Supporting Information

Environmental Science and Technology

Pesticide Risks in Small Streams – How to Get as Close as Possible to the Stress Imposed on Aquatic Organisms

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Content:

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SI 1: Additional study site information

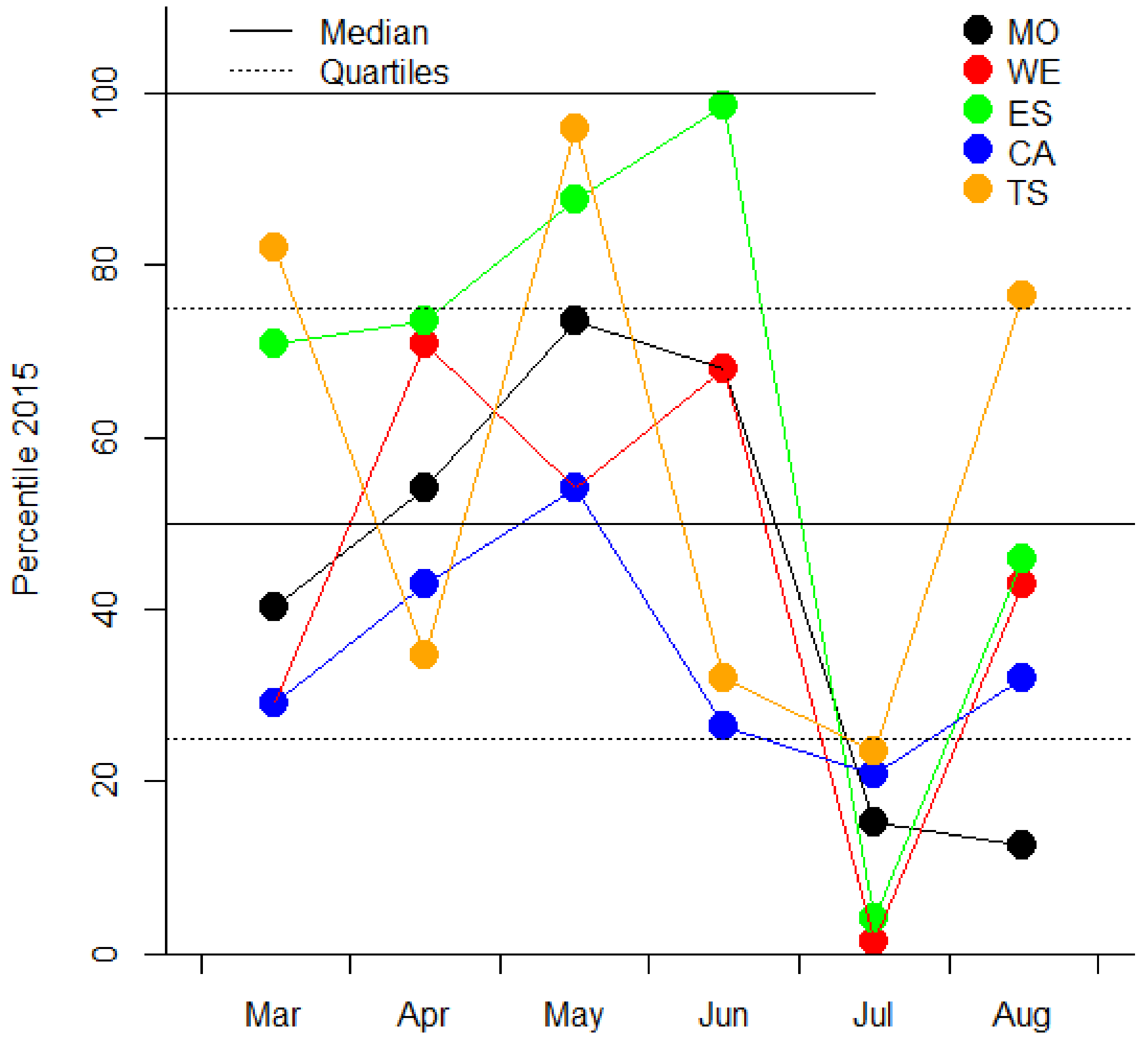


Figure SI 1.1. Comparison of monthly precipitation in 2015 with the distribution of 36 previous years (1980 – 2015). The full year 2015 was neither extremely wet nor extremely dry throughout the entire season in all of the sites. Single months at certain stations do show rarely occuring precipitation sums, i.e., very dry in July at all sites, very wet in May at Tsatonire, and very wet in June at Eschelisbach. Stream name abbreviations: Mooskanal (Mo), Weierbach (We), Eschelisbach (Es), Canale Piano di Magadino (Ca) and Tsatonire (Ts)

Mooskanal (3.4 km^2, SO: 2)

Canale Piano di Magadino (9.0 km^2, SO: 4)

Weierbach (1.6 km^2, SO: 1)

Tsatonire (2.4 km^2, SO: 2)

Eschelisbach (2.0 km^2, SO: 2)
(Photograph: Esther Michel, eawag)

Figure SI 1.2. Pictures of the five small streams (catchment area and stream order (SO) are indicated)

SI 2: Additional substance information

SI 2.1 Information on Sampling and on MS-Settings

Table SI 2.1.1: Sampling procedures

Aspect	Chosen procedure
Sample transport	Weekly (sent to lab by express delivery and frozen upon arrival)
Sample storage	-20°C until analysis
Field blanks	2 per sampling site
Autosampler	ISCO Sampler equipped with glass bottles and PTFE suction line

Table SI 2.1.2: HPLC gradient used for the chromatographic separation on an Atlantis T3 column

Time [min]	H2O +vs 0.1% FA %	MeOH + 0.1 % FA %	Flow [µL/min]
0.0	87	13	300
5.0	87	13	300
20.0	5	95	300
29.0	5	95	300
29.5	87	13	300
35.0	87	13	300

FA: formic acid

Table SI 2.1.3: Settings for the QExactive mass spectrometer

Parameter	positive	negative
ESI settings		
Spray voltage	4000 V	3000 V
Capillary temperature	320 °C	320 °C
S-Lens RF voltage	50 V	50 V
Probe Heater Temp	50°C	50°C
Sheath Gas Flow (Arb)	40	40
Aux Gas Flow (Arb)	10	10
Spare Gas Flow (Arb)	0	0
Orbitrap settings		
MS1		
Scan range (m/z)	100 - 1000	100 - 1000
Mass resolution (m/z 200)	140,000	140,000
Automatic Gain Control	1e6	1e6
Max Injection time	100 ms	100 ms
MS2		
Mass resolution (m/z 200)	17,500	17,500
Automatic Gain Control	1e5	1e5
Max Injection time	100 ms	100 ms
Acquisition type	data-dependent	data-dependent
Data- dependent loop count	5	5
Isolation window (m/z)	1	1
Collision energy normalized	compound-optimized	compound-optimized
Dynamic exclusion	8 s	8 s

Arb: arbitrary units, ms: milli seconds, s: seconds

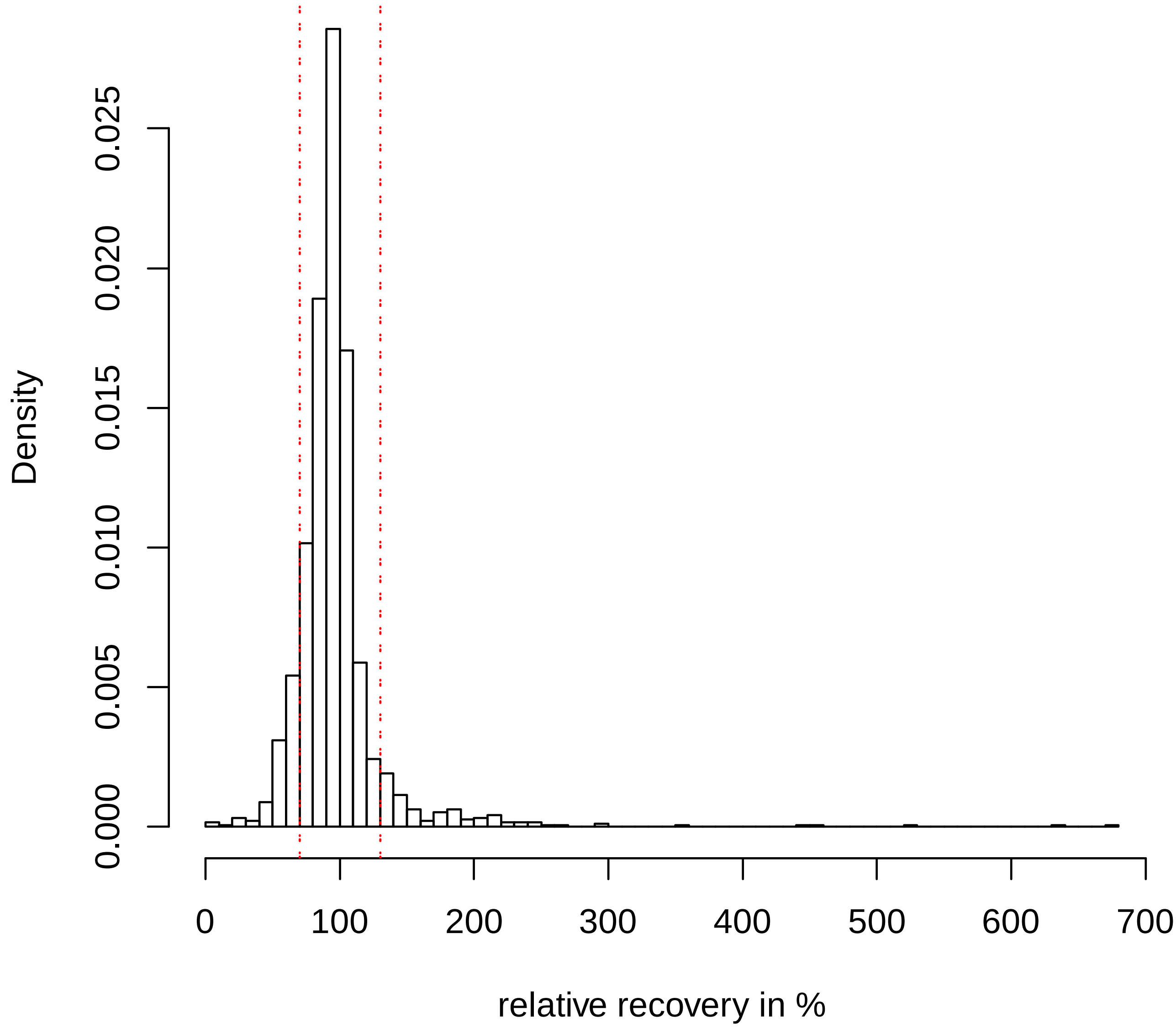


Figure SI 2.1.4 Average analyte recoveries of detected compounds in spiked stream samples. For each stream and each sequence 1-2 recoveries were determined. 83% of the recoveries were within the range of 70-130%. For compounds with own internal standard 99% of recoveries were within the range of 70-130%.

SI 2.2 Pesticide Type, LOQs, Quality-Level, Scenario-Selection, Detection

Substance	CAS Number	Pesticide Type [1]	LOQ-Range [2]	Quality [3]	Included in "historic" scenario	Included in list of 38 priority PPP	Detection
2,4-D	94-75-7	H	1 - 10	1		1	Yes
Aclonifen	74070-46-5	H	9 - 15	2			Yes
Alachlor	15972-60-8	H	1 - 7	1 [4]	1		No
Amidosulfuron	120923-37-7	H	1 - 7	2			Yes
Atraton	1610-17-9	H	0.5 - 2.2	2			No
Atrazine	1912-24-9	H	0.4 - 1	1	1	1	Yes
Beflubutamid	113614-08-7	H	2	3			No
Benoxacor	98730-04-2	H(S)	2	3			No
Bentazon	25057-89-0	H	1 - 3	1		1	Yes
Bromacil	314-40-9	H	2 - 3	2			No
Bromoxynil	1689-84-5	H	1 - 6	2			Yes
Butafenacil	134605-64-4	H	4	3			No
Butralin	33629-47-9	H	2	3			No
Carbetamide	16118-49-3	H	2 - 4	2			No
Carfentrazone-ethyl	128639-02-1	H	3	3			No
Chloridazon	1698-60-8	H	0.5 - 2	1	1	1	Yes
Chlorotoluron	15545-48-9	H/B	0.5 - 15	1	1	1	Yes
Chlorpropham (CIPC)	101-21-3	H	30	3			No
Cinidon-ethyl	142891-20-1	H	NA	3			No
Clethodim	99129-21-2	H	2	3			No
Clodinafop-propargyl	105512-06-9	H	4	3			No
Clomazone	81777-89-1	H	0.5 - 1	2			Yes
Cloquintocet-mexyl	99607-70-2	H(S)	2.5	2			No
Cycloxydim	101205-02-1	H	1 - 3	2			No
Dicamba	1918-00-9	H	8 - 65	1 [4]		1	Yes
Dichlorprop-P	15165-67-0	H	1 - 7	1 [4]			No
Diflufenican	83164-33-4	H	1 - 6.5	1 [4]			Yes
Dimefuron	34205-21-5	H	1 - 6	2			Yes
Dimethachlor	50563-36-5	H	1 - 2.7	2			Yes
Dimethenamid	87674-68-8	H	0.4 - 1.6	1	1		Yes
Diuron	330-54-1	H/B	0.5 - 4	1	1	1	Yes
Ethofumesate	26225-79-6	H	3 - 8	2	1	1	Yes
Florasulam	145701-23-1	H	50	3			No
Flufenacet	142459-58-3	H	0.4 - 2	2			Yes
Flumioxazin	103361-09-7	H	50	2			No
Flupyrsulfuron-methyl	144740-54-5	H	5	2			No
Flurochloridon	61213-25-0	H	5	2			No
Fluroxypyr	69377-81-7	H	1 - 10	2			Yes
Foramsulfuron	173159-57-4	H	0.5 - 2	2			Yes
Haloxyfop	69806-34-4	H	1 - 5	2			Yes
Hexazinon	51235-04-2	H	1	2			No
Imazamox	114311-32-9	H	1 - 15	2			Yes
Iodosulfuron-methyl	144550-36-7	H	2 - 5	2			Yes
Ioxynil	1689-83-4	H	0.5 - 8	2			Yes
Isoproturon	34123-59-6	H/B	0.5 - 5	1	1	1	Yes
Isoxadifen-ethyl	163520-33-0	H(S)	2	2			No
Isoxaflutole	141112-29-0	H	8 - 10	2			No
Lenacil	2164-08-1	H	0.5 - 3	2			Yes
Linuron	330-55-2	H	1 - 5	1 [4]	1	1	Yes
MCPA	94-74-6	H	1 - 4	1		1	Yes
MCPB	94-81-5	H	0.5 - 15	1 [4]			Yes
MCPP (Mecoprop)	93-65-2	H/B	1 - 7	1			Yes
Mefenpyr-diethyl	135590-91-9	H(S)	0.5 - 2	2			Yes
Mesosulfuron-methyl	208465-21-8	H	0.5 - 4	2			Yes

Substance	CAS Number	Pesticide Type [1]	LOQ-Range [2]	Quality [3]	Included in "historic" scenario	Included in list of 38 priority PPP	Detection
Mesotrione	104206-82-8	H	3 - 10	1			Yes
Metamitron	41394-05-2	H	0.5 - 3	2	1	1	Yes
Metazachlor	67129-08-2	H	0.5 - 2	2	1	1	Yes
Metolachlor	51218-45-2	H	0.5 - 6	1	1		Yes
Metosulam	139528-85-1	H	1	2			No
Metoxuron	19937-59-8	H	2.5	2	1		No
Metribuzin	21087-64-9	H	0.4 - 2	2		1	Yes
Metsulfuron-methyl	74223-64-6	H	1 - 3	1			Yes
Monolinuron	1746-81-2	H/B	0.5 - 3	2	1		Yes
Monuron	150-68-5	H	0.5 - 3	2			Yes
Napropamide	15299-99-7	H	0.5 - 6	2		1	Yes
Nicosulfuron	111991-09-4	H	1 - 7	1		1	Yes
Orbencarb	34622-58-7	H	0.5 - 3	2	1		Yes
Oryzalin	19044-88-3	H	1 - 4	2			Yes
Oxadiargyl	39807-15-3	H	7	3			No
Oxasulfuron	144651-06-9	H	0.5 - 1	2			No
Pethoxamid	106700-29-2	H	1	2			No
Picloram	1918-02-1	H	400	3			No
Pinoxaden	243973-20-8	H	1	2			No
Propachlor	1918-16-7	H	0.5 - 2	2	1		Yes
Propaquizafop	111479-05-1	H	2 - 10	2			No
Propyzamide	23950-58-5	H	1 - 4	2	1		Yes
Prosulfocarb	52888-80-9	H	0.5 - 4	2			Yes
Prosulfuron	94125-34-5	H	1 - 2	2			No
Pyraflufen-ethyl	129630-19-9	H	40	3			No
Pyroxsulam	422556-08-9	H	0.5 - 4	2			Yes
Quinoclamine	2797-51-5	H	0.5 - 6	2			No
Quizalofop-P-ethyl	100646-51-3	H	2	3			No
Rimsulfuron	122931-48-0	H	1 - 6	2			Yes
Simeton	673-04-1	H	0.4 - 1	2			Yes
Sulcotrione	99105-77-8	H	1 - 7	1			Yes
Sulfentrazon	122836-35-5	H	2 - 3	2			No
Sulfosulfuron	141776-32-1	H	1	2			Yes
Tebutam	35256-85-0	H	0.4 - 4	1			Yes
Tembotrione	335104-84-2	H	2 - 10	2			Yes
Tepraloxydim	149979-41-9	H	0.5 - 3	2			Yes
Terbacil	5902-51-2	H	0.5 - 4	2			Yes
Terbumeton	33693-04-8	H	0.5 - 1	2			No
Terbuthylazine	5915-41-3	H/B	0.5 - 2.3	1	1	1	Yes
Terbutryn	886-50-0	H/B	0.5 - 1.5	2	1	1	Yes
Thiencarbazone	317815-83-1	H	2 - 6	2			No
Thifensulfuron-methyl	79277-27-3	H	1 - 5	2			Yes
Tralkoxydim	87820-88-0	H	2	3			No
Triasulfuron	82097-50-5	H	2	3			No
Tribenuron-methyl	101200-48-0	H	2 - 5	2			Yes
Triflusulfuron-methyl	126535-15-7	H	0.9 - 2	2			Yes
Tritosulfuron	142469-14-5	H	2 - 3	2			Yes
Azaconazole	60207-31-0	F	2	3			No
Azoxystrobin	131860-33-8	F	1 - 5	1 [4]		1	Yes
Benalaxyl	71626-11-4	F	0.5 - 1	2			No
Benthiavalicarb-isopropyl	177406-68-7	F	0.4 - 2	2			Yes
Bitertanol	55179-31-2	F	2	3			No
Bixafen	581809-46-3	F	1 - 5	2			Yes
Boscalid	188425-85-6	F	1 - 6	1 [4]		1	Yes
Bupirimate	41483-43-6	F	0.5 - 2	2			Yes
Carbendazim	10605-21-7	F/B	0.5 - 2	1		1	Yes

Substance	CAS Number	Pesticide Type [1]	LOQ-Range [2]	Quality [3]	Included in "historic" scenario	Included in list of 38 priority PPP	Detection
Carboxin	5234-68-4	F	2	3			No
Cyazofamid	120116-88-3	F	0.5 - 2	2			Yes
Cyflufenamid	180409-60-3	F	1 - 5	2			Yes
Cymoxanil	57966-95-7	F	4 - 200	2			No
Cyproconazole	94361-06-5	F/B	0.5 - 1.7	2		1	Yes
Cyprodinil	121552-61-2	F	0.5 - 2.4	1 [4]		1	Yes
Diethofencarb	87130-20-9	F	1 - 3	2			Yes
Difenoconazole	119446-68-3	F	0.5 - 1	2			Yes
Dimethomorph	110488-70-5	F	1 - 10	2			Yes
Epoxiconazole	133855-98-8	F	0.5 - 4.4	1 [4]		1	Yes
Famoxadone	131807-57-3	F	50	2			No
Fenamidone	161326-34-7	F	0.5 - 1.5	2			Yes
Fenbuconazole	114369-43-6	F	2	3			No
Fenhexamid	126833-17-8	F	0.4 - 4	2			Yes
Fenpropidin	67306-00-7	F	0.5 - 15	2			Yes
Fenpropimorph	67564-91-4	F/B	0.5 - 10	2	1		Yes
Fluazinam	79622-59-6	F	0.5 - 8	2			Yes
Fludioxonil	131341-86-1	F	0.5 - 2	2			Yes
Fluopicolide	239110-15-7	F	1 - 5	2			Yes
Fluopyram	658066-35-4	F	0.5 - 3	2			Yes
Fluoxastrobin	361377-29-9	F	0.5 - 1	2			No
Fluquinconazole	136426-54-5	F	30	3			No
Flusilazole	85509-19-9	F	0.5 - 2	2			Yes
Flutolanil	66332-96-5	F	1 - 2	2			Yes
Fuberidazole	3878-19-1	F	2	3			No
Imazalil	35554-44-0	F/B	2	3			No
Iprovalicarb	140923-17-7	F	0.4 - 3	2		1	Yes
Kresoxim-methyl	143390-89-0	F	0.5 - 4	2			Yes
Mandipropamid	374726-62-2	F	0.9 - 5	2			Yes
Mepanipyrim	110235-47-7	F	0.5 - 3	2			Yes
Mepronil	55814-41-0	F	2	3			No
Metalaxyl-M	57837-19-1	F	0.4 - 9	1 [4]	1	1	Yes
Metconazole	125116-23-6	F	0.5 - 2	2			Yes
Metrafenone	220899-03-6	F	1 - 5.6	2			Yes
Myclobutanil	88671-89-0	F	0.5 - 2.6	2			Yes
Penconazole	66246-88-6	F	0.5 - 2	2	1		Yes
Pencycuron	66063-05-6	F	0.5 - 4	2			Yes
Picoxystrobin	117428-22-5	F	1 - 2	2			Yes
Prochloraz	67747-09-5	F	0.5 - 6	1			Yes
Propamocarb	24579-73-5	F	0.5 - 4.1	2		1	Yes
Propiconazole	60207-90-1	F/B	0.5 - 2	1	1		Yes
Proquinazid	189278-12-4	F	1 - 3	2			No
Prothioconazole	178928-70-6	F	10	2			No
Pyraclostrobin	175013-18-0	F	0.5 - 4	2			Yes
Pyrifenox	88283-41-4	F	2	3			No
Pyrimethanil	53112-28-0	F	0.9 - 5	1 [4]		1	Yes
Quinoxyfen	124495-18-7	F	0.4 - 2	2			Yes
Spiroxamine	118134-30-8	F	0.5 - 25	2			Yes
Tebuconazole	107534-96-3	F/B	0.5 - 1.5	1	1	1	Yes
Thiabendazole	148-79-8	F/B	0.5 - 7	2			No
Thiophanate-methyl	23564-05-8	F	3	3			No
Tolclofos-methyl	57018-04-9	F	5	2			No
Triadimenol	55219-65-3	F	0.4 - 2	2			No
Triazoxide	72459-58-6	F	1 - 2	2			No
Trifloxystrobin	141517-21-7	F	1 - 5	2			Yes
Triflumizole	99387-89-0	F	0.5 - 2	2			Yes

