Supporting Information

Transformation of Biocides Irgarol and Terbutryn in the Biological Wastewater Treatment

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Chemicals and Standards

Stock solutions of analytes (1 mg mL^{-1}) were prepared in methanol. Stock solutions of internal standards (0.1 mg mL^{-1}) were dissolved in the same solvents as respective analytes. A standard solution of all target analytes was prepared in methanol at a concentration of 10, 1, 0.1, and 0.01 µg mL^{-1}. A standard solution of all surrogate standards was also prepared in methanol at a concentration of 1 µg mL^{-1}. The stock solutions were stored in the freezer at -20°C. The diluted standard solutions of analytes and surrogates were stored in the dark at 4°C and renewed at least very 3 months.

Information about WWTPs

The five sampled WWTPs (WWTP 1-5) are conventional plants equipped with a mechanical treatment (screen, grit removal, primary clarifier) followed by an activated sludge treatment with denitrification and nitrification as well as phosphate removal and a secondary sedimentation. WWTP 1 is equipped with a unit for biological phosphate removal located behind the primary clarifier. The parameters such as population equivalents (PE), daily flow rate, hydraulic retention time (HRT), and sludge retention time (SRT) of the activated sludge treatment of the WWTPs were as follows: WWTP 1: 20,000 PE, 8,000 m^3 d^{-1}, 3.5 d, and 10.3 d; WWTP 2: 34,800 PE, 10,100 m^3 d^{-1}, 1.8 d, and 12 d; WWTP 3: 37,000 PE, 7,500 m^3 d^{-1}, 2.9 d, and 19 d; WWTP 4: 60,400 PE, 13,000 m^3 d^{-1}, 1.6 d, and 12-14 d; WWTP 5: 320,000 PE, 61,000 m^3 d^{-1}, 6 h, and 12 d.

Streams and Rivers Sampling

TABLE S1. Overview of sampling locations in the Hessian Ried region (June 2012).

Sampling location	GPS coordinates		Comment to sampling location	pH	T [°C]	σ [µS cm^{-1}]	O_2 [mg L^{-1}]	O_2 %
HR_01	N 49° 58.628'	E 08° 30.438'	Geräthsbach before mouth	7.8	18.2	830	8.8	98
HR_02.1	N 49° 58.246'	E 08° 32.991'	Geräthsbach before WWTP 3	7.8	18.5	850	7.2	80
HR_02.2	N 49° 58.711'	E 08° 30.452'	Geräthsbach after WWTP 3	7.4	19.2	852	8.7	97
HR_03	N 49° 58.493'	E 08° 30.064'	Gundbach before mouth Schwarzbach	7.7	17.8	883	8.9	96
HR_04	N 49° 58.212'	E 08° 33.434'	Schwarzbach after mouth	7.7	18.1	835	8.4	90
HR_05	N 50° 1.622'	E 08° 39.755'	Hengstbach before WWTP 2	8.5	20.7	662	8.5	98
HR_06	N 50° 6.932'	E 08° 50.093'	Bieber	8.1	22.9	801	8.0	97
HR_07	N 50° 6.961'	E 08° 50.08'	Rodau after Bieber	8.1	22.0	1050	8.0	96
HR_08	N 50° 6.903'	E 08° 50.132'	Rodau before Bieber	8.0	21.1	1291	8.2	96
HR_09	N 49° 41.199'	E 08° 24.766'	Weschnitz before mouth Halbmaasgraben	9.0	25.8	655	8.0	100
HR_10	N 49° 41.762'	E 08° 25.133'	Halbmaasgraben after WWTP 1	7.8	27.9	975	7.6	99
HR_11	N 49° 41.932'	E 08° 24.603'	Weschnitz after mouth Halbmaasgraben	8.7	26.5	657	*	*
HR_12	N 50° 1.753'	E 08° 39.457'	Schwarzbach after WWTP 2	7.4	21.0	1150	7.3	84
HR_13	N 49° 45.1'	E 08° 28.34'	Winkelbach before Rhine	8.8	25.4	696	*	*
HR_14	N 49° 47.772'	E 08° 28.185'	Modau	9.1	23.8	741	*	*

T = temperature, σ = electrical conductivity, * sonde was defect

TABLE S2. Proportion of treated wastewater of the mean discharge in the Hessian Ried region.

