.0
1.50	0.10	0.0	100.0
6.00	0.10	0.0	100.0
8.00	1.00	0.0	100.0
9.00	1.00	0.0	100.0
10.00	1.00	100.0	0.0
13.00	1.00	100.0	0.0

Table S10. Temperature programme applied in GC-method for chemical analysis of 150 pesticides.

rate (°C/min)	temperature (°C)	time (min)
	35	5
10	180	5
3	200	5
25	280	5

SPME measurement reliability and assurance of non-depletive equilibration

To check for differences between individual fibers within one sediment sample, the pyrene concentration in three fibers from a single sediment sample from the Wittenkade was analyzed. The relative standard deviation between these fibers was 1%. In addition, a 33% increase in pyrene concentration was observed in the Wittenkade when comparing the 1-month to the 2-month samples. Therefore, the PAH concentrations in this experiment were determined by using one 2-month equilibrated SPME fiber per site (n=1). To investigate the variation in pesticide accumulation in SPME fibers between replicates and equilibration times, pesticide concentrations in two 1 month exposed and one two month exposed fibers in the Sexbierum sediment were compared. Pesticide concentration correspondence between the two 1-month exposed replicates was on average 96% (88-108 %; 6 detected compounds) for LC analysed compounds and 129% (58-282%; 4 detected compounds) for GC analysed compounds. Pesticide concentration correspondence between the 1- and 2-month exposed replicates was on average 90% (63-115%) for LC analysed compounds and 72% (39-117%) for GC analysed compounds. Hence, variation was greater for GC analysed compounds compared to LC analysed compounds. This may be due to the required additional sample treatment before GC analysis, but may also partly be attributable to the longer equilibration times required for compounds with higher $\log K_{OW}$ values which are targeted in GC analysis. This is further illustrated by the observation that the detected levels of GC analysed compounds were generally lower in the one month than the two month equilibrated fibers. One month exposed SPME fibers were used for pesticide analyses, implying that the detected pore water concentrations for GC analysed pesticides may be an underestimation of the actual concentrations in the sediment cores.

A hypothetical calculation can effectively illustrate that non-depletive equilibration of SPME fibers with the sediment pore water was achieved:

Each used 4 cm SPME fiber has a polymer volume of approximately 0.6 mL, which roughly equates to 0.6 mg of polymer material. As three fibers were exposed per treatment, 1.8 mg of polymer material was equilibrated with the sediment. Per treatment, 5 g of wet sediment was used, which

roughly equates to 3 g sediment dry-weight. The lowest OC content measured in the used sediments, which was hence the worst-case scenario for potential depletive equilibration, was 0.5 %, equating to approximately 15 mg of OC per treatment. Thus, 15 mg of OC was equilibrated with 1.8 mg of polymer material, leaving a considerable margin for non-depletive equilibration of the SPME fibers with the sediments in the present study design.

Table S11. Freely dissolved contaminant concentrations detected in sediments from sites with different land uses. AS = artificial sediment, other location codes are defined in Table S2, n.m. = not measured.

