

Leaching and transformation of film preservatives in paints induced by combined exposure to UV radiation and water contact under controlled laboratory conditions

Supplementary Materials

Ute Schoknecht, Helena Mathies, Jan Lisec*

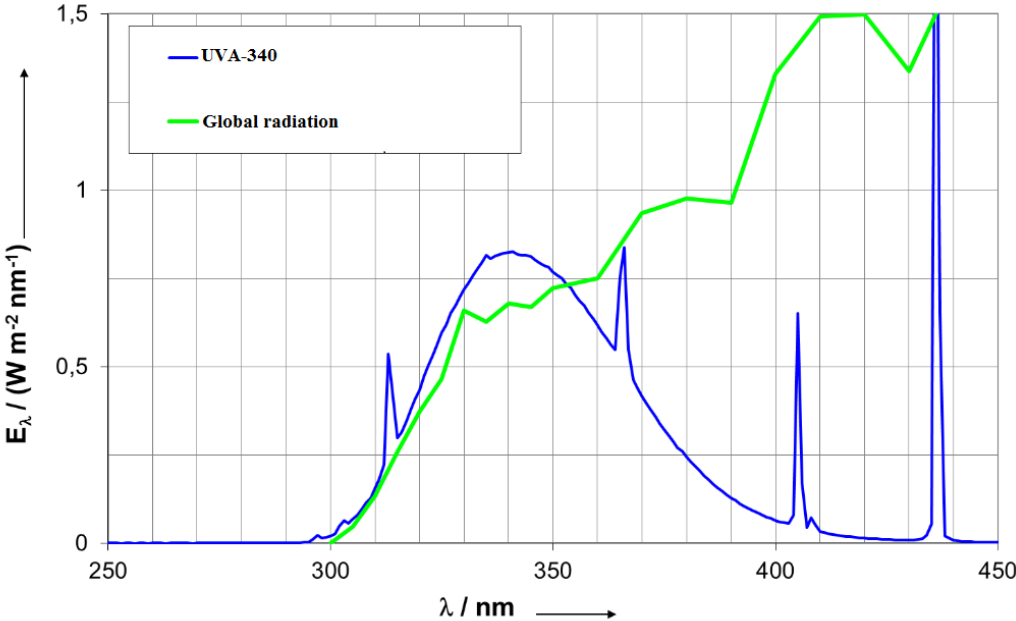
Federal Institute for Materials Research and Testing, Unter den Eichen 87, 12205 Berlin

Supplementary S1. Composition of the investigated paints

Ingredient	Red paint	White paint
	Percent by weight	Percent by weight
Water	17.32	17.32
Cellulose ether	0.19	0.19
Sodium hydroxide solution 20%	0.19	0.19
Na-Polyacrylate 35%	0.28	0.28
Polymer defoaming agent	0.28	0.28
Methylisothiazolinone/Benzisothiazolinone	0.19	0.19
TiO ₂ chloride type, Color index: P.W. 6	0.00	9.21
Iron oxide red / Fe ₂ O ₃ / color index P.R. 101	9.21	0.00
Mica D: 50 38 μ	4.46	4.46
CaCO ₃ D: 50 5 μ	13.86	13.86
CaCO ₃ D: 50 15 μ	22.77	22.77
Styrene acrylate 50 % MFT ca. 20 Grad	27.72	27.72
Silicone resin emulsion modified polysiloxane 55%	0.99	0.99
Acrylate thickener 25%	0.28	0.28
Dipropylene glycol n-butylether	1.29	1.29
Dispersion containing 25% Terbutryn ^a	0.20	0.20
Dispersion containing 50% Diuron ^a	0.10	0.10
Dispersion containing 8% OIT ^a	0.62	0.62
Dispersion containing 50% Carbendazim ^a	0.10	0.11
Sum	100	100

^a biocide dispersions including surfactants

Supplementary S2. Typical spectrum of UVA-340 lamps compared to global radiation



Supplementary S3. Analytical method

LC-MS Analysis

LC-System: Agilent 1100 Series
Detector: Agilent 6130 Series Quadrupole
Column: Phenomenex Synergi™, 4 µm Hydro-RP 80 Å, 150 mm x 2 mm
Column temperature: 30°C
Eluent: A: 0.2% acetic acid in water (Millipore Quality)
B: acetonitrile, LC-MS quality (Chemsolute)
Flow: 0.5 ml min⁻¹
Injection volume: 10 µl
Gradient:

Time	Solvent A	Solvent B
min	%	%
1	90	10
4	50	50
10	25	75
11	10	90
11.5	90	10
15	90	10

Quadrupole temperature: 100°C
MSD spray chamber: API-ES
Drying gas flow: 12 l min⁻¹ nitrogen
Nebulizer pressure: 40 psig
Drying gas temperature: 300°C
Capillary voltage: positive mode: 1500 V, negative mode: 1500 V