Substance	CAS Number	Pesticide Type [1]	LOQ-Range [2]	Quality [3]	Included in "historic" scenario	Included in list of 38 priority PPP	Detection
Triforine	26644-46-2	F	15	3			No
Triticonazole	131983-72-7	F	150	3			No
Zoxamid	156052-68-5	F	2	3			No
Acephate	30560-19-1	I	25	3			No
Aldicarb	116-06-3	I	7 - 15	2			No
Bifenazat	149877-41-8	I	2	3			No
Buprofezin	69327-76-0	I	0.5 - 2	2			Yes
Carbofuran	1563-66-2	I	1 - 6	2			Yes
Chlorantraniliprole	500008-45-7	I	2 - 5	2			No
Chlorfenvinphos	470-90-6	I	2	2			No
Chlorpyrifos	2921-88-2	I/B	2 - 45	1	1	1	Yes
Chlorpyrifos-methyl	5598-13-0	I/B	9 - 55	1		1	Yes
Clofentezine	74115-24-5	I	80	3			No
Clothianidin	210880-92-5	I/B	1 - 2	1			Yes
Cyromazine	66215-27-8	I/B	25	2			No
Diafenthiuron	80060-09-9	I	6	3			No
Diazinon	333-41-5	I/B	0.4 - 1	1	1	1	Yes
Diflubenzuron	35367-38-5	I/B	1 - 2	2			Yes
Dimethoate	60-51-5	I	1 - 3	1	1	1	Yes
Fenazaquin	120928-09-8	I	2	3			No
Fenoxycarb	79127-80-3	I	0.5 - 1	2			Yes
Fenpyroximate	134098-61-6	I	4	3			No
Fipronil	120068-37-3	I/B	0.5 - 6	2			Yes
Flonicamid	158062-67-0	I	0.4 - 2	2			Yes
Hexaflumuron	86479-06-3	I/B	70	3			No
Hexythiazox	78587-05-0	I	3	3			No
Imidacloprid	138261-41-3	I/B	0.5 - 2	1		1	Yes
Indoxacarb	173584-44-6	I/B	6	3			No
Methidathion	950-37-8	I	1	2			No
Methiocarb	2032-65-7	I	1 - 7	1			Yes
Methomyl	16752-77-5	I/B	0.4 - 9	2			Yes
Methoxyfenozide	161050-58-4	I	0.5 - 2.4	2		1	Yes
Mevinphos	7786-34-7	I	2	3			No
Novaluron	116714-46-6	I	1	2			No
Phosmet	732-11-6	I	15	3			No
Piperonyl butoxide	51-03-6	I/B	2 - 15	2			Yes
Pirimicarb	23103-98-2	I	3 - 7.5	1	1	1	Yes
Pirimiphos-methyl	29232-93-7	I	2	3			No
Pymetrozine	123312-89-0	I	2 - 2.5	2			Yes
Spinosyn A	131929-60-7	I	8	3			No
Spirodiclofen	148477-71-8	I	1	2			No
Spirotetramat	203313-25-1	I	0.5 - 1	2			Yes
Tebufenozide	112410-23-8	I	0.5 - 4	2			Yes
Tebufenpyrad	119168-77-3	I	2	3			No
Thiacloprid	111988-49-9	I/B	1 - 2.6	2		1	Yes
Thiamethoxam	153719-23-4	I/B	0.4 - 3	1		1	Yes
Triazamat	112143-82-5	I	2	3			No

[1] H: Herbicide, H(S): Safener, F: Fungicide, I: Insecticide, B: also registered as biocide

[2] Limit of quantification in surface water matrix (determined for each stream in each of the measurement sequences)

[3] Q = 1: Quantified with isotope labeled structure identical internal standard
Q = 2: Quantified with isotope labeled structure non-identical internal standard
Q = 3: Semi-quantifiable - processed and quantified with a single one-point calibration

[4] Use of both structure identical and non-identical internal standards within the five measurement sequences

SI 2.3 Chronic (CQC) and Acute quality criteria (AQC) and labels for the three taxonomic groups [1]

Substance	CAS-Nr	CQC (ng/L)	AQC (ng/L)	Label CQC	Label AQC	Source
2,4-D	94-75-7	600	4000	P	P	OZ HP
Aclonifen	74070-46-5	120	120	PV	P	EU-WFD 2013; List of priority substances
Amidosulfuron	120923-37-7	874	1760	P	P	Kontiokari & Mattsoff 2011
Atrazine	1912-24-9	600	2000	PIV	P	EU-WFD 2013; List of priority substances
Azoxystrobin	131860-33-8	200	550	PI	PIV	OZ HP
Bentazon	25057-89-0	270000	470000	PV	P	OZ HP
Benthiavalicarb-isopropyl	177406-68-7	20000		PIV		OZ ad hoc
Bixafen [2]	581809-46-3	170	950	IV	PV	OZ ad hoc
Boscalid	188425-85-6	11600	11600	PV	PIV	OZ HP
Bromoxynil [3]	1689-84-5	500	3000	P	P	INERIS
Bupirimate [4]	41483-43-6	6000		PIV		RIVM (Ctgb)
Buprofezin	69327-76-0	2250		IV		OZ ad hoc
Carbendazim	10605-21-7	340	530	IV	IV	OZ HP
Carbofuran	1563-66-2	16	280	I	I	OZ ad hoc
Chloridazon	1698-60-8	10000	190000	P	P	OZ HP
Chlorotoluron	15545-48-9	600	2400	P	P	OZ HP
Chlorpyrifos	2921-88-2	0.46	16	I	I	EU-WFD 2013; List of priority substances
Chlorpyrifos-methyl [5]	5598-13-0	0.2	3	I	I	RIVM ad hoc
Clomazone [3]	81777-89-1	2000	14000	P	P	INERIS
Clothianidin	210880-92-5	200	2900	I	I	Kontiokari & Mattsoff 2011
Cyazofamid	120116-88-3	250	2500	PI	PIV	NIBIO
Cyflufenamid	180409-60-3	2400	2400	IV	IV	OZ ad hoc
Cyproconazole	94361-06-5	1250	1250	PIV	P	OZ HP
Cyprodinil	121552-61-2	330	3300	I	I	OZ HP
Diazinon	333-41-5	12	24	I	I	OZ HP
Dicamba	1918-00-9	2200	52000	PV	P	OZ HP
Diethofencarb	87130-20-9	3200	140000	IV	PIV	OZ ad hoc
Difenoconazole	119446-68-3	760	7800	IV	PIV	RIVM
Diflubenzuron	35367-38-5	4	210	I	I	OZ ad hoc
Diflufenican	83164-33-4	10	45	P	P	INERIS
Dimefuron	34205-21-5	8	800	P	P	OZ ad hoc
Dimethachlor	50563-36-5	46	6600	P	P	OZ ad hoc
Dimethenamid [6]	163515-14-8	130	1600	P	P	RIVM
Dimethoate	60-51-5	70	977	IV	I	OZ HP
Dimethomorph	110488-70-5	5600	34000	IV	PIV	INERIS
Diuron	330-54-1	70	250	P	P	OZ HP
Epoxiconazole	106325-08-0	200	240	PV	P	OZ HP
Ethofumesate	26225-79-6	3100	260000	PI	PIV	OZ HP
Fenamidone	131807-57-3	950	950	IV	I	OZ ad hoc
Fenhexamid	126833-17-8	5600	13400	PV	PV	OZ ad hoc
Fenoxycarb	79127-80-3	0.3	26	I	PIV	RIVM Bericht 2008
Fenpropidin	67306-00-7	78	980	P	P	Kontiokari & Mattsoff 2011
Fenpropimorph	67564-91-4	16	100000	V	PIV	Kontiokari & Mattsoff 2011
Fipronil	120068-37-3	0.7	14	I	I	OZ ad hoc
Flonicamid [4]	158062-67-0	62000		PIV		OZ ad hoc
Fluazinam	79622-59-6	290	4500	IV	PIV	Kontiokari & Mattsoff 2011
Fludioxonil	131341-86-1	100	23000	PIV	PIV	Kontiokari & Mattsoff 2011
Flufenacet	142459-58-3	137	610	P	P	RIVM (Ctgb)
Fluopicolide	239110-15-7	710	710	P	PV	RIVM
Fluopyram	658066-35-4	13500	25100	PIV	PIV	OZ ad hoc
Fluroxypyr (free acid)	69377-81-7	123000	1230000	PIV	PIV	NIBIO
Flusilazole	85509-19-9	2300	4200	PV	PIV	OZ ad hoc
Flutolanil	66332-96-5	18000	320000	PIV	PIV	Kontiokari & Mattsoff 2011
Foramsulfuron	173159-57-4	10	100	P	P	OZ ad hoc
Haloxyfop [4]	69806-34-4	110000		PIV		RIVM helpdesk water
Imazamox	114311-32-9	450	2100	P	P	OZ ad hoc

Substance	CAS-Nr	CQC (ng/L)	AQC (ng/L)	Label CQC	Label AQC	Source
Imidacloprid	138261-41-3	13	100	I	I	OZ HP
Iodosulfuron-methyl	144550-36-7	40	83	P	P	Kontiokari & Mattsoff 2011
Ioxynil	1689-83-4	130	2700	P	P	Kontiokari & Mattsoff 2011
Iprovalicarb	140923-17-7	190000	190000	PIV	PIV	OZ HP
Isoproturon	34123-59-6	640	2400	P	P	OZ HP
Kresoxim-methyl	143390-89-0	630	630	PIV	PI	RIVM
Lenacil [7]	2164-08-1	1000	1200	P	P	UBA (Jahnel et al. 2004)
Linuron	330-55-2	260	1370	PV	P	OZ HP
Mandipropamid	374726-62-2	14600	14600	IV	PIV	OZ ad hoc
MCPA	94-74-6	260	1500	P	P	OZ HP
MCPB	94-81-5	430		PV		UBA (Jahnel et al. 2006)
Mecoprop-p [8]	16484-77-8	3600	187000	P	PV	OZ HP
Mefenpyr-diethyl	135590-91-9	1650	16500	PIV	PV	OZ ad hoc
Mepanipyrim	110235-47-	580	2300	PIV	PIV	OZ ad hoc
Mesosulfuron-methyl	208465-21-8	16	36	P	P	OZ ad hoc
Mesotrion	104206-82-8	77	770	P	P	Andersson & Kreuger
Metalaxyl-M	70630-17-0	98000	98000	PIV	PI	OZ HP
Metamitron	41394-05-2	4000	39000	P	P	OZ HP
Metazachlor	67129-08-2	20	280	P	P	OZ HP
Metconazole	125116-23-6	291	210000	PV	PIV	RIVM (Ctgb)
Methiocarb	2032-65-7	2	160	I	I	RIVM (Ctgb)
Methomyl	16752-77-5	160	3000	I	I	OZ ad hoc
Methoxyfenozide	161050-58-4	360	3700	I	PIV	OZ HP
Metolachlor [9]	51218-45-2	690	3300	PV	P	OZ HP
Metrafenone	220899-03-	2250	7100	PIV	PIV	OZ ad hoc
Metribuzin	21087-64-9	58	870	P	P	OZ HP
Metsulfuron-methyl	74223-64-6	10	30	P	P	RIVM
Monolinuron	1746-81-2	150	150	P	P	RIVM
Monuron	150-68-5	200		PIV		RIVM ad hoc
Myclobutanil	88671-89-0	4000	4000	PIV	PIV	OZ HP
Napropamide	15299-99-7	5120	6800	P	PIV	OZ HP
Nicosulfuron	111991-09-4	8.7	85	P	P	OZ HP
Orbencarb	34622-58-7	Too few data on ecotoxicological endpoints. Maximum measured concentration: 4.1 ng/L				
Oryzalin	19044-88-3	328	1540	P	P	OZ ad hoc
Penconazol	66246-88-6	4200	4200	PIV	PV	Kontiokari & Mattsoff 2011
Pencycuron [10]	66063-05-6	1340	2700	PI	PIV	LAWA
Picoxystrobin [10]	117428-22-5	25	50	PIV	PI	RIVM ad hoc
Piperonyl butoxide	51-03-6	240	2400	PIV	PI	OZ ad hoc
Pirimicarb	23103-98-2	90	1800	I	I	OZ HP
Prochloraz	67747-09-5	1560	1560	PIV	PI	OZ ad hoc
Propachlor	1918-16-7	20	520	PV	P	OZ ad hoc
Propamocarb	25606-41-1	1030000	1030000	PIV	PIV	OZ HP
Propiconazol	60207-90-1	1800	2100	PV	P	Kontiokari & Mattsoff 2011
Propyzamide	23950-58-5	520	83000	PIV	PI	OZ ad hoc
Prosulfocarb	52888-80-9	600	12000	PI	PIV	Kontiokari & Mattsoff 2011
Pymetrozine	123312-89-0	2500	306000	I	PI	OZ ad hoc
Pyraclostrobin	175013-18-0	200	600	IV	IV	Kontiokari & Mattsoff 2011
Pyrimethanil	53112-28-0	1500	32000	IV	PIV	OZ HP
Pyroxsulam	422556-08-9	68	257	P	P	OZ ad hoc
Quinoxyfen	124495-18-7	150	2700	PIV	PIV	EU-WFD 2013; List of priority substances
Rimsulfuron	122931-48-0	9	5000	P	P	INERIS
Simeton	673-04-1	Too few data on ecotoxicological endpoints. Maximum measured concentration: 2.1 ng/L				
Spirotetramat	203313-25-	2000	85000	PIV	PIV	OZ ad hoc
Spiroxamin	118134-30-8	32	52.2	PV	P	OZ ad hoc
Sulcotrion	99105-77-8	100	5100	P	P	UBA (Wenzel et al. 2014)
Sulfosulfuron	141776-32-1	50	96	P	P	Kontiokari & Mattsoff 2011
Tebuconazol	107534-96-3	240	1400	PIV	PI	OZ HP

Substance	CAS-Nr	CQC (ng/L)	AQC (ng/L)	Label CQC	Label AQC	Source
Tebufenozide	112410-23-8	570	19000	PI	PI	OZ ad hoc
Tebutam	35256-85-0	5600	56000	PIV	PIV	OZ ad hoc
Tembotrione	335104-84-2	320	848	P	P	OZ ad hoc
Tepraloxydim	149979-41-9	110000	110000	PV	PIV	Kontiokari & Mattsoff 2011
Terbacil	5902-51-2	11	1100	P	P	OZ ad hoc
Terbuthylazin	5915-41-3	220	1280	PI	P	OZ HP
Terbutryn	886-50-0	65	340	P	PI	OZ HP
Thiacloprid	111988-49-9	10	80	I	I	OZ HP
Thiamethoxam	153719-23-4	200	1400	I	I	OZ HP
Thifensulfuron-methyl	79277-27-3	50	130	P	P	Kontiokari & Mattsoff 2011
Tribenuron-methyl	101200-48-0	100	430	P	P	NIBIO
Trifloxystrobin	141517-21-7	270	810	PIV	PIV	RIVM (Ctgb)
Triflumizole	99387-89-0	2900	57000	PIV	PIV	RIVM (Ctgb)
Triflusulfuron-methyl	126535-15-7	130	280	P	P	RIVM
Tritosulfuron	142469-14-5	750	4760	P	P	Kontiokari & Mattsoff 2011

[1] Retrieved on January 24th 2017.
All QC given in ng/L. Labels for three organism groups plants (P), invertebrates (I) and vertebrates (V). The labeling depends on the method used for deriving the respective QC. For the assessment factor method as well as the mesocosm method described in the EU Technical Guidance for Deriving EQS (2011) the QC of each substance is labeled for all taxonomic groups (P, I and/or V) for which the lowest relevant toxicity value is within a factor of 10 of the overall lowest toxicity value. Based on the precautionary principle taxa without toxicity data are added to the labels of the corresponding QC. For the SSD method the labeling consists of all taxonomic groups (P, I and/or V) from which the QC relevant SSD was constructed.

[2] CQC is based on secondary poisoning (otherwise 460 ng/L)
Bixafen ad hoc QC – Assessment of secondary poisoning
According to the TGD for EQS (EC, 2011) a QC for secondary poisoning has to be calculated if the log Kow value is ≥ 3 and/or the bioconcentration factor (BCF) is > 100. The BCF of Bixafen is 695 accordingto the EFSA draft assessment report (EFSA 2011). Hence, a QC for secondary poisoning is calculated below. The lowest valid toxicity value is a NOAEL of 3.3 mg /kg body weight /day. It results from a multi-generation study with rats (EFSA 2011). With a conversion factor of 8.33 (for rat multi-generation studies) the following NOECoral results:

$$\mathrm{NOEC_{oral}} = 8.33 * 3.3 \frac{mg}{kg\ body weight} * \mathrm{day}^{-1} = 27.5 \frac{\mathrm{mg}}{\mathrm{kg\ food}}$$

This results in the following QC (or QS for the more commonly used term quality standard) for secondary poisoning (AF_{oral} = 30, because of chronic rat study):

$$\mathrm{QS_{biota,secpois}} = \frac{\mathrm{TOX_{oral}}}{\mathrm{AF_{oral}}} = \frac{27.5\ \ \mathrm{mg/kg\ food}}{30} = 0.12\ \mathrm{mg/kg\ food}$$

This can be converted into a water concentration of:

$$\mathrm{QS_{water,secpois}} = \frac{\mathrm{QS_{biota,secpois}}}{\mathrm{BCF} * \mathrm{BMF}} = \frac{0.12\ \mathrm{mg/kg\ food}}{695 * 1} = 0.000173\ \mathrm{mg/l}$$

EFSA (2011) Draft Assessment Report (DAR) - public version - Initial risk assessent provided by the rapporteur Member State United Kingdom for the new active substance Bixafen of the review programme referred to in Article 11(1) of Regulation (EC) No 1107/2009, Volume 3, Annex B9 July 2011.
EC (2011) Common Implementation Strategy for the Water Framework Directive (2000/60/EC) Technical Report - 2011 - 055 Guidance Document No. 27 Technical Guidance For Deriving Environmental Quality Standards.

[3] AQC OZ ad hoc based on data from INERIS
[4] no AQC available
[5] AQC ad hoc OZ based on RIVM ad hoc
[6] QC for Dimethenamid-P
[7] AQC OZ ad hoc based on Jahnel et al. 2004
[8] QC derived for Mecoprop-P
[9] QC derived for S-Metolachlor
[10] AQC OZ ad hoc

Sources

report	weblink
Andersson & Kreuger (2011)	Andersson M., Kreuger J.(2011) Preliminära riktvärden för växtskyddsmedel i ytvatten - Beräkning av riktvärden för 64 växtskyddsmedel som saknar svenska riktvärden. Teknisk rapport 144, Department of Soil and Environment Swedish University of Agricultural Sciences, Uppsala, Sweden.
INERIS	http://www.ineris.fr/substances/fr/page/9
Kontiokari & Mattsoff (2011)	Kontiokari V. , Mattsoff L. (2011) Proposal of Environmental Quality Standards for Plant Protection Products. THE FINNISH ENVIRONMENT 7, Finnish Environment Institute, Helsinki, Finland.
LAWA	https://webetox.uba.de/webETOX/index.do
NIBIO	http://www.bioforsk.no/ikbViewer/page/prosjekt/tema/artikkel?p_dimension_id=18844&p_menu_id=18851&p_sub_id=18845&p_document_id=91227&p_dim2=18854
OZ HP	http://www.ecotoxcentre.ch/expert-service/quality-standards/proposals-for-acute-and-chronic-quality-standards/?_ga=2.207532311.523493197.1507810479-1837988877.1458219369
OZ ad hoc	See separate File: SI_Table_2_2_and_2_3_QC_SPEZ_2015.xlsx (sheet: SI Table 2.4 ad hoc QC)
RIVM	https://rvs.rivm.nl/zoeksysteem/
UBA	https://webetox.uba.de/webETOX/index.do

SI 2.4 Underlying ecotoxicological data for substances with ad hoc estimations of QC in SI 2.3

See separate File *SI_Table_2_3_and_2_4_QC_SPEZ_2015.xlsx* – includes also SI Table 2.3 in table-format

SI 2.5 $RQ_{\_EQS\_Taxa}$ – Rationale for taxon specific mixture risk assessment

Mixture risk quotients are calculated by summing up the resulting risk quotients. Summing up risk quotients based on water quality criteria tends to overestimate the actual risk to aquatic life if the measured substances specifically affect different taxonomic group(s). For mixtures of pesticides this is highly likely. Therefore, a taxon-specific calculation of the mixture risk is needed. There are basically two different approaches for taxon-specific mixture risk assessment.

The one closest to mixture toxicity theory is the RQ_{STU}-approach (STU sum of toxic units). It is based on the separate prediction of the acute mixture toxicity for algae, daphnids and fish [1]. In a second step the highest resulting toxic unit is multiplied by an assessment factor, which is 1000 for assessing chronic mixture risks from acute toxicity data.

The $RQ_{\_EQS\_Taxa}$ approach [2] on the other hand is based on the analysis of the relative sensitivity of the different taxa to each measured substance. Based on this analysis labels for three organism groups plants (P), invertebrates (I) and vertebrates (V) are added to each quality criterion (separately for the acute and chronic quality criterion).

The decision for the $RQ_{\_EQS\_Taxa}$ approach was mainly driven by the fact that algae and daphnids are not always good representatives for plant and invertebrate sensitivity towards herbicides and insecticides. For sulfonylurea herbicides for example duckweed is several orders of magnitude more sensitive than algae. The same applies to neonicotinoids where insects are several orders of magnitude more sensitive than daphnids.

AQC and CQC were labeled based on the method used for the derivation of the respective QC. For the assessment factor method as well as the mesocosm method [3] the QC of each substance is labeled for all taxonomic groups (P, I and/or V) for which the lowest relevant toxicity value is within a factor of 10 of the overall lowest toxicity value. Based on the precautionary principle taxa without toxicity data are added to the labels of the corresponding QC. Data availability for plant protection products is usually good. Therefore, precautionary labeling was an exception. For the SSD method the labeling consists of all taxonomic groups (P, I and/or V) from which the QC relevant SSD was constructed.

