SUPPORTING INFORMATION TO ARTICLE:

Indicators for the exposure assessment of transformation products of organic micropollutants

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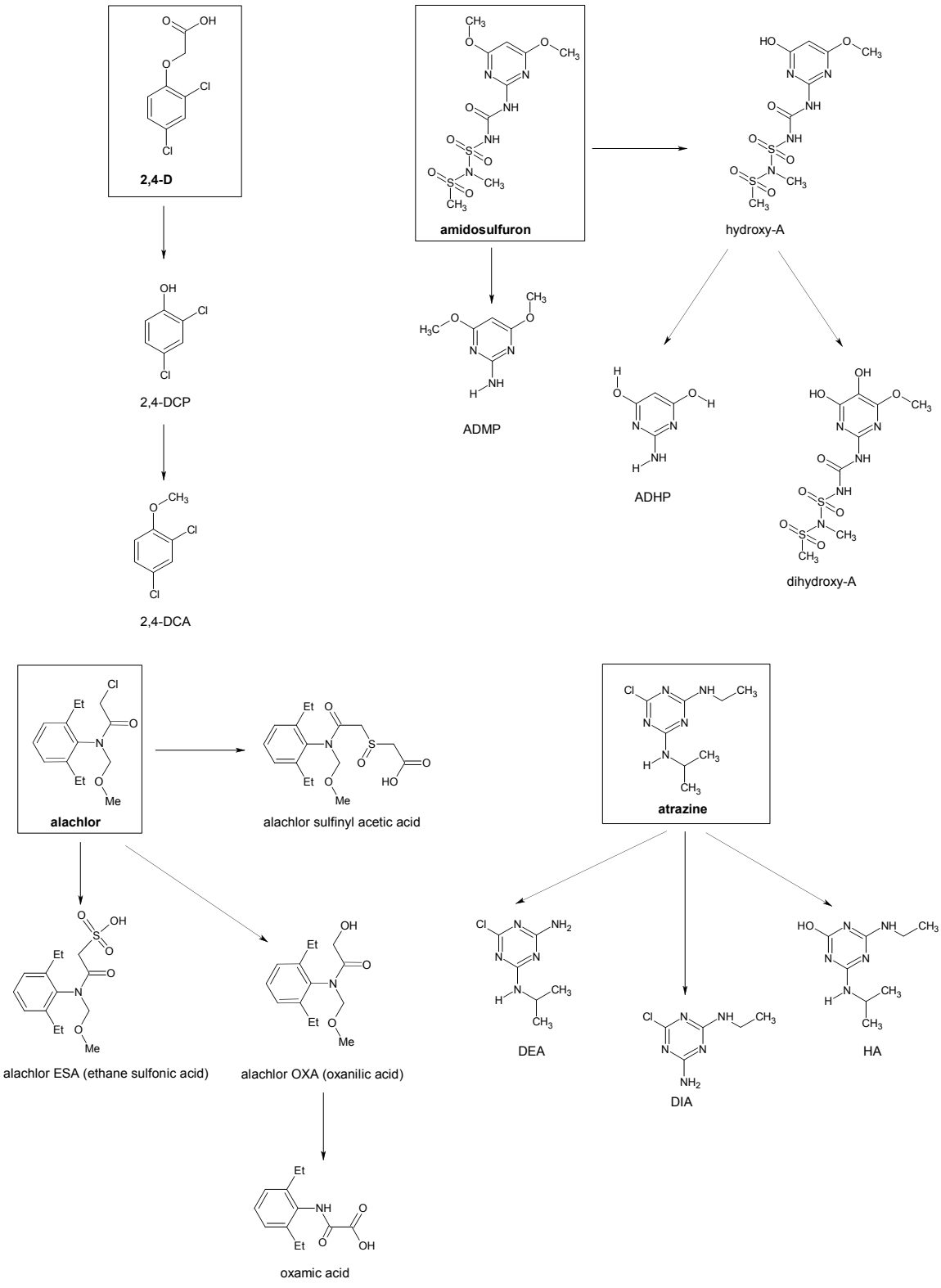
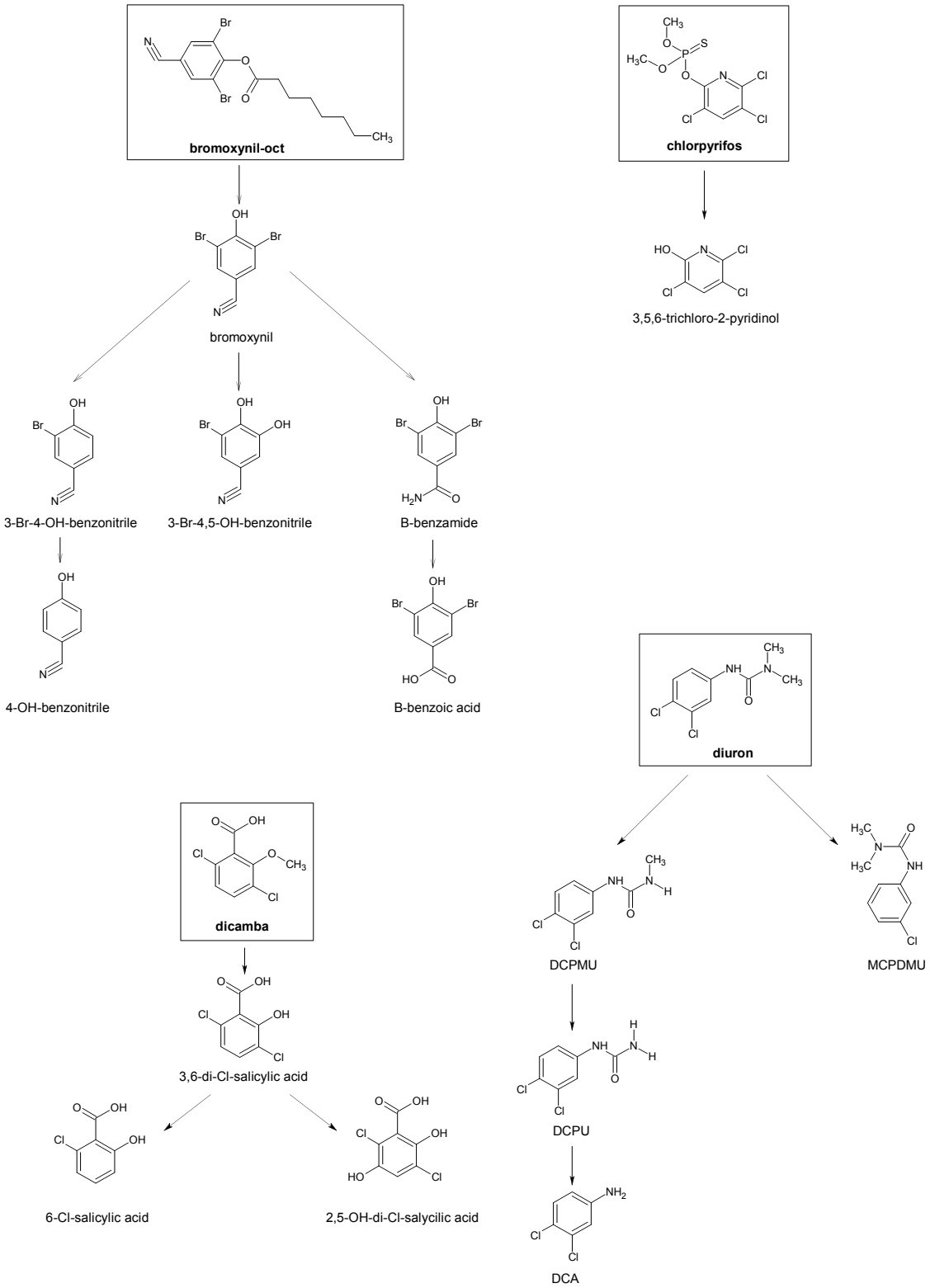
Content:

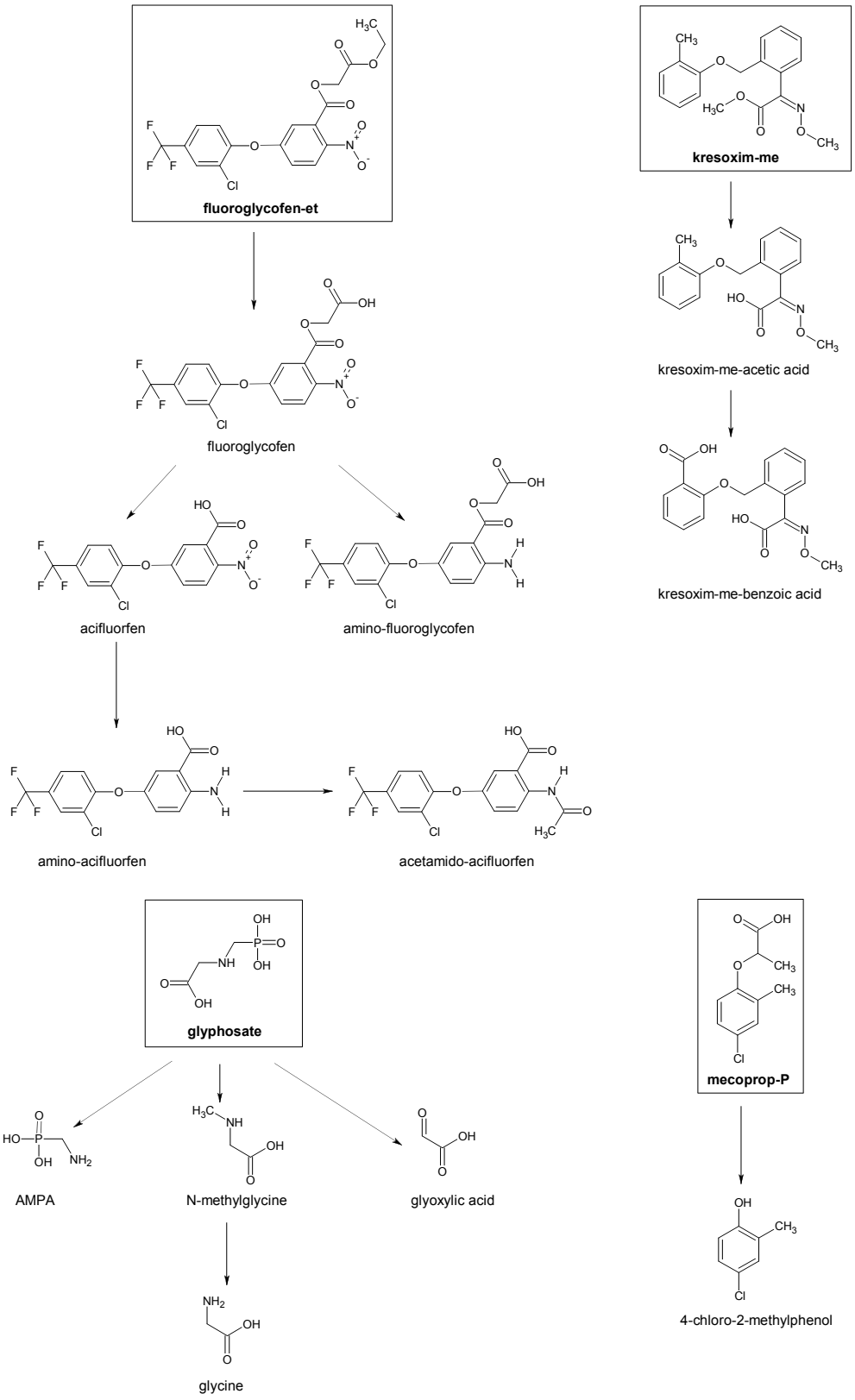
SI-1: List of case study pesticides and their transformation schemes (Table S1)