GPS coordinates		Name of the measuring points	[%]
N 49° 58.634'	E 08° 30.385'	Schwarzbach, Mörfelden-Walldorf-Mörfelden, Gundbach	29
N 50° 6.932'	E 08° 50.092'	Bieber, Mühlheim am Main	65
N 50° 7.837'	E 08° 49.650'	Rodau, Mühlheim am Main, mouth Rodau	58
N 50° 6.939'	E 08° 50.104'	Rodau, Mühlheim am Main-Brückfeld, before Bieber	65
N 49° 41.205'	E 08° 24.753'	Weschnitz, Biblis-Wattenheim, bridge L3261 before Wattenheim	9
N 49° 41.757'	E 08° 25.134'	Halbmaasgraben, Biblis, after WWTP 1	24
N 49° 41.925'	E 08° 24.601'	Weschnitz, Biblis-Wattenheim, after mouth Halbmaasgraben	9
N 49° 45.094'	E 08° 28.341'	Winkelbach, Gernsheim, before Rhine	25
N 49° 47.771'	E 08° 28.181'	Modau, Stockstadt am Rhein, bridge B44, before mouth Fanggraben	22

data from P.Seel, Hessian Agency for the Environment and Geology

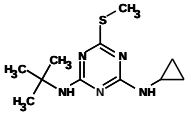
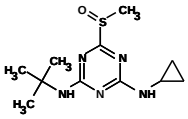
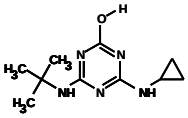
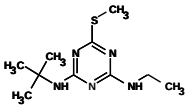
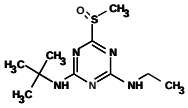
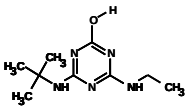
HR-MS analysis via LTQ Orbitrap Velos

10 mM ammonium formate was used as mobile phase A and acetonitrile as mobile phase B. The gradient of mobile phase A was as follows: start with 100%, after 6 min decrease to 70% within 1 min, decrease to 20% within 17 min, kept isocratic for 6 min, return to the initial conditions (100%) within 2 min which were hold for the last 5 min. The total run time was 37 min. The flow rate was adjusted to 400 µl min^{-1} and the column oven temperature on 40°C.

The injection volume of the sample was 10 µL. A Fusion-RP 80Å column (150 x 3 mm, 4 µm; Phenomenex, Aschaffenburg, Germany) was used for chromatographic separation.

The ESI source parameters for the LC-LTQ-Orbitrap-MS measurements were set as follows: capillary temperature, 275°C; capillary voltage, 3.0 kV; heater temperature, 380°C; sheath gas flow rate, 45 arbitrary units (AU); aux gas flow rate, 15 AU; S-lens RF level, 69%. Data dependent acquisition was used to prepare MS spectra as follows: a full scan (50 – 450 m/z; positive mode) was performed followed by MS^2 and MS^3 scans for the two most intense ions with an intensity of > 10,000 counts per second (cps) and > 1000 cps, respectively. CID (collision induced dissociation) and HCD (high-energy collision dissociation) with normalized collision energies of 35% and 80% were used for fragmentation. In addition, dynamic exclusion was applied (exclusion of masses for which three MS^n experiments have been performed, exclusion duration, 30 s) enabling also MS^n experiments for less abundant ions, e.g. during co-elution of different substances. External calibration was performed prior to the analysis of each batch to ensure accurate mass determinations with a resolution of 60,000.

TABLE S3. Overview of the accurate mass measurements of irgarol, terbutryn, and their TPs performed by HR-MS (LTQ Orbitrap Velos) electrospray ionization in positive ion mode.

substance	(proposed) substance structure	$[M+H]^+$	molecular formula	measd./calc. mass	mass error [ppm]	RDB	loss
Irgarol		**m/z 254**	$C_{11}H_{20}N_5S$	254.1433/ 254.1434	-0.4	4.5	-
		m/z 198	$C_7H_{12}N_5S$	198.0808/ 198.0808	-0.1	4.5	C_4H_8
		m/z 83	$C_4H_7N_2$	83.06080/ 83.0604	5.3	2.5	$C_7H_{13}N_3S$
Irgarol sulfoxide		**m/z 270**	$C_{11}H_{20}ON_5S$	270.1381/ 270.1383	-0.8	4.5	-
		m/z 214	$C_7H_{12}ON_5S$	214.0756/ 214.0757	-0.3	4.5	C_4H_8
		m/z 196	$C_7H_{10}N_5S$	196.0650/ 196.0651	-0.6	5.5	H_2O, C_4H_8
		m/z 168	$C_6H_{10}ON_5$	168.0879/ 168.0880	-0.8	4.5	CH_2S, C_4H_8
2-hydroxy Irgarol		**m/z 224**	$C_{10}H_{18}ON_5$	224.1509/ 224.1506	1.3	4.5	-
		m/z 168	$C_6H_{10}ON_5$	168.0882/ 168.0880	1.5	4.5	C_4H_8
		m/z 126	$C_5H_8ON_3$	126.0664/ 126.0662	1.5	3.5	C_4H_8, CH_2N_2
		m/z 86	$C_2H_4ON_3$	86.0348/ 86.0349	-0.6	2.5	C_4H_8, CH_2N_2, C_3H_4
Terbutryn		**m/z 242**	$C_{10}H_{20}N_5S$	242.1433/ 242.1434	-0.2	3.5	-
		m/z 186	$C_6H_{12}N_5S$	186.0807/ 186.0808	-0.6	3.5	C_4H_8
		m/z 91	$C_2H_7N_2S$	91.0322/ 91.0325	-3.2	0.5	C_4H_8, $C_4H_5N_3$
Terbutryn sulfoxide		**m/z 258**	$C_{10}H_{20}ON_5S$	258.1381/ 258.1383	-0.9	3.5	-
		m/z 240	$C_{10}H_{18}N_5S$	240.1277/ 240.1277	-0.3	4.5	H_2O
		m/z 202	$C_6H_{12}ON_5S$	202.0757/ 202.0757	0.1	3.5	C_4H_8
		m/z 184	$C_6H_{10}N_5S$	184.0651/ 184.0651	-0.2	4.5	H_2O, C_4H_8
2-hydroxy Terbutryn		**m/z 212**	$C_9H_{18}ON_5$	212.1510/ 212.1506	2	3.5	-
		m/z 156	$C_5H_{10}ON_5$	156.0882/ 156.0880	1.4	3.5	C_4H_8
		m/z 114	$C_4H_8ON_3$	114.0663/ 114.0662	0.8	2.5	C_4H_8, CH_2N_2
		m/z 86	$C_5H_{12}N$	86.0347/ 86.0349	-2.2	2.5	C_4H_8, CH_2N_2, C_2H_4