[1] Backhaus and Faust 2012 Predictive Environmental Risk Assessment of Chemical Mixtures: A Conceptual Framework ES&T 46: 2564−2573
[2] Junghans, M.; Kunz, P.; Werner, I., Toxizität von Mischungen - Aktuelle, praxisorenitierte Ansätze für die Beurteilung von Gewässerproben. Aqua & Gas 2013, 5, 54-61. The paper can be downloaded via http://www.oekotoxzentrum.ch/media/100659/2013_junghans_mischungtox_aqua-gas.pdf
[3] European Commission Common Implementation Strategy for the Water Framework Directive. Technical Guidance for Deriving Environmantal Quality Standards; 2011.

SI 3: Measured concentrations

SI 3.1 Repository of original data

Original concentration data available at https://doi.org/10.25678/000022

Table SI 3.2 Number of samples taken and number of measured pooled samples per site

	Mooskanal	Weierbach	Eschelisbach	Canale Piano di Magadino	Tsatonire
Start of campaign [1]	2015.03.02 12:00	2015.03.03 12:00	2015.03.03 12:00	2015.03.04 12:00	2015.03.02 12:00
End of campaign [1]	2015.08.28 12:00	2015.08.31 00:00	2015.08.30 12:00	2015.09.02 12:00	2015.08.30 12:00
Number of samples taken (Interruptions in days [2])	321 (18.5)	360 (0.5)	360 (0)	313 (22+4.5)	330 (16)
Number of pooled samples measured [3]	34	55	60	49	51

[1] Central European Time during daylight saving time (UTC + 2 h)

[2] Interruptions were caused either by technical problems with the autosampler or damage to sample jars during transport. Furthermore, the very dry conditions in the south of Switzerland during summer 2015 resulted in 22 days of missing samples in the Canale di Piano Magadino during August caused by low water levels. During that dry period 4.5 days had sufficient water levels to take samples. These were measured but excluded from evaluations as comparison with QC is not meaningful.

[3] Lower number of samples measured in the Mooskanal because it had the lowest water flow and was expected to show slower concentration changes than the other streams

SI 3.3: Measured concentrations single compounds

SI 3.3.1 Detection frequency (DF) and maximum concentrations (Max. conc.) of all detected herbicides in the five streams

Substance	AQC [1]	Mooskanal, BE	Weierbach, BL	Eschelisbach, TG	Canale Piano di Magadino, TI	Tsatonire, VS	all	No. of streams with detections	Type [2]
2,4-D	4000	2.2% (4.8 ng/L)	19.4% (430 ng/L)	22.2% (130 ng/L)	3.9% (30 ng/L)	11.2% (84 ng/L)	11.78% (430 ng/L)	5	H
Aclonifen	120	0.6% (22 ng/L)	1.1% (1500 ng/L)	0% (<LOQ)	0.3% (41 ng/L)	0% (<LOQ)	0.4% (1500 ng/L)	3	H
Amidosulfuron	1760	0% (<LOQ)	4.4% (46 ng/L)	0% (<LOQ)	0% (<LOQ)	0% (<LOQ)	0.88% (46 ng/L)	1	H
Atrazine	2000	100% (1200 ng/L)	99.7% (22 ng/L)	96.4% (7.4 ng/L)	44.1% (1.1 ng/L)	50.6% (4.9 ng/L)	78.16% (1200 ng/L)	5	HX
Bentazon	470000	93.1% (17 ng/L)	89.2% (2000 ng/L)	92.5% (620 ng/L)	4.9% (49 ng/L)	0% (<LOQ)	55.94% (2000 ng/L)	4	H
Bromoxynil	3000	18.1% (4.4 ng/L)	14.2% (6.3 ng/L)	0.3% (3.8 ng/L)	0.3% (5.1 ng/L)	0% (<LOQ)	6.58% (6.3 ng/L)	4	H
Chloridazon	190000	44.9% (110 ng/L)	92.5% (300 ng/L)	96.4% (120 ng/L)	0% (<LOQ)	0.3% (4.8 ng/L)	46.82% (300 ng/L)	4	H
Clomazone	14000	0% (<LOQ)	60% (14 ng/L)	0.3% (1.1 ng/L)	1.6% (1.6 ng/L)	0% (<LOQ)	12.38% (14 ng/L)	3	H
Dicamba	52000	0.6% (110 ng/L)	41.7% (460 ng/L)	47.8% (900 ng/L)	26.3% (500 ng/L)	0.3% (33 ng/L)	23.34% (900 ng/L)	5	H
Diflufenican	45	0% (<LOQ)	64.7% (480 ng/L)	0% (<LOQ)	0% (<LOQ)	0% (<LOQ)	12.94% (480 ng/L)	1	H
Dimefuron	800	0% (<LOQ)	37.8% (15 ng/L)	0% (<LOQ)	0% (<LOQ)	1.5% (12 ng/L)	7.86% (15 ng/L)	2	HX
Dimethachlor	6600	0% (<LOQ)	18.3% (240 ng/L)	0% (<LOQ)	0% (<LOQ)	0% (<LOQ)	3.66% (240 ng/L)	1	H
Dimethenamid	1600	51.4% (110 ng/L)	63.6% (280 ng/L)	17.5% (50 ng/L)	0% (<LOQ)	0% (<LOQ)	26.5% (280 ng/L)	3	H
Ethofumesate	26000	25.9% (120 ng/L)	77.8% (4400 ng/L)	11.4% (97 ng/L)	6.9% (27 ng/L)	0% (<LOQ)	24.4% (4400 ng/L)	4	H
Flufenacet	610	8.4% (14 ng/L)	8.1% (32 ng/L)	18.6% (300 ng/L)	3.3% (7.1 ng/L)	0% (<LOQ)	7.68% (300 ng/L)	4	H
Fluroxypyr	1230000	5.9% (94 ng/L)	44.4% (270 ng/L)	27.8% (270 ng/L)	0.3% (15 ng/L)	0% (<LOQ)	15.68% (270 ng/L)	4	H
Foramsulfuron	100	4% (31 ng/L)	0% (<LOQ)	2.2% (32 ng/L)	0% (<LOQ)	0% (<LOQ)	1.24% (32 ng/L)	2	H
Haloxyfop	NA	29% (220 ng/L)	1.4% (2.4 ng/L)	41.1% (170 ng/L)	0% (<LOQ)	0% (<LOQ)	14.3% (220 ng/L)	3	H
Imazamox	2100	0% (<LOQ)	0% (<LOQ)	2.2% (74 ng/L)	15.1% (14 ng/L)	0% (<LOQ)	3.46% (74 ng/L)	2	H
Iodosulfuron-methyl	83	0% (<LOQ)	6.7% (110 ng/L)	0% (<LOQ)	0% (<LOQ)	0% (<LOQ)	1.34% (110 ng/L)	1	H
Ioxynil	2700	31.5% (39 ng/L)	80.3% (260 ng/L)	0.3% (10 ng/L)	0% (<LOQ)	0.3% (3.2 ng/L)	22.48% (260 ng/L)	4	H
Lenacil	1200	42.1% (76 ng/L)	61.9% (44 ng/L)	21.4% (7.4 ng/L)	0% (<LOQ)	0% (<LOQ)	25.08% (76 ng/L)	3	H
Linuron	1370	65.4% (160 ng/L)	75.3% (1100 ng/L)	12.5% (78 ng/L)	100% (560 ng/L)	93.6% (2800 ng/L)	69.36% (2800 ng/L)	5	H
MCPA	1500	43% (16 ng/L)	65.3% (1600 ng/L)	35.6% (390 ng/L)	6.9% (30 ng/L)	15.8% (44 ng/L)	33.32% (1600 ng/L)	5	H
MCPB	NA	0.6% (47 ng/L)	35.8% (20000 ng/L)	0% (<LOQ)	0% (<LOQ)	0% (<LOQ)	7.28% (20000 ng/L)	2	H
Mefenpyr-diethyl	16500	0% (<LOQ)	6.4% (37 ng/L)	0% (<LOQ)	0% (<LOQ)	0% (<LOQ)	1.28% (37 ng/L)	1	H(S)
Mesosulfuron-methyl	36	3.7% (7.2 ng/L)	17.2% (360 ng/L)	1.4% (7.4 ng/L)	0% (<LOQ)	0% (<LOQ)	4.46% (360 ng/L)	3	H
Mesotrione	770	4% (56 ng/L)	2.8% (33 ng/L)	16.4% (400 ng/L)	26.6% (72 ng/L)	0% (<LOQ)	9.96% (400 ng/L)	4	H
Metamitron	39000	60.1% (580 ng/L)	77.5% (10000 ng/L)	61.1% (850 ng/L)	0.3% (1.5 ng/L)	0% (<LOQ)	39.8% (10000 ng/L)	4	H
Metazachlor	280	88.2% (83 ng/L)	100% (1200 ng/L)	0% (<LOQ)	26.6% (41 ng/L)	0% (<LOQ)	42.96% (1200 ng/L)	3	H
Metolachlor	3300	24.9% (85 ng/L)	100% (5000 ng/L)	75.3% (990 ng/L)	92.8% (1500 ng/L)	0.3% (0.6 ng/L)	58.66% (5000 ng/L)	5	H
Metribuzin	870	68.2% (77 ng/L)	58.3% (16 ng/L)	87.5% (230 ng/L)	46.4% (65 ng/L)	0% (<LOQ)	52.08% (230 ng/L)	4	H
Metsulfuron-methyl	30	3.7% (16 ng/L)	4.4% (5.1 ng/L)	0.6% (15 ng/L)	0% (<LOQ)	0% (<LOQ)	1.74% (16 ng/L)	3	H
Monuron	NA	0% (<LOQ)	0% (<LOQ)	0.8% (2 ng/L)	0% (<LOQ)	34.5% (6.1 ng/L)	7.06% (6.1 ng/L)	2	HX
Napropamide	6800	11.2% (14 ng/L)	29.4% (39 ng/L)	92.5% (4900 ng/L)	5.6% (4.7 ng/L)	0.3% (22 ng/L)	27.8% (4900 ng/L)	5	H
Nicosulfuron	85	9% (76 ng/L)	39.7% (160 ng/L)	37.2% (180 ng/L)	3.9% (40 ng/L)	0% (<LOQ)	17.96% (180 ng/L)	4	H
Orbencarb	NA	0% (<LOQ)	8.1% (4.1 ng/L)	0% (<LOQ)	0% (<LOQ)	0% (<LOQ)	1.62% (4.1 ng/L)	1	HX
Oryzalin	1540	0% (<LOQ)	0% (<LOQ)	9.2% (140 ng/L)	22.7% (440 ng/L)	0.3% (6.4 ng/L)	6.44% (440 ng/L)	3	H
Propachlor	520	34.9% (130 ng/L)	0% (<LOQ)	0% (<LOQ)	0% (<LOQ)	0% (<LOQ)	6.98% (130 ng/L)	1	HX

Substance	AQC [1]	Mooskanal, BE	Weierbach, BL	Eschelisbach, TG	Canale Piano di Magadino, TI	Tsatonire, VS	all	No. of streams with detections	Type [2]
Propyzamide	83000	95.3% (360 ng/L)	58.1% (430 ng/L)	4.7% (300 ng/L)	18.1% (190 ng/L)	0% (<LOQ)	35.24% (430 ng/L)	4	H
Prosulfocarb	12000	27.7% (140 ng/L)	0.3% (7.9 ng/L)	0.3% (2.5 ng/L)	16.4% (7.2 ng/L)	0% (<LOQ)	8.94% (140 ng/L)	4	H
Pyroxsulam	257	0% (<LOQ)	3.1% (5.6 ng/L)	0% (<LOQ)	0% (<LOQ)	0% (<LOQ)	0.62% (5.6 ng/L)	1	H
Rimsulfuron	5000	0% (<LOQ)	11.1% (26 ng/L)	0% (<LOQ)	0.3% (2 ng/L)	0% (<LOQ)	2.28% (26 ng/L)	2	H
Simeton	NA	0.3% (0.5 ng/L)	26.4% (0.9 ng/L)	0.3% (0.6 ng/L)	0% (<LOQ)	0.6% (2.1 ng/L)	5.52% (2.1 ng/L)	4	HX
Sulcotrione	5100	0.3% (1.9 ng/L)	0% (<LOQ)	0.3% (9.6 ng/L)	0% (<LOQ)	0% (<LOQ)	0.12% (9.6 ng/L)	2	H
Sulfosulfuron	96	0% (<LOQ)	0% (<LOQ)	0% (<LOQ)	0% (<LOQ)	13.3% (2.8 ng/L)	2.66% (2.8 ng/L)	1	H
Tebutam	56000	0% (<LOQ)	6.9% (3.7 ng/L)	0% (<LOQ)	0% (<LOQ)	0% (<LOQ)	1.38% (3.7 ng/L)	1	HX
Tembotrione	848	0.3% (7 ng/L)	0% (<LOQ)	14.2% (63 ng/L)	0% (<LOQ)	0% (<LOQ)	2.9% (63 ng/L)	2	H
Tepraloxydim	110000	29.3% (21 ng/L)	11.1% (3000 ng/L)	0.3% (1.2 ng/L)	0% (<LOQ)	0% (<LOQ)	8.14% (3000 ng/L)	3	H
Terbacil	1100	0% (<LOQ)	0% (<LOQ)	9.2% (2.4 ng/L)	0% (<LOQ)	0% (<LOQ)	1.84% (2.4 ng/L)	1	HX
Thifensulfuron-methyl	130	0.3% (5.5 ng/L)	2.5% (1.6 ng/L)	0.6% (12 ng/L)	0% (<LOQ)	0% (<LOQ)	0.68% (12 ng/L)	3	H
Tribenuron-methyl	430	0% (<LOQ)	0% (<LOQ)	23.6% (70 ng/L)	0% (<LOQ)	0.3% (4.5 ng/L)	4.78% (70 ng/L)	2	H
Triflusulfuron-methyl	280	0% (<LOQ)	0.3% (2.3 ng/L)	3.9% (1.7 ng/L)	0% (<LOQ)	0% (<LOQ)	0.84% (2.3 ng/L)	2	H
Tritosulfuron	4760	0% (<LOQ)	40% (83 ng/L)	0% (<LOQ)	0% (<LOQ)	0% (<LOQ)	8% (83 ng/L)	1	H
Chlorotoluron	2400	0% (<LOQ)	19.2% (7.5 ng/L)	0% (<LOQ)	0% (<LOQ)	0% (<LOQ)	3.84% (7.5 ng/L)	1	H/BX
Diuron	250	37.1% (6.6 ng/L)	3.1% (180 ng/L)	21.1% (810 ng/L)	19.4% (35 ng/L)	98.2% (3000 ng/L)	35.78% (3000 ng/L)	5	H/B
Isoproturon	2400	29.9% (11 ng/L)	90% (40000 ng/L)	0% (<LOQ)	0.3% (9.3 ng/L)	0.6% (2.2 ng/L)	24.16% (40000 ng/L)	4	H/B
MCPP (Mecoprop)	187000	0.6% (8.7 ng/L)	80.3% (4000 ng/L)	51.1% (340 ng/L)	58.9% (310 ng/L)	57.6% (450 ng/L)	49.7% (4000 ng/L)	5	H/B
Monolinuron	150	0% (<LOQ)	0.8% (5 ng/L)	0.3% (2 ng/L)	0% (<LOQ)	21.5% (13 ng/L)	4.52% (13 ng/L)	3	HX/B
Terbuthylazine	1280	26.5% (98 ng/L)	86.9% (230 ng/L)	78.3% (840 ng/L)	60.5% (41 ng/L)	98.2% (3400 ng/L)	70.08% (3400 ng/L)	5	H/BX
Terbutryn	340	33% (4 ng/L)	27.2% (12 ng/L)	0% (<LOQ)	0.3% (1.5 ng/L)	33.6% (11 ng/L)	18.82% (12 ng/L)	4	HX/B

[1] Acute Quality Criteria

[2] H: Herbicide; H(S): Safener; HX: legacy herbicide (not registered as plant protection product in 2015); BX: legacy biocide (not registered as biocide in 2015)

SI 3.3.2 Detection frequency (DF) and maximum concentrations (Max. conc.) of all detected fungicides in the five streams

SubstanceName	AQC [1] (ng/L)	Mooskanal	Weierbach	Eschelisbach	Canale Piano di Magadino	Tsatonire	all	No. of streams with detections	Type [2]
Azoxystrobin	550	70.4% (180 ng/L)	100% (1700 ng/L)	96.4% (3000 ng/L)	81.6% (230 ng/L)	89.4% (32 ng/L)	87.56% (3000 ng/L)	5	F
Benthiavalicarb-isopropyl	NA	0% (<LOQ)	0% (<LOQ)	0% (<LOQ)	0.3% (0.9 ng/L)	4.2% (10 ng/L)	0.9% (10 ng/L)	2	F
Bixafen	950	0% (<LOQ)	23.1% (220 ng/L)	0.3% (6.6 ng/L)	0% (<LOQ)	0% (<LOQ)	4.68% (220 ng/L)	2	F
Boscalid	11600	23.7% (11 ng/L)	85.6% (180 ng/L)	77.8% (120 ng/L)	1% (5.3 ng/L)	48.5% (240 ng/L)	47.32% (240 ng/L)	5	F
Bupirimate	NA	0% (<LOQ)	0% (<LOQ)	83.1% (710 ng/L)	0% (<LOQ)	0% (<LOQ)	16.62% (710 ng/L)	1	F
Cyazofamid	2500	0% (<LOQ)	3.6% (1.8 ng/L)	0% (<LOQ)	0% (<LOQ)	22.1% (170 ng/L)	5.14% (170 ng/L)	2	F
Cyflufenamid	2400	0% (<LOQ)	0% (<LOQ)	0% (<LOQ)	0.3% (1.9 ng/L)	18.5% (14 ng/L)	3.76% (14 ng/L)	2	F
Cyprodinil	3300	12.1% (8.8 ng/L)	94.7% (210 ng/L)	58.9% (690 ng/L)	16.4% (28 ng/L)	87% (160 ng/L)	53.82% (690 ng/L)	5	F
Diethofencarb	140000	4.7% (7.3 ng/L)	26.1% (440 ng/L)	0% (<LOQ)	0% (<LOQ)	0% (<LOQ)	6.16% (440 ng/L)	2	F
Difenoconazole	7800	37.4% (36 ng/L)	74.4% (87 ng/L)	70.3% (67 ng/L)	61.2% (140 ng/L)	52.7% (23 ng/L)	59.2% (140 ng/L)	5	F
Dimethomorph	34000	1.2% (4.9 ng/L)	59.2% (120 ng/L)	25.3% (8.9 ng/L)	8.6% (18 ng/L)	74.5% (410 ng/L)	33.76% (410 ng/L)	5	F
Epoxiconazole	240	7.2% (2.3 ng/L)	89.7% (250 ng/L)	53.1% (25 ng/L)	4.9% (3.7 ng/L)	0% (<LOQ)	30.98% (250 ng/L)	4	F
Fenamidone	950	77.3% (140 ng/L)	49.7% (17 ng/L)	5.3% (4.6 ng/L)	11.2% (59 ng/L)	0% (<LOQ)	28.7% (140 ng/L)	4	F
Fenhexamid	13400	0% (<LOQ)	2.8% (2.2 ng/L)	56.9% (570 ng/L)	2.3% (4.2 ng/L)	41.5% (340 ng/L)	20.7% (570 ng/L)	4	F
Fenpropidin	980	0% (<LOQ)	14.2% (1.1 ng/L)	0% (<LOQ)	6.9% (1.3 ng/L)	34.8% (20 ng/L)	11.18% (20 ng/L)	3	F
Fluazinam	4500	0% (<LOQ)	0% (<LOQ)	5% (24 ng/L)	0% (<LOQ)	0% (<LOQ)	1% (24 ng/L)	1	F
Fludioxonil	23000	0.3% (2.5 ng/L)	46.1% (20 ng/L)	71.7% (540 ng/L)	24% (30 ng/L)	79.4% (220 ng/L)	44.3% (540 ng/L)	5	F
Fluopicolide	710	7.5% (6.8 ng/L)	0% (<LOQ)	0% (<LOQ)	8.6% (13 ng/L)	0.3% (3.5 ng/L)	3.28% (13 ng/L)	3	F
Fluopyram	25100	4% (2.4 ng/L)	36.7% (120 ng/L)	92.2% (6000 ng/L)	30.9% (67 ng/L)	49.4% (310 ng/L)	42.64% (6000 ng/L)	5	F
Flusilazole	4200	10% (0.7 ng/L)	98.6% (160 ng/L)	23.6% (3.9 ng/L)	13.2% (0.7 ng/L)	33.9% (10 ng/L)	35.86% (160 ng/L)	5	F
Flutolanil	320000	0% (<LOQ)	7.5% (66 ng/L)	0% (<LOQ)	0% (<LOQ)	0% (<LOQ)	1.5% (66 ng/L)	1	F
Iprovalicarb	190000	0% (<LOQ)	6.9% (5.2 ng/L)	0.8% (2.5 ng/L)	2% (10 ng/L)	14.5% (19 ng/L)	4.84% (19 ng/L)	4	F
Kresoxim-methyl	630	0% (<LOQ)	1.1% (60 ng/L)	10.6% (35 ng/L)	0% (<LOQ)	0% (<LOQ)	2.34% (60 ng/L)	2	F
Mandipropamid	14600	11.5% (14 ng/L)	11.7% (55 ng/L)	0% (<LOQ)	53.6% (92 ng/L)	13.9% (22 ng/L)	18.14% (92 ng/L)	4	F
Mepanipyrim	2300	0% (<LOQ)	0% (<LOQ)	0% (<LOQ)	0% (<LOQ)	33% (220 ng/L)	6.6% (220 ng/L)	1	F
Metalaxyl-M	98000	34.3% (120 ng/L)	16.1% (150 ng/L)	91.4% (170 ng/L)	92.8% (73 ng/L)	30.3% (19 ng/L)	52.98% (170 ng/L)	5	F
Metconazole	210000	0% (<LOQ)	86.9% (36 ng/L)	0% (<LOQ)	0% (<LOQ)	0% (<LOQ)	17.38% (36 ng/L)	1	F
Metrafenone	7100	0% (<LOQ)	0.3% (13 ng/L)	0% (<LOQ)	4.3% (6.3 ng/L)	98.5% (400 ng/L)	20.62% (400 ng/L)	3	F
Myclobutanil	4000	0% (<LOQ)	0.6% (6.9 ng/L)	51.7% (43 ng/L)	7.9% (2.6 ng/L)	59.1% (100 ng/L)	23.86% (100 ng/L)	4	F
Penconazole	4200	0% (<LOQ)	3.6% (1.9 ng/L)	53.1% (14 ng/L)	48.7% (24 ng/L)	95.8% (150 ng/L)	40.24% (150 ng/L)	4	F
Pencycuron	2700	30.2% (10 ng/L)	0% (<LOQ)	2.5% (5.5 ng/L)	0% (<LOQ)	0% (<LOQ)	6.54% (10 ng/L)	2	F
Picoxystrobin	50	0% (<LOQ)	0% (<LOQ)	0.3% (5.1 ng/L)	0% (<LOQ)	0% (<LOQ)	0.06% (5.1 ng/L)	1	F
Prochloraz	1560	0% (<LOQ)	1.4% (29 ng/L)	5% (220 ng/L)	0% (<LOQ)	0% (<LOQ)	1.28% (220 ng/L)	2	F
Propamocarb	1030000	85.7% (660 ng/L)	41.4% (150 ng/L)	11.9% (30 ng/L)	66.8% (530 ng/L)	0% (<LOQ)	41.16% (660 ng/L)	4	F
Pyraclostrobin	600	0% (<LOQ)	0% (<LOQ)	0% (<LOQ)	2.3% (4.5 ng/L)	0% (<LOQ)	0.46% (4.5 ng/L)	1	F
Pyrimethanil	32000	26.5% (130 ng/L)	56.1% (580 ng/L)	11.7% (64 ng/L)	0% (<LOQ)	35.5% (10 ng/L)	25.96% (580 ng/L)	4	F
Quinoxyfen	2700	0% (<LOQ)	0% (<LOQ)	0% (<LOQ)	0% (<LOQ)	41.2% (33 ng/L)	8.24% (33 ng/L)	1	F
Spiroxamine	52.2	3.7% (0.6 ng/L)	14.2% (0.7 ng/L)	0% (<LOQ)	14.1% (5.7 ng/L)	46.4% (600 ng/L)	15.68% (600 ng/L)	4	F
Trifloxystrobin	810	0% (<LOQ)	0% (<LOQ)	2.8% (50 ng/L)	0% (<LOQ)	0% (<LOQ)	0.56% (50 ng/L)	1	F
Triflumizole	57000	0% (<LOQ)	0% (<LOQ)	0% (<LOQ)	0% (<LOQ)	0.9% (23 ng/L)	0.18% (23 ng/L)	1	F

