toxics

MDPI

Supplementary Materials: Environmental Risk of Pesticides for Fish in Small- and Medium-Sized Streams of Switzerland

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Table S1. Sources of chemical-analytical data from monitoring studies conducted in Switzerland 2012–18.

Campaign	Reference	Link to data
NAWA 2012	Moschet et al., 2014	https://doi.org/10.1021/es500371t
NAWA 2015	Spycher et al., 2018	https://doi.org/10.25678/000022
NAWA 2017	Spycher et al., 2019	https://doi.org/10.25678/0000GG
Pyrethroids 2017 & 2018	Rösch et al., 2019a, b	https://doi.org/10.25678/0001C7

Table S5. Effect values (in µg/L) for the most sensitive fish species (LC_{50}, NOEC), highest environmental concentration (MEC_{max}; in µg/L) and mode of action of highly relevant pesticides. 1) 14 d composite sample (chronic exposure); 2) 3–3.5 d (acute exposure) composite sample; an assessment factor of 10 was applied to the LC_{50} and NOEC to derive acute and chronic PNECs, respectively. NA: not measured.

Pesticide type	Fish-relevant substances	LC_{50}	NOEC	MEC_{max} 2012[1]	MEC_{max} 2015[2]	MEC_{max} 2015[1]	MEC_{max} 2017[2]	MEC_{max} 2017[1]	MEC_{max} 2018[1]	Primary mode of action
Insecticides	Chlorpyrifos	1.3	0.14	NA	0.039	0.01093	0.021	0.00855	0.0021	Inhibition of acetylcholinesterase
	Chlorpyrifos-methyl	12.6	4.7	NA	0.21	0.00975	0.063	0.01575	0.015	Inhibition of acetylcholinesterase
	Diazinon	90	2.4	0.043	0.59	0.06343	0.0068	0.0068	NA	Inhibition of acetylcholinesterase
	Cypermethrin	0.39	0.03	NA	NA	NA	0.00098	0.00049	0.0038	Disruption of sodium channels
	λ-Cyhalothrin	0.08	0.031	NA	NA	NA	0.031	0.00775	0.00097	Disruption of sodium channels
	Deltamethrin	0.15	0.017	NA	NA	NA	<LOQ	0.00	0.077	Disruption of sodium channels
	Permethrin	1.5	0.66	NA	NA	NA	0.00065	0.00016	0.019	Disruption of sodium channels
Herbicides	Diuron	500	33.4	0.052	3	1.27464	0.093	0.02325	NA	Photosythesis II inhibition
	Linuron	890	21	0.27	2.8	0.748	0.63	0.2295	NA	Photosythesis II inhibition
	S-Metolachlor	3900	30	0.96	5	2.650	0.72	0.2785	NA	Inhibition of long-chain fatty acids
	Pendimethalin	138	6.3	NA	NA	NA	0.48	0.181	NA	Inhibition of mitosis
Fungicides	Carbendazim	7	11	0.065	0.5	0.35214	1.3	0.33648	NA	Damage to cytoskeleton and motor proteins
	Epoxiconazole	3140	3	0.064	0.25	0.05448	0.33	0.10938	NA	Inhibition of sterole biosynthesis
	Fenpropimorph	2300	0.16	0.015	0.0015	0.00046	0.58	0.2	NA	Inhibition of sterole biosynthesis
	Fluazinam	55	2.9	NA	0.024	0.00176	0.23	0.1	NA	Disruption of cellular respiration
	Fluopyram	980	135	NA	6	2.81071	3	1.95	NA	Disruption of cellular respiration
	Pyraclostrobin	6	2	0.0605	0.0045	0.00056	0.0023	0.00105	NA	Disruption of cellular respiration
	Spiroxamine	2410	2	0.016	0.6	0.07507	<LOQ	<LOQ	NA	Inhibition of sterole biosynthesis

Table S6. Sublethal effect data for data-rich relevant pesticides. Data were selected based on environmental relevance in Swiss creeks (≤ MEC_{max} detected in monitoring studies 2012–18). No data was available in this concentration range for S-metolachlor, epoxiconazole, fenpropimorph, fluazinam, fluopyram, flusilazole, pyraclostrobin, spiroxamine and permethrin.