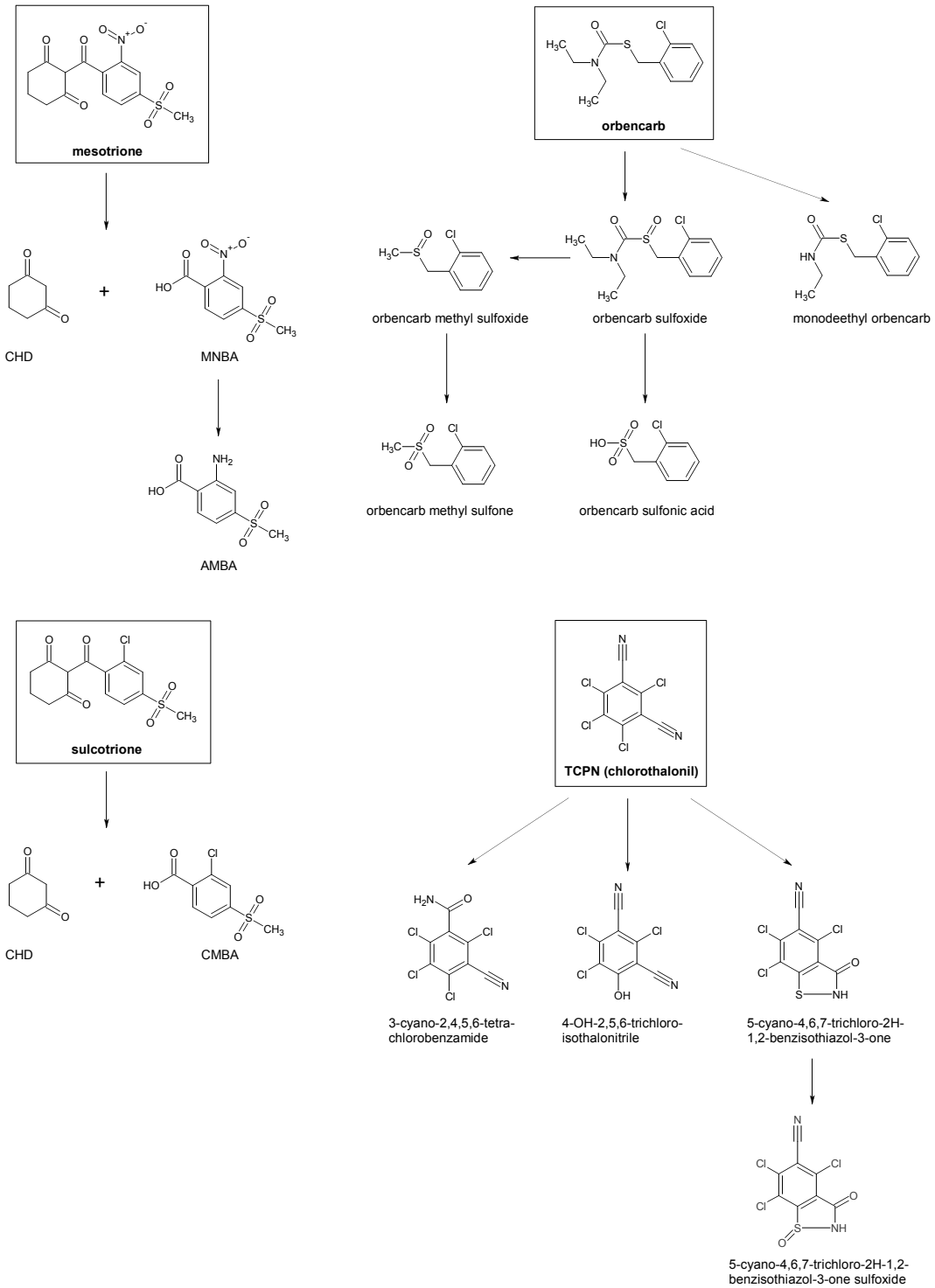
Table S1: List of 16 case study pesticides, including their CAS number and substance class ([a] herbicide, [b] fungicide, [c] insecticide).

Substance	CAS number	Substance class
2,4-D [a]	94-75-7	phenoxyacetic acid
alachlor [a]	15972-60-8	chloroacetanilide
amidosulfuron [a]	120923-37-7	sulfonylurea
atrazine [a]	1912-24-9	triazine
bromoxynil-oct [a]	1689-99-2	aromatic nitrile
chlorpyrifos [c]	2921-88-2	organothiophosphate
dicamba [a]	1918-00-9	benzoic acid
diuron [a]	330-54-1	phenylurea
fluoroglycofen-et [a]	77501-90-7	nitrophenyl ether
glyphosate [a]	1071-83-6	organophosphate
kresoxim-me [b]	143390-89-0	strobilurin
mecoprop-P [a]	16484-77-8	phenoxyacetic acid
mesotrione [a]	104206-82-8	triketone
orbencarb [a]	34622-58-7	thiocarbamate
sulcotrione [a]	99105-77-8	triketone
TCPN (chlorothalonil) [b]	1897-45-6	aromatic nitrile


2,4-D
2,4-DCP
2,4-DCA
amidosulfuron
ADMP
hydroxy-A
ADHP
dihydroxy-A
alachlor
alachlor sulfinyl acetic acid
alachlor ESA (ethane sulfonic acid)
alachlor OXA (oxanilic acid)
oxamic acid
atrazine
DEA
DIA
HA


bromoxynil-oct
chlorpyrifos
bromoxynil
3,5,6-trichloro-2-pyridinol
3-Br-4-OH-benzonitrile
3-Br-4,5-OH-benzonitrile
B-benzamide
4-OH-benzonitrile
B-benzoic acid
diuron
dicamba
DCPMU
MCPDMU
3,6-di-Cl-salicylic acid
DCPU
6-Cl-salicylic acid
2,5-OH-di-Cl-salycilic acid
DCA


fluoroglycofen-et
kresoxim-me
fluoroglycofen
kresoxim-me-acetic acid
kresoxim-me-benzoic acid
acifluorfen
amino-fluoroglycofen
amino-acifluorfen
acetamido-acifluorfen
glyphosate
mecoprop-P
AMPA
N-methylglycine
glyoxylic acid
4-chloro-2-methylphenol
glycine


mesotrione
CHD
MNBA
AMBA
orbencarb
orbencarb methyl sulfoxide
orbencarb sulfoxide
monodeethyl orbencarb
orbencarb methyl sulfone
orbencarb sulfonic acid
sulcotrione
CHD
CMBA
TCPN (chlorothalonil)
3-cyano-2,4,5,6-tetra-chlorobenzamide
4-OH-2,5,6-trichloro-isothalonitrile
5-cyano-4,6,7-trichloro-2H-1,2-benzisothiazol-3-one
5-cyano-4,6,7-trichloro-2H-1,2-benzisothiazol-3-one sulfoxide

SI-2: Rules for deriving K_{oc} and compartmental half-lives from EPI Suite output; list of half-life and K_{oc} values used (Tables S2 and S3)

Derivation of half-lives

The compartmental half-lives were collected from handbooks, registration information from the EU, US EPA and the UK, and from primary scientific literature. If several experimental data were found for one substance, the geometric mean was taken as input value. The rate constants from the different degradation processes, i.e., photolysis, hydrolysis and biodegradation, were summed up to obtain an overall dissipation rate. For the calculation of aqueous photolysis rate constants, light attenuation over the depth of the water bodies was accounted for. Photolysis in soil was not considered.