Substance	AQC [1] (ng/L)	BE	BL	TG	TI	VS	all	No. of streams with detections	Type [2]
Carbendazim	530	45.2% (55 ng/L)	73.9% (500 ng/L)	75.8% (180 ng/L)	37.5% (70 ng/L)	94.2% (96 ng/L)	65.32% (500 ng/L)	5	F/B
Cyproconazole	1250	17.8% (11 ng/L)	99.7% (91 ng/L)	4.4% (4.3 ng/L)	0.3% (1.4 ng/L)	1.5% (2.7 ng/L)	24.74% (91 ng/L)	5	F/B
Fenpropimorph	100000	3.7% (1.5 ng/L)	0% (<LOQ)	0% (<LOQ)	0% (<LOQ)	5.8% (0.8 ng/L)	1.9% (1.5 ng/L)	2	F/B
Propiconazole	2100	25.2% (70 ng/L)	77.5% (120 ng/L)	2.5% (1.8 ng/L)	1% (1.3 ng/L)	7% (3.1 ng/L)	22.64% (120 ng/L)	5	F/B
Tebuconazole	1400	63.9% (85 ng/L)	100% (130 ng/L)	45% (11 ng/L)	19.4% (12 ng/L)	67.9% (100 ng/L)	59.24% (130 ng/L)	5	F/B

[1] Acute Quality Criteria

[2] F: Fungicide, F/B: Registered as plant protection product and biocide

SI 3.3.3 Detection frequency (DF) and maximum concentrations (Max. conc.) of all detected insecticides in the five streams

Substance	AQC [1] (ng/L)	Mooskanal	Weierbach	Eschelisbach	Canale Piano di Magadino	Tsatonire	all	No. of streams with detections	Type [2]
Buprofezin	NA	0% (<LOQ)	0% (<LOQ)	0% (<LOQ)	35.5% (120 ng/L)	0% (<LOQ)	7.1% (120 ng/L)	1	I
Carbofuran	280	0% (<LOQ)	0.8% (5.5 ng/L)	29.2% (38 ng/L)	0% (<LOQ)	0% (<LOQ)	6% (38 ng/L)	2	IX
Dimethoate	977	44.5% (22 ng/L)	30.3% (590 ng/L)	83.1% (1600 ng/L)	1% (1.5 ng/L)	27.9% (79 ng/L)	37.36% (1600 ng/L)	5	I
Fenoxycarb	26	0% (<LOQ)	0.6% (17 ng/L)	0.6% (25 ng/L)	0% (<LOQ)	0% (<LOQ)	0.24% (25 ng/L)	2	I
Flonicamid	NA	3.4% (5 ng/L)	0% (<LOQ)	21.9% (62 ng/L)	0% (<LOQ)	0% (<LOQ)	5.06% (62 ng/L)	2	I
Methiocarb	160	0% (<LOQ)	14.4% (170 ng/L)	1.4% (22 ng/L)	0% (<LOQ)	0% (<LOQ)	3.16% (170 ng/L)	2	I
Methoxyfenozide	3700	0% (<LOQ)	0% (<LOQ)	92.5% (36 ng/L)	0.7% (3.1 ng/L)	0.9% (17 ng/L)	18.82% (36 ng/L)	3	I
Pirimicarb	1800	0% (<LOQ)	13.9% (86 ng/L)	20.8% (240 ng/L)	13.5% (18 ng/L)	14.8% (71 ng/L)	12.6% (240 ng/L)	4	I
Pymetrozine	306000	7.8% (6.6 ng/L)	0% (<LOQ)	0% (<LOQ)	31.9% (54 ng/L)	1.5% (2.9 ng/L)	8.24% (54 ng/L)	3	I
Spirotetramat	85000	0% (<LOQ)	0.3% (1 ng/L)	0.6% (2.9 ng/L)	0% (<LOQ)	0% (<LOQ)	0.18% (2.9 ng/L)	2	I
Tebufenozide	19000	0% (<LOQ)	0% (<LOQ)	62.8% (43 ng/L)	0.3% (7.6 ng/L)	74.5% (160 ng/L)	27.52% (160 ng/L)	3	I
Chlorpyrifos	16	6.2% (17 ng/L)	0% (<LOQ)	3.3% (14 ng/L)	0% (<LOQ)	13% (39 ng/L)	4.5% (39 ng/L)	3	I/BX
Chlorpyrifos-methyl	3	0% (<LOQ)	0% (<LOQ)	2.5% (210 ng/L)	0% (<LOQ)	0% (<LOQ)	0.5% (210 ng/L)	1	I/BX
Clothianidin	2900	4.7% (24 ng/L)	56.4% (23 ng/L)	49.2% (36 ng/L)	7.2% (2 ng/L)	0% (<LOQ)	23.5% (36 ng/L)	4	I/B
Diazinon	24	38.3% (3.4 ng/L)	5.6% (3.3 ng/L)	35.6% (590 ng/L)	60.9% (9.6 ng/L)	45.2% (10 ng/L)	37.12% (590 ng/L)	5	IX/BX
Diflubenzuron	210	0% (<LOQ)	6.9% (38 ng/L)	0% (<LOQ)	0% (<LOQ)	0% (<LOQ)	1.38% (38 ng/L)	1	I/B
Fipronil	14	3.1% (1.9 ng/L)	6.1% (24 ng/L)	1.4% (0.7 ng/L)	0% (<LOQ)	12.4% (10 ng/L)	4.6% (24 ng/L)	4	IX/B
Imidacloprid	100	4% (17 ng/L)	15.8% (43 ng/L)	56.7% (40 ng/L)	1.3% (9.4 ng/L)	13% (11 ng/L)	18.16% (43 ng/L)	5	I/B
Methomyl	3000	4.4% (6.7 ng/L)	0.3% (34 ng/L)	49.4% (6000 ng/L)	0% (<LOQ)	0.3% (91 ng/L)	10.88% (6000 ng/L)	4	I/BX
Piperonyl butoxide	2400	0% (<LOQ)	51.1% (59 ng/L)	0% (<LOQ)	5.3% (6.3 ng/L)	1.5% (7.8 ng/L)	11.58% (59 ng/L)	3	I/B
Thiacloprid	80	21.5% (45 ng/L)	29.4% (860 ng/L)	32.8% (250 ng/L)	0.3% (23 ng/L)	0.6% (1.6 ng/L)	16.92% (860 ng/L)	5	I/B
Thiamethoxam	1400	4% (7.3 ng/L)	47.8% (120 ng/L)	39.4% (1000 ng/L)	0.7% (29 ng/L)	23% (5.5 ng/L)	22.98% (1000 ng/L)	5	I/B

[1] Acute Quality Criteria

[2] I: Insecticide; IX: Legacy insecticide (not registered as plant protection product in 2015); BX: Legacy biocide (not registered as biocide in 2015)

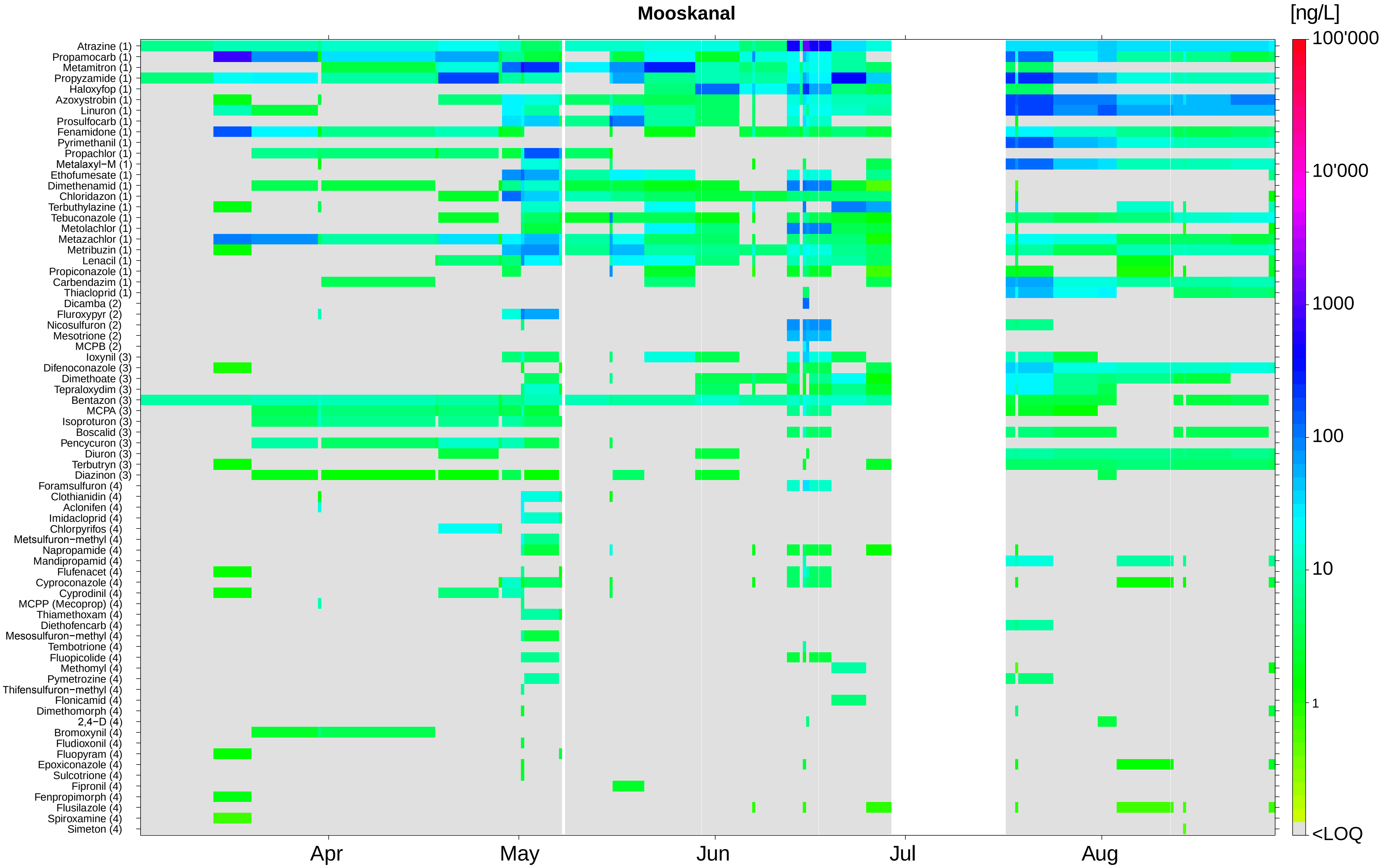


Figure SI 3.4.1 Exposure Profile of Mooskanal with 74 detected compounds grouped into groups 1-4 by low or high detection frequency and maximal concentration. Within groups the compounds are ordered by decreasing maximal concentration. White color indicates interruptions of sampling.

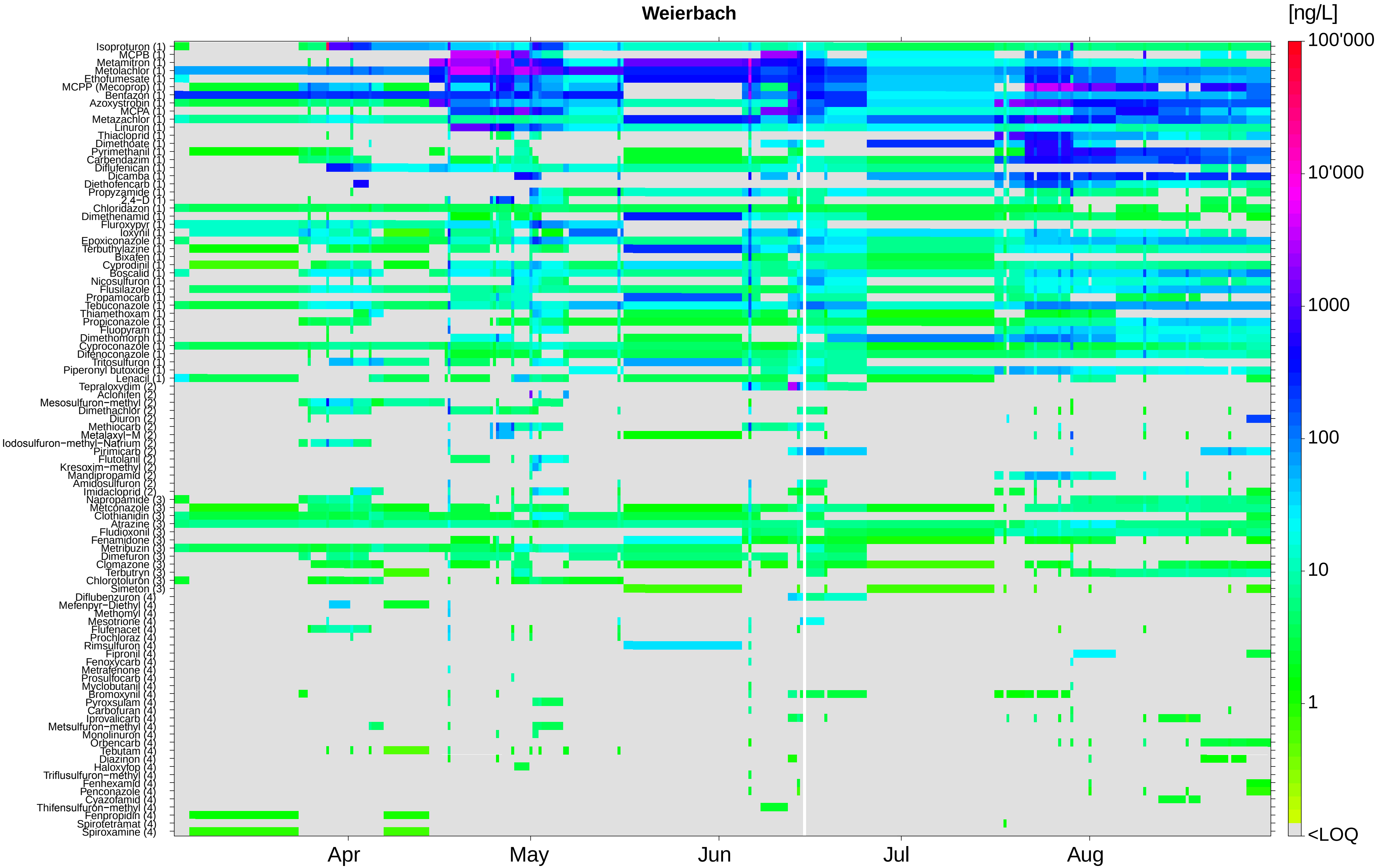


Figure SI 3.4.2 Exposure Profile of Weierbach with 98 detected compounds grouped into groups 1-4 by low or high detection frequency and maximal concentration. Within groups the compounds are ordered by decreasing maximal concentration. White color indicates an interruption of sampling.

Figure SI 3.4.3 (corresponding to Figure 2 in article and therefore not shown here)

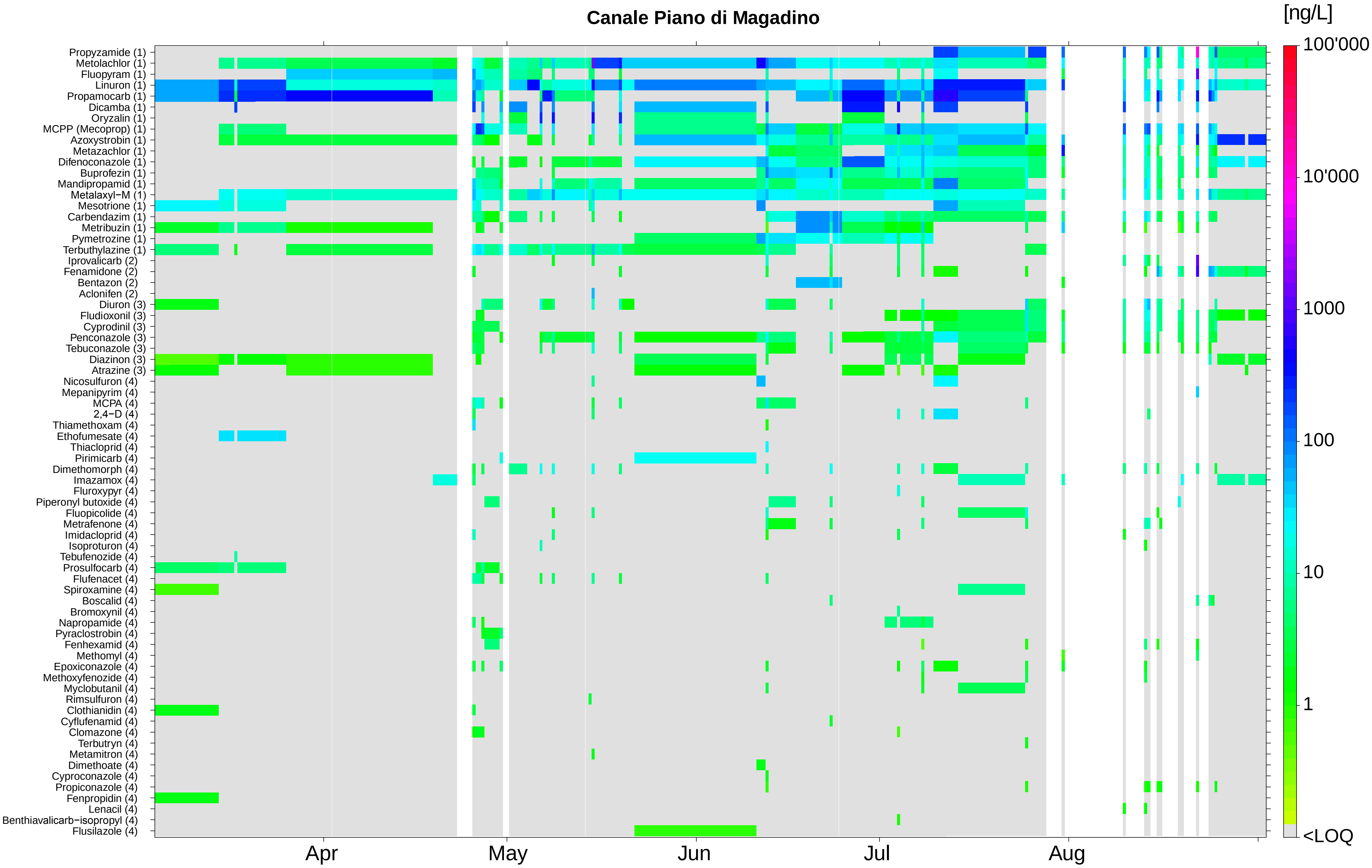


Figure SI 3.4.4 Exposure Profile of Canale Piano di Magadino with 72 detected compounds grouped into groups 1-4 by low or high detection frequency and maximal concentration. Within groups the compounds are ordered by decreasing maximal concentration. White color indicates an interruption of sampling.

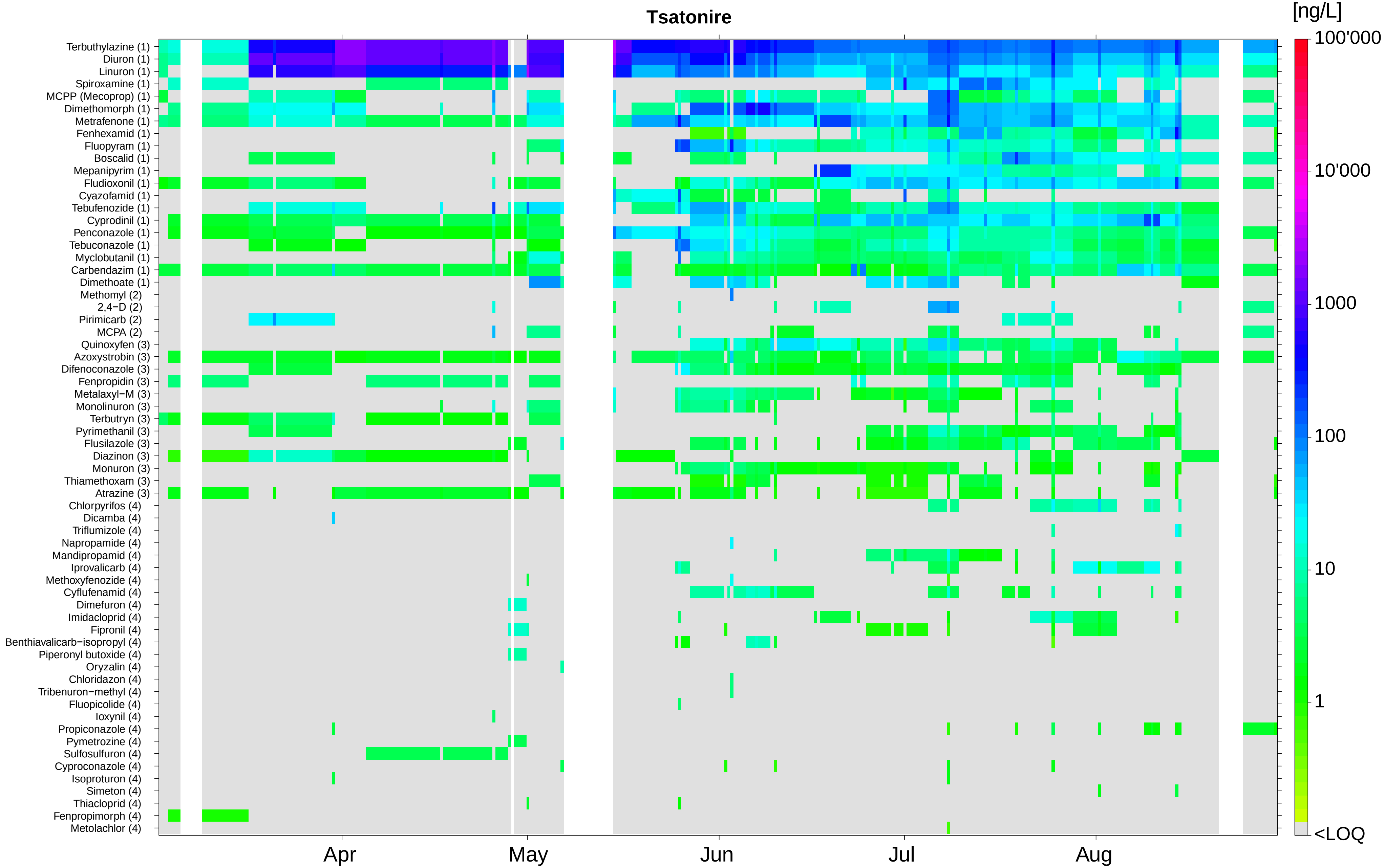


Figure SI 3.4.5 Exposure Profile of Tsatonire with 64 detected compounds grouped into groups 1-4 by low or high detection frequency and maximal concentration. Within groups the compounds are ordered by decreasing maximal concentration. White color indicates an interruption of sampling.