Isolation of Irgarol TP (Sulfoxide) via semipreparative HPLC-UV

Milli-Q water was used as mobile phase A and acetonitrile as mobile phase B. For the separation of the analytes an eluent gradient was applied. The proportion of mobile phase A was changed as follows: start with 95%, after 2 min decrease to 10% within 18 min, kept isocratic for 6 min, return to the initial conditions (95%) within 1 min which were hold for the last 8 min. The total run time was 35 min. The flow rate was adjusted to 2 mL min^{-1} and the column oven temperature on 40°C. The injection volume of the sample was 400 µL.

NMR analysis

^{1}H-NMR (700 MHz) and ^{13}C-NMR (176 MHz) were performed on Bruker AVANCE III 700 NMR spectrometers with a 5 mm BBI probe equipped with a z-gradient. The spectra were obtained with π/2-pulse lengths of 9.3 μs (^{1}H) and 14.5 μs (^{13}C) and a sweep width of 10330 Hz (20.6 ppm) for ^{1}H and 29700 Hz (236 ppm) for ^{13}C, all nuclei with a relaxation delay of 2 s. Proton and carbon spectra were referenced using the remaining solvents signals (DMSO-d_5H_1=2.49 ppm and ^{13}C-DMSO-d_6=39.5 ppm) as an internal standard. The nitrogen setup was done with $CH_3{}^{15}NO_2$ with a value of 0 ppm in Aceton-d_6. The temperature was kept at 298.3 K and calibrated with a standard ^{1}H methanol NMR sample. The control of the temperature was realized with a VTU (variable temperature unit) and an accuracy of +/- 0.1K, which was checked with the standard Bruker Topspin 2.1 software.

A standard ^{1}H NMR spectrum was measured with 64 transients. The carbon spectrum was kept with a J-modulated spin-echo for ^{13}C-nuclei coupled to ^{1}H to determine number of attached protons with decoupling during acquisition. All ^{13}C NMR measurements were done with 4096 number of scans.

All the 2D ^{1}H,^{13}C- heteronuclear single quantum correlations (HSQC via double inept transfer and phase sensitive using Echo/Antiecho-TPPI gradient selection with decoupling during acquisition) were run with 4096 points in f2 and 512 points in f1 dimension. Before Fourier transformation, the data were zero filled to 1024 points in f1 and multiplied by a window function (q-sine bell or sine bell) in both dimension. The following parameters were used to obtain optimal results: 1JCH=145Hz for optimizing observable intensities of cross peaks from one bond 1H-X correlation.

The assignment of the protons was accomplished by 2D-1H,1H COSY (correlated spectroscopy). The spectroscopic widths of the homo-nuclear 2D COSY experiments were typically 7000 Hz in both dimension (f1 and f2) and the relaxation delay 1.2 s.

Identification by NMR

The chemical structure of the synthesized irgarol sulfoxide was confirmed by NMR experiments (^{1}H NMR, ^{13}C NMR, ^{1}H,^{1}H-COSY, and ^{1}H,^{13}C-HSQC). The comparison between the ^{1}H NMR (Figure S1) and the ^{13}C NMR (Figure S2) spectra of irgarol and irgarol sulfoxide reveals no differences in the ^{1}H and ^{13}C chemical shifts of the tertiary butyl group as well as at the cyclopropyl group and the triazine ring. In contrast, the ^{1}H and ^{13}C chemical shifts of the methylthioether group are significantly increased from δ_H 2.36 ppm (irgarol) to δ_H 2.74 ppm (irgarol sulfoxide) and δ_C 11.92 ppm (irgarol) to δ_C 23.42 ppm (irgarol sulfoxide), respectively. This confirmed the oxidation of the methylthio group to the sulfoxide and thus the chemical identity of the synthesized irgarol sulfoxide.