If there were no experimental data available, the half-lives were estimated using the US EPA EPI (Estimation Programs Interface) Suite™ (Version 3.12). In the EPI Suite™ programme it is suggested that, in order to derive compartmental half-lives, results from the BIOWIN Primary Survey Model be translated into water half-life categories and that soil and sediment half-lives are derived from these water half-lives by using multiplication factors of 2 and 9, respectively. Evidence from pesticide fate research, however, shows that for most compounds the water and soil half-lives are similar or that the water half-life is even higher. Since the basis for a more scientifically sound factor is lacking, we kept the factor of 2 to derive unknown soil half-lives from EPI Suite output but also multiplied estimated water half-lives with a factor of 2 to account for the observed higher recalcitrance in water and the fact that only parts of the water column will be biologically and photolytically active. Half-lives for the dissolved fraction in sediments were set equal to water half-lives, thus accounting for the aerobic and mixed nature of the surface sediment layer.

Table S2: Soil, water and air half-life values as used in the calculations. For empirical values the number of experimental data points and the original references are given. In some cases, half-lives of TPs are derived from compartmental degradation studies as described in SI-3. These cases are indicated as "ff calculations". Where no experimental data was available half-lives were derived from the BIOWIN program as described above. All values for half-lives in air are derived from the AOPWIN program assuming an OH radical concentration in air of 5×10^5 molecules/cm^3.

	$t_{1/2,\ soil}$ (d)	*n*	ref	$t_{1/2,\ water}$ (d)	*n*	ref	$t_{1/2,\ air}$ (d)
2,4-D	5.53	12	(1-3)	47.8	3	(1-3)	5.39
2,4-DCP	6.64	3	(1-3) (ff calculations)	17.3		BIOWIN	30.3
2,4-DCA	12.2	2	(1-3) (ff calculations)	75		BIOWIN	12.1
alachlor	9.09	6	(2-5)	104	4	(2,6)	0.17
alachlor OXA	47.9	2	(2,5) (ff calculations)	649	2	(6) (ff calculations)	0.68
oxamic acid	40.0	3	(5)	17.3		BIOWIN	0.49

alachlor ESA	322	5	(4,5) (ff calculations)	649	2	(6) (ff calculations)	0.7
alachlor sulfinyl acetic acid	214	2	(5) (ff calculations)	17.3		BIOWIN	0.14
amidosulfuron	19. 6	8	(2)	118	2	(2)	2.94
hydroxy-A	17.5	3	(7)	17.3		BIOWIN	0.16
ADHP	31.0		BIOWIN	17.3		BIOWIN	0.16
dihydroxy-A	17.3		BIOWIN	17.3		BIOWIN	0.16
ADMP	17.3		BIOWIN	17.3		BIOWIN	0.16
atrazine	33.9	469	(8)	230		(9)	0.19
DEA	33.3	10	(8)	300		(10)	0.43
DIA	32.2	6	(8)	300		(10)	0.89
HA	88.3	10	(8)	300		(10)	0.29
bromoxynil-oct	2.74	2	(5)	0.94	3	(1,5)	4.34
bromoxynil	13.9	8	(11)	9.45	2	(1)	153
3-Br-4-OH-benzonitrile	17.3		BIOWIN	17.3		BIOWIN	17.6
4-OH-benzonitrile	17.3		BIOWIN	17.3		BIOWIN	5.33
3-Br-4,5-OH-benzonitrile	17.3		BIOWIN	17.3		BIOWIN	14.8
B-benzamide	17.3		BIOWIN	17.3		BIOWIN	13.6
B-benzoic acid	30		BIOWIN	30		BIOWIN	39.9
chlorpyrifos-me	11.2	2	(3,12)	13.2	9	(12)	0.55
3,5,6-trichloro-2-pyridonol	45.4	1	(7)	30		BIOWIN	182
dicamba	12.3	3	(3,13,14)	60		BIOWIN	10.7
3,6-di-Cl-salicylic acid	71.3	2	(7) (ff calculations)	17.3		BIOWIN	10.1
6-Cl-salicylic acid	17.3		BIOWIN	17.3		BIOWIN	3.44
2,5-OH-di-Cl-salicylic acid	17.3		BIOWIN	17.3		BIOWIN	15.4
diuron	50.3	14	(5,15-23)	45.1	3	(5)	2.94
DCPMU	48.0	3	(15,22) (ff calculations)	30		BIOWIN	3.11
MCPDMU	34.5	2	(17,18)	17.3		BIOWIN	1
DCPU	30	1	(22)	17.3		BIOWIN	3.29
DCA	1.87	2	(17,24)	17.3		BIOWIN	1.45
fluoroglycofen-et	10.7	2	(2)	1.71	3	(2)	13.1
fluoroglycofen	1	1	(2)	3.93	2	(1,2)	16.3
acifluorfen	55.4	3	(13,14)	36.8	2	(14), BIOWIN	37.1
amino-acifluorfen	30		BIOWIN	30		BIOWIN	1.00
acetamido-acifluorfen	30		BIOWIN	30		BIOWIN	7.13
amino-fluoroglycofen	17.3		BIOWIN	17.3		BIOWIN	1.10
glyphosate	11.7	13	(1,3,5,13,14,25-29)	11.4	5	(1)	0.41
AMPA	111	3	(1,5,28)	19.8	1	(30)	1.07
glyoxylic acid	2.5		BIOWIN	2.5		BIOWIN	2.44
N-methylglycine	4.66		BIOWIN	4.66		BIOWIN	0.45
glycine	4.66		BIOWIN	4.66		BIOWIN	1.15
kresoxim-me	2.19	4	(1,3)	2.26	2	(1,2)	0.84
kresoxim-me-acetic acid	27.2	3	(1,3)	359	2	(2,3)	0.83
kresoxim-me-benzoic acid	4.66		BIOWIN	4.66		BIOWIN	1.56
mecoprop-P	10.6	10	(1-3)	59.5	2	(1,31)	1.84
4-chloro-2-methylphenol	16.3	3	(1,2,7) (ff calculations)	17.3		BIOWIN	2.63
mesotrione	12.7	14	(32)	30		BIOWIN	4.41
MNBA	17.3		BIOWIN	17.3		BIOWIN	20.1
CHD	17.3		BIOWIN	17.3		BIOWIN	5.45
AMBA	17.3		BIOWIN	17.3		BIOWIN	3.18
orbencarb	21.1	3	(33)	17.3		BIOWIN	1.26
monodeethyl orbencarb	17.3		BIOWIN	17.3		BIOWIN	1.5
orbencarb sulfoxide	17.3		BIOWIN	17.3		BIOWIN	1.1
orbencarb methyl sulfoxide	17.3		BIOWIN	17.3		BIOWIN	0.46
orbencarb methyl sulfone	17.3		BIOWIN	17.3		BIOWIN	3.2
orbencarb sulfonic acid	17.3		BIOWIN	17.3		BIOWIN	11.7