Signals

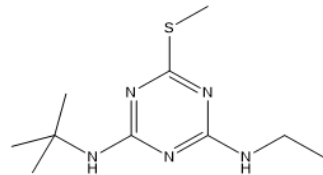
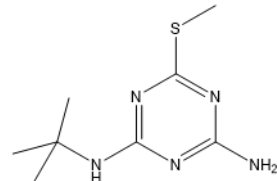
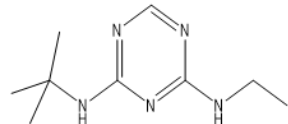
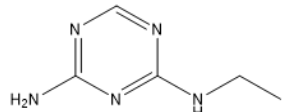
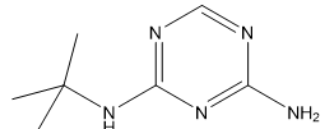
Substance	Code	Retention time	Mode	Signal M+1	Signal M-1	Calibration range	Recovery from paint
		min		m/z	m/z		
Terbutryn		8.93	positive	242		0.0004 - 0.2	94
Terbumeton		7.04	positive	226		0.001 - 0.5	79
2-Hydroxy terbutryn	TBOH	5.13	positive	212		0.002 - 1.0	85
Desethyl-2-hydroxy-terbutryn	TBOH-DesE	1.54	positive	184		0.004 - 2.0	56
Desethyl terbutryn	TB-DesE	7.17	positive	214		0.002 - 1.0	72
Terbutryn sulfoxide	TBSO	7.16	positive	258		0.002 - 0.5	69
Diuron		7.95	positive	233		0.002 - 2.0	76
1-(3,4-Dichlorophenyl-3) - methyl urea	DCPMU	7.49	negative		218	0.002 - 0.2	44
1-(3,4-Dichlorophenyl)-urea	DCPU	7.04	negative		203	0.001 - 0.05	75
Dichloroaniline		7.08	positive	162		0.005 - 5	50
Monuron		7.02	positive	199		0.002 - 0.10	76
Carbendazim		3.70	positive	192		0.002 - 2.0	120
Octylisothiazolinone	OIT	10.28	positive	214		0.005 - 1.0	93

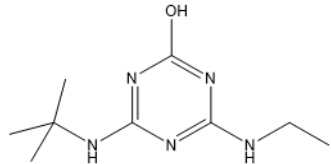
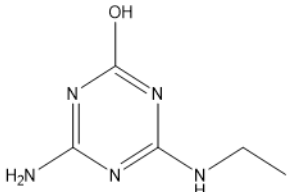
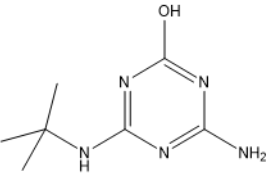
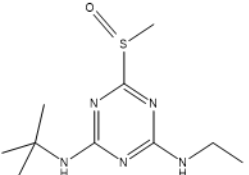
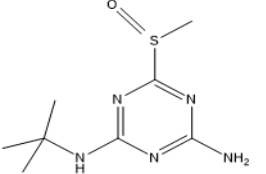
A matrix signal was observed for the same retention time and m/z as for TB-DesE.

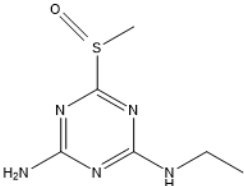
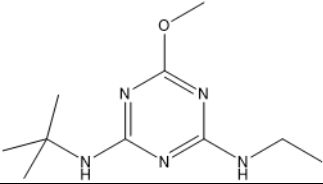
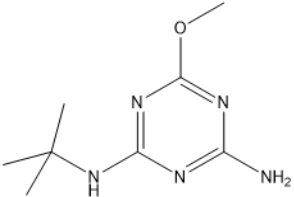
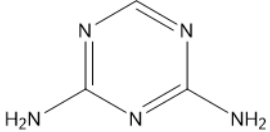
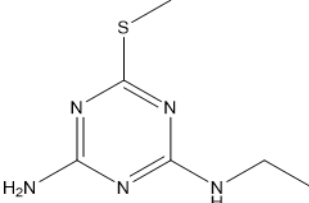
Standards