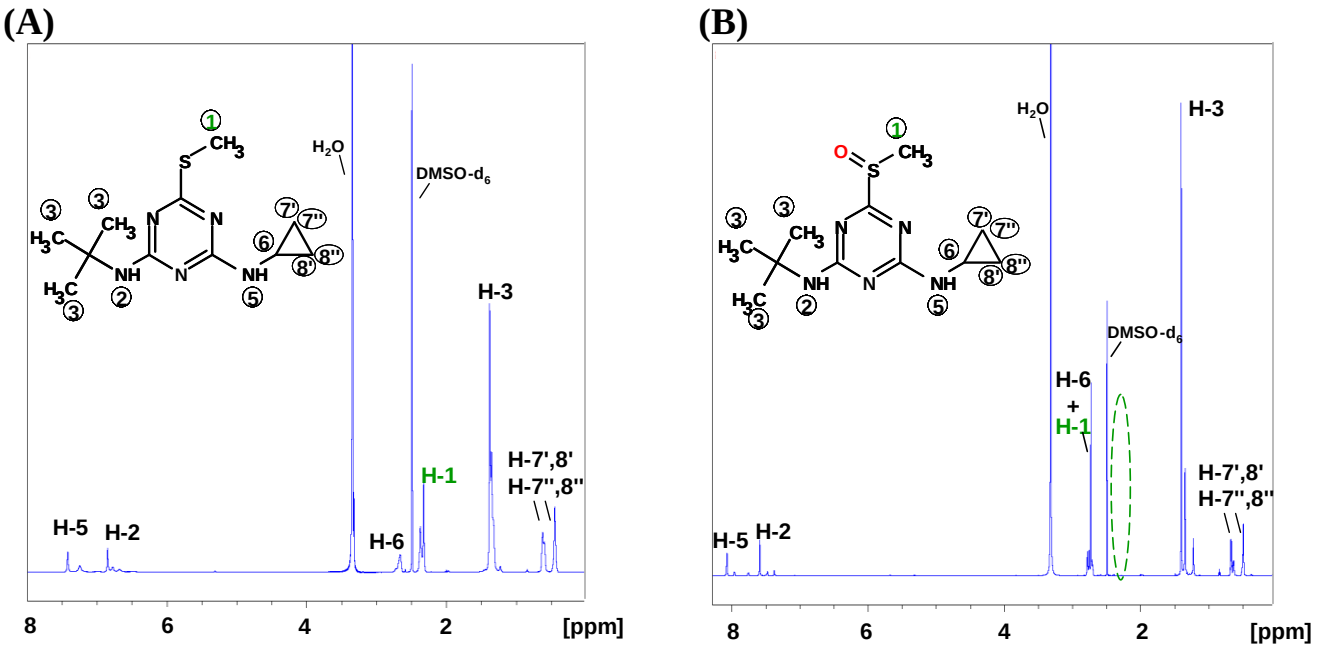


FIGURE S1. ^{1}H-NMR spectra of irgarol (A) and irgarol sulfoxide (B). Samples were measured at 298.3 K in DMSO-*d*$_6$.