sulcotrione	11.5	6	(14,28,34-37)	30		BIOWIN	4.27
CMBA	56.5	3	(28)	17.3		BIOWIN	19.1
CHD	17.3		BIOWIN	17.3		BIOWIN	5.45
TCPN	12.4	15	(2,3,38-47)	1.1	3	(2,5,14)	5190
4-OH-2,5,6-trichloroisothalonitrile	34.1	5	(40,41,45,48) (ff calculations), (14)	30		BIOWIN	111
3-CN-2,4,5,6-tetrachlorobenzamide	30		BIOWIN	30		BIOWIN	15.8
5-CN-4,6,7-tri-Cl-2H-1,2-benzisothiazol-3-one	30		BIOWIN	30		BIOWIN	5.54
5-CN-4,6,7-tri-Cl-2H-1,2-benzisothiazol-3-one sulfoxide	30		BIOWIN	30		BIOWIN	5.82

Derivation of organic carbon-water partition coefficients

Whenever possible, experimental organic carbon-water partition coefficients (K_{oc}) were used as given in the first column of Table S3. In all other cases, several rules were applied to achieve internal consistency between measured and estimated K_{oc} values within a substance family and to best possibly benefit from measured values (for an overview on final K_{oc} values used and methods to derived them see Table S3): For non-ionic substances, unknown K_{oc} values of the TPs were calculated starting from the experimental K_{oc} value of the parent pesticide. PCKOCWIN was then used to derive the incremental difference in log K_{oc} between the parent pesticide and the TP under conside–ration, which was then added to the experimental value of the parent to yield the log K_{oc} of the TP. For anionic TPs of neutral parent pesticides, plausible correction factors were applied to the PCKOCWIN estimates to account for the enhanced partitioning of negatively charged species into water, i.e., factors of 0.5 for substance with pK_a close to 7, and of 0.1 for substances with pK_a < 6. For anionic TPs of anionic parent pesticides that were structurally very similar to the parent, the K_{oc} value of the parent was conside–red the best estimate.

Table S3: K_{oc} values used in the calculations. Where no empirical K_{oc} values were available, different extrapolation rules were applied to ensure internal consistency within substance families. Extrapolation methods used (for details see main text): [a] PCKOCWIN neutral: PCKOCWIN prediction used without further modification; [b] Analogy anionic: For structurally very similar anionic TPs of anionic parent pesticides the K_{oc} value of the parent was used; [c] PCKOCWIN anionic: Correction factor applied to the PCKOCWIN estimates to account for the higher partitioning of negatively charged species into water (factors of 0.5 for substance with pK_a close to 7, and of 0.1 for substances with pK_a < 6); [d] PCKOCWIN increment: K_{oc} values of the TPs calculated starting from the experimental K_{oc} value of the parent pesticide. PCKOCWIN used to derive the incremental difference

in log K_{oc} between the parent pesticide and the TP. Difference added to the experimental value of the parent to yield the log K_{oc} of the TP; [e] Analogy glyphosate: Zwitterionic compounds. PCKOCWIN predictions adjusted to account for enhanced sorption in analogy to glyphosate and AMPA.

Compound	K_{oc}, experimental	PCKOCWIN	K_{oc}, extrapolated	pKa (estimated or experimental)	Extrapolation method
2,4-D	38	29		2.73	
2,4-DCP	293	718		7.89	
2,4-DCA		315		xx	PCKOCWIN neutral [a]
alachlor	177	185		xx	
alachlor OXA	4.5	10		2.75	
oxamic acid		10	4.5	2.98	analogy anionic [b]
alachlor ESA	52	10		0.25	
alachlor sulfinyl acetic acid		10	4.5	2.59	analogy anionic [b]
amidosulfuron	17	10		3.58	
hydroxy-A	40	10		1.76	
ADHP		13	1.3	3.10	PCKOCWIN anionic [c]
dihydroxy-A		10	40	1.04	analogy anionic [b]
ADMP	410	10		xx	
atrazine	129	230		xx	
DEA	56	86		xx	
DIA	61	56		xx	
HA	793	230		5.15	
bromoxynil-oct	639	4850		xx	
bromoxynil	161	435		3.86	
3-Br-4-OH-benzonitrile		263	26	5.86	PCKOCWIN anionic [c]
4-OH-benzonitrile		159	80	7.43	PCKOCWIN anionic [c]
3-Br-4,5-OH-benzonitrile		435	44	5.16 / 7.08	PCKOCWIN anionic [c]
B-benzamide		228	23	5.32	PCKOCWIN anionic [c]
B-benzoic acid		64	6.4	4.72 / 3.34	PCKOCWIN anionic [c]
chlorpyrifos-me	3610	2010		xx	
3,5,6-trichloro-2-pyridonol	102	237		3.69	
dicamba	2.0	29		1.97	
3,6-di-Cl-salicylic acid	504	66	6.5	1.75 / 5.36	PCKOCWIN anionic [c]
6-Cl-salicylic acid		40	4.0	2.05 / 7.06	PCKOCWIN anionic [c]
2,5-OH-di-Cl-salicylic acid		108	11	1.7 / 5.55	PCKOCWIN anionic [c]
diuron	541	136		xx	
DCPMU	651	115		xx	
MCPDMU		327	327	xx	PCKOCWIN increment [d]
DCPU		449	449	xx	PCKOCWIN increment [d]
DCA	270	120		xx	
fluoroglycofen-et	262	15400		xx	
fluoroglycofen		1560	113	3.27	analogy anionic [b]
acifluorfen	113	3130		2.50	
amino-acifluorfen		733	113	3.80	analogy anionic [b]
acetamido-acifluorfen		624	113	xx	analogy anionic [b]
amino-fluoroglycofen		366	113	2.78	analogy anionic [b]
glyphosate	15900	19		2.3 / 5.6 / 10.9	
AMPA	5210	1.9		1.9 / 5.4 / 10	
glyoxylic acid		1.0	0.1	3.30	PCKOCWIN anionic [c]
N-methylglycine		1.3	313	2.35	analogy glyphosate [e]
glycine		1.0	250	2.37	analogy glyphosate [e]
kresoxim-me	302	40700		xx	