	Substance	MEC_{max}[1] (µg/L)	$LOEC$[2] (µg/L)	Effect (exposure duration)	Fish species and life stage	Reference
Insecticides	Chlorpyrifos	0.039	0.002*	Altered mating behavior in males (1–2 d); reduced number and survival of offspring (14 d)	*Poecilia reticulate*; adult	[1]
			0.005	Reduced AChE[3] activity in head (4 d)	*Odontesthes bonariensis*; larvae	[2]
	Diazinon	0.59	0.0036*	Reduced AChE activity; oxidative stress (5, 15, 30 d)	*Cyprinus carpio*	[3]
			0.3	Altered blood plasma hormone level, reduced level of expressible milt (5 d)	*Salmo salar*; mature males	[4]
			0.47[s]	Reduced fecundity, females (108 d)	*Cyprinodon variegatus*; adult	[5]
			0.55	Reduced growth rate of offspring (6–8 mo)	*Salvelinus fontinalis*; adult	[6]
	Cypermethrin	0.0038	<0.004	Reduced olfactory response to pheromone (PGF2α); Altered blood plasma hormone level, reduced priming effect on milt (5 d)	*Salmo salar*; mature males	[7]
	λ-Cyhalothrin	0.031	0.0004*	DNA damage in erythrocytes (1, 2 d)	*Gambusia affinis*	[8]
			0.005*	Increased hematocrit; DNA damage in erythrocytes; reduced AChE and catalase activity (4 d)	*Prochilodus lineatus*; juvenile	[9]
	Deltamethrin	0.077	0.060	Reduced plasma IgM (28 d)	*Gobiocypris rarus*	[63]
			0.035	Reduced female wet weight in F0 generation (260 d)	*Pimephales promelas ; complete life-cycle*	[64]
			0.049	Reduced dry weight (35 d)	*Cyprinodon variegatus ; eggs (24-48h old)*	[64]
Herbicides	Linuron	2.8	1.0	Reduced vitellogenin concentration in females (21 d)	*Pimephales promelas*; adult	[10]
			1.7	Changes in gene expression (lipid and steroid biosynthesis; cellular stress) (4 d)	*Salmo trutta*; mature males	[11]
	Diuron	3	0.057	Oxidative stress; altered activity of biotransformation enzymes (7 d)	*Oreochromis niloticus*; mature males	[12]
			0.1	Reduction of primary ovarian follicles (25 d)	*Oreochromis niloticus*; mature females	[13]
			0.1	Reduced growth and condition factor; changes in thyroid hormone levels (15 d)	*Menidia beryllina*; juvenile	[14]
			0.2	Reduction in blood plasma testosterone levels (25 d)	*Oreochromis niloticus*; mature males	[15]
			0.2	Changes in gene expression of vitellogenin and activity of cytochrome P450 aromatase (7 d)	*Oreochromis mossambica*; juvenile, male	[16]

			1	Increase of micronuclei in erythrocytes, DNA damage in liver cells and spermatocytes (14, 21 d)	*Danio rerio*; adult, male	[17]
	Pendimethalin	0.48	0.5	Reduced antioxidant defense in gill and liver (28 d)	*Oncorhynchus mykiss*	[18]
			0.5	Changes in adrenaline level, AChE activity, Na^+/K^+-ATPase activity, monoaminoxidase activity, and oxidative stress (4 d)	*Channa punctata*	[19,20]
Fungicides	Carbendazim	0.5	0.16	Changes in swimming behavior (5 d)	*Danio rerio*; larvae	[21]
	Azoxystrobin	3	0.1	Changes in gene expression (oxidative stress, endocrine disruption, immune response) (1, 2, 3 d)	*Danio rerio*; larvae	[22]
			0.25	Changes in anti-oxidative and detoxification enzyme activity/malondialdehyde concentration in liver (7, 14, 21, 28 d)	*Danio rerio*; adult	[23]
			0.5	Increase of micronuclei in erythrocytes, DNA damage in liver cells and spermatocytes (7, 14, 21 d)	*Danio rerio*; adult, male	[17]
			1	Oxidative stress and genotoxicity in liver (7, 14, 21, 28 d)	*Danio rerio*; adult	[24]
			2	Changes in gene expression of *cyp11a, hsd3b, cyp19a* in gonads, *vtg1, vtg2* in liver (21 d)	*Danio rerio*; adult, male	[25]

[1] MEC_{max} from NAWA SPEZ monitoring studies 2015-18; [2] lowest effect concentration; [3] AChE – acetyl cholinesterase; * pesticide applied as product formulation; [S] in saltwater.