			reference		urban					WWTP			agriculture		
		Unit	AS	SP	WK	WBV	WD	BG	OBV	HI	EI	UT	BW	WL	SX
metals	Cd	μg/L	-	-	-	-	-	0.04	0.03	-	0.04	-	-	-	-
	Cr	μg/L	0.02	0.1	0.2	0.9	0.6	0.6	2.1	0.1	0.1	0.1	0.1	0.1	0.4
	Cu	μg/L	0.7	0.2	2.0	7.2	6.6	8.9	6.3	2.2	0.7	1.6	0.2	0.1	2.3
	Ni	μg/L	-	-	1.9	7.8	8.2	6.1	3.4	0.8	1.7	1.9	-	-	5.0
	Pb	μg/L	0.2	0.1	0.5	0.8	1.0	2.0	0.8	0.1	0.1	0.6	0.1	0.1	0.1
	Zn	μg/L	0.2	0.5	6.0	11.5	13.6	15.7	6.5	4.4	2.5	4.8	0.5	1.3	1.5
PAHs	phenanthrene	μg/L	-	0.9	22.2	-	-	42.4	-	6.3	1.5	4.8	0.7	1.7	0.5
	pyrene	μg/L	-	0.02	2.4	0.3	0.1	6.3	0.1	0.6	0.2	0.5	0.1	0.1	0.01
WWTP markers	HHCB	ng/L	-	-	-	-	-	-	-	40.2	10.7	46.8	-	-	-
	bisphenol A	ng/L	88	96	n.m.	177	445	68	165	658	919	896	90	666	56
	nonylphenol	ng/L	153	194	172	125	190	200	1086	311	151	380	-	147	-
	triclosan	ng/L	-	-	-	-	-	-	-	2944	-	2442	-	-	-
pesticides	azoxystrobin	ng/L	-	-	-	-	-	-	-	-	-	-	-	2528	4802
	bixafen	ng/L	-	-	-	-	-	-	-	-	-	-	-	-	72.6
	boscalid	ng/L	-	-	-	-	-	-	-	-	-	-	-	2649	1091
	chlorpyrifos	ng/L	-	-	-	-	-	-	-	-	-	-	-	8.6	-
	dicofol	ng/L	-	-	-	-	-	0.2	-	-	-	0.2	-	-	-
	diflufenican	ng/L	-	-	-	-	-	-	-	-	3.3	-	-	-	-
	esfenvalerate	ng/L	-	-	-	-	-	-	-	-	-	-	-	2.9	0.3
	fluopicolide	ng/L	-	-	-	-	-	-	-	-	-	-	-	-	1067
	flutolanil	ng/L	-	-	-	-	-	-	-	-	-	-	252	-	117
	lambda-cyhalothrin	ng/L	-	-	-	-	-	-	-	-	-	-	-	-	0.04
	pencycuron	ng/L	-	-	-	-	-	-	-	-	-	-	-	-	64.9

prosulfocarb	ng/L	-	0.7	-	0.7	-	0.3	1.1	0.4	0.7	0.9	0.4	5.7	8.8
tebuconazole	ng/L	-	-	-	-	-	-	-	-	-	-	-	-	11.7
tri-allate	ng/L	-	-	-	0.6	0.9	0.5	0.8	0.6	-	0.8	0.4	2.3	-

SI 4 – Physical chemical sediment characteristics.

Materials and methods - Physical chemical characterization of sediment. *Particle size distribution.* All sediments were subjected to the dry sieving method (Cammeraat & Imeson, 1998). One sediment sample (>20 gr) per location was oven-dried at 30 ˚C and then fractionated using mesh sieves to obtain eight size fractions. Sieves were shaken for 5 min at 40 Hz using a horizontal shaking machine (AS 200 basic; Retsch, Aartselaar, Belgium) and each fraction was weighed.

C:N ratio and Total Organic Carbon content (TOC). One sediment core per location was dried and homogenized, and approximately 20 gr was ground using a planetary mill (Pulverisette 5; Fritsch, Idar-Oberstein, Germany) for 5 minutes at 400 rpm. Approximately 5 mg of ground sediment was used to determine the total C and N content in duplicate on an element analyzer (Vario El cube; Elementar, Langenselbold Germany). Total inorganic carbon (TIC) content was determined in duplicate based on weight loss by dissolution of $CaCO_3$ using a soliTIC module attached to the element analyser. By subtracting the TIC content from the total carbon content in the samples, the total organic carbon (TOC) content in the sediments was determined.

Cammeraat, L. H.; Imeson, A. C. Deriving indicators of soil degradation from soil aggregation studies in southeastern Spain and southern France. *Geomorphology* **1998**, *23* (2–4), 307–321.

Table S12. Characteristics of the investigated sediments. TOC = total organic carbon; N = nitrogen content; C:N = carbon to nitrogen ratio; ND = not determined; * calculated.

name code	fraction <63 μm (%)	TOC (%)	N (%)	C:N
AS (artificial sediment)	13.28	5.00*	ND	ND
SP (reference)	1.12	3.12	0.22	14.5
WK	1.09	4.69	0.17	28.2
WBV	4.29	7.88	0.72	10.9
WD	3.08	7.83	0.65	12.1
BG	8.51	9.31	0.4	23.2
OBV	1.19	6.89	0.38	18.0
HI	0.41	1.90	0.11	17.6
EI	7.01	2.08	0.18	11.6
UT	0.20	3.37	0.14	24.2
BW	1.51	0.45	0.05	8.3
WL	1.23	0.45	0.03	13.2
SX	2.11	1.48	0.18	8.1

Results - Physical chemical sediment characteristics. Sediment characteristics varied among the different sediments (Table S12). All field collected sediments contained >90% sand (>63 μm), and the fraction <63 μm ranged between 0.2% (UT) and 8.51% (BG). Except for the three most sandy field sediments (UT, HI and WK), this is within the particle size range between the reference location (SP, 1.1%) and the artificial sediment (13.3%). The percentage TOC was highest in the urban sediments (4.7 - 9.3 %), and lowest in the agricultural sediments (0.5-1.5 %). The C:N ratio, an indicator of the nutritional value of the organic matter, ranged between 8.1 (SX) and 28.2 (WK), but no land use related pattern in C:N ratio became apparent.