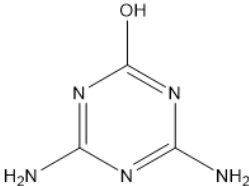
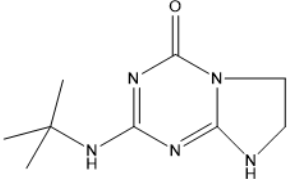
Substance	Code	CAS	Supplier	Purity
Terbutryn		886-50-0	Dr. Ehrenstorfer	99.0%
Terbumeton		33693-04-8	Sigma-Aldrich	99.2%
2-Hydroxy terbutryn	TBOH	66753-07-9	Sigma-Aldrich	98.6%
Desethyl-2-hydroxy-terbutryn	TBOH-DesE	66753-06-89	Neochema	10 µg ml ⁻¹
Desethyl terbutryn	TB-DesE	30125-65-6	Neochema	99.8%
Terbutryn sulfoxide	TBSO	82985-33-9	Neochema	98.5%
Diuron		330-53-1	Sigma-Aldrich	> 98.0%
1-(3,4-Dichlorophenyl-3) - methyl urea	DCPMU	3567-62-2	Dr. Ehrenstorfer	99.0%
1-(3,4-Dichlorophenyl)-urea	DCPU	2327-02-8	Neochema	100 µg ml ⁻¹
3-(3,4-dichlorophenyl)-1-formyl-1-methylurea	DCPFMU	76409-92-2	Sigma-Aldrich	contained DCPMU
Dichloroaniline	DCA	95-76-1	Ultra Scientific	≥ 98.0%
Monuron		150-68-5	Sigma-Aldrich	99.9%
Carbendazim		10605-21-7	Sigma-Aldrich	99.5%
Octylisothiazolinone	OIT	26530-20-1	Dr. Ehrenstorfer	99.5%

Supplementary S4. Transformation products of terbutryn and diuron

No	Substance	Code	CAS	Mass in g mol ⁻¹	Molecular formula	Structure
1	Terbutryn		886-50-0	241.356*	C ₁₀ H ₁₉ N ₅ S	
2	Desethyl-terbutryn	TB-DesE	30125-65-6	213.303*	C ₈ H ₁₅ N ₅ S	
3	Desthiomethyl-terbutryn	TB-DesS	73956-51-1	195.265*	C ₉ H ₁₇ N ₅	
4	Desthiomethyl-desbutyl-terbutryn	TB-DesS-DesB	30368-49-1	139.158*	C ₅ H ₉ N ₅	
5	Desthiomethyl-desethyl-terbutryn	TB-DesS-DesE	73956-52-2	167.212*	C ₇ H ₁₃ N ₅	

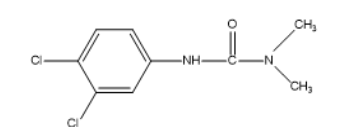
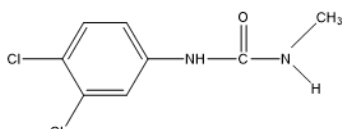
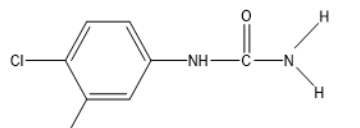
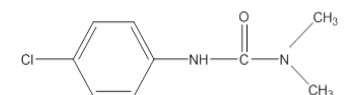
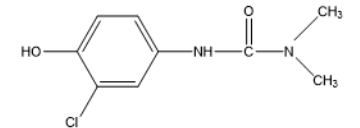
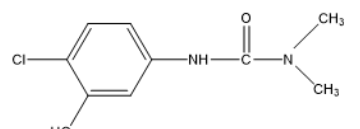
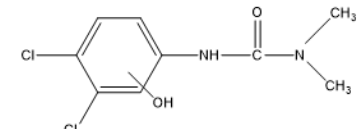
6	2-Hydroxy-terbutryn	TBOH	66753-07-9	211.264*	C ₉ H ₁₇ N ₅ O	
7	Desbutyl-2-hydroxy-terbutryn	TBOH-DesB		155.159**	C ₅ H ₉ N ₅ O	
8	Desethyl-2-hydroxy-terbutryn	TBOH-DesE	66753-06-8	183.211*	C ₇ H ₁₃ N ₅ O	
9	Terbutrynsulfoxid	TBSO	82985-33-9	257.356*	C ₁₀ H ₁₉ N ₅ OS	
10	Desethyl-terbutrynsulfoxid	TBSO-DesE		229.306**	C ₈ H ₁₅ N ₅ OS	

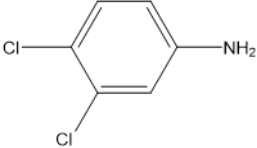
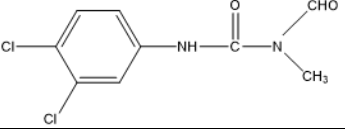
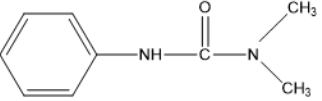
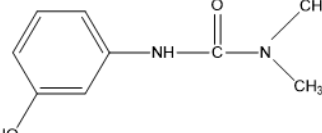
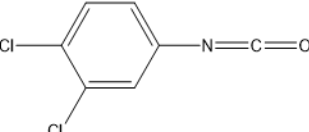
11	Desbutyl-terbutrynsulfoxid	TB-SO-DesB		201.252**	$C_6H_{11}N_5OS$	
12	Terbumeton	Terbumeton	33693-04-8	225.291*	$C_{10}H_{19}N_5O$	
13	Desethyl-terbumeton	Terbumeton-DesE	30125-64-5	197.238*	$C_8H_{15}N_5O$	
14	2,4-Diamino-1,3,5-triazin		504-08-5	111.105*	$C_3H_5N_5$	
15	Desbutyl-terbutryn	TB-DesB		184.252**	$C_6H_{11}N_5S$	