SI 3.5: Sum of measured concentrations and precipitation

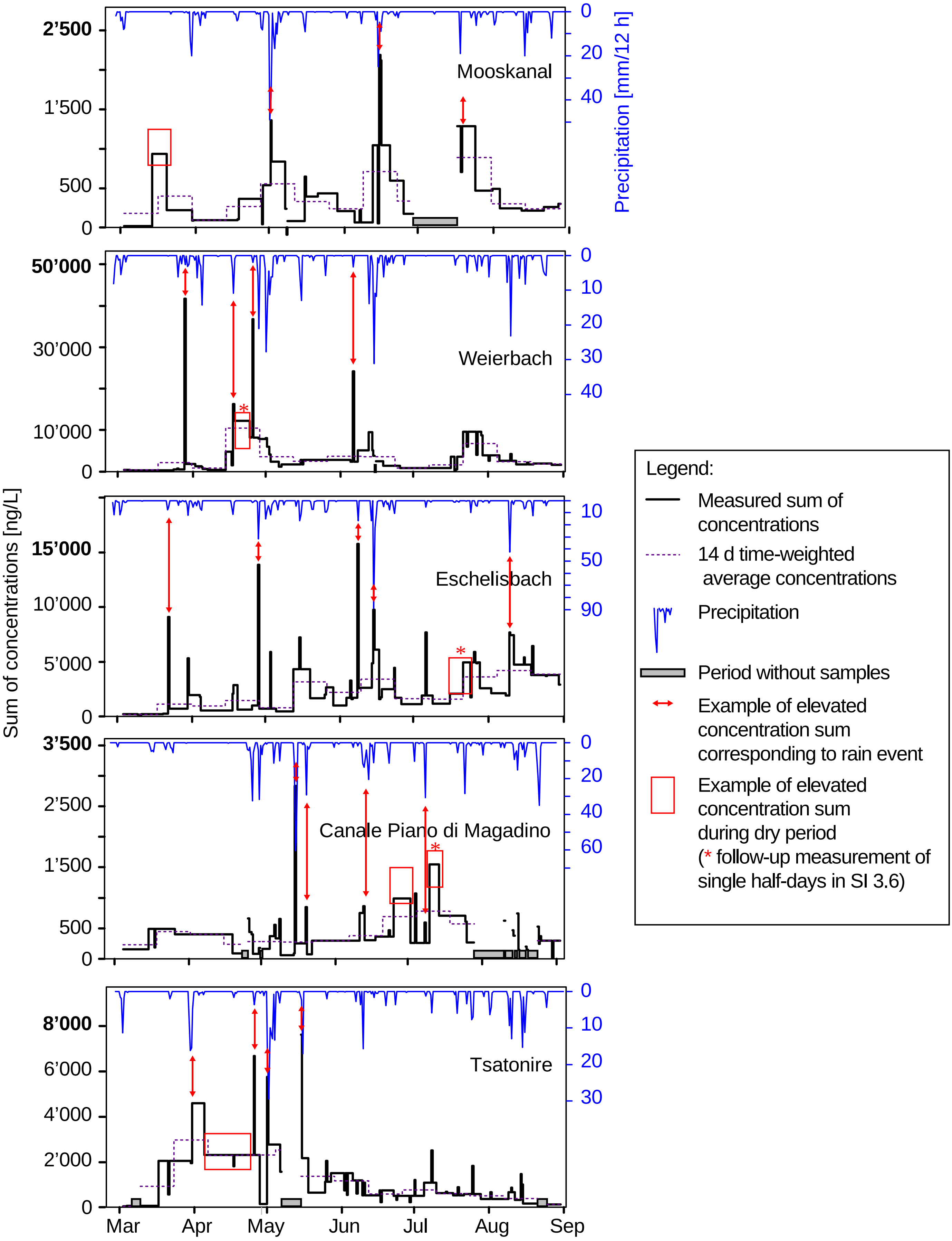
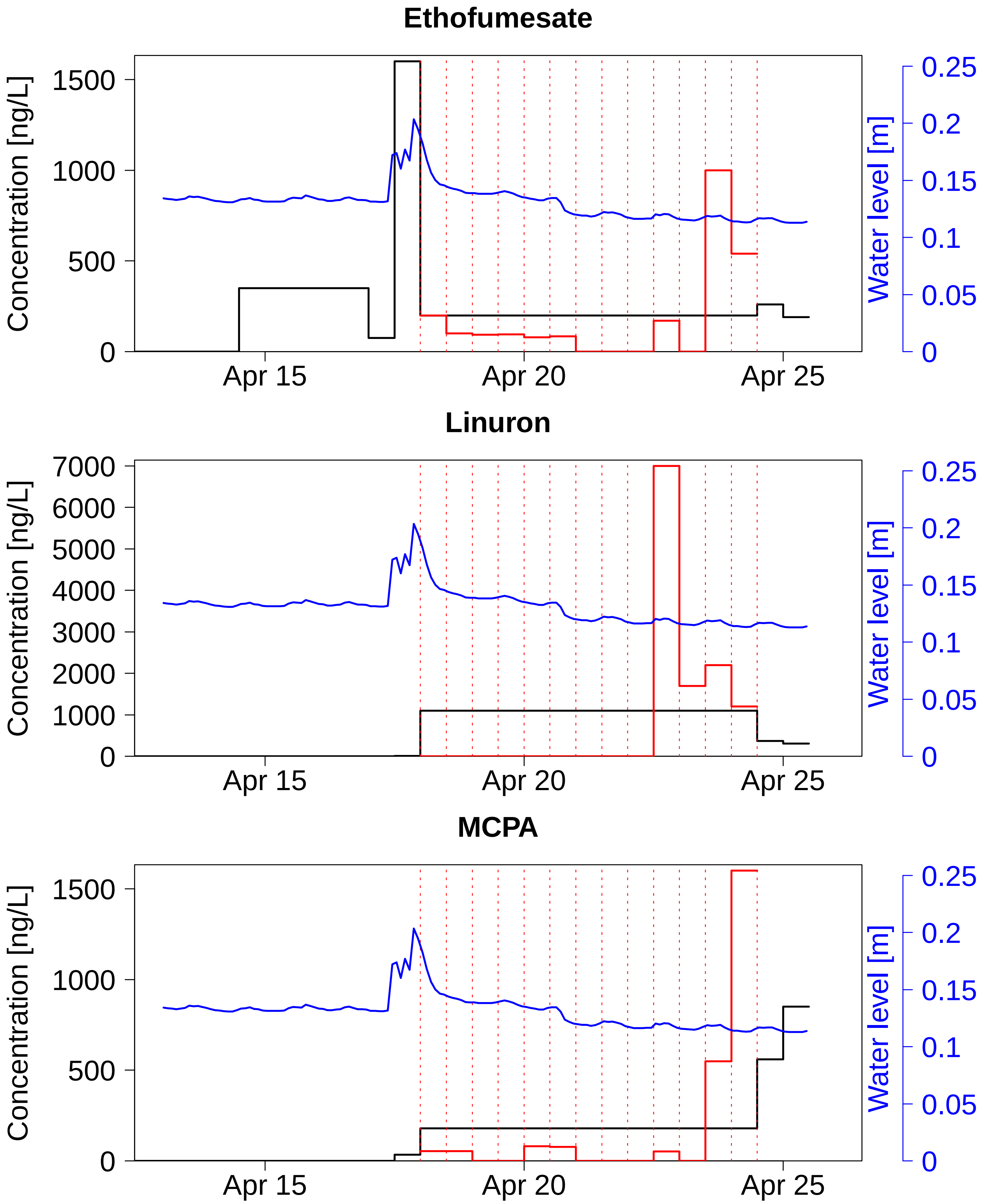


Figure SI 3.5 Sum of concentrations of all PPP including precipitation in the five catchments. Three pooled samples with elevated concentrations were later measured with full temporal resolution (SI 4.5)

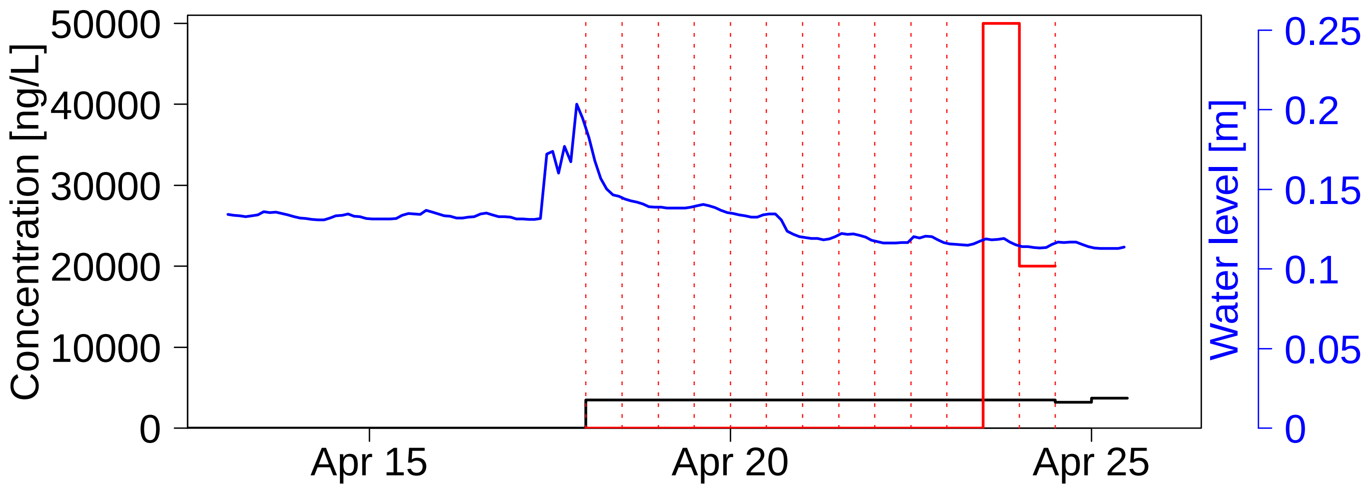
SI 3.6: Follow-up measurements on increased concentrations during dry periods

SI 3.6.1 Additional measurements during low flow conditions in the Weierbach

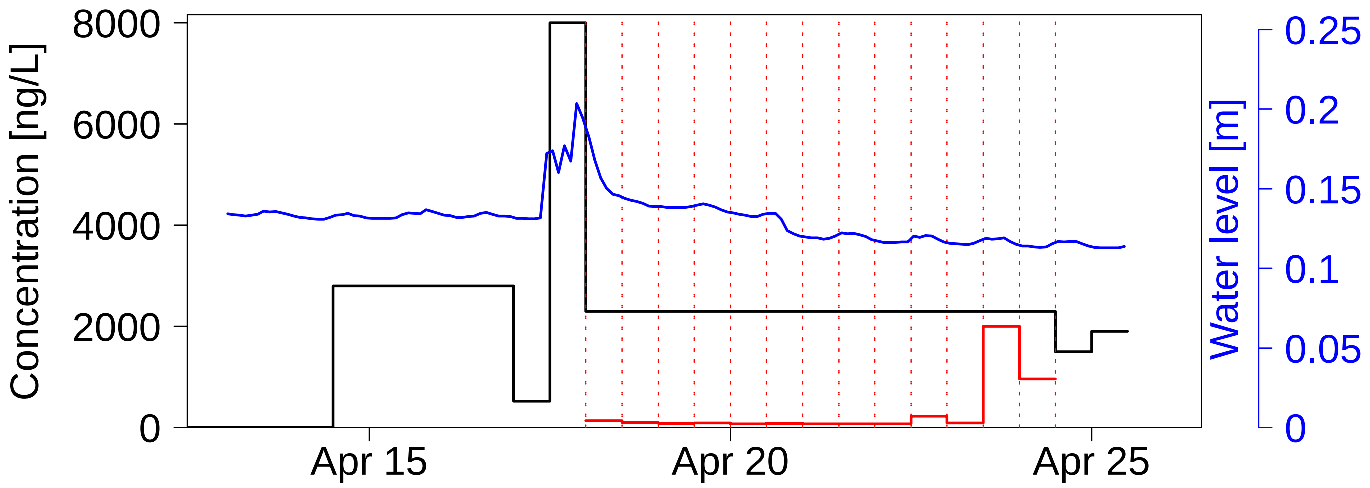
The black line represent the original data with the pooled samples designated by a * in SI 3-4. The 6 compounds having the highest concentrations in the composite sample from April 18th (0:00) to April 24th (12:00) were measured 8 month later using each of the 13 half-day samples separately (red line).



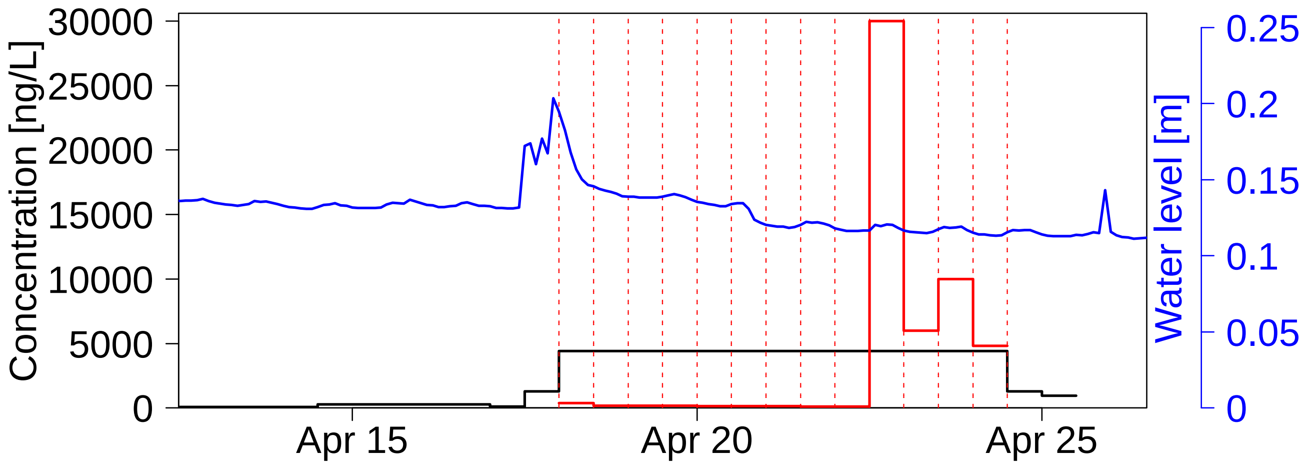
MCPB



Metamitron



Metolachlor

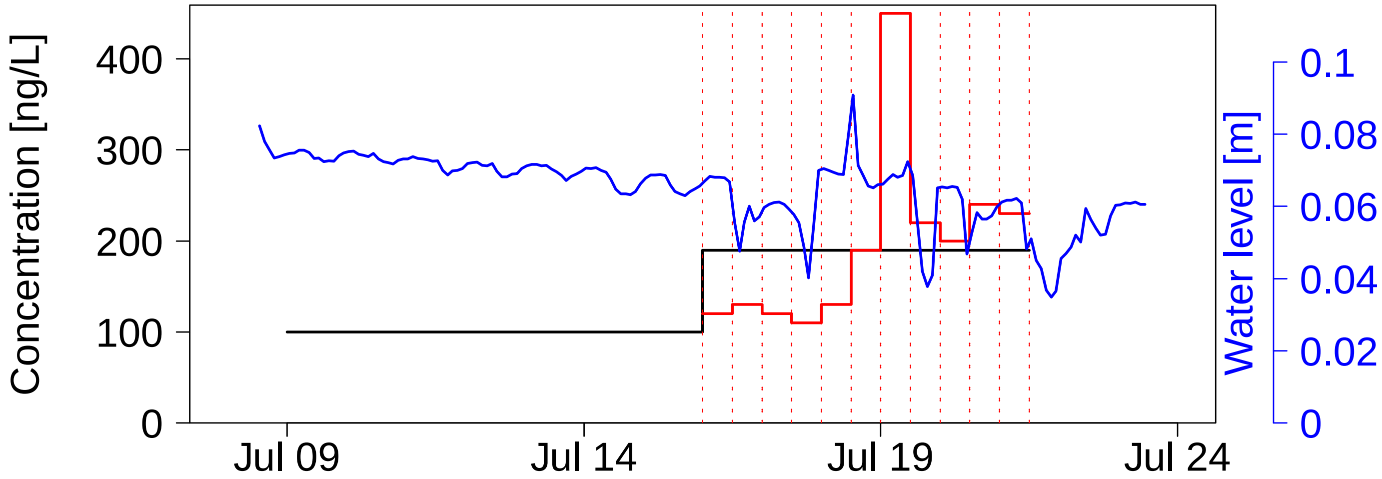


Interpretation: The concentration profiles of the six compounds show dramatic increases on single half-days during a long period of low flow conditions. This cannot be explained by rain-induced surface runoff and/or input via the drainage system and must have other reasons e.g., spills, irrigation or drift.

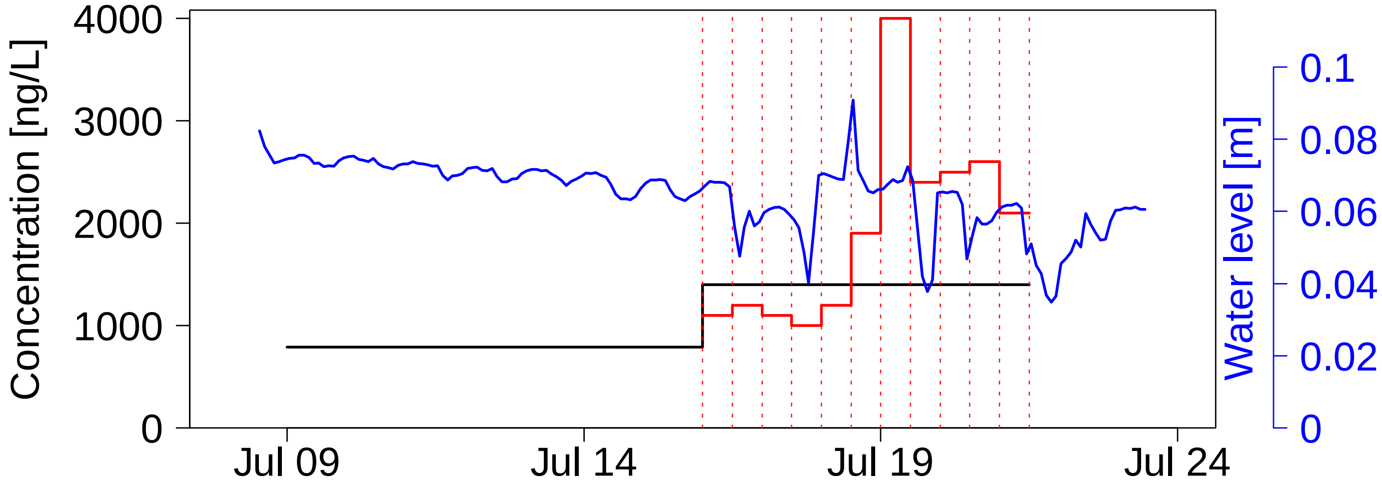
SI 3.6.2 Additional measurements during low flow conditions in the Eschelisbach

The black line represent the original data with the pooled samples designated by a * in SI 3-4. The 2 compounds having the highest concentrations in the composite sample from July 16th (0:00) to July 21th (12:00) were measured 8 month later using each of the 11 half-day samples separately (red line).