SI 5 – Data analyses and toxicity indices.

Statistical analysis of bioassay responses

In order to increase the field relevance of the 28 d *C. riparius* life cycle whole sediment bioassays, results of the contaminated sites were compared to the reference site (SP), rather than to the artificial sediment. As such, the artificial sediment served purely as a control of test performance and test organism viability, while the reference field sediment served as an uncontaminated reference for the field sediments, representative of midge survival, emergence and emergence time on natural sediments. Since the survival and emergence data of the whole sediment bioassays were not normally distributed, a Mann-Whitney U test was performed, to test for statistical differences between the reference and contaminated sediments. The mean emergence time (EmT_{50}), i.e. the day at which 50% emergence occurred, was calculated for each field location as well as for the artificial sediment by plotting the cumulative number of emerged midges against time, normalised to percentages for each treatment.[1] Since emergence times between males and females differ, this was done separately for each gender. Non-linear regression was performed using the logistic curve containing the EmT_{50} as a parameter. Significant differences between the reference site and all other treatments were checked using a one-way ANOVA with Dunnett's multiple comparison post-hoc test with significance level at $p < 0.05$. Statistical analyses were performed in SPSS® (IBM SPSS Statistics, Version 24, Armonk, NY, USA) for survival and emergence data, and in GraphPad Prism® (GraphPad Software Inc., Version 5.00, San Diego, CA, USA) for EmT_{50} calculations.

Toxicity index calculations

Three previously described toxicity indices were calculated to determine the potential toxicity of the detected contaminant concentrations in the sediments. A cumulative EAR of the mixture of detected compounds ($EAR_{mixture}$) was calculated for each location by summing the EAR profiles of each of the compounds using the R package *ToxEval*[2] as previously described.[3] For metals, no toxicity data were available within the USEPA ToxCast database[4] at the time of writing, and these were hence excluded from $EAR_{mixture}$ calculations.

Toxic pressures of individual chemicals, expressed as potentially affected fractions (PAF), were derived using previously reported chronic NOEC SSDs.[5] Subsequently, mixture toxic pressures, expressed as msPAF-NOEC, were derived assuming mixture toxicity according to the "mixed model" by De Zwart and Posthuma (2005).[6]

A literature search was performed to obtain reported ecotoxicity data for the detected compounds with identical endpoints for a single species, to allow for TU calculations. Effect concentrations were collected from the USEPA ECOTOX database[10] and peer-reviewed scientific literature. When no records were available through the former sources, effect concentrations were obtained from the University of Hertfordshire Pesticides Property Database,[11] adhering to an A5 data quality distinction of records. For *C. riparius*, no sufficiently homogeneous dataset with effect concentrations was available for reliable TU calculation, and hence it was decided to use reported acute (48 h) 50% toxic effect concentrations (EC_{50}) of the detected compounds to *D. magna* (Table S13), given the extensive data availability for this species and its common use as model organism for toxicity to aquatic invertebrates. Cumulative TUs were calculated by summing the lowest reported TU values for separate compounds per location assuming response additivity, in which TU was defined as the ratio of the measured concentration of a given compound to its EC_{50}.[7]

Bioassay responses were summarised in a toxicity index in which each location was attributed a point for the occurrence of lethal and sublethal effects respectively.

$EAR_{mixture}$ values ≥ 1 indicate that measured compounds are at a concentration expected to produce bioactivity for a given endpoint.[3] For msPAF, a threshold value for acceptable risk of 5% was previously adopted based on EU-WFD policy.[8] For TU, a threshold value of 0.1, based on European Commission Uniform Principles, was previously used for risk interpretation in surface water.[12]

(1)   Vogt, C.; Nowak, C.; Diogo, J. B.; Oetken, M.; Schwenk, K.; Oehlmann, J. Multi-Generation Studies with Chironomus Riparius - Effects of Low Tributyltin Concentrations on Life History Parameters and Genetic Diversity. *Chemosphere* **2007**, *67* (11), 2192–2200. https://doi.org/10.1016/j.chemosphere.2006.12.025.