kresoxim-me-acetic acid	20	7610		3.49	
kresoxim-me-benzoic acid		23100	20	3.44 / 3.6	analogy anionic [b]
mecoprop-P	25	49		3.78	
4-chloro-2-methylphenol	175	718		9.71	
mesotrione	52	142		3.10	
MNBA		12	1.2	1.76	PCKOCWIN anionic [c]
CHD		1.4	0.1	5.30	PCKOCWIN anionic [c]
AMBA		10	1.0	3.72	PCKOCWIN anionic [c]
orbencarb	440	2730		xx	
monodeethyl orbencarb		1140	183	xx	PCKOCWIN increment [d]
orbencarb sulfoxide		6020	970	xx	PCKOCWIN increment [d]
orbencarb methyl sulfoxide		307	50	xx	PCKOCWIN increment [d]
orbencarb methyl sulfone		353	57	xx	PCKOCWIN increment [d]
orbencarb sulfonic acid		35	3.5	0.27	PCKOCWIN anionic [c]
sulcotrione	55	199		3.13	
CMBA		17	1.7	4.60	PCKOCWIN anionic [c]
CHD		1.4	0.1	5.30	PCKOCWIN anionic [c]
TCPN	3130	2390		xx	
4-OH-2,5,6-trichloroisothalonitrile	371	2390		1.00	
3-CN-2,4,5,6-tetrachlorobenzamide		238	312	xx	PCKOCWIN increment [d]
5-CN-4,6,7-tri-Cl-2H-1,2-benzisothiazol-3-one		290	380	xx	PCKOCWIN increment [d]
5-CN-4,6,7-tri-Cl-2H-1,2-benzisothiazol-3-one sulfoxide		60	79	xx	PCKOCWIN increment [d]

SI-3: Method for calculation of fractions of formation and half-lives from degradation studies

Empirical fractions of TP formation in soil and water (ff_s and ff_w) were calculated from information from compartmental degradation studies where available. If first order kinetics are assumed, it can be shown that the time elapsed between the start of a degradation study and the time when the maximal concentration of transformation product y is reached (t^{y}_{max}) is a function of the degradation rate constants of precursor x (k^x) and transformation product y (k^y) (see eq 1). The maximal amount of a transformation product y formed (c^{y}_{max}) in that degradation study is further a function of the fraction of formation (ff^{xy}) of transformation product y out of precursor x (see eq 2).

$$t^{y}_{max} = \frac{\ln k^x - \ln k^y}{k^x - k^y} \quad (1)$$

$$c^{y}_{max} = ff^{xy} \cdot c^{x}_{0} \left(\frac{k^x}{k^y} \right)^{\frac{k^y}{k^y - k^x}} \quad (2)$$

Results of degradation studies in which transformation products are specifically identified are usually given in terms of maximal percentage of transformation product formed (c^{y}_{max}/c^{x}_{0}) and the time it takes to reach this maximum (t^{y}_{max}). The degradation rate constant of the precursor x (k^x) can usually be deduced from the time-course of precursor concentrations assuming first-order kinetics. The degradation rate constant of the transformation product y (k^y) can then be deduced by numerically solving eq 1. With the known maximal percentage of transformation product formed (c^{y}_{max}/c^{x}_{0}) and the two degradation rate constants k^x and k^y, the fraction of formation ff^{xy} can be calculated according to eq 3.

$$ff^{xy} = \frac{c^{y}_{max}}{c^{x}_{0}} \left(\frac{k^x}{k^y} \right)^{\frac{k^y}{k^x - k^y}} \quad (3)$$

SI-4: Complete results from persistence calculations (Table S4)

Table S4: Results from persistence calculations sorted in order of descending JP values. (JP: Joint Persistence, PP: Primary Persistence of PC, Q = JP/PP, CTP_i: Contribution to persistence of transformation product *i*, $CTP_{i,j}$: Contribution to persistence of transformation product *i* in environmental compartment *j* (*j* = s (soil), w (water), a (air)).