16	2-Hydroxy-4,6-diamino-1,3,5-triazin	TBOH-DesB-DesE	645-92-1	127.105*	C ₃ H ₆ N ₅ O	
17	Terbutryn-TP-210	TP-210		209.251**	C ₉ H ₁₅ N ₅ O	

*data from Chemspider (<http://www.chemspider.com/>)

**calculated (<https://www.chemie.de/tools/>)

No	Substance	Code	CAS	Mass in g mol ⁻¹	Molecular formula	Structure
1	Diuron		330-54-1	233.094*	C ₉ H ₁₀ Cl ₂ N ₂ O	
2	Desmethyl-diuron 1-(3,4-dichlorophenyl)-3-methylurea	DCPMU	3567-62-2	219.068*	C ₈ H ₈ Cl ₂ N ₂ O	
3	3,4-Dichlorophenylurea	DCPU	2327-02-8	205.041*	C ₇ H ₆ Cl ₂ N ₂ O	
4	Monuron 3-(4-chlorophenyl)-1,1-dimethylurea	Diuron-DesCl	150-68-5	198.649*	C ₉ H ₁₁ ClN ₂ O	
5	3-(4-Chloro-3-hydroxyphenyl)-1-1-dimethylurea	Diuron-OH P1	69342-26-3	214.649*	C ₉ H ₁₁ ClN ₂ O ₂	
6	3-(3-Chloro-4-hydroxyphenyl)-1-1-dimethylurea	Diuron-OH P2	34637-13-3	214.649*	C ₉ H ₁₁ ClN ₂ O ₂	
7	Hydroxylated diuron	Diuron-OH		250.102**	C ₉ H ₁₁ Cl ₂ N ₂ O ₂	

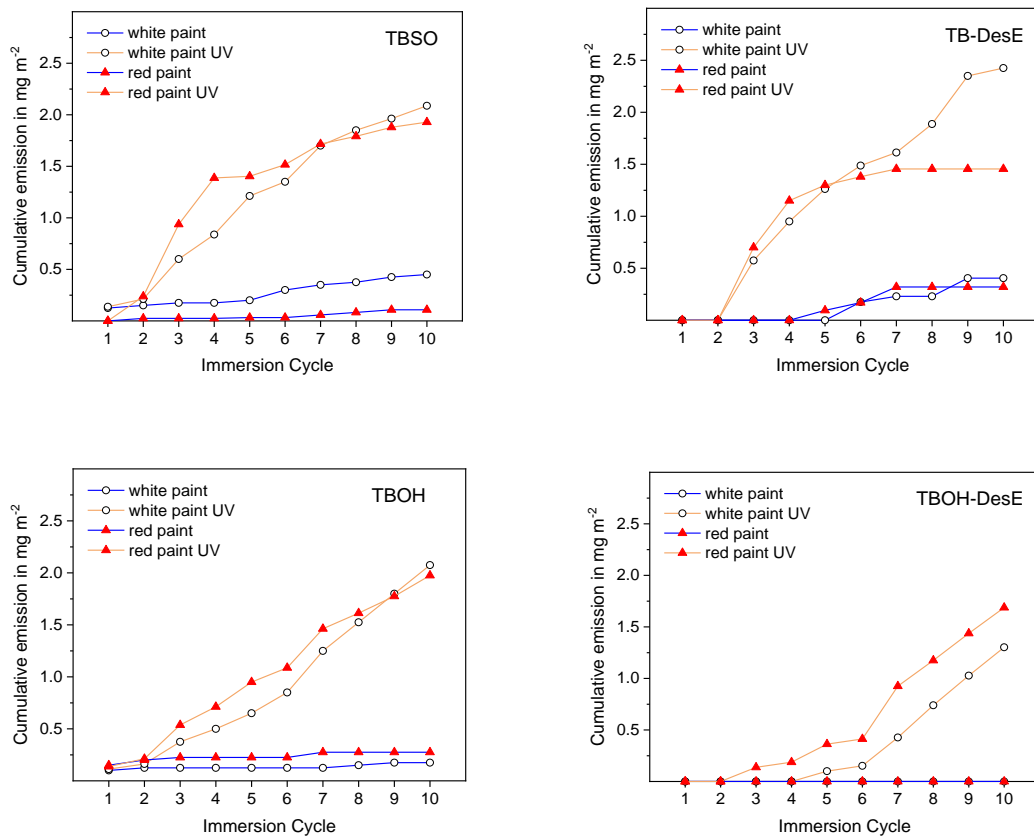
8	Dichloroaniline	DCA	95-76-1	162.017*	C ₆ H ₅ Cl ₂ N	
9	3-(3,4-Dichlorophenyl)-1-formyl-1-methylurea (2 isomeres)	DCPFMU	76409-92-2	247.078*	C ₉ H ₈ Cl ₂ N ₂ O ₂	
10	Fenuron 1,1-dimethyl-3-phenylurea		101-42-8	164.204*	C ₉ H ₁₂ N ₂ O	
11	Hydroxyfenuron 3-(3-hydroxyphenyl)-1-1-dimethylurea		4849-46-1	180.204*	C ₉ H ₁₂ N ₂ O ₂	
12	3,4-Dichlorophenyl isocyanate	DCPI	102-36-3	188.011*	C ₇ H ₃ Cl ₂ NO	
13	Monuron-dimer			395.288**	C ₁₈ H ₂₀ Cl ₂ N ₄ O ₂	
14	Monuron-diuron-dimer			429.734**	C ₁₈ H ₁₉ Cl ₃ N ₄ O ₂	
15	Monuron-denuron-dimer			360.843**	C ₁₈ H ₂₁ ClN ₄ O ₂	
16	Fenuron-dimer			326.398**	C ₁₈ H ₂₂ N ₄ O ₂	