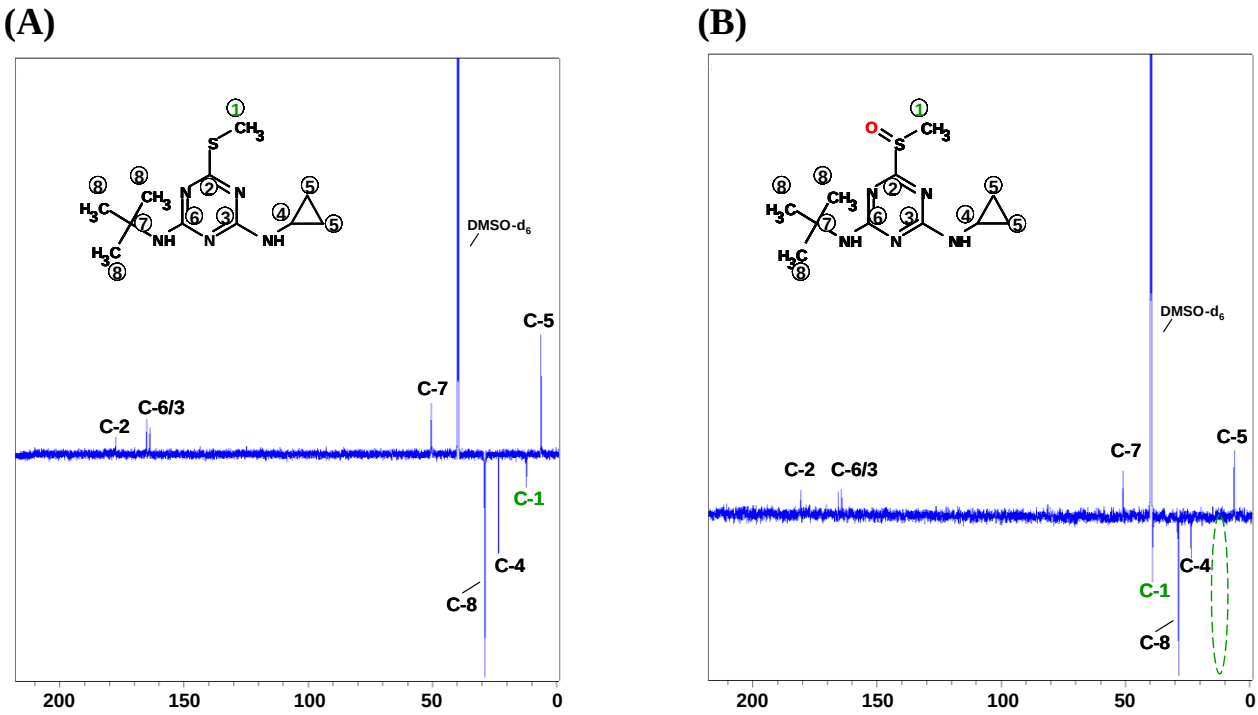


FIGURE S2. ^{13}C-NMR spectra of irgarol (A) and irgarol sulfoxide (B). Samples were measured at 298.3 K in DMSO-*d*$_6$.

Analysis of Batch Samples and Environmental Samples from WWTPs as well as Streams and Rivers

10 mM ammonium formate was used as mobile phase A and acetonitrile as mobile phase B. The gradient of mobile phase A was as follows: start with 90%, after 0.3 min decrease to 30% within 1 min, decrease to 0% within 7.7 min, kept isocratic for 3 min, return to the initial conditions (90%) within 0.1 min which were hold for the last 2.9 min. The total run time was 15 min. The flow rate was adjusted to 600 µl min^{-1} and the column oven temperature on 30°C. The injection volume of the sample was 10 µL. A Fusion-RP 80Å column (150 x 3 mm, 4 µm; Phenomenex, Aschaffenburg, Germany) was used for chromatographic separation.

The detection was performed by multiple reaction monitoring (MRM), whereby two to three transitions (one for quantification and up to two for confirmation) were selected for the TPs. The MS/MS parameters (Table S4) were optimized for the individual compounds in

continuous flow mode via direct injection of standard solutions (1 µg mL^{-1}) with a syringe pump (10 µL min^{-1}).

The recovery of the target analytes (Table S5) was assessed within each sample series and for each matrix (surface water, WWTP effluent and influent) by spiking the analytes to a final concentration (25, 50 and 100 ng L^{-1}, at least n = 4). Absolute recoveries were determined by comparing the peak areas of spiked samples with the peak areas in an external standard containing the same amount of analytes. The relative recoveries were calculated by dividing the quantified concentrations with the spiked concentrations. The limit of quantification (LOQ) was defined as the lowest calibration point in the linear regression with a signal to noise ratio (S/N) of at least 10 for transition q1 and 3 for transition q2 and q3. For the quantification an external calibration with 11 calibration points (0-200 ng) was used by adding surrogate standards (irgarol-d_9 and terbutryn-d_5). Linear regression was applied with a weighting factor of 1/x.

Non-spiked sludge samples (blank batch samples) were used as reference samples e.g. for the kinetic experiments/mass balances (sludge was diluted with WWTP 5 effluent). The non-spiked batch samples were also measured as the spiked batch samples. The measured concentrations of non-spiked batch samples are shown in Table S6. In the calculations of kinetics and mass balances the analyte concentration of non-spiked batch samples were subtracted from the analyte concentration of spiked batch samples.

TABLE S4. Retention time, precursor ion, product ions and MS parameters used for LC-MS/MS detection of irgarol, terbutryn and their respective TPs.

Compound	RT[a] [min]	q_1 transition	q_2 transition	q_3 transition	DP[b] [V]	CE[c] ($q_1/q_2/q_3$) [eV]	CXP[d] ($q_1/q_2/q_3$) [V]
Irgarol	5.92	254 → 198	254 → 83	-	70	26/41/-	6/6/-
Irgarol sulfoxide	4.45	270 → 196	270 → 168	270 → 214	56	27/27/23	14/10/20
Terbutryn	5.93	242 → 91	242 → 186	-	50	38/25/-	5/15/-
Terbutryn sulfoxide	4.40	258 → 184	258 → 202	258 → 240	21	27/25/19	16/16/12
M1	4.76	214 → 68	214 → 110	-	50	10/3/-	37/10/-
Irgarol-d_9	5.88	263 → 199	263 → 92	-	40	29/40/-	16/15/-
Terbutryn-d_5	5.91	247 → 191	247 → 91	-	50	24/41/-	12/5/-

[a] RT = Retention time, [b] DP = Declustering potential, [c] CE = Collision energy, [d] CXP = Collision cell exit potential

TABLE S5. Linearity of calibration curves, limit of quantification and recoveries in the investigated matrices with 95% confidence intervals after subtracting the background concentration. For calculation of relative recoveries, different amounts (10 or 12.5 ng) of analytes were added depending on the sampled matrix.