Compound name	JP (d)	Q	CTP_i (d)	$CTP_{i,s}$ (d)	$CTP_{i,w}$ (d)	$CTP_{i,a}$ (d)
atrazine	212.1	2.5	84.3	39.4	44.8	0.0
DEA			52.0	7.7	44.3	0.0
DIA			23.0	2.9	20.1	0.0
HA			52.9	29.3	23.6	0.0
alachlor	201.1	12.5	16.1	11.5	4.6	0.0
alachlor OXA			7.7	3.5	4.0	0.1
alachlor ESA			164.5	25.2	139.3	0.0
alachlor sulfinyl acetic acid			11.1	7.0	4.1	0.0
alachlor oxamic acid			1.7	1.0	0.7	0.0
kresoxim-me	169.5	54.3	3.1	2.9	0.2	0.0
kresoxim-me-acetic-acid			163.7	19.7	144.0	0.0
kresoxim-me-benzoic acid			2.7	2.5	0.2	0.0
diuron	128.5	1.8	71.7	64.3	7.4	0.0
DCPMU			28.7	25.9	2.8	0.0
MCPDMU			20.1	18.4	1.8	0.0
DCPU			7.0	6.3	0.8	0.0
DCA			0.9	0.3	0.6	0.0
fluoroglycofen-et	102.3	7.1	14.4	14.0	0.2	0.1
fluoroglycofen			1.5	1.0	0.4	0.0
acifluorfen			48.1	38.7	9.4	0.0
amino-fluoroglycofen			2.7	2.3	0.4	0.0
amino-acifluorfen			19.8	14.8	5.0	0.0
acetamido-acifluorfen			15.9	10.5	5.4	0.0
amidosulfuron	98.4	1.3	74.0	19.1	54.9	0.0
hydroxy-A			10.5	6.1	4.5	0.0
ADMP			3.2	0.0	3.2	0.0
ADHP			7.0	2.6	4.4	0.0
dihydroxy-A			3.7	1.8	1.9	0.0
mesotrione	78.3	3.5	22.3	15.4	6.9	0.0
MNBA			20.0	9.8	10.2	0.0
CHD, mesotrione			20.0	9.4	10.6	0.0
AMBA			16.0	4.6	11.5	0.0
sulcotrione	72.4	3.5	20.6	14.1	6.4	0.0
CMBA			31.9	17.2	14.7	0.0
CHD, sulcotrione			19.9	9.5	10.4	0.0
dicamba	69.2	1.6	43.1	11.1	31.9	0.0
3,6-di-Cl-salicylic acid			17.6	9.0	8.5	0.0
6-Cl-salicylic acid			4.3	0.6	3.7	0.0
2,5-OH-di-Cl-salicylic acid			4.3	0.6	3.7	0.0
glyphosate	60.9	3.6	16.9	15.7	1.2	0.0
AMPA			39.8	39.2	0.6	0.0
glyoxylic acid			1.0	0.8	0.2	0.0
N-methylglycine			1.8	1.7	0.1	0.0
glycine			1.4	1.3	0.1	0.0
TCPN	59.5	2.9	20.9	16.4	0.1	4.4
4-OH-2,5,6-trichloroisothalonitrile			26.5	24.1	2.5	0.0
3-CN-2,4,5,6-tetrachlorobenzamide			9.5	9.1	0.5	0.0
5-CN-4,6,7-tri-Cl-2H-1,2-benzisothiazol-3-one			1.4	0.0	1.4	0.0
5-CN-4,6,7-tri-Cl-2H-1,2-benzisothiazol-3-one sulfoxide			1.1	0.0	1.1	0.0
orbencarb	55.6	2.0	27.5	26.7	0.6	0.2
monodeethyl orbencarb			9.0	8.4	0.7	0.0
orbencarb sulfoxide			9.0	8.7	0.3	0.0
orbencarb methyl sulfoxide			3.6	3.0	0.6	0.0
orbencarb sulfonic acid			3.6	2.2	1.4	0.0
orbencarb methyl sulfone			2.9	2.1	0.8	0.0
bromoxynil-oct	48.4	11.7	4.2	3.5	0.0	0.6
bromoxynil			15.5	15.0	0.5	0.0
3-Br-4-OH-benzonitrile			0.1	0.0	0.1	0.0
3-Br-4,5-OH-benzonitrile			0.4	0.0	0.4	0.0
B-benzamide			13.5	10.6	2.9	0.0
4-OH-benzonitrile			0.1	0.0	0.1	0.0
B-benzoic acid			14.7	7.8	6.9	0.0
2,4-D	45.7	1.0	44.5	7.0	37.5	0.0
2,4-DCP			1.0	0.7	0.3	0.0
2,4-DCA			0.2	0.1	0.0	0.0
mecoprop-p	30.5	1.1	28.9	12.3	16.6	0.0
4-chloro-2-methylphenol			1.6	1.1	0.5	0.0
chlorpyrifos-me	27.1	1.9	14.6	14.5	0.0	0.1
3,5,6-trichloro-2-pyridonol			12.5	10.7	1.7	0.0

SI-5: Complete RAC rankings (Table S5); Use survey data from Greifensee catchment (Table S6)

Table S5: RAC and RAC Greifensee ranks and values for all compounds (RAC: Relative Aquatic Concentration; RAC Greifensee: Relative Aquatic Concentration in the Greifensee catchment). Compounds sorted according to RAC rank. All values normalized to atrazine. Quality of input data indicated for degradation rate constants k_s and k_w (***: >2 empirical values, **: 1-2 empirical values or estimated from degradation study, *: estimated using BIOWIN), for organic carbon-water partition coefficient K_{oc} (+++: >2 empirical values, ++: 1-2 empirical values or analogy reasoning, +: estimated using PCKOCWIN), and for fractions of formation, ff_s and ff_w (°°°: deduced from >1 empirical degradation studies, °°: deduced from 1 empirical degradation study, °: generic, –: No *ff* because compound is PC).