Table S7. Toxic effect data for data-rich relevant pesticides shown in Figure 3. LC50: 50% survival after 96 h; NOEC: reduced growth, impaired development or reproduction after ≥28 d; sublethal: non-apical sublethal effects.

Substance	Effect category	Effect concentration (µg/L)	Reference
Linuron	sublethal	1	[10]
Linuron	sublethal	1.7	[11]
Linuron	sublethal	30	[26]
Linuron	sublethal	31.5	[27]
Linuron	sublethal	10	[28]
Linuron	sublethal	30	[29]
Linuron	LC50	2900	[30]
Linuron	LC50	3100	[30]
Linuron	LC50	8600	[30]
Linuron	LC50	9600	[30]
Linuron	LC50	890	[30]
Linuron	NOEC	21	[30]
Diuron	sublethal	0.1	[14]
Diuron	sublethal	78	[31]
Diuron	sublethal	0.057	[12]
Diuron	sublethal	0.2	[15]
Diuron	sublethal	5	[34]
Diuron	sublethal	0.1	[13]
Diuron	LC50	500	[30]
Diuron	LC50	710	[30]
Diuron	LC50	1100	[30]
Diuron	LC50	2800	[30]
Diuron	LC50	6300	[30]
Diuron	LC50	6700	[30]
Diuron	LC50	7700	[30]
Diuron	LC50	7800	[30]
Diuron	LC50	14700	[30]
Diuron	NOEC	33.4	[30]
Diuron	NOEC	220	[30]
Diuron	NOEC	410	[30]
Diazinon	sublethal	0.3	[4]
Diazinon	sublethal	0.47	[5]
Diazinon	sublethal	0.55	[6]
Diazinon	sublethal	2.9	[33]
Diazinon	sublethal	0.0036	[3]
Diazinon	sublethal	45	[34]
Diazinon	sublethal	60	[35]
Diazinon	sublethal	0.675	[36]
Diazinon	sublethal	1	[37]
Diazinon	sublethal	100	[38]
Diazinon	LC50	90	[14]
Diazinon	LC50	168	[30]
Diazinon	LC50	770	[30]
Diazinon	LC50	1470	[30]
Diazinon	LC50	1600	[30]
Diazinon	LC50	4300	[30]
Diazinon	LC50	8900	[30]
Diazinon	NOEC	200	[30]
Diazinon	NOEC	16.5	[30]