Azoxystrobin



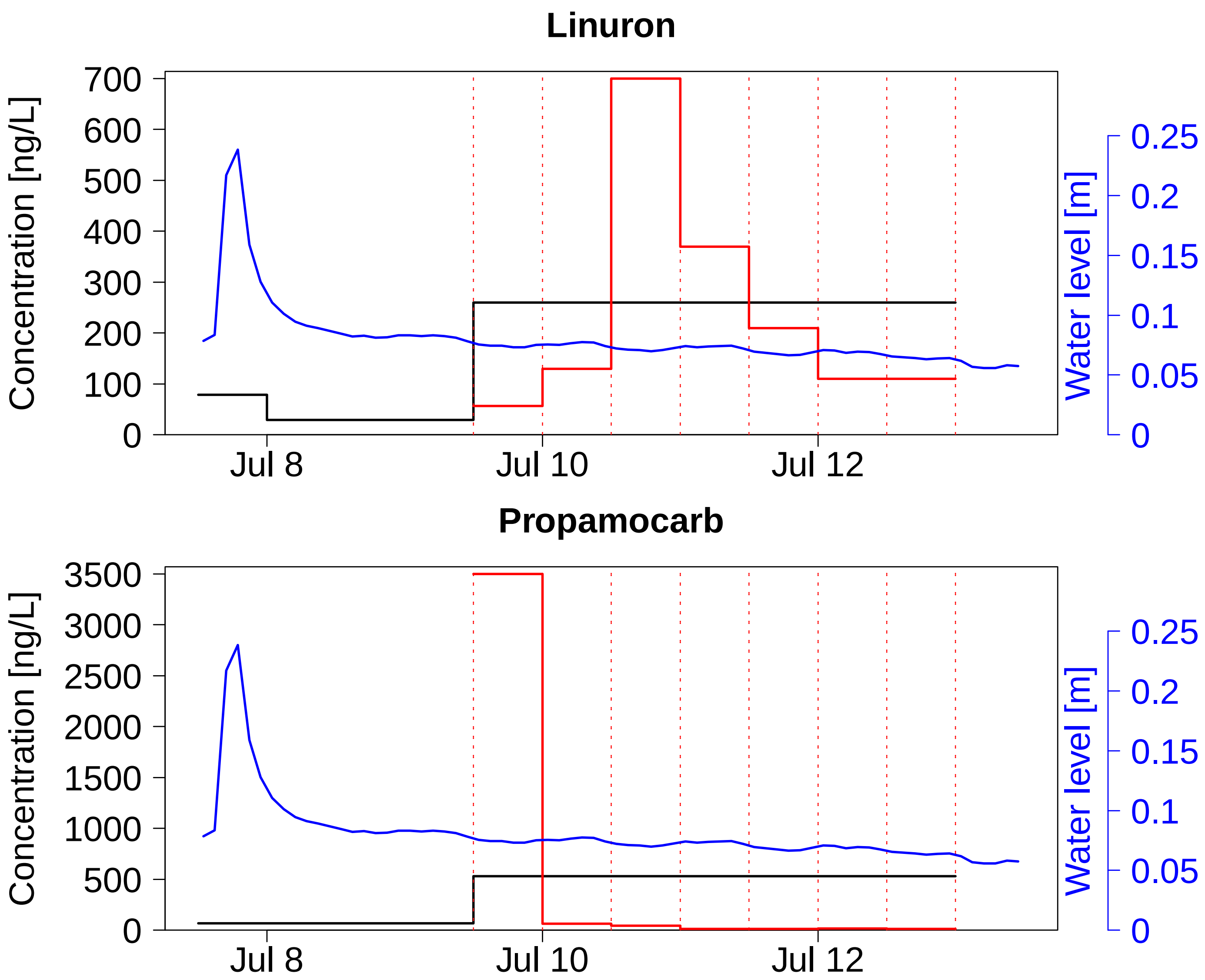
Fluopyram



Note: It is unclear why the concentrations of fluopyram remained constantly close or above 1000 ng/L throughout the generally dry months of July as spills or other types of improper handling would cause sharper peaks. Transfer via irrigation water might be a possible explanation.

SI 3.6.3 Additional measurements during low flow conditions in the Canale Piano di Magadino

The black line represent the original data with the pooled samples designated by a * in SI 3-4. The 2 compounds having the highest concentrations in the composite sample from July 10th (0:00) to July 13th (12:00) were measured 8 month later using each of the 7 half-day samples separately (red line).



Note: Propamocarb has a very sharp peak on a single half-days during a low flow condition. This cannot be explained by rain-induced surface runoff and/or input via the drainage system and must have other reasons e.g., spills, irrigation or drift. Linuron probably has the same entry path although the case is less clear as the increase is distributed over a longer time.

Table SI 3.6.4: Agreement between analysis of single half-days and pooled samples:

Compound	Site (Figure in SI)	Average concentration of half-day samples [ng/L]	Concentration of pooled sample [ng/L]	$C_{average}/C_{pooled}$
Ethofumesate	Weierbach (SI 3.6.1)	182	200	90.9%
Linuron	"	931	1100	84.6%
MCPA	"	190	180	105.6%
MCPB	"	5385	3500	153.8%
Metamitron [1] (Metamitron-desamino)	"	312 (1166)	2300 (350)	13.6% (333%)
Metolachlor	"	4027	350	91.5%
Azoxystrobin	Eschelisbach (SI 3.6.2)	195	190	102.4%
Fluopyram	"	1918	1400	137.0%
Linuron	Canale (SI 3.6.3)	241	260	92.7%
Propamocarb	"	523	530	98.7%

[1] The value in braces is the concentration of the transformation product metamitron-desamino. The metamitron-concentration in the pooled sample is consistently higher than the follow-up measurement (cf. SI Figure 3.6.1) due to transformation of metamitron during storage (and/or freezing and thawing). The sum of parent and transformation product were in better agreement: mean sum of 1478 ng/L for the single half-days and 2650 ng/l for pooled sample and $C_{average}/C_{pooled}$ reaching 55.8%. No additional transformation products were measured.

SI 4: Risk assessment and scenario analysis

SI 4.1: Single Substance RQs vs. RQ_{mix}

Figure SI 4.1.1

Top panel: Single substance acute risk quotient (ARQ) profiles of compounds with maxima above 0.1 in Mooskanal calculated with measured environmental concentrations (MEC)

Lower panels: Mixture ARQ profiles (ARQ_{mix}) for the three taxonomic groups calculated with MEC, i.e., using the original data (ORIG), and the scenarios for reduced temporal resolution (TR) based on 14d C_{twa}, reduced substance selection (SS) based on the 28 most frequently measured compounds and reduced seasonal coverage (SC) (no separate bar shown because this would correspond to the ORIG bar for time period April-July only), plus ARQ_{mix} calculated with all three factors combined (TR+SS+SC). Water quality class based on general approach for micropollutants assessment [1].

[1] Kase, R.; Eggen, R. I. L.; Junghans, M.; Götz, C.; Hollender, J., Assessment of Micropollutants from Municipal Wastewater- Combination of Exposure and Ecotoxicological Effect Data for Switzerland. In Waste Water - Evaluation and Management, Garcia Einschlag, F. S., Ed. 2011; pp 31-54)

Figure SI 4.1.2

Top panel: Single substance acute risk quotient (ARQ) profiles of compounds with maxima above 0.1 in Weierbach calculated with measured environmental concentrations (MEC)

Lower panels: Mixture ARQ profiles (ARQ_{mix}) for the three taxonomic groups calculated with MEC, i.e., using the original data (ORIG), and the scenarios for reduced temporal resolution (TR) based on 14d C_{twa}, reduced substance selection (SS) based on the 28 most frequently measured compounds and reduced seasonal coverage (SC) (no separate bar shown because this would correspond to the ORIG bar for time period April-July only), plus ARQ_{mix} calculated with all three factors combined (TR+SS+SC). Water quality class based on general approach for micropollutants assessment [1].

[1] Kase, R.; Eggen, R. I. L.; Junghans, M.; Götz, C.; Hollender, J., Assessment of Micropollutants from Municipal Wastewater-Combination of Exposure and Ecotoxicological Effect Data for Switzerland. In Waste Water - Evaluation and Management, Garcia Einschlag, F. S., Ed. 2011; pp 31-54)

Figure SI 4.1.3 (corresponding to Figure 3 in article and therefore not shown here)

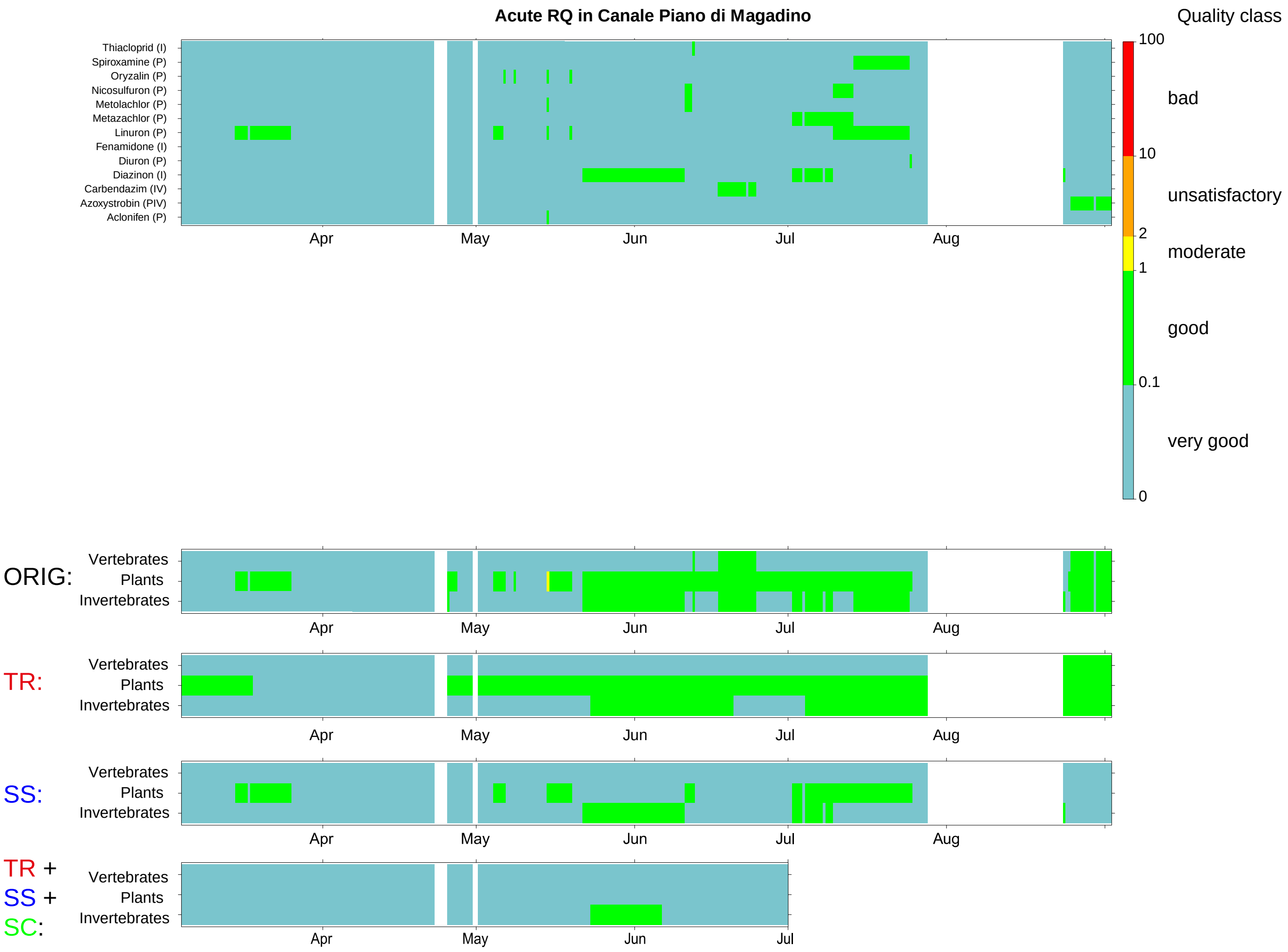


Figure SI 4.1.4

Top panel: Single substance acute risk quotient (ARQ) profiles of compounds with maxima above 0.1 in Canale Piano di Magadino calculated with measured environmental concentrations (MEC)

Lower panels: Mixture ARQ profiles (ARQ_{mix}) for the three taxonomic groups calculated with MEC, i.e., using the original data (ORIG), and the scenarios for reduced temporal resolution (TR) based on 14d C_{twa}, reduced substance selection (SS) based on the 28 most frequently measured compounds and reduced seasonal coverage (SC) (no separate bar shown because this would correspond to the ORIG bar for time period April-July only), plus ARQ_{mix} calculated with all three factors combined (TR+SS+SC). Water quality class based on general approach for micropollutants assessment [1].

[1] Kase, R.; Eggen, R. I. L.; Junghans, M.; Götz, C.; Hollender, J., Assessment of Micropollutants from Municipal Wastewater-Combination of Exposure and Ecotoxicological Effect Data for Switzerland. In Waste Water - Evaluation and Management, Garcia Einschlag, F. S., Ed. 2011; pp 31-54)

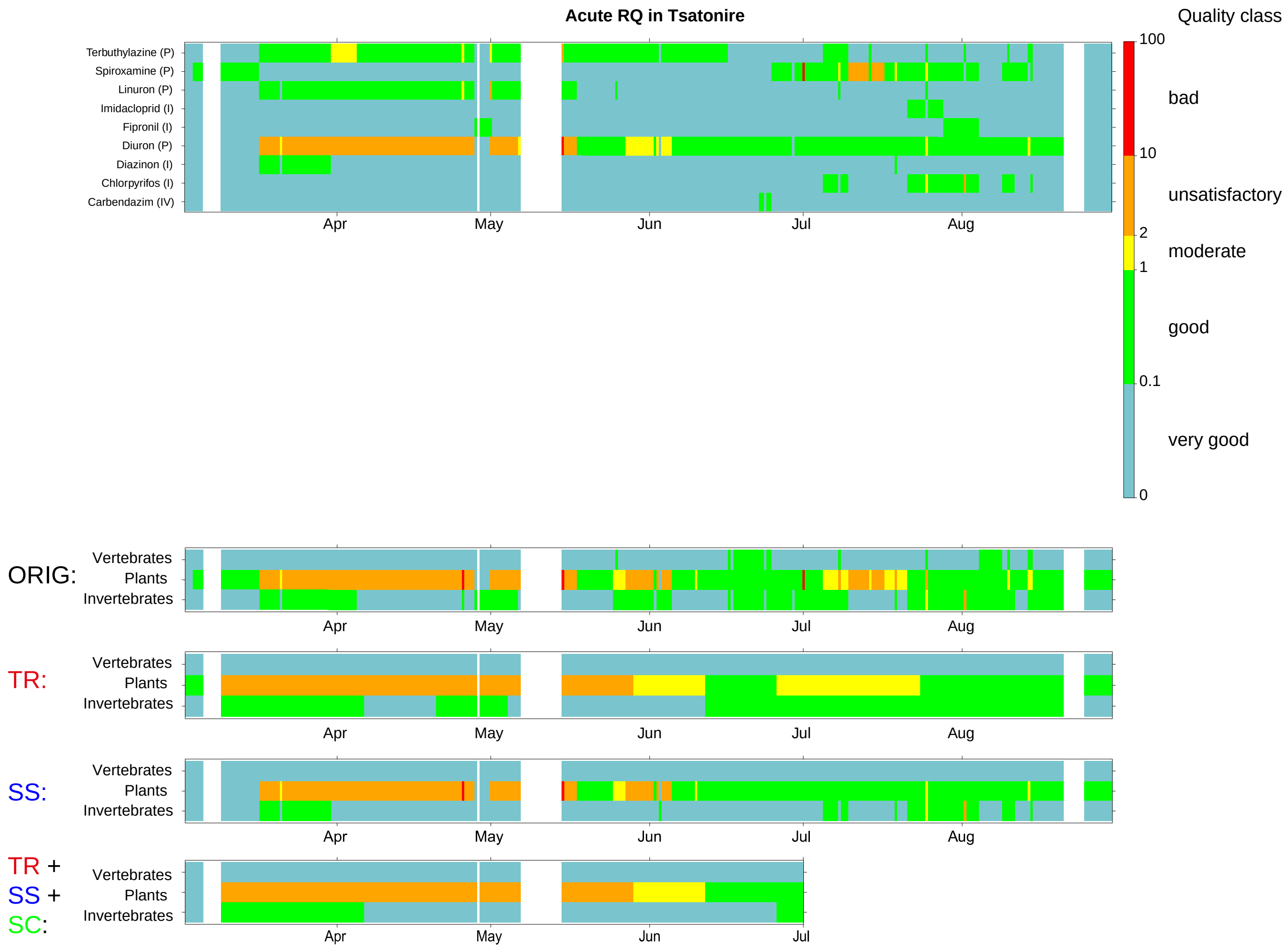


Figure SI 4.1.5

Top panel: Single substance acute risk quotient (ARQ) profiles of compounds with maxima above 0.1 in the Tsatonire calculated with measured environmental concentrations (MEC)

Lower panels: Mixture ARQ profiles (ARQ_{mix}) for the three taxonomic groups calculated with MEC, i.e., using the original data (ORIG), and the scenarios for reduced temporal resolution (TR) based on 14d C_{twa}, reduced substance selection (SS) based on the 28 most frequently measured compounds and reduced seasonal coverage (SC) (no separate bar shown because this would correspond to the ORIG bar for time period April-July only), plus ARQ_{mix} calculated with all three factors combined (TR+SS+SC). Water quality class based on general approach for micropollutants assessment [1].

[1] Kase, R.; Eggen, R. I. L.; Junghans, M.; Götz, C.; Hollender, J., Assessment of Micropollutants from Municipal Wastewater-Combination of Exposure and Ecotoxicological Effect Data for Switzerland. In Waste Water - Evaluation and Management, Garcia Einschlag, F. S., Ed. 2011; pp 31-54)

SI 4.2: Details on acute RQ_{mix}

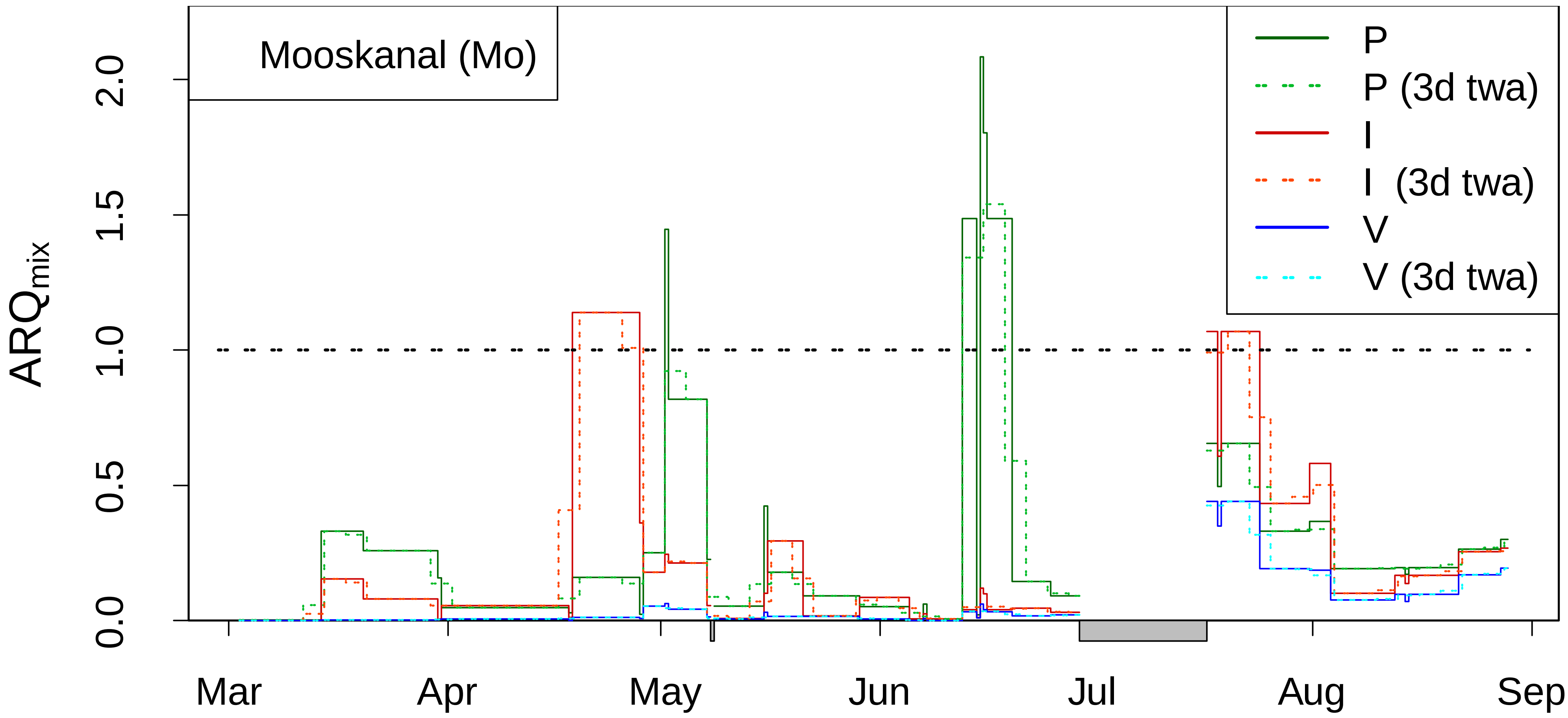


Figure SI 4.2.1 Sum of acute risk quotients (ARQ_{mix}) for plants (P), invertebrates (IV) and vertebrates (V) determined in Mooskanal based on original measurements (solid lines) and 3day time-weighted average concentrations (colored dashed lines). The black dashed line indicates an ARQ_{mix} of 1.

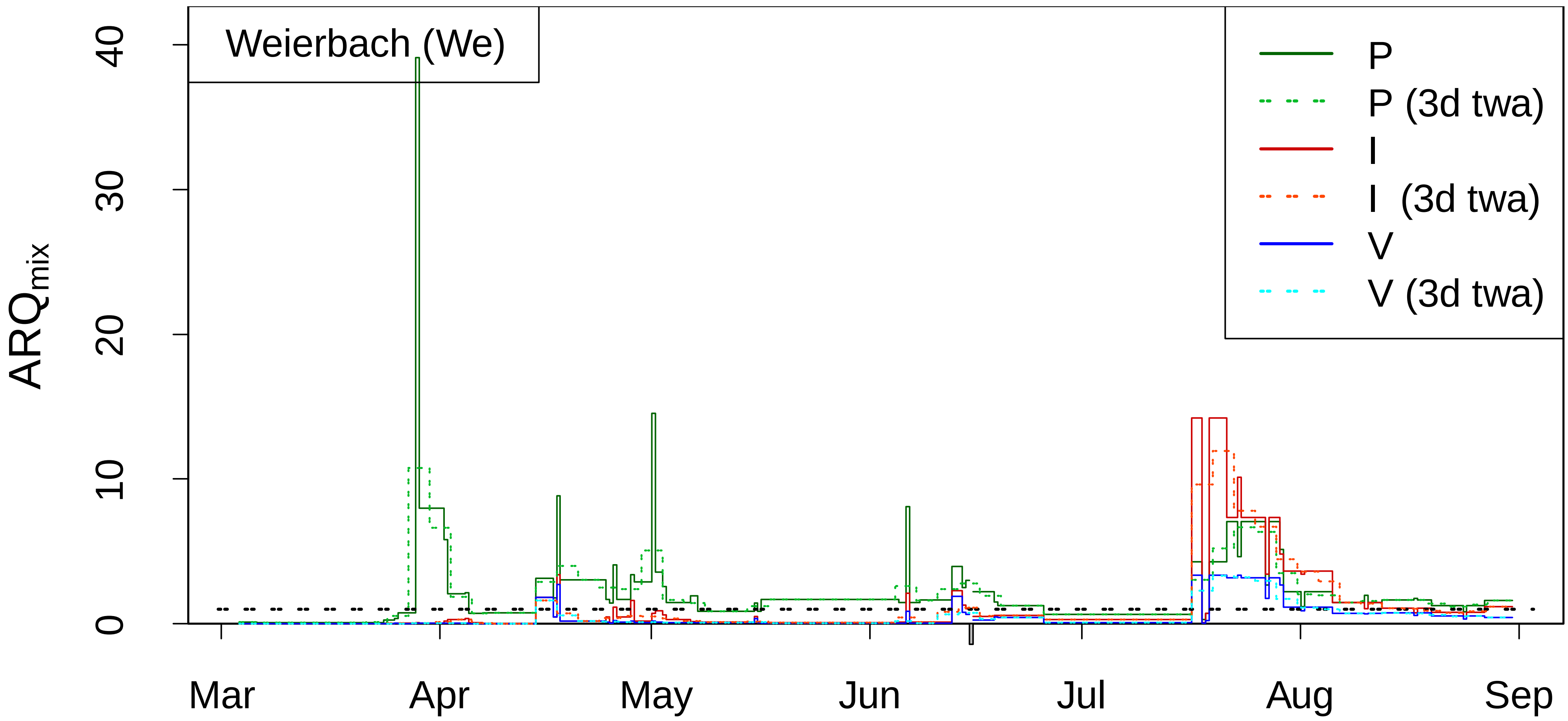


Figure SI 4.2.2 Sum of acute risk quotients (ARQ_{mix}) for plants (P), invertebrates (IV) and vertebrates (V) determined in Weierbach based on original measurements (solid lines) and 3 day time-weighted average concentrations (colored dashed lines). The black dashed line indicates an ARQ_{mix} of 1.