(2)   De Cicco, L. A.; Corsi, S. R.; Villeneuve, D. L.; Blackwell, B.; Ankley, G. T. ToxEval: Evaluation of Measured Concentration Data Using the ToxCast High-Throughput Screening Database or a User-Defined Set of Concentration Benchmarks, R package version 1.0.0, 2018 http://usgs-r.github.io/toxEval/index.html (accessed Sep 3, 2019).

(3)   Blackwell, B. R.; Ankley, G. T.; Bradley, P. M.; Houck, K. A.; Makarov, S. S.; Medvedev, A. V.; Swintek, J.; Villeneuve, D. L. Potential Toxicity of Complex Mixtures in Surface Waters from a Nationwide Survey of United States Streams: Identifying in Vitro Bioactivities and Causative Chemicals. *Environ. Sci. Technol.* **2019**, *53* (2), 973–983. https://doi.org/10.1021/acs.est.8b05304.

(4)   U.S. EPA. iCSS ToxCast Dashboard, https://comptox.epa.gov/dashboard/ (accessed Sep 3, 2019).

(5)   Posthuma, L.; van Gils, J.; Zijp, M. C.; van de Meent, D.; de Zwart, D. Species Sensitivity Distributions for Use in Environmental Protection, Assessment, and Management of Aquatic Ecosystems for 12 386 Chemicals. *Environ. Toxicol. Chem.* **2019**, *38* (4), 703–711. https://doi.org/10.1002/etc.4373.

(6)   De Zwart, D.; Posthuma, L. Complex Mixture Toxicity for Single and Multiple Species: Proposed Methodologies. *Environ. Toxicol. Chem.* **2005**, *24* (10), 2665–2676. https://doi.org/10.1897/04-639R.1.

(7)   Sprague, J. B. Measurement of Pollutant Toxicity to Fish-III. Sublethal Effects and "Safe" Concentrations. *Water Res.* **1971**, *5* (6), 245–266. https://doi.org/10.1016/0043-1354(71)90171-0.

(8)   Lindim, C.; de Zwart, D.; Cousins, I. T.; Kutsarova, S.; Kühne, R.; Schüürmann, G. Exposure and Ecotoxicological Risk Assessment of Mixtures of Top Prescribed Pharmaceuticals in Swedish Freshwaters. *Chemosphere* **2019**, *220*, 344–352. https://doi.org/10.1016/J.CHEMOSPHERE.2018.12.118.

(9)   Bundschuh, M.; Goedkoop, W.; Kreuger, J. Evaluation of Pesticide Monitoring Strategies in Agricultural Streams Based on the Toxic-Unit Concept - Experiences from Long-Term Measurements. *Sci. Total Environ.* **2014**, *484* (1). https://doi.org/10.1016/j.scitotenv.2014.03.015.

(10)   U.S. EPA. ECOTOX Database, https://cfpub.epa.gov/ecotox/ (accessed Sep 3, 2019).

(11)   University   of   Hertfordshire,   Pesticide   Properties   Database   (PPDB),

http://sitem.herts.ac.uk/aeru/iupac/%0A (accessed Sep 3, 2019).

(12)   Bundschuh, M.; Goedkoop, W.; Kreuger, J. Evaluation of Pesticide Monitoring Strategies in

Agricultural Streams Based on the Toxic-Unit Concept - Experiences from Long-Term

Measurements.   *Sci.   Total   Environ.*   **2014**,   *484*   (1),   84–91.

https://doi.org/10.1016/j.scitotenv.2014.03.015.