*data from Chemspider (<http://www.chemspider.com/>)

**calculated (<https://www.chemie.de/tools/>)

Supplementary S5. Emission curves of transformation products

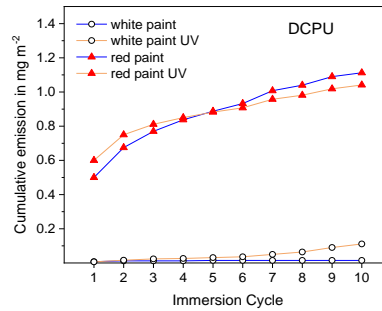
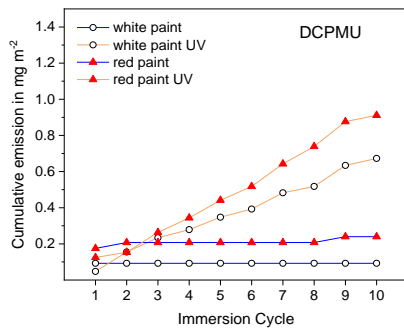
Transformation products of terbutryn in eluates



Emission curves for transformation products of terbutryn during immersion cycles. Test specimens of white and red paints were either kept in a dark room at $21 \pm 2^\circ\text{C}$ and $60 \pm 5\%$ relative humidity between the immersion cycles or exposed to UV radiation (indicated by “UV”).

Transformation products were mainly observed after UV radiation. TBOH-DesE – a secondary transformation product – is formed only later during the experiment. Small amounts of TBSO (mainly in the white paint eluates), TB-DesE and TBOH (in eluates from both paints) were also formed by water contact.