Analyte	correlation coefficient (r)	WWTP influent				WWTP effluent				surface water			
		LOQ [ng L^{-1}]	n	absolute recovery[a] [%]	relative recovery[b] [%]	LOQ [ng L^{-1}]	n	absolute recovery[a] [%]	relative recovery[b] [%]	LOQ [ng L^{-1}]	n	absolute recovery[a] [%]	relative recovery[b] [%]
Irgarol	0.9960	2	36	35 ± 4	112 ± 6	1	36	73 ± 2	93 ± 3	1	15	59 ± 4	103 ± 5
Irgarol sulfoxide	0.9982	5	36	17 ± 1	58 ± 5	1	36	41 ± 2	56 ± 2	1	15	34 ± 4	63 ± 5
Terbutryn	0.9919	3	36	28 ± 3	82 ± 4	1	36	57 ± 2	81 ± 4	1	15	41 ± 8	84 ± 11
Terbutryn sulfoxide	0.9993	4	4	53 ± 5	79 ± 5	1	4	44 ± 4	61 ± 3	1	4	37 ± 5	70 ± 6
M1	0.9990	4	36	10 ± 2	49 ± 5	1	36	40 ± 2	56 ± 3	1	15	30 ± 4	65 ± 5

[a] Calculated in comparison to a non-enriched standard solution; [b] Calculated using the recovery of the spiked surrogate standard

TABLE S6. Background concentration of irgarol, terbutryn and their TPs in non-spiked batch samples consisting of activated sludge diluted with effluent from WWTP 5 (Oct. 2012).

Irgarol	Irgarol sulfoxide	Terbutryn	Terbutryn sulfoxide	M1
[ng L^{-1}]				
7.5	2.1	23.3	7.9	2.7

Mass Balances

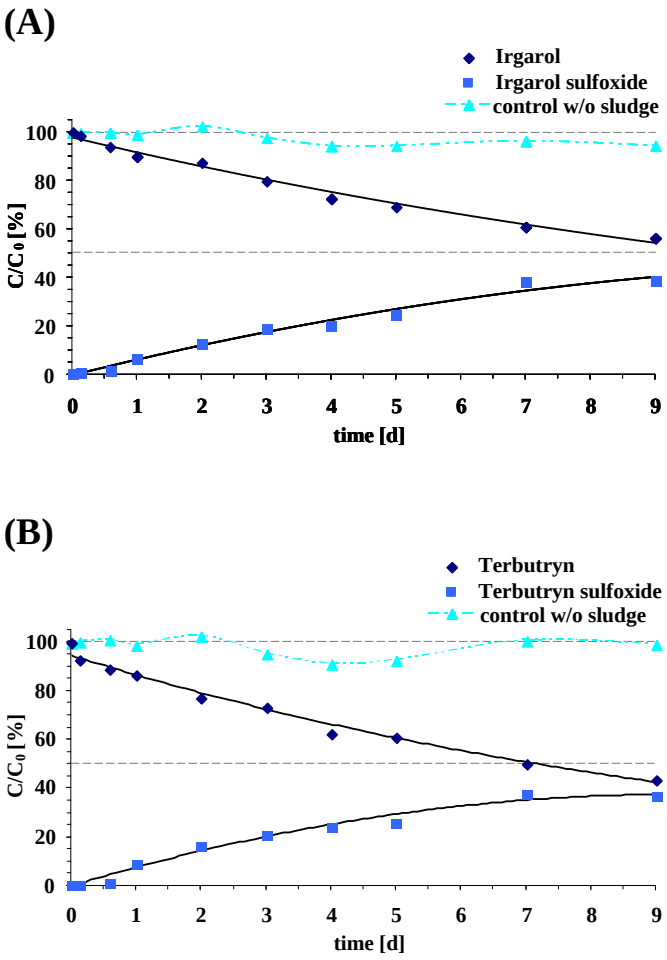
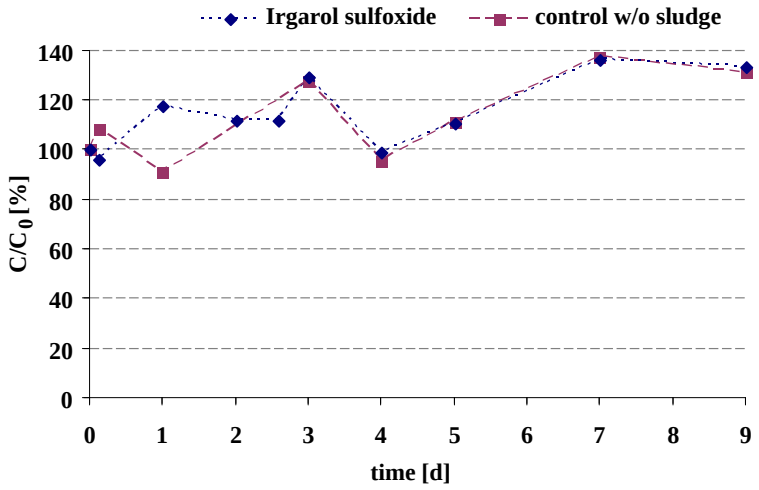