Diazinon	NOEC	2.4	[30]
Cypermethrin	sublethal	0.1	[7]
Cypermethrin	sublethal	0.15	[39]
Cypermethrin	sublethal	0.4	[40]
Cypermethrin	sublethal	0.443	[41]
Cypermethrin	sublethal	0.004	[7]
Cypermethrin	sublethal	0.04	[42]
Cypermethrin	sublethal	0.16	[43]
Cypermethrin	LC50	0.4	[30]
Cypermethrin	LC50	0.43	[30]
Cypermethrin	LC50	1.2	[30]
Cypermethrin	LC50	2.1	[30]
Cypermethrin	LC50	1.47	[30]
Cypermethrin	LC50	1.98	[30]
Cypermethrin	LC50	0.71	[30]
Cypermethrin	LC50	1.77	[30]
Cypermethrin	LC50	1.11	[30]
Cypermethrin	LC50	0.39	[30]
Cypermethrin	LC50	3.82	[30]
Cypermethrin	LC50	1.37	[30]
Cypermethrin	LC50	2.4	[30]
Cypermethrin	NOEC	2.79	[30]
Cypermethrin	NOEC	0.03	[30]
Cypermethrin	NOEC	0.077	[30]
Cypermethrin	NOEC	0.37	[30]
Cyhalothrin	sublethal	1	[44]
Cyhalothrin	sublethal	0.0004	[8]
Cyhalothrin	sublethal	0.005	[9]
Cyhalothrin	sublethal	0.15	[45]
Cyhalothrin	sublethal	0.65	[46]
Cyhalothrin	sublethal	0.8	[47]
Cyhalothrin	sublethal	0.3	[48]
Cyhalothrin	LC50	0.078	[30]
Cyhalothrin	LC50	0.16	[30]
Cyhalothrin	LC50	0.21	[30]
Cyhalothrin	LC50	0.24	[30]
Cyhalothrin	LC50	0.49	[30]
Cyhalothrin	LC50	0.78	[30]
Cyhalothrin	LC50	1.6	[30]
Cyhalothrin	LC50	0.7	[30]
Cyhalothrin	LC50	0.807	[30]
Cyhalothrin	NOEC	0.031	[30]
Cyhalothrin	NOEC	0.25	[30]
Chlorpyrifos	sublethal	0.002	[1]
Chlorpyrifos	sublethal	0.12	[49]
Chlorpyrifos	sublethal	0.661	[50]
Chlorpyrifos	sublethal	0.88	[51]
Chlorpyrifos	sublethal	1.2	[52]
Chlorpyrifos	sublethal	0.005	[2]
Chlorpyrifos	sublethal	0.6	[53]
Chlorpyrifos	sublethal	0.625	{54]
Chlorpyrifos	sublethal	1	[55]
Chlorpyrifos	sublethal	0.661	[56]

Chlorpyrifos	sublethal	1.16	[57]
Chlorpyrifos	sublethal	2.25	[58]
Chlorpyrifos	LC50	1.3	[30]
Chlorpyrifos	LC50	1.3	[30]
Chlorpyrifos	LC50	1.7	[30]
Chlorpyrifos	LC50	1.78	[30]
Chlorpyrifos	LC50	4.2	[30]
Chlorpyrifos	LC50	4.7	[30]
Chlorpyrifos	LC50	8.5	[29]
Chlorpyrifos	LC50	8.5	[30]
Chlorpyrifos	LC50	10	[30]
Chlorpyrifos	LC50	12.5	[30]
Chlorpyrifos	LC50	130	[30]
Chlorpyrifos	LC50	136	[30]
Chlorpyrifos	LC50	250	[30]
Chlorpyrifos	LC50	250	[30]
Chlorpyrifos	LC50	520	[30]
Chlorpyrifos	LC50	806	[30]
Chlorpyrifos	NOEC	0.27	[30]
Chlorpyrifos	NOEC	0.75	[30]
Chlorpyrifos	NOEC	0.28	[30]
Chlorpyrifos	NOEC	0.38	[30]
Chlorpyrifos	NOEC	0.51	[30]
Chlorpyrifos	NOEC	5	[30]
Carbendazim	sublethal	4	[59]
Carbendazim	sublethal	20	[59]
Carbendazim	sublethal	0.16	[21]
Carbendazim	LC50	440	[30]
Carbendazim	LC50	1080	[30]
Carbendazim	LC50	7	[30]
Carbendazim	LC50	100	[30]
Carbendazim	LC50	390	[30]
Carbendazim	NOEC	11	[30]
Azoxytrobin	sublethal	0.1	[22]
Azoxytrobin	sublethal	0.25	[23]
Azoxytrobin	sublethal	0.5	[17]
Azoxytrobin	sublethal	1	[24]
Azoxytrobin	sublethal	2	[25]
Azoxytrobin	sublethal	10	[60]
Azoxytrobin	sublethal	20	[61]
Azoxytrobin	sublethal	200	[62]
Azoxytrobin	LC50	470	[30]
Azoxytrobin	LC50	1100	[30]
Azoxytrobin	LC50	1380	[30]
Azoxytrobin	LC50	1600	[30]
Azoxytrobin	LC50	1650	[30]
Azoxytrobin	NOEC	147	[30]

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Table S8. Acute toxicity data (96 h LC50) for data-rich relevant pesticides shown in SI Figure S2. All data were examined for validity and relevance by the Ecotox Centre, Dübendorf, Switzerland (https://www.oekotoxzentrum.ch) and can be obtained upon request from info@oekotoxzentrum.ch.