Table S13. Reported aquatic acute (48 h) EC_{50} values for the detected compounds to *D. magna*, used for TU calculations.

compound	unit	EC_{50}	notes	used for TU calculation	reference	DOI/web adress
Cd	µg/L	3		•	Yim et al., 2006	10.1016/j.jhazmat.2005.11.107
Cd	µg/L	13.5			Meyer et al., 2014	10.1002/etc.2787
Cd	µg/L	39			Nelson et al, 1984	10.1002/etc.5620030212
Cd	µg/L	58.16			Attar & Maly, 1982	10.1007/BF01055205
Cd	µg/L	65			Biesinger & Christensen, 1972	10.1139/f72-269
Cd	µg/L	69			Dave et al., 1981	10.1016/0306-4492(81)90105-2
Cd	µg/L	142			Lari et al., 2017	10.1016/j.jhazmat.2017.03.060
Cd	µg/L	170			Teodorovic et al., 2009	10.2478/s11535-009-0048-7
Cd	µg/L	310			Meng et al., 2008	10.1109/ICBBE.2008.298
Cd	µg/L	1880			Khangarot & Ray, 1989	10.1016/0147-6513(89)90071-7
Cr	µg/L	160		•	Fargassova 1994	10.1007/BF00192051
Cr	µg/L	1790			Khangarot & Ray, 1989	10.1016/0147-6513(89)90071-7
Cr	µg/L	9070			Meng et al., 2008	10.1109/ICBBE.2008.298
Cu	µg/L	4		•	Yim et al., 2006	10.1016/j.jhazmat.2005.11.107
Cu	µg/L	9.8			Biesinger & Christensen, 1972	10.1139/f72-269
Cu	µg/L	31.8			Borgmann & Charlton, 1984	10.1016/S0380-1330(84)71855-7
Cu	µg/L	34.5			Lari et al., 2017	10.1016/j.jhazmat.2017.03.060
Cu	µg/L	41			Elnabarawy et al., 1986	10.1002/etc.5620050409
Cu	µg/L	66.8			De Schamphelaere et al 2005	10.1016/j.chemosphaere.2004.06.039
Cu	µg/L	93			Khangarot & Ray, 1989	10.1016/0147-6513(89)90071-7
Cu	µg/L	103			Meyer et al., 2014	10.1002/etc.2787
Cu	µg/L	168			De Schamphelaere et al 2002	10.1016/S1532-0456(02)00087-X
Cu	µg/L	820			Meng et al., 2008	10.1109/ICBBE.2008.298
Ni	µg/L	510		•	Biesinger & Christensen, 1972	10.1139/f72-269
Ni	µg/L	1068			Pane et al., 2003	10.1021/es034317l
Ni	µg/L	1120			Biesinger & Christensen, 1972	10.1139/f72-270
Ni	µg/L	1503			Lari et al., 2017	10.1016/j.jhazmat.2017.03.060

Ni	μg/L	7290		Khangarot & Ray, 1989	10.1016/0147-6513(89)90071-7
Ni	μg/L	7300		Khangarot et al.,1987	10.1002/aheh.19870150415
Ni	μg/L	7590		Khangarot & Ray, 1989	10.1016/0147-6513(89)90071-7
Pb	μg/L	95	•	Yim et al., 2006	10.1016/j.jhazmat.2005.11.107
Pb	μg/L	450		Biesinger & Christensen, 1972	10.1139/f72-269
Pb	μg/L	1815		Elnabarawy et al., 1986	10.1002/etc.5620050409
Pb	μg/L	1880		Offem & Ayotunde, 2008	10.1007/s11270-008-9632-0
Pb	μg/L	2630		Khangarot et al.,1987	10.1002/aheh.19870150415
Pb	μg/L	3610		Khangarot & Ray, 1989	10.1016/0147-6513(89)90071-7
Pb	μg/L	3730		Fargassova 1994	10.1007/BF00192051
Pb	μg/L	5100		Meng et al., 2008	10.1109/ICBBE.2008.298
Pb	μg/L	74730		Teodorovic et al., 2009	10.2478/s11535-009-0048-7
Zn	μg/L	100	•	Biesinger & Christensen, 1972	10.1139/f72-269
Zn	μg/L	300		Yim et al., 2006	10.1016/j.jhazmat.2005.11.107
Zn	μg/L	319		Lari et al., 2017	10.1016/j.jhazmat.2017.03.060
Zn	μg/L	330		De Schamphelaere et al 2005	10.1016/j.chemosphere.2004.06.039
Zn	μg/L	410		Teodorovic et al., 2009	10.2478/s11535-009-0048-7
Zn	μg/L	560		Khangarot & Ray, 1989	10.1016/0147-6513(89)90071-7
Zn	μg/L	696		Meyer et al., 2014	10.1002/etc.2787
Zn	μg/L	779		Attar & Maly, 1982	10.1007/BF01055205
Zn	μg/L	920		Hall et al. 1986	10.1111/j.1752-1688.1986.tb00763.x
Zn	μg/L	2800		Bowmer et al., 1998	10.1016/S0045-6535(98)00116-7
phenanthrene	μg/L	207	•	Abernethy et al., 1986	10.1016/0166-445X(86)90062-7
phenanthrene	μg/L	383		Muñoz & Tarazona, 1993	10.1007/BF00197195
phenanthrene	μg/L	410		Pagnout et al., 2006	10.1016/j.ecoenv.2006.03.005
phenanthrene	μg/L	500		Baun et al., 2008	10.1016/j.aquatox.2007.11.019
phenanthrene	μg/L	570		Feldmannová et al., 2006	10.1002/tox.20198
phenanthrene	μg/L	604		Verrhiest et al., 2001	10.1023/A:10122230
phenanthrene	μg/L	700		Millemann et al., 1984	10.1577/1548-8659(1984)113<74:CATTAO>2.0.CO;2
phenanthrene	μg/L	843		Eastmond et al., 1984	10.1007/BF01055652
phenanthrene	μg/L	950		Xie et al., 2006	10.1897/05-256R.1