Transformation products of diuron in eluates

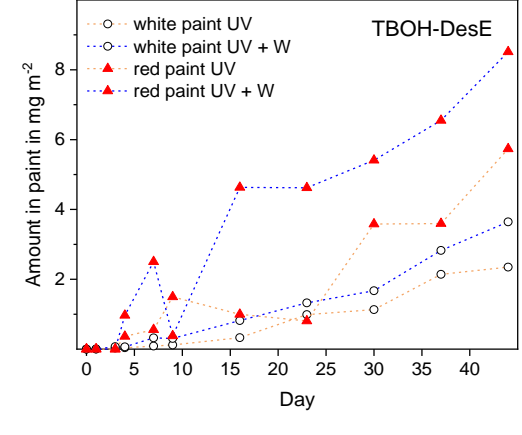
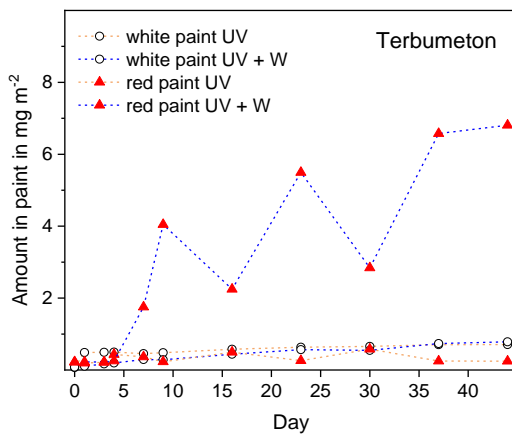
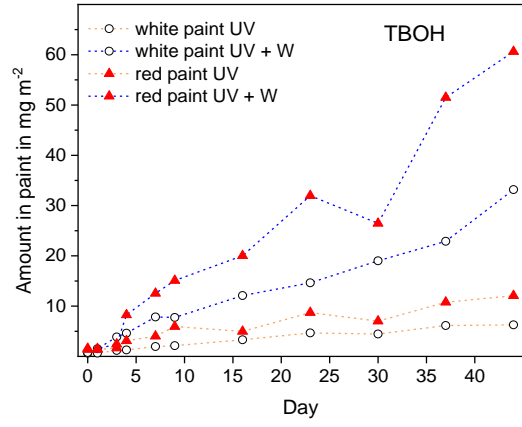
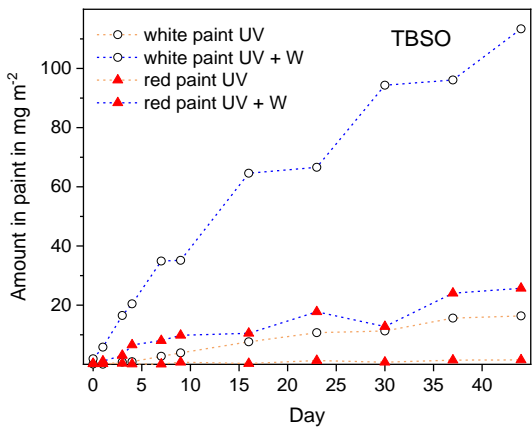
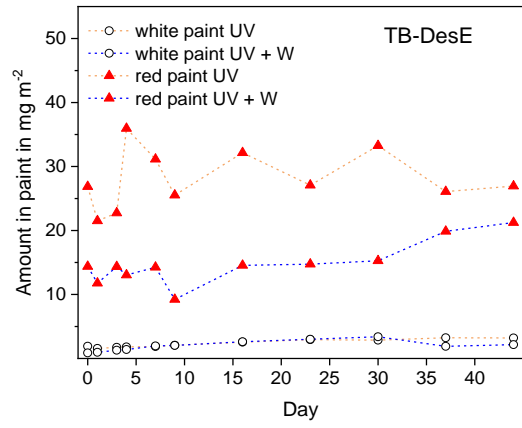
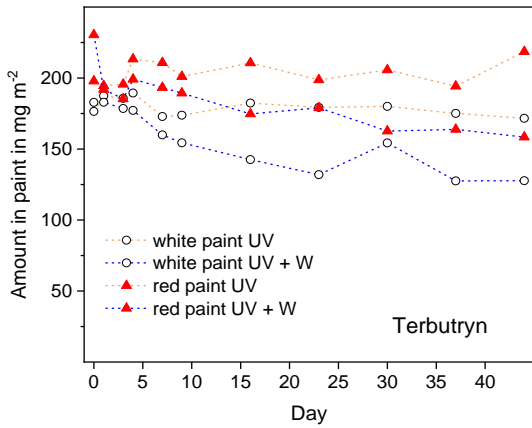


Emission curves for transformation products of diuron during immersion cycles. Test specimens of white and red paints were either kept in a dark room at $21 \pm 2^\circ\text{C}$ and $60 \pm 5\%$ relative humidity or exposed to UV radiation (indicated by "UV").

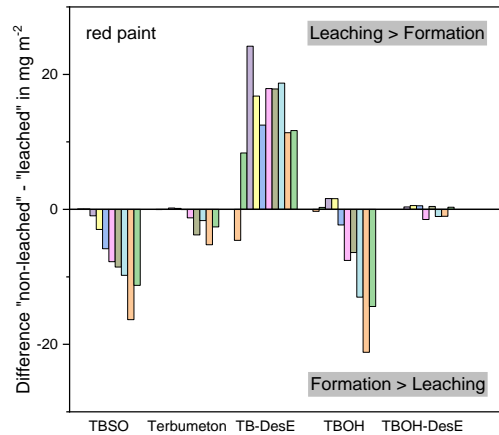
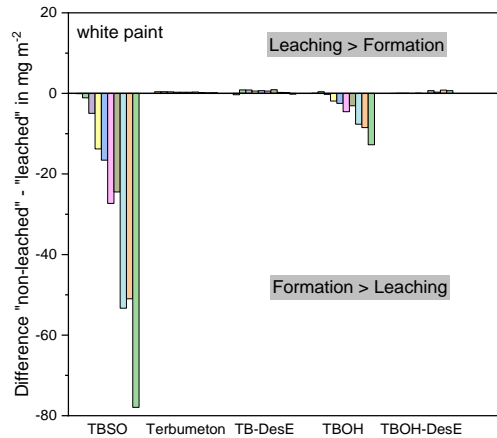
DCPMU was formed due to UV radiation in both paints, with slightly greater amounts in the red paint. DCPU was already present in the red paint at the beginning of the experiment. A small amount was formed in the white paint later during the experiment, probably as a secondary transformation product from DCPMU.