Substance	LC50 (µg/L)	Fish species	Family	Order
azoxystrobin	470	*Oncorhynchus mykiss*	Salmonidae	Salmoniformes
azoxystrobin	1100	*Lepomis macrochirus*	Centrarchidae	Perciformes
azoxystrobin	1380	*Oryzias latipes*	Adrianichthyidae	Beloniformes
azoxystrobin	1600	*Cyprinus carpio*	Cyprinidae	Cypriniformes
azoxystrobin	1650	*Misgurnus anguilicaudatus*	Cobitidae	Cypriniformes
azoxystrobin	660	*Cyprinodon variegatus*	Cyprinodontidae	Cyprinodontiformes
carbendazim	440	*Cyprinus carpio*	Cyprinidae	Cypriniformes
carbendazim	1080	*Danio rerio*	Cyprinidae	Cypriniformes
carbendazim	7	*Ictalurus punctatus*	Ictaluridae	Siluriformes
carbendazim	100	*Oncorhynchus mykiss*	Salmonidae	Salmoniformes
carbendazim	390	*Salmo trutta*	Salmonidae	Salmoniformes
chlorpyrifos	1.3	*Leuresthes tenuis*	Atherinopsidae	Atheriniformes
chlorpyrifos	1.3	*Menidia peninsulae*	Atherinopsidae	Atheriniformes
chlorpyrifos	1.7	*Menidia menidia*	Atherinopsidae	Atheriniformes
chlorpyrifos	1.78	*Lepomis macrochirus*	Centrarchidae	Perciformes
chlorpyrifos	4.2	*Menidia beryllina*	Atherinopsidae	Atheriniformes
chlorpyrifos	4.7	*Pungitius pungitius*	Gasterosteidae	Gasterosteiformes
chlorpyrifos	8.5	*Oncorhynchus mykiss*	Salmonidae	Salmoniformes
chlorpyrifos	8.5	*Gasterosteus aculeatus*	Gasterosteidae	Gasterosteiformes
chlorpyrifos	10	*Leuciscus Idus*	Cyprinidae	Cypriniformes
chlorpyrifos	12.5	*Sander vitreus*	Percidae	Perciformes
chlorpyrifos	130	*Pimephales promelas*	Cyprinidae	Cypriniformes
chlorpyrifos	136	*Cyprinidon variegatus*	Cyprinodontidae	Cyprinodontiformes
chlorpyrifos	250	*Oryzias latipes*	Adrianichthyidae	Beloniformes
chlorpyrifos	250	*Rutilus rulitus*	Cyprinidae	Cypriniformes
chlorpyrifos	520	*Opsanus beta*	Batrachoididae	Batrachoidiformes
chlorpyrifos	806	*Ictalurus punctatus*	Ictaluridae	Siluriformes
cyhalothrin	0.078	*Leuciscus Idus*	Cyprinidae	Cypriniformes
cyhalothrin	0.16	*Ictalurus punctatus*	Ictaluridae	Siluriformes
cyhalothrin	0.21	*Lepomis macrochirus*	Centrarchidae	Perciformes
cyhalothrin	0.24	*Oncorhynchus mykiss*	Salmonidae	Salmoniformes
cyhalothrin	0.49	*Gasterosteus aculeatus*	Gasterosteidae	Gasterosteiformes
cyhalothrin	0.78	*Danio rerio*	Cyprinidae	Cypriniformes
cyhalothrin	1.6	*Oryzias latipes*	Adrianichthyidae	Beloniformes
cyhalothrin	0.7	*Pimephales promelas*	Cyprinidae	Cypriniformes
cyhalothrin	0.807	*Cyprinodon variegatus*	Cyprinodontidae	Cyprinodontiformes
cypermethrin	0.4	*Scardinius erythrophthalmus*	Cyprinidae	Cypriniformes
cypermethrin	0.43	*Cnesterodon decemmaculatus*	Poecilidae	Cyprinodontiformes
cypermethrin	1.2	*Salmo trutta*	Salmonidae	Salmoniformes
cypermethrin	2.1	*Oreocchromis niloticus*	Cichlidae	Cichliformes
cypermethrin	1.47	*Galaxius maculatus*	Galaxiidae	Osmeriformes
cypermethrin	1.98	*Pseudaphritis urvillii*	Pseudaphritidae	Perciformes
cypermethrin	0.71	*Cyprinus carpio*	Cyprinidae	Cypriniformes
cypermethrin	1.77	*Brachidanio rerio*	Cyprinidae	Cypriniformes
cypermethrin	1.11	*Lepomis macrochirus*	Centrarchidae	Perciformes
cypermethrin	0.39	*Oncorhynchus mykiss*	Salmonidae	Salmoniformes
cypermethrin	3.82	*Oryzias latipes*	Adrianichthyidae	Beloniformes
cypermethrin	1.37	*Pimephales promelas*	Cyprinidae	Cypriniformes
cypermethrin	2.4	*Cyprinodon variegatus*	Cyprinodontidae	Cyprinodontiformes
diazinon	90	*Oncorhynchus mykiss*	Salmonidae	Salmoniformes
diazinon	168	*Lepomis macrochirus*	Centrarchidae	Perciformes
diazinon	770	*Salvelinus fontinalis*	Salmonidae	Salmoniformes
diazinon	1470	*Cyprinidon variegatus*	Cyprinodontidae	Cyprinodontiformes
diazinon	1600	*Jordanella floridae*	Cyprinodontidae	Cyprinodontiformes
diazinon	4300	*Pimephales promelas*	Cyprinidae	Cypriniformes