phenanthrene	μg/L	1159		Bobra et al., 1983	10.1016/0045-6535(83)90118-2
pyrene	μg/L	74.1	•	Clément et al., 2007	10.1080/10406630591007260
pyrene	μg/L	91		Abernethy et al., 1986	10.1016/0166-445X(86)90062-7
pyrene	μg/L	133		Pagnout et al., 2006	10.1016/j.ecoenv.2006.03.005
pyrene	μg/L	1820.25		Bobra et al., 1983	10.1016/0045-6535(83)90118-2
HHCB	ng/L	194000	•	Chen et al., 2015	10.1007/s00128-015-1543-3
HHCB	ng/L	3330000		Pablos et al., 2015	10.1007/s11356-015-4119-1
bisphenol A	ng/L	7750000		Brennan et al., 2006	10.1016/j.chemosphere.2005.11.046
bisphenol A	ng/L	9940000		Mansilha et al., 2013	10.1007/s11356-013-1614-0
bisphenol A	ng/L	10000000		Chen et al., 2002	10.1002/tox.10035
bisphenol A	ng/L	10200000		Alexander et al., 1988	10.1002/etc.5620070104
bisphenol A	ng/L	12800000		Hirano et al., 2004	10.1248/jhs.50.97
nonylphenol	ng/L	180000	•	Hirano et al., 2004	10.1248/jhs.50.97
nonylphenol	ng/L	190000		Comber et al., 1993	10.1016/0043-1354(93)90086-W
triclosan	ng/L	241766		Sengupta et al., 2015	10.1016/j.chemosphere.2015.02.027
triclosan	ng/L	338000		Wang et al., 2013	10.1016/j.jhazmat.2013.07.007
triclosan	ng/L	390000		Orvos et al., 2002	10.1002/etc.5620210703
triclosan	ng/L	856800		Silva et al., 2015	10.1016/j.ecoenv.2015.02.022
azoxystrobin	ng/L	71000	•	Warming et al., 2009	10.1897/08-279.1
azoxystrobin	ng/L	98000		Warming et al., 2009	10.1897/08-279.1
azoxystrobin	ng/L	277000		Warming et al., 2009	10.1897/08-279.1
azoxystrobin	ng/L	340000		Ochoa-Acuña et al., 2009	10.1007/s10646-009-0298-1
bixafen	ng/L	1200000	quality: A5	University of Hertfordshire, Pesticide Properties Database	http://sitem.herts.ac.uk/aeru/iupac/
boscalid	ng/L	5330000	quality: A5 •	University of Hertfordshire, Pesticide Properties Database	http://sitem.herts.ac.uk/aeru/iupac/
chlorpyrifos	ng/L	190	•	Kikuchi et al., 2000	10.1006/eesa.2000.195
chlorpyrifos	ng/L	325		Diamantino et al., 1998	10.1007/s001289900
chlorpyrifos	ng/L	480		Rubach et al., 2011	10.1007/s00244-010-9582-6
chlorpyrifos	ng/L	600		Moore et al., 1998	10.1007/s002449900299
chlorpyrifos	ng/L	740		Palma et al., 2008	10.1007/s00128-008-9517-3
chlorpyrifos	ng/L	900		Matsumoto et al., 2009	n.a.
chlorpyrifos	ng/L	1220		Demetrio et al., 2014	10.1007/s00128-014-1336-0