Compound name	RAC rank	RAC relative to atrazine	RAC Greifensee rank	RAC Greifensee relative to atrazine	Data quality				
					k_s	k_w	K_{oc}	ff_s	ff_w
CMBA	1	3.3	1	1.08	**	*	+	°	°
dicamba	2	2.63	5	0.32	***	*	+++	–	–
amidosulfuron	3	2.33	33	0.0039	***	**	+++	–	–
kresoxim-me-acetic acid	4	2.23	19	0.015	***	**	+++	°	°
CHD	5	2.10	3	0.69	*	*	+	°	°
MNBA	6	2.01	64	0	*	*	+	°	°
AMBA	7	1.46	64	0	*	*	+	°	°
alachlor ESA	8	1.43	11	0.084	**	**	+++	°°°	°°°
3,6-di-Cl-salicylic acid	9	1.35	8	0.16	***	*	+++	–	–
B-benzoic acid	10	1.26	13	0.048	*	*	+	°	°°
alachlor sulfinyl acetic acid	11	1.08	12	0.064	**	*	++	°°°	°°
mecoprop-P	12	1.07	6	0.24	***	**	+++	–	–
atrazine	**13**	**1.00**	**2**	**1.00**	***	***	+++	–	–
acifluorfen	14	0.80	39	0.0020	***	*	+++	°°	°
alachlor OXA	15	0.78	14	0.046	**	**	+++	°°°	°°°
B-benzamide	16	0.78	17	0.030	*	*	+	°°	°°
mesotrione	17	0.72	64	0	**	*	+++	–	–
sulcotrione	18	0.62	7	0.20	***	*	+++	–	–
ADHP	19	0.57	44	0.00097	**	*	+	°°	°
amino-acifluorfen	20	0.51	42	0.0013	*	*	++	°	°
DEA	21	0.41	4	0.41	***	***	+++	°°°	°°°
2,4-D	22	0.39	21	0.012	***	**	+++	–	–
diuron	23	0.37	29	0.0069	***	**	+++	–	–
orbencarb sulfonic acid	24	0.36	18	0.027	*	*	+	°	°
hydroxy-A	25	0.34	48	0.00057	**	*	+++	°°°	°°
acetamido-acifluorfen	26	0.32	46	0.00083	*	*	++	°	°
3,5,6-trichloro-2-pyridonol	27	0.29	64	0	**	*	+++	°°	°
6-Cl-salicylic acid	28	0.27	15	0.033	*	*	+	°	°
2,5-OH-di-Cl-salicylic acid	29	0.25	16	0.031	*	*	+	°	°
alachlor	30	0.21	20	0.012	***	***	+++	–	–
4-OH-2,5,6-trichloroiso-thalonitrile	31	0.20	32	0.0046	***	*	+++	°°	°
oxamic acid	32	0.16	24	0.0096	**	*	++	°°°	°°
MCPDMU	33	0.16	36	0.0029	***	*	+	°	°
orbencarb	34	0.15	22	0.011	**	*	+++	–	–
DIA	35	0.15	9	0.15	***	***	+++	°°°	°°°
DCPMU	36	0.14	37	0.0026	***	*	+++	°°°	°°
HA	37	0.14	10	0.14	***	***	+++	°°°	°°°
bromoxynil	38	0.14	31	0.0051	***	**	+++	°°°	°°°
monodeethyl orbencarb	39	0.13	23	0.0097	*	*	+	°	°
orbencarb methyl sulfoxide	40	0.13	25	0.0096	*	*	+	°	°
dihydroxy-A	41	0.13	52	0.00021	*	*	++	°	°
orbencarb methyl sulfone	42	0.11	27	0.0084	*	*	+	°	°
3-CN-2,4,5,6-tetrachloro-benzamide	43	0.084	41	0.0020	*	*	+	°	°°
kresoxim-me-benzoic acid	44	0.076	49	0.00051	*	*	++	°	°°
3-Br-4,5-OH-benzonitrile	45	0.065	38	0.0024	*	*	+	°°	°
amino-fluoroglycofen	46	0.061	54	0.00016	*	*	++	°	°
fluoroglycofen	47	0.050	55	0.00013	**	**	++	°°°	°°°

DCPU	48	0.045	45	0.00083	**	*	+	°	°
orbencarb sulfoxide	49	0.045	35	0.0033	*	*	+	°	°
ADMP	50	0.042	57	0.00007	*	*	+++	°°	°
4-chloro-2-methylphenol	51	0.027	30	0.0060	**	*	+++	°°°	°°°
AMPA	52	0.022	26	0.0086	***	**	+++	°	°
glyoxylic acid	53	0.021	28	0.0081	*	*	+	°	°
3-Br-4-OH-benzonitrile	54	0.019	47	0.00072	*	*	+	°°	°°
DCA	55	0.014	51	0.00026	**	*	+	°°	°
2,4-DCP	56	0.014	50	0.00042	**	*	+++	°°	°
glycine	57	0.010	34	0.0039	*	*	+	°	°
chlorpyrifos-me	58	0.010	64	0	**	**	+++	–	–
5-CN-4,6,7-tri-Cl-2H-1,2-benzisothiazol-3-one	59	0.007	53	0.00016	*	*	+	°°	°
N-methylglycine	60	0.005	40	0.0020	*	*	+	°	°
fluoroglycofen-et	61	0.005	61	0.00001	**	**	+++	–	–
4-OH-benzonitrile	62	0.003	56	0.00011	*	*	+	°°	°
glyphosate	63	0.003	43	0.0010	***	***	+++	–	–
kresoxim-me	64	0.002	60	0.00002	***	**	+++	–	–
2,4-DCA	65	0.002	58	0.00006	**	*	+	°°	°
5-CN-4,6,7-tri-Cl-2H-1,2-benzisothiazol-3-one sulfoxide	66	0.001	59	0.00002	*	*	+	°°	°
bromoxynil-oct	67	0.00003	62	5.2922E-07	**	**	+++	–	–
TCPN	68	0.000002	63	5.1911E-08	***	**	+++	–	–

Table S6: Estimates of yearly amounts of parent pesticide usage in the Greifensee catchment (kg/a). The data are extrapolated from a stratified survey encompassing 10-15% of all farmers in the area (Keller, L. and M. Amaundruz, *Pflanzenschutzmittel-verbrauchserhebung der Jahre 1997-2003 in den Einzugsgebieten Greifensee*, Murtensee und Baldeggersee. 2004, LBL, Lindau, SRVA, Lausanne). Average yearly usage was calculated over those years where usage was indicated. If no usage is indicated for a given substance and year, this does not necessarily mean that the substance has not been used at all, but could also be due to the number of random samples being too low. Yearly usage amounts marked with [a] are therefore particularly uncertain.

	Yearly usage (kg/a)							**Average yearly usage (kg/a)**
	1997	1998	1999	2000	2001	2002	2003	
atrazine	460	449	432	454	500	409	407	**444**
glyphosate	57	220	245	155	114	178	215	**169**
sulcotrione	135	142	150	175	170	119	128	**145**
mecoprop-P	110	122	141	137	116	53	15	**99**
dicamba	69	74	73	46	30	32	49	**53**
orbencarb	38	50				10		**33** [a]
alachlor		14					38	**26** [a]
2,4-D	2.1	19	28	23	13	3.3	4.9	**13**
TCPN (chlorothalonil)	8.2	8.1				2.9	23	**11** [a]
bromoxynil	1.1	9.2	6.2	11	14	17	1.5	**8.6**
diuron			15	4.1	13	0.2		**8.2** [a]
bromoxynil-oct	5.8		13	4.6	3.6			**6.8** [a]
kresoxim-me	1.0	2.6	2.2	5.3	3.8			**3.0** [a]
fluoroglycofen-et	1.2	1.1						**1.1** [a]
amidosulfuron	0.1	1.4	0.3	0.6	0.8	1.7	0.3	**0.7**
chlorpyrifos-me								**0.0** [a]
mesotrione								**0.0** [a]

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