diazinon	8900	*Entosphenus tridentatus*	Petromyzontidae	Petromyzontiformes
diuron	500	*Morone saxatilis*	Moronidae	Perciformes
diuron	710	*Oncorhynchus clarki*	Salmonidae	Salmoniformes
diuron	1100	*Salvelinus namaycush*	Salmonidae	Salmoniformes
diuron	2800	*Lepomis macrochirus*	Centrarchidae	Perciformes
diuron	6300	*Mugil cephalus*	Mugilidae	Mugiliformes
diuron	6700	*Cyprinodon variegatus*	Cyprinodontidae	Cyprinodontiformes
diuron	7700	*Pimaphales promelas*	Cyprinidae	Cypriniformes
diuron	7800	*Oryzias melastigma*	Adrianichthyidae	Beloniformes
diuron	14700	*Oncorhynchus mykiss*	Salmonidae	Salmoniformes

Table S9. Fish species resident in small to medium-sized streams in Switzerland and their current status (NAWA TREND Monitoring [1,2]).

Species	**Red List Status**
Chondrostoma nasus	Critically endangered
Salmo trutta lacustris	Endangered
Lampetra planeri	Endangered
Thymallus thymallus	Vulnerable
Alburnoides bipunctatus	Vulnerable
Leuciscus souffia	Vulnerable
Cyprinus carpio	Vulnerable
Anguilla anguilla	Vulnerable
Cobitis taenia	Vulnerable
Salmo trutta fario	Near threatened
Gasterosteus aculeatus	Near threatened
Cottus gobio	Near threatened
Barbus barbus	Near threatened
Perca fluviatilis	Least concern
Esox lucius	Least concern
Leuciscus cephalus	Least concern
Leuciscus leuciscus	Least concern
Rutilus rutilus	Least concern
Scardinius erythrophthalmus	Least concern
Tinca tinca	Least concern
Lota lota	Least concern
Gobio gobio	Least concern
Phoxinus phoxinus	Least concern
Barbatula barbartula	Least concern
Gymnocephalus cernuus	Least concern

1 Kirchhofer, A.; Breitenstein, M.; Zaugg, B. Rote Liste der Fische und Rundmauler der Schweiz. Umwelt-Vollzug Nr. 0734; Bundesamt für Umwelt, Bern, und Schweizer Zentrum für die Kartographie der Fauna, Neuenburg, Switzerland.**2007**; p. 64.