chlorpyrifos	ng/L	7120			Liu et al., 2012	10.1016/j.ecoenv.2012.02.014
chlorpyrifos	ng/L	14500			Perez et al., 2015	10.1007/s10646-015-1489-6
chlorpyrifos	ng/L	580000			Loureiro et al., 2010	10.1002/etc.198
dicofol	ng/L	200000		•	Haeba et al., 2008	10.1065/espr2007.12.466
diflufenican	ng/L	240000		•	Weyman et al., 2012	10.1002/etc.1856
diflufenican	ng/L	240000	quality: A5		University of Hertfordshire, Pesticide Properties Database	http://sitem.herts.ac.uk/aeru/iupac/
esfenvalerate	ng/L	270		•	Fairchild et al., 1992	10.1002/etc.5620110111
esfenvalerate	ng/L	270	quality: A5		University of Hertfordshire, Pesticide Properties Database	http://sitem.herts.ac.uk/aeru/iupac/
esfenvalerate	ng/L	1160			Bjergager et al., 2012	10.1016/j.aquatox.2011.12.001
fluopicolide	ng/L	1800000	quality: A5	•	University of Hertfordshire, Pesticide Properties Database	http://sitem.herts.ac.uk/aeru/iupac/
flutolanil	ng/L	6800000	quality: A5	•	University of Hertfordshire, Pesticide Properties Database	http://sitem.herts.ac.uk/aeru/iupac/
flutolanil	ng/L	10000000			Matsumoto et al., 2009	n.a.
lambda-cyhalothrin	ng/L	360	quality: A5	•	University of Hertfordshire, Pesticide Properties Database	http://sitem.herts.ac.uk/aeru/iupac/
lambda-cyhalothrin	ng/L	391			Barata et al., 2006	10.1016/j.aquatox.2006.01.013
lambda-cyhalothrin	ng/L	1040			Mokry & Hoagland, 1990	10.1002/etc.5620090811
pencycuron	ng/L	300000	quality: A5	•	University of Hertfordshire, Pesticide Properties Database	http://sitem.herts.ac.uk/aeru/iupac/
pencycuron	ng/L	10000000			Matsumoto et al., 2009	n.a.
prosulfocarb	ng/L	510000	quality: A5	•	University of Hertfordshire, Pesticide Properties Database	http://sitem.herts.ac.uk/aeru/iupac/
tebuconazole	ng/L	750000		•	Ochoa-Acuňa et al., 2009	10.1007/s10646-009-0298-1
tebuconazole	ng/L	2790000	quality: A5		University of Hertfordshire, Pesticide Properties Database	http://sitem.herts.ac.uk/aeru/iupac/
tebuconazole	ng/L	3631000			Li et al., 2015	10.1016/j.chemosphere.2014.11.031
tri-allate	ng/L	80000		•	Buhl & Faerber, 1989	10.1007/BF01055019
tri-allate	ng/L	91000			Peterson & Hulting, 2004	10.1614/WS-03-149R
tri-allate	ng/L	91000	quality: A5		University of Hertfordshire, Pesticide Properties Database	http://sitem.herts.ac.uk/aeru/iupac/

Table S14. Toxicity indices and the top contributing compounds per index and location, calculated based on detected freely dissolved contaminant concentrations in sediments of 12 field locations.

			toxicity index			
location	$EAR_{mixture}$	top contaminant	msPAF (%)	top contaminant	TU	top contaminant
SP	0.22	bisphenol A	17.1	nonylphenol	0.05	Cu
WK	0.06	phenanthrene	46.7	pyrene	0.70	Cu
WBV	0.41	bisphenol A	40.4	Cu	1.95	Cu
WD	1.02	bisphenol A	43.4	nonylphenol	1.81	Cu
BG	0.28	bisphenol A	74.5	pyrene	2.73	Cu
OBV	0.38	bisphenol A	59.1	nonylphenol	1.69	Cu
HI	1.79	bisphenol A	40.4	nonylphenol	0.65	Cu
EI	2.11	bisphenol A	19.5	nonylphenol	0.22	Cu
UT	2.28	bisphenol A	41.7	nonylphenol	0.50	Cu
BW	0.22	bisphenol A	0.7	pyrene	0.06	Cu
WL	1.77	bisphenol A	26.9	nonylphenol	0.14	chlorpyrifos
SX	0.56	azoxystrobin	21.1	azoxystrobin	0.68	Cu

SI 6 – Bioassay quality criteria and midge emergence.