FIGURE S3. Mass balance [%] of irgarol (A) and terbutryn (B) in batch systems using diluted activated sludge (1:10 with effluent, 0.40 g_{SS} L^{-1}). Irgarol and terbutryn were spiked at a concentration of 0.5 µg L^{-1}. Filtered effluent without sludge was used as negative control to examine the influence of abiotic transformation processes. Calculations were done on a molar basis (mol L^{-1}).

(A)



(B)

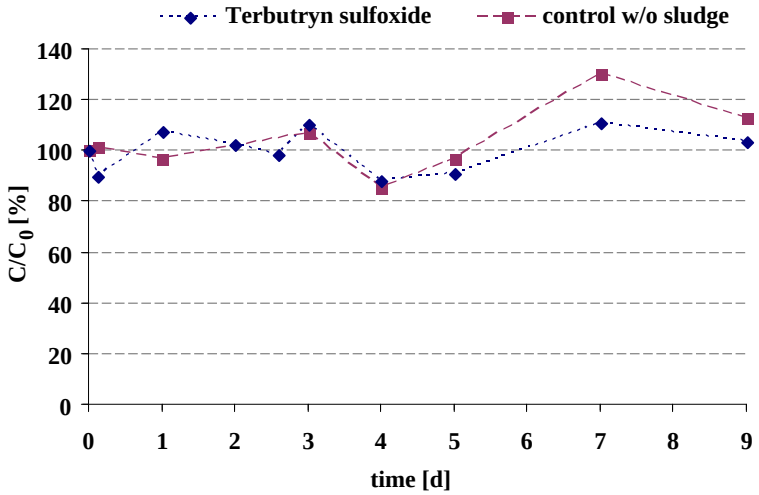


FIGURE S4. Batch experiment of irgarol sulfoxide (A) and terbutryn sulfoxide (B) in batch systems using diluted activated sludge (1:10 with effluent, 0.40 g_{SS} L^{-1}). The TPs were spiked with concentrations of 0.2 µg L^{-1}. Filtered effluent without sludge was used as negative control to examine the influence of abiotic transformation processes.

Sorption[1,2]

Batch experiments

Sorbed proportion onto sludge/suspended solids in wastewater can be estimated as follows:

The sludge-water distribution coefficient $K_{d,sec}$ (L $kg_{dw\ sludge}^{-1}$) for irgarol ($K_{d,sec}$ = 140 ± 10 L kg_{TSS}^{-1}) and terbutryn ($K_{d,sec}$ = 160 ± 10 L kg_{TSS}^{-1}) are reported by Wick et al.[1]

$$K_{d,sec} = \frac{C_s}{C_w} \quad \rightarrow \quad C_s = K_{d,sec} \cdot C_w$$

where C_s (µg $kg_{dw\ sludge}^{-1}$) is the sorbed concentration and C_w (µg L^{-1}) is the soluble concentration.

$$\text{Percent sorption} = \frac{100 \cdot K_{d,sec} \cdot X_{SS}}{1 + K_{d,sec} \cdot X_{SS}}$$

where X_{SS} is the concentration of total suspended solids (TSS).[2]

The measured concentration of TSS in the activated sludge used for the batch experiments was 4 g_{SS} L^{-1}. Due to a dilution of 1:10, the final TSS concentration in the batch reactors was 0.4 g_{SS} L^{-1}. The following values were used: $K_{d,sec}$ = 0.160 L g_{TSS}^{-1} (160 L kg_{TSS}^{-1}) and X_{SS} = 0.4 g_{SS} L^{-1}.

$$\text{Percent sorption} = \frac{100 \cdot 0.160 \cdot 0.4}{1 + 0.160 \cdot 0.4} = \underline{6\%}$$

Thus, it can be estimated that about 6% of irgarol and terbutryn are sorbed onto sludge, while about 94% remains dissolved.

WWTPs

Removal in WWTPs by sorption and withdrawal of excess sludge can be predicted as follows:

$$\text{Percent sorption} = \frac{100 \cdot K_{d,sec} \cdot X_{SP}}{1 + K_{d,sec} \cdot X_{SP}}$$

where X_{SP} is the sludge production (quantity of sludge generated per unit of wastewater treated).[3]

Assuming the typically sludge production of 0.2 g L^{-1} [4] and the used $K_{d,sec}$ = 0.160 L g_{TSS}^{-1} (160 L kg_{TSS}^{-1}):

$$\text{Percent sorption} = \frac{100 \cdot 0.160 \cdot 0.2}{1 + 0.160 \cdot 0.2} = \underline{3\%}$$

Hence, removal by sorption during wastewater treatment can be estimated to be about 3%.