2 Spalinger, L.; Dönni, W.; Guthruf, J. *NAWA TREND BIOLOGIE 2. Kampagne (2015) Fachbericht Fische, Report*; Bundesamt für Umwelt: Bern, Switzerland, **2017**; p. 75.

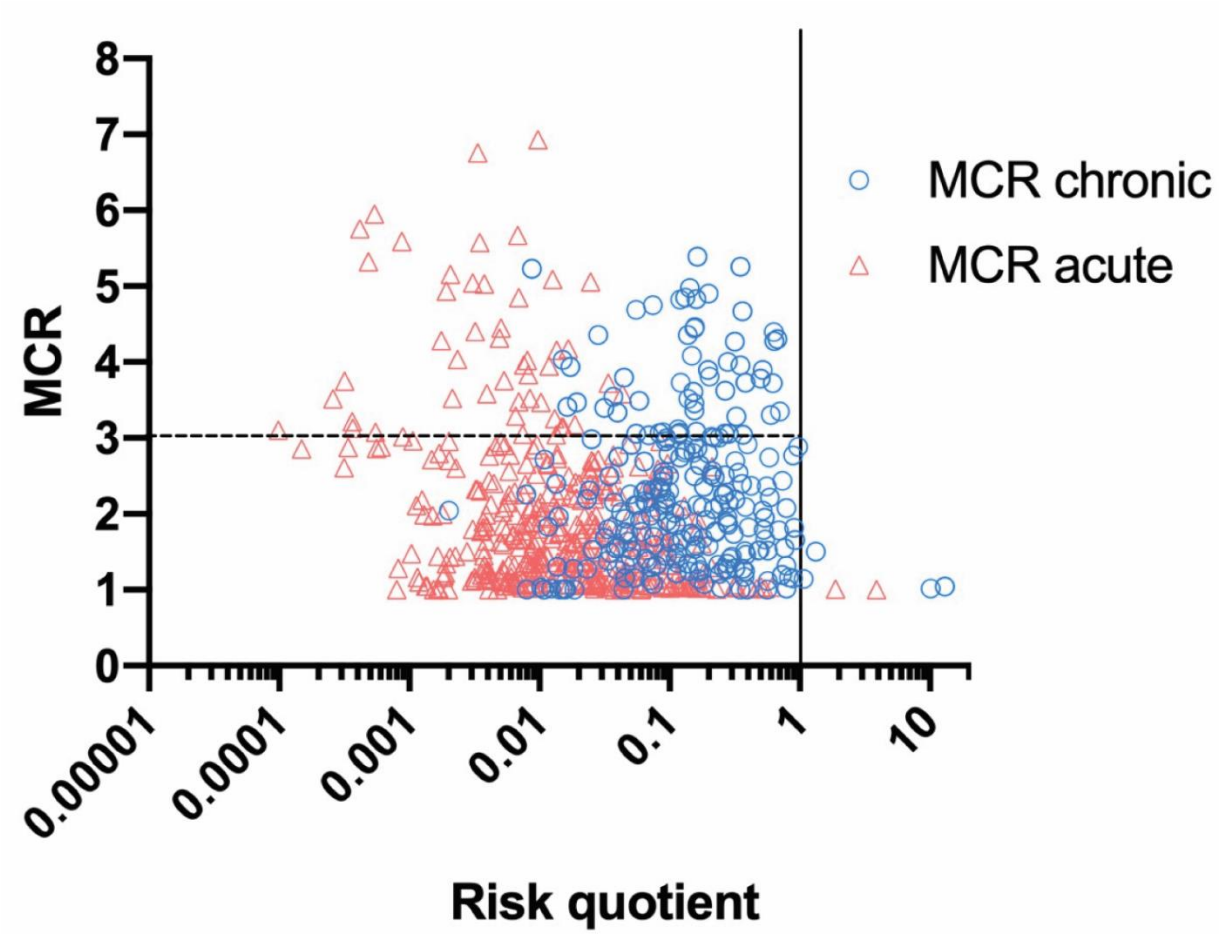

Figure S1. Maximum cumulative ratios (MCR) as a function of the mixture risk quotient of pesticides detected in water samples from monitoring campaigns 2012-2018. The MCR corresponds to the number of pesticides in the sample that drive the mixture risk quotient.