SI 6 Active substances and transformation products in paints during the experiments

Terbutryn and transformation products in paints



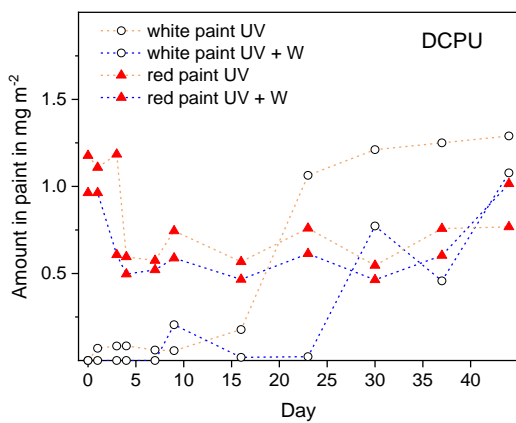
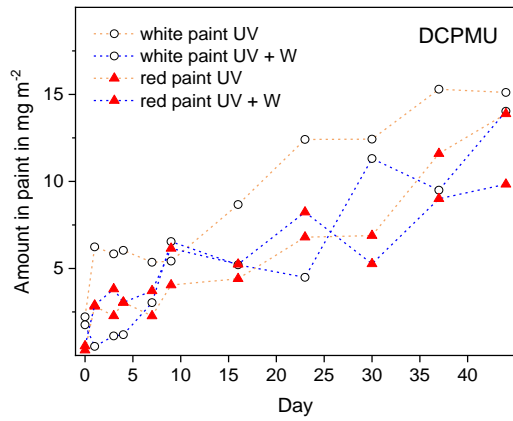
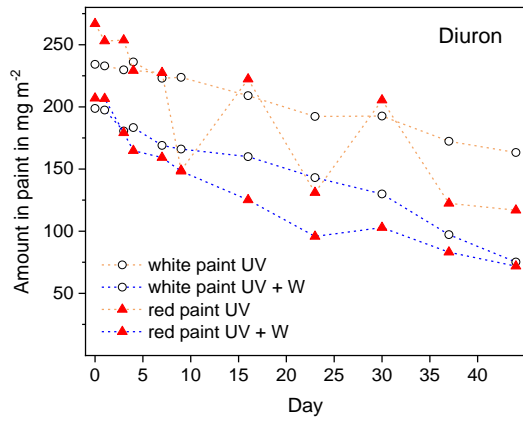
Amount of terbutryn and transformation products in the paint layers at selected days of the experiment.



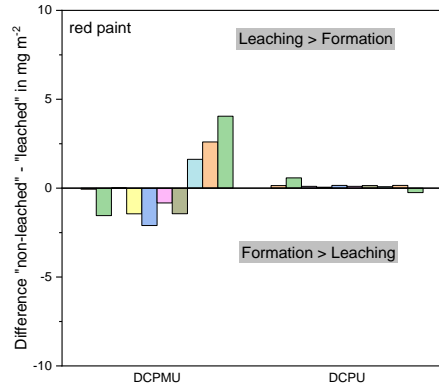
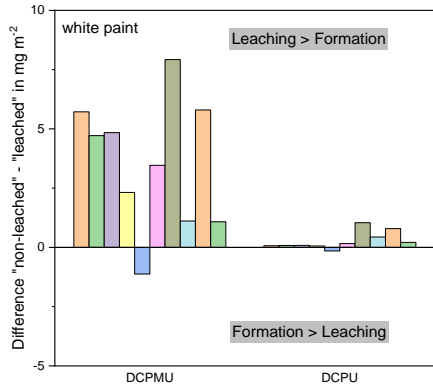
Differences for the amounts of transformation products of terbutryn in test specimens that were exposed to UV (“non-leached”) and test specimens that were exposed to UV and water (“leached”).

The differences of TBSO and TBOH tend to increase during the experiment in favor of the samples that were exposed to water contact, indicating that formation of these transformation products proceeds faster than leaching. This is especially pronounced in the white paint. In contrast to that, leaching of TB-DesE from the red paint is preferred to its formation.