Table S15. Quality control measurements (average ± st.err), i.e. pH, O$_2$, conductivity and NH$_4^+$ on day 28 of the experiment. * 1 core omitted from analyses due to low oxygen saturation.

| land use	location	name code	pH	O$_2$ (% saturation)	conductivity (μS/cm)	NH$_4^+$ (mg/L)
Reference	Science Park	SP	8.8 ± 0,0	86 ± 3	1334 ± 37	0.1 ± 0.0
	Wittenkade	WK	8.8 ± 0,0	86 ± 1	1739 ± 96	0.0 ± 0.0
	Wittenburgervaart	WBV	8.6 ± 0,0	90 ± 0	4238 ± 235	0.1 ± 0.0
Urban	Westerdok	WD	8.5 ± 0,1	92 ± 0	4764 ± 207	0.1 ± 0.0
	Bickersgracht	BG	8.6 ± 0,0	87 ± 0	3416 ± 677	0.1 ± 0.0
	Oostenburgervaart	OBV	8.7 ± 0,1	84 ± 1	2348 ± 223	0.0 ± 0.0
	Hilversum	HI	7.9 ± 0,1	63 ± 2*	817 ± 89	0.3 ± 0.1
WWTP	Eindhoven	EI	8.2 ± 0,1	62 ± 1	891 ± 53	0.2 ± 0.0
	Utrecht	UT	8.6 ± 0,0	54 ± 4*	1117 ± 62	0.2 ± 0.0
	Balgweg	BW	8.7 ± 0,0	91 ± 1	1299 ± 55	0.1 ± 0.0
agriculture	Westland	WL	8.8 ± 0,0	86 ± 1	1154 ± 42	0.0 ± 0.0
	Sexbierum	SX	8.6 ± 0,1	60 ± 5	5654 ± 231	1.1 ± 0.7
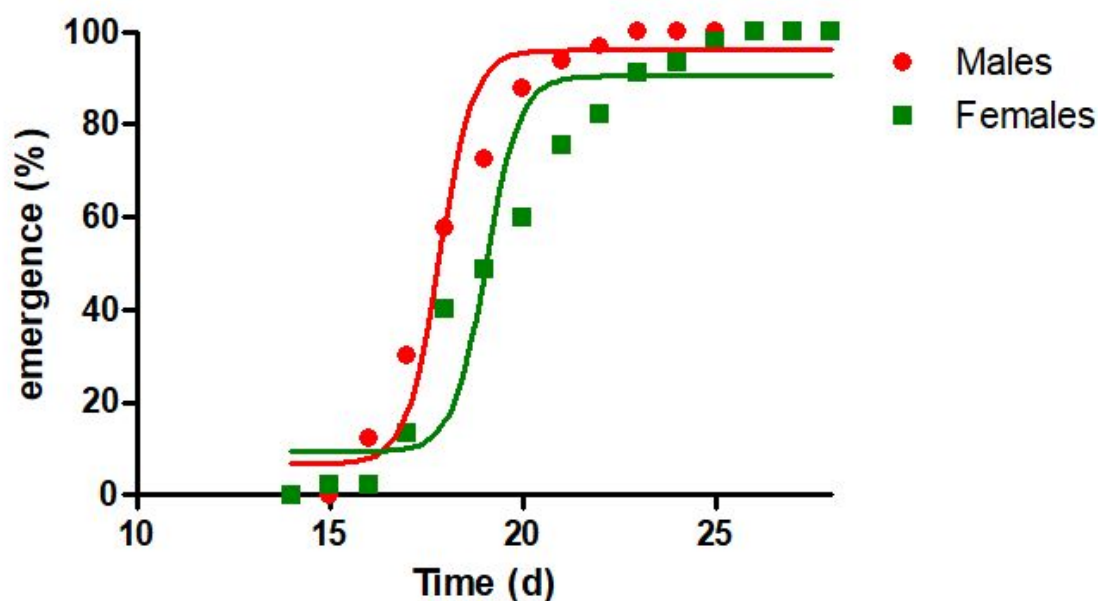
Figure S2. Curve fit of the log logistic model to emergence time of *C. riparius* males (red circles) and females (green squares) after 28 d exposure to whole sediment cores from the reference site.