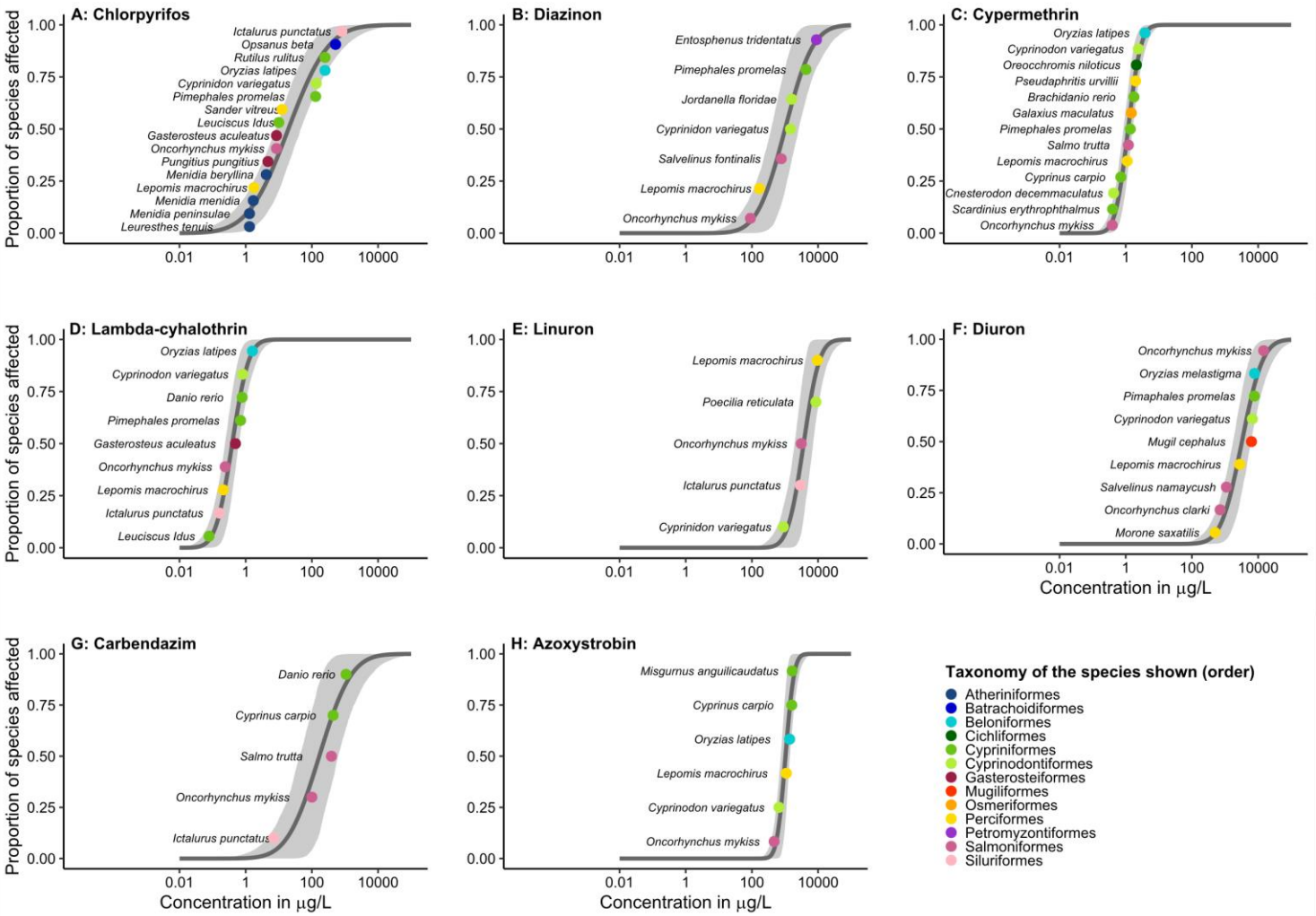

Figure S2. Species sensitivity distributions (SSDs) for data-rich relevant pesticides.