Diuron and transformation products in paints



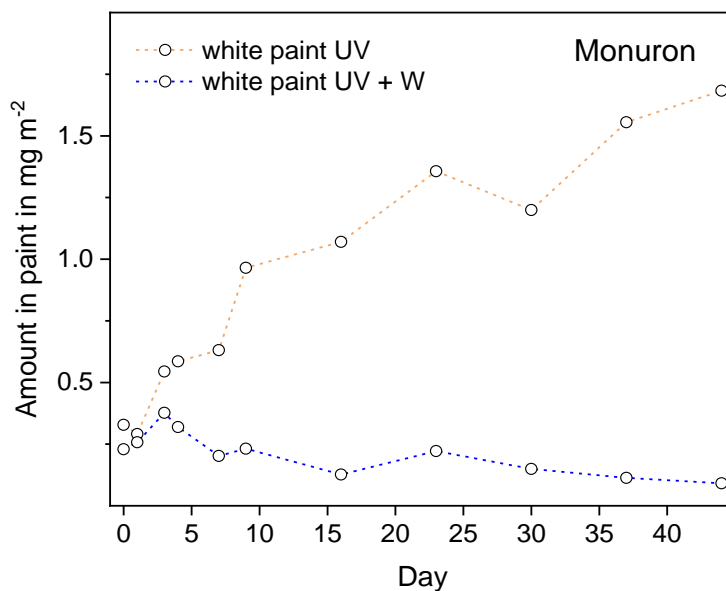
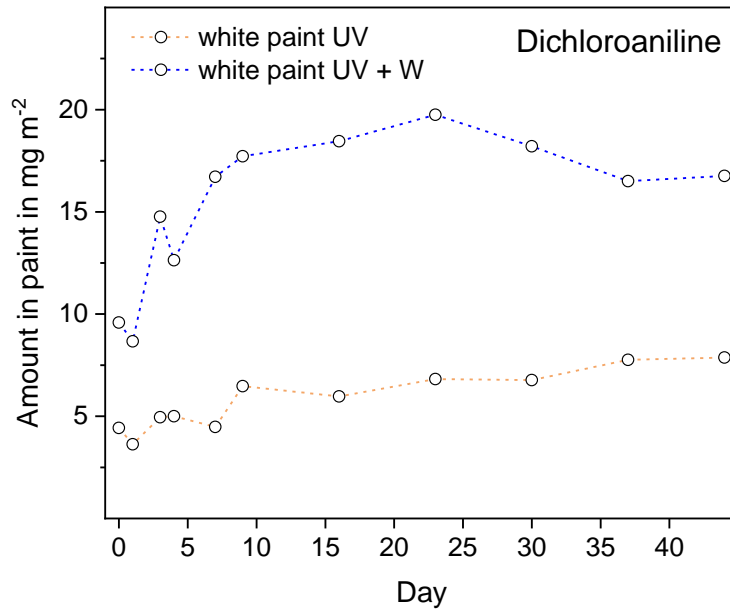
Amount of diuron and transformation products in the paint layers at selected days of the experiment.



Differences for the amounts of transformation products of diuron in test specimens that were exposed to UV (“non-leached”) and test specimens that were exposed to UV and water (“leached”).

Generally, the observed differences were very small. For DCPMU in the white paint, the differences slightly tend towards leaching in favor of formation.

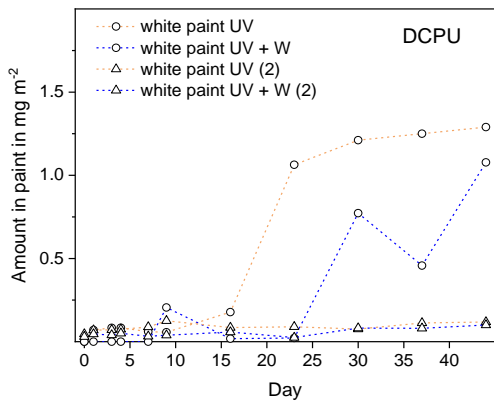
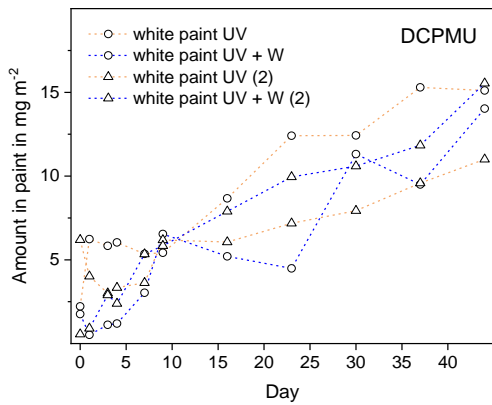
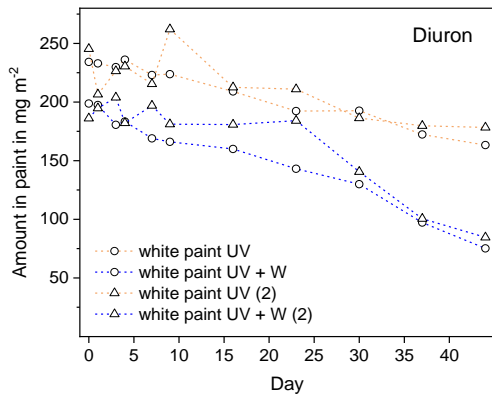
Results of post-test analysis of methanolic extracts from the white paint for additional transformation products of diuron



Amount of dichloroaniline and monuron in the paints at selected days of the experiment

Greater amounts of dichloroaniline were detected if the test specimens were exposed to water in addition to UV radiation. Small amounts of monuron were formed under the influence of UV radiation and probably effectively leached during the immersion cycles.

Comparison of the results from the original analysis and repeated analysis after long-term storage



Comparison of the results for diuron, DCPMU and DCPU at selected days of the experiment from the original analysis and the repeated analysis (2) after storage of the methanolic extracts for 3 years at 8°C

Results for diuron and DCPMU were in similar ranges for both analyses, whereas the small amounts of DCPU were not detected during the second analysis.