The amount sorbed to suspended solids in the influent was calculated to assess possible losses by filtration of samples. The TSS concentration of the raw wastewater was 0.3 g_{SS} L^{-1} at a maximum.

$$\text{Percent sorption} = \frac{100 \cdot K_{d,sec} \cdot X_{SS}}{1 + K_{d,sec} \cdot X_{SS}}$$

where X_{SS} is the concentration of TSS.[2] The following values were used:

$K_{d,sec}$ = 0.160 L g_{TSS}^{-1} (160 L kg_{TSS}^{-1}) and X_{SS} = 0.3 g_{SS} L^{-1}.

$$\text{Percent sorption} = \frac{100 \cdot 0.160 \cdot 0.3}{1 + 0.160 \cdot 0.3} = \underline{4.6\%}$$

Thus, it can be estimated that less than 5% of irgarol and terbutryn were sorbed to suspended solids in the influent and losses by filtration were negligible.

Suspended solids in streams

Sorbed proportion onto suspended solids can be estimated as follows:

$K_{d,sec}$ values were normalized for comparison with literature data to the fraction of total organic carbon f_{OC} (kg_{OC} $kg_{dw\ sludge}^{-1}$) resulting in the K_{OC} (L kg_{OC}^{-1}):

$$K_{OC} = \frac{K_{d,sec}}{f_{OC}} \quad \rightarrow \quad C_s = K_{Oc} \cdot C_w \cdot f_{OC}$$

The organic carbon normalized soil-water distribution coefficient (K_{OC}) value is for irgarol log K_{OC} = 3.0 (sediment)[5] and for terbutryn log K_{OC} = 2.9 (soil)[6].

$$\text{Percent sorption} = \frac{100 \cdot K_{OC} \cdot X_{SS}}{1 + K_{OC} \cdot X_{SS}}$$

The following values were used: K_{OC} = 1 L g_{OC}^{-1} and X_{SS} = 0.03 g_{SS} L^{-1}.

$$\text{Percent sorption} = \frac{100 \cdot 1 \cdot 0.03}{1 + 1 \cdot 0.03} = \underline{2.9\%}$$

It can be estimated that at maximum about 3% of irgarol and terbutryn are sorbed onto suspended solids, while about 97% remain dissolved. Thus, it can be expected that sorption of

irgarol and terbutryn are negligible also for suspended solids in rivers as already mentioned for sludge.

Environmental Occurrence of Transformation Products

Streams and Rivers.

TABLE S7. Concentrations of irgarol, terbutryn and their TPs in stream and small river grab samples (LOQ = 1 ng L^{-1}).

Sampling location	Irgarol		Irgarol sulfoxide		Sum		Terbutryn		Terbutryn sulfoxide		Sum		M1	
	Concentration of sampling (1st[a]/ 2nd[b]) [ng L^{-1}]													
HR_01	10	9.6	15	9.5	25	19	34	38	24	28	58	66	3.3	3.4
HR_02.1	11	10	17	10	28	20	21	34	21	29	42	63	3.4	3.1
HR_02.2	n.d.	9.0	n.d.	8.2	n.d.	17	n.d.	47	n.d.	26	n.d.	73	n.d.	2.9
HR_03	5.8	3.9	4.3	3.6	10	8	24	24	16	23	40	47	6.3	4.9
HR_04	8.5	7.7	12	8.2	21	16	33	32	22	26	55	58	4.6	4.3
HR_05	1.8	1.3	14	8.2	15	9.5	11	11	5.9	4	16.9	15	1.9	1.6
HR_06	15	15	15	14	30	29	50	60	25	31	75	91	5.2	5.9
HR_07	12	11	8.6	8.7	21	20	51	58	21	25	72	83	4.2	5.8
HR_08	5.4	7.1	4.3	4.1	10	11	46	55	16	19	62	74	3.1	4.7
HR_09	20	22	2.2	1.8	22	24	98	100	8.2	9	106	109	7.7	6.7
HR_10	3.2	2.4	<LOQ	<LOQ	3.2	2.4	90	88	5.0	5	95	93	2.7	3.7
HR_11	19	21	2.3	2.0	21	23	102	99	9.0	10	111	109	6.5	6.3
HR_12	nd	4.8	nd	5.6	nd	10	nd	41	nd	34	nd	75	nd	7.4
HR_13	nd	2.7	nd	1.2	nd	3.9	nd	40	nd	10	nd	50	nd	2.1
HR_14	nd	3.1	nd	1.9	nd	5.0	nd	36	nd	13	nd	49	nd	2.3
AA-EQS[c]	2.5 ng L^{-1}						65 ng L^{-1}							

[a] sampling during wet weather periods (11.06.2012), [b] sampling during dry weather periods (28.06.2012),

[c] this parameter is the EQS expressed as an annual average value (AA-EQS) for inland surface waters (12.08.2013)

nd: not determined

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