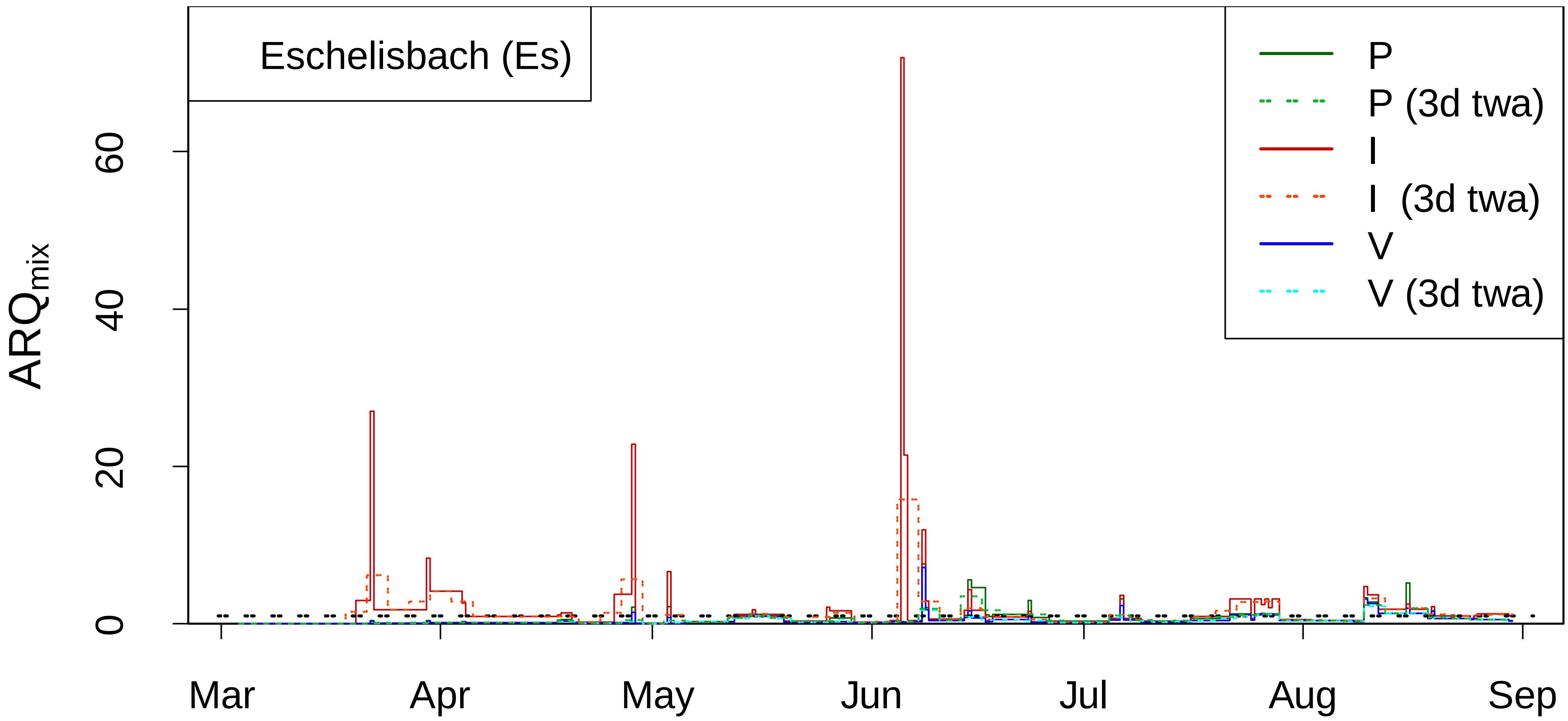


Figure SI 4.2.3 Sum of acute risk quotients (ARQ_{mix}) for plants (P), invertebrates (IV) and vertebrates (V) determined in Eschelisbach based on original measurements (solid lines) and 3 day time-weighted average concentrations (colored dashed lines). The black dashed line indicates an ARQ_{mix} of 1.

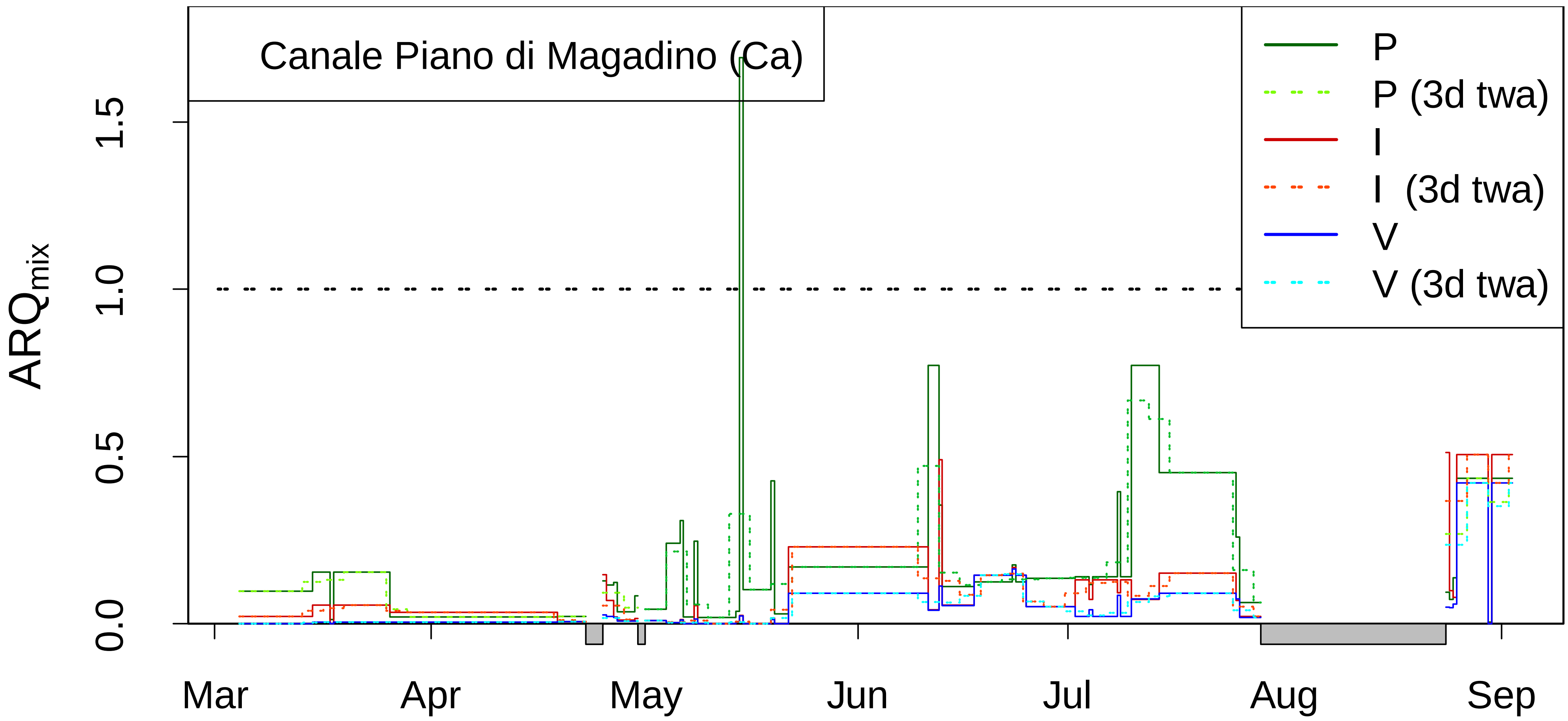


Figure SI 4.2.4 Sum of acute risk quotients (ARQ_{mix}) for plants (P), invertebrates (IV) and vertebrates (V) determined in Canale Piano di Magadino based on original measurements (solid lines) and 3 day time-weighted average concentrations (colored dashed lines). The black dashed line indicates an ARQ_{mix} of 1.

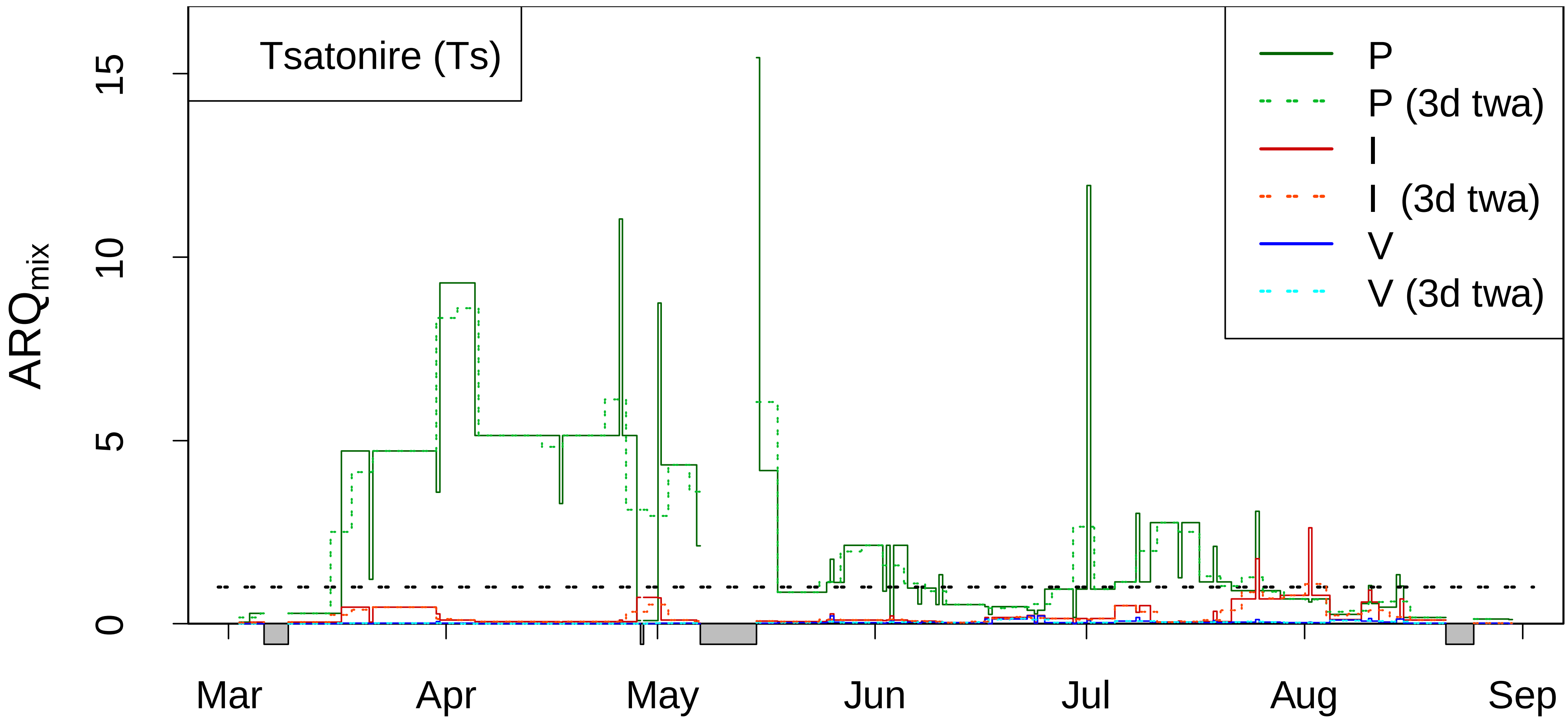


Figure SI 4.2.5 Sum of acute risk quotients (ARQ_{mix}) for plants (P), invertebrates (IV) and vertebrates (V) determined in Tsatonire based on original measurements (solid lines) and 3 day time-weighted average concentrations (colored dashed lines). The black dashed line indicates an ARQ_{mix} of 1.

SI 4.3: Details on Chronic Risk Quotients

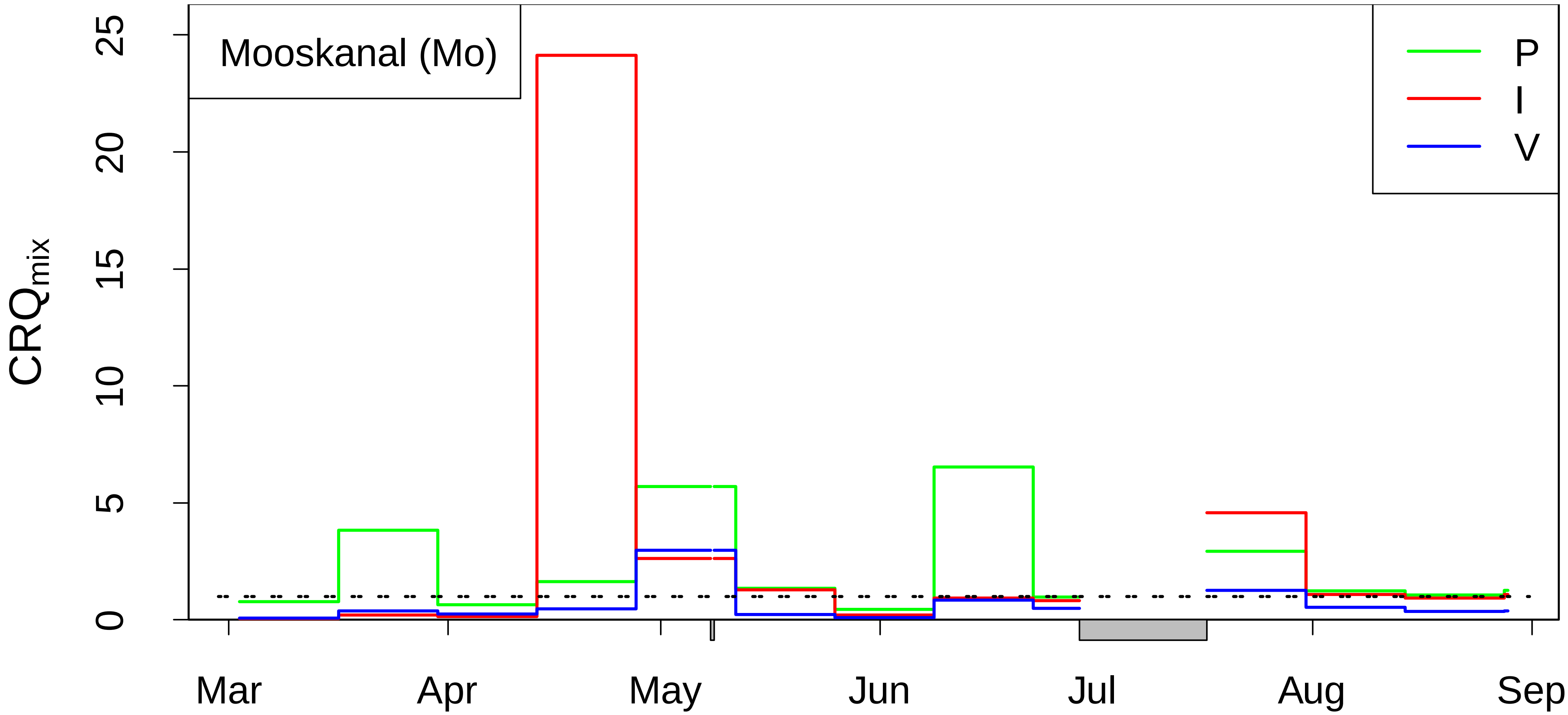


Figure SI 4.3.1 Sum of chronic risk quotients (CRQ_{mix}) for plants (P), invertebrates (IV) and vertebrates (V) determined in Mooskanal based on two-week time-weighted average concentrations (14d-C_{twa}). The dashed line indicates a CRQ_{mix} of 1.

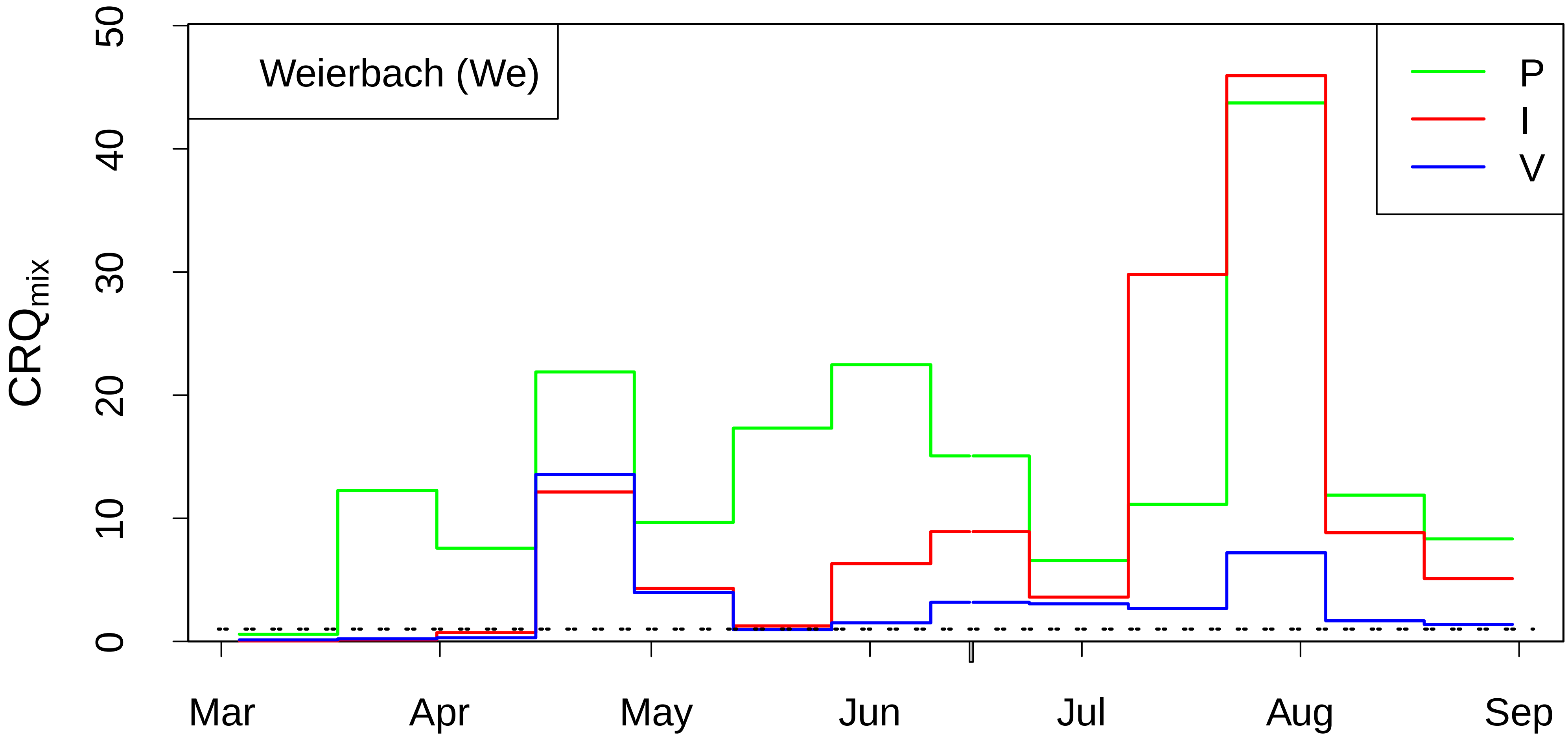


Figure SI 4.3.2 Sum of chronic risk quotients (CRQ_{mix}) for plants (P), invertebrates (IV) and vertebrates (V) determined in Weierbach based on two-week time-weighted average concentrations (14d-C_{twa}). The dashed line indicates a CRQ_{mix} of 1.

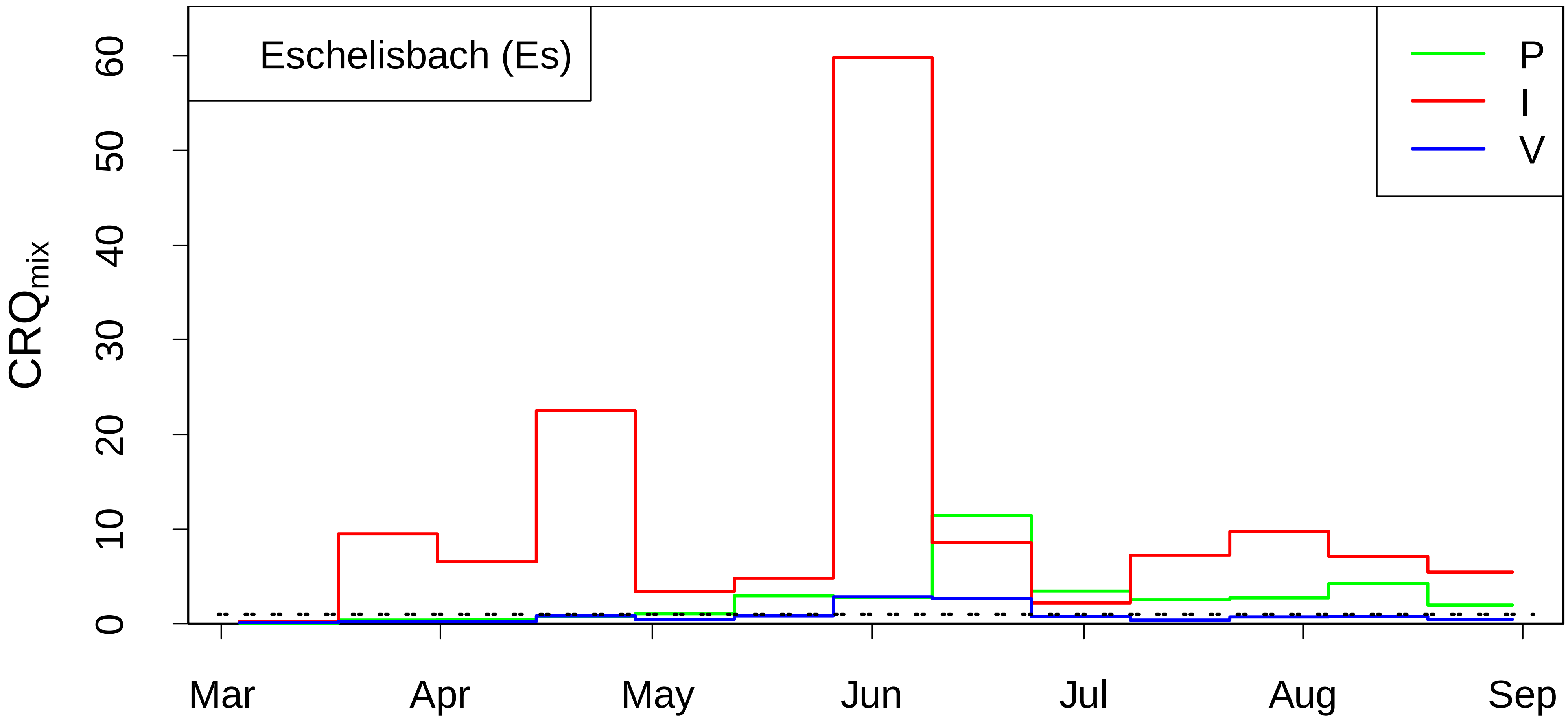


Figure SI 4.3.3 Sum of chronic risk quotients (CRQ_{mix}) for plants (P), invertebrates (IV) and vertebrates (V) determined in Eschelisbach based on two-week time-weighted average concentrations (14d-C_{twa}). The dashed line indicates a CRQ_{mix} of 1.

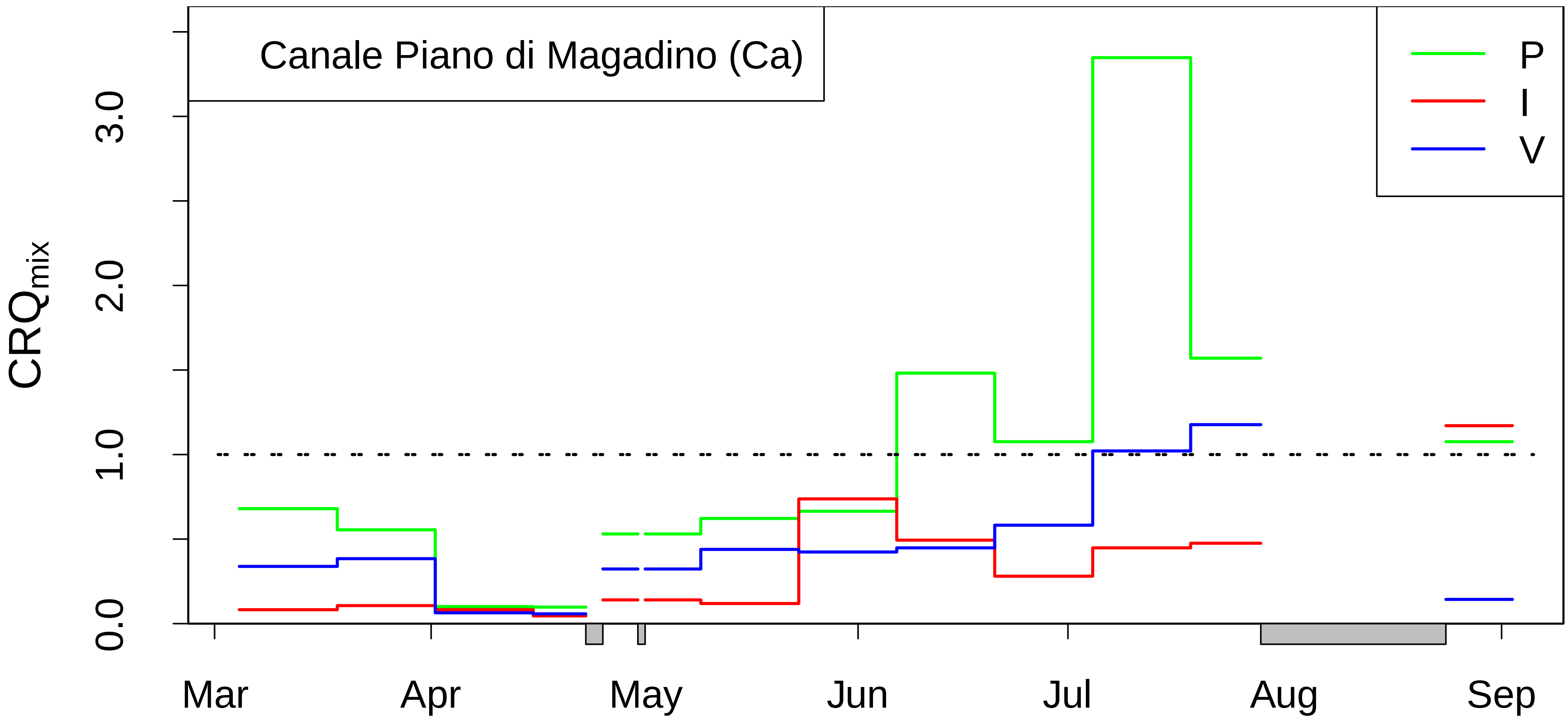


Figure SI 4.3.4 Sum of chronic risk quotients (CRQ_{mix}) for plants (P), invertebrates (IV) and vertebrates (V) determined in Canale Piano di Magadino based on two-week time-weighted average concentrations (14d-C_{twa}). The dashed line indicates a CRQ_{mix} of 1.

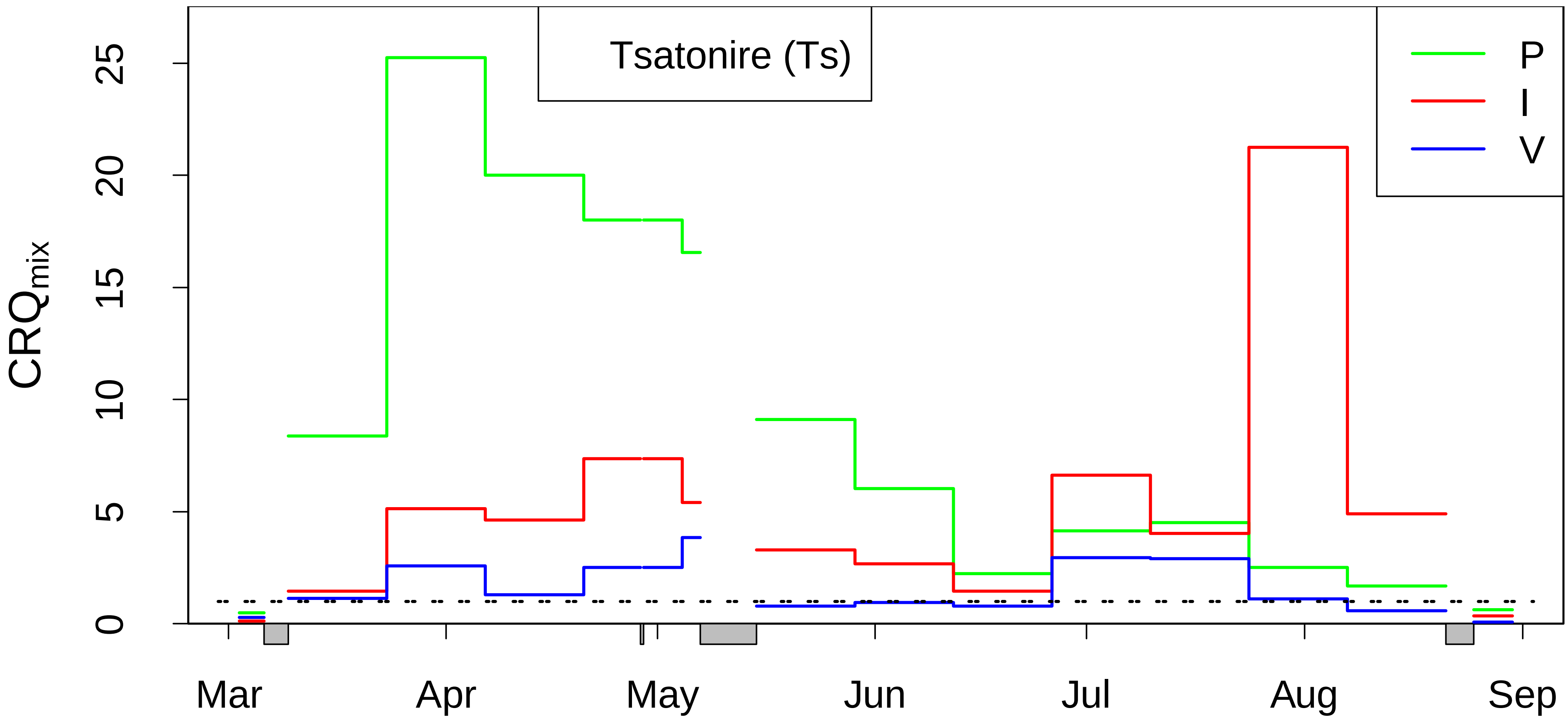


Figure SI 4.3.5 Sum of chronic risk quotients (CRQ_{mix}) for plants (P), invertebrates (IV) and vertebrates (V) determined in Tsatonire based on two-week time-weighted average concentrations (14d-C_{twa}). The dashed line indicates a CRQ_{mix} of 1.

SI 4.4: Details on Scenarios for Risk Assessment

Effects on acute risk quotient of mixture (ARQ_{mix}) if either temporal resolution, number of compounds or temporal coverage are lowered. Column "Original" is based on high temporal resolution (composite half-day samples during rain event and pooled samples during dry periods), full set of 213 compounds and 6 months coverage. Light grey columns contain the scenarios relevant to evaluate historic routine monitoring data (i.e., 14-day time weighted averages or 28 historically most frequent or 4-months coverage from March to June or all three scenarios combined). Dark grey columns contain the scenarios potentially resulting in an improved coverage of acute risks (i.e., 3-day time weighted averages or 38 compounds recommended for monitoring or both scenarios combined).

Table SI 4.4.1 Time with ARQ_{mix} > 1 in %

Stream	Organism Group	Original	Temporal resolution		Substance selection		Seasonal coverage [b]	All combined	
			3d-C_{twa}	14d-C_{twa}	28 most frequent cpds	38 recommended cpds	4 months	3d C_{twa}, 38 recommended, 6 months	14d-C_{twa}, 28 most frequent, 4 months
Mo	P	4.4	3.7	0	0	4.0	5.9	3.7	0
	I	10.3	7.5	0	5.9	10.3	8.1	5.6	0
	V	0	0.0	0	0	0.0	0	0.0	0
We	P	63.6	66.7	84.4	26.9	51.1	59.2	53.3	35.3
	I	24.2	23.3	23.3	0	22.5	5.9	21.9	0
	V	12.8	11.7	15.6	0	12.8	3.8	11.7	0
Es	P	15.6	20.0	15.6	0.6	14.7	9.6	15.0	0
	I	35.8	41.7	61.1	9.4	31.9	31	40.0	23.4
	V	10.8	10.0	7.8	0	7.5	2.5	8.3	0
Ca[a]	P	0.3	0.0	0	0	0.0	0.4	0.0	0
	I	0	0.0	0	0	0.0	0	0.0	0
	V	0	0.0	0	0	0.0	0	0.0	0
Ts	P	49.1	57.0	69.1	38.2	38.2	57.1	42.4	79.3
	I	0.6	1.8	0	0.6	0.6	0	0.0	0
	V	0	0.0	0	0	0.0	0	0.0	0

[a] 4.5 days during period with many interruptions excluded as 3d and 14d-C_{twa} not meaningful during this time

[b] Figures calculated for four instead of six months. As a consequence the percent of time with ARQ_{mix} > 1 can increase (if proportionally more exceedances occur in the first 4 months)

Abbreviations:

Mo: Mooskanal, We: Weierbach, Es: Eschelisbach, Ca: Canale Piano di Magadino, Ts: Tsatonire

P: Plants, I: Invertebrates, V: Vertebrates

Table SI 4.4.2 Maximum ARQ_{mix} of whole sampling campaign. Light grey columns contain the data used for Figure 4 of the article and dark grey columns the data for SI Figure 4.6.

Stream	Organism Group	Original	Temporal resolution		Substance selection		Seasonal coverage	All combined	
			3d-C_{twa}	14d-C_{twa}	28 most frequent cpds	38 recommended cpds	4 months	3d C_{twa}, 38 recommended, 6 months	14d-C_{twa}, 28 most frequent, 4 months
Mo	P	2.1	1.5	0.8	0.7	1.5	2.1	1.2	0.3
	I	1.1	1.1	0.8	1.1	1.1	1.1	1.1	0.7
	V	0.4	0.4	0.3	0	0.4	0.1	0.4	0
We	P	39.1	10.8	4.6	16.8	17	39.1	6.5	1.4
	I	14.2	11.9	5.6	0.7	14.2	3.4	11.9	0.2
	V	3.4	3.3	2.2	0.2	3.4	2.7	3.3	0
Es	P	7.6	3.5	1.7	3.3	6.2	7.6	2.4	0.2
	I	72.0	15.8	4.4	24.6	71.9	72	15.7	2.7
	V	7.1	2.2	1.2	0	5.8	7.1	2.1	0
Ca[a]	P	1.7	0.7	0.4	1	0.7	1.7	0.6	0.1
	I	0.5	0.5	0.4	0.4	0.5	0.5	0.5	0.1
	V	0.4	0.4	0.3	0	0.4	0.2	0.4	0
Ts	P	15.4	8.6	6.4	15.4	15.3	15.4	8.6	6.3
	I	2.6	1.1	0.7	2.5	2.5	0.7	0.9	0.3
	V	0.2	0.1	0.1	0	0.2	0.2	0.1	0

[a] Canale Piano di Magadino not shown in figures due to to generally low ARQ_{mix}. Furthermore, 4.5 days during period with many interruptions excluded as 3d and 14d-C_{twa} not meaningful during this time

Abbreviations:
Mo: Mooskanal, We: Weierbach, Es: Eschelisbach, Ca: Canale Piano di Magadino, Ts: Tsatonire
P: Plants, I: Invertebrates, V: Vertebrates

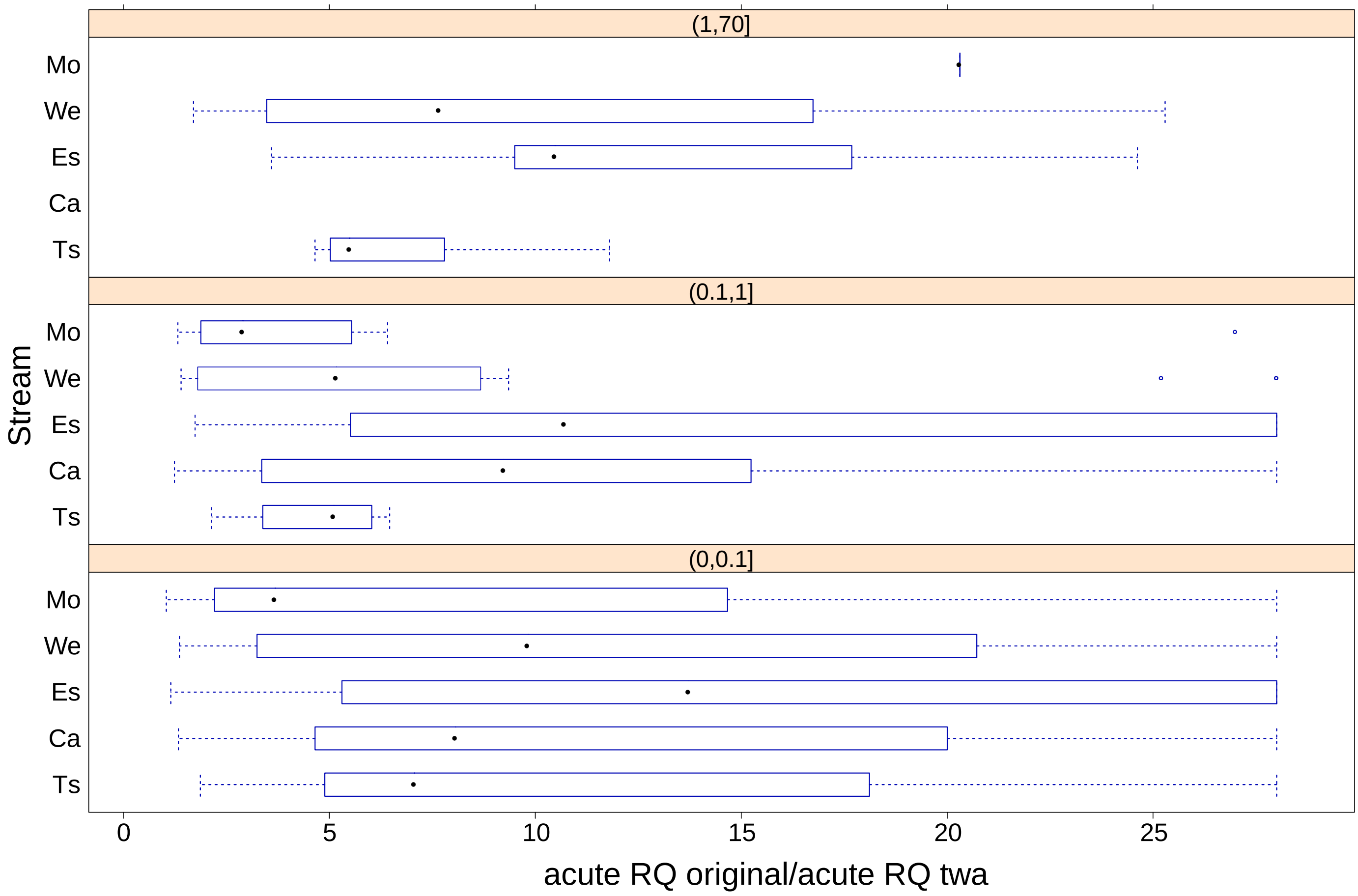


Figure SI 4.5 Single substance evaluation of acute risks: For each compound the highest risk quotient determined with the original measured concentrations was compared to the one determined for the 14-day time-weighted average (at the corresponding half-day). The values used for the boxplots were split in three groups according to their original RQ with intervals ranging from 0 to 0.1 (low risk), 0.1 to 1 (slight risk) and > 1 (elevated risk). The number of cases in the three groups is *n* = 28 for (1,70], *n* = 71 for (0.1,1] and *n* = 277 for (0,0.1]. Stream name abbreviations: Mooskanal (Mo), Weierbach (We), Eschelisbach (Es), Canale Piano di Magadino (Ca) and Tsatonire (Ts)

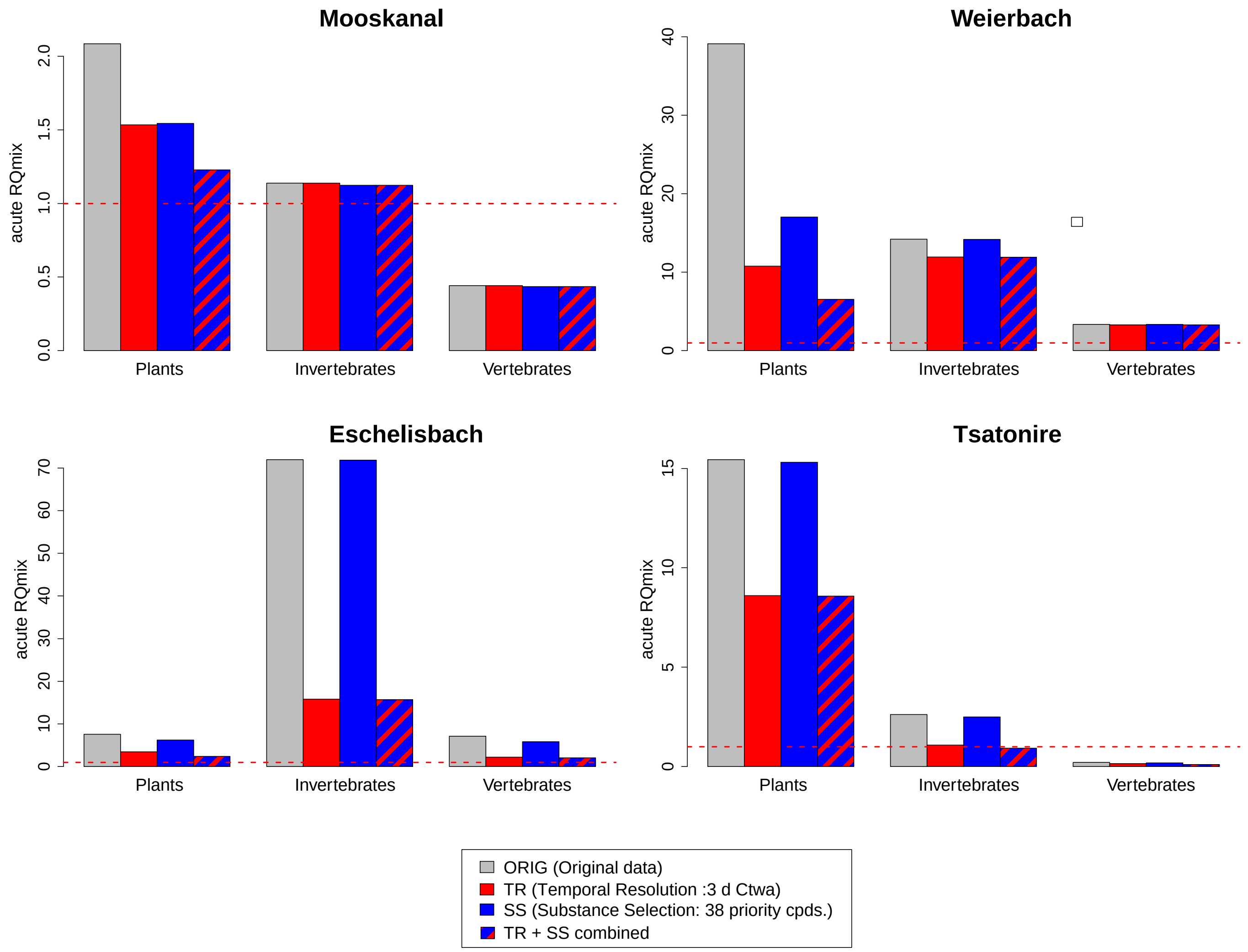


Figure SI 4.6 Highest ARQ_{mix} of whole season at the four sites with exceedances of acute quality criteria. Grey bars show the results obtained with the measured environmental concentrations of all compounds (ORIG). Colored bars show the results of different scenarios: reduced temporal resolution (TR) based on 3d-C_{twa}, reduced substance selection (SS) based on the 38 priority compounds recommended for monitoring in Switzerland and ARQ_{mix} calculated with both factors combined (TR+SS). The dashed red line indicates an ARQ_{mix} of 1. The Canale Piano di Magadino is not shown due to generally low ARQ_{mix} (but values are given in SI Table 4.4.2)