Leaching and Transformation of Film Preservatives in Paints Induced by Combined Exposure to Ultraviolet Radiation and Water Contact under Controlled Laboratory Conditions

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Abstract: Stormwater from urban areas can transport biocidally active substances and related transformation products from buildings into the environment. The occurrence of these substances in urban runoff depends on the availability of water, and on ultraviolet radiation exposure that causes photolytic reactions. In a systematic laboratory study, painted test specimens were exposed to either ultraviolet radiation, water contact, or a combination of both. Leaching of the biocidally active substances carbendazim, diuron, octylisothiazolinone, terbutryn, and selected transformation products of terbutryn and diuron were observed under various exposure conditions. Remaining concentrations of these substances in the paint were quantified. It was demonstrated that the distribution of active substances and transformation products in eluates and in the coatings themselves differs with exposure conditions. Strategies for environmental monitoring of biocide emissions need to consider the most relevant transformation products. However, environmental concentrations of biocidally active substances and transformation products depend on earlier exposure conditions. As a consequence, monitoring data cannot describe emission processes and predict expected leaching of biocidally active substances from buildings if the data are collected only occasionally.

Keywords: substance release; construction products; biocides; transformation; UV radiation; water contact

1. Introduction

Stormwater in urban area transports substances that originate from building materials and are mobilized by precipitation. Several studies demonstrated that biocidally active substances (hereafter referred to as "biocides") and transformation products occurred in urban runoff [1–6]. Film preservatives in coatings are a possible source [7–10]. These biocidal products are intended to migrate from the coatings into a water film on the surface and prevent the growth of algae and fungi on the building surfaces. Therefore, a certain water solubility of these substances is required, leading to unwanted transport with runoff water from buildings into the environment. The marketing and use of biocidal products, e.g., film preservatives (product type 7, PT 7), is regulated by the European Biocidal Products Regulation (BPR) [11]. This regulation requires an authorization procedure that includes environmental risk assessments. An estimate of the released amounts of biocides is basic information for this evaluation of environmental risks. However, biocides emission from building materials is a complex process [12] that depends on variable use conditions. The formation and release of transformation products is a particular challenge, not only in relation to the occurrence of numerous additional substances in water samples but also in relation to the possible environmental hazard of these substances. Transformation products are to be included in mass balances and risk evaluations. The transformation of terbutryn [9] and OIT (octylisothiazolinone) [10] from coatings was investigated in field studies. Analysis of transformation products in water samples was the subject of several

current studies [1–13]. Hensen et al. [14] propose an approach to evaluate the ecotoxicity of transformation products.

Usually, findings of biocides and transformation products in urban surface waters originate from occasional measurement campaigns. It can be expected that the reported concentrations depend on the actual exposure conditions and cannot describe the whole emission process. In addition, it is not clear whether monitoring results reflect low or high values during this process. Knowledge of conditions that influence the transformation of biocides can be useful in interpreting these randomly obtained results. Hydrolysis and photolysis can be expected to be the main transformation reactions in building materials that are exposed to outdoor conditions. Biocides in rather thin layers of coatings on the surfaces of buildings are intensely exposed to interaction via water contact and ultraviolet (UV) radiation, due to varying wet and dry phases.

Here, we present the results of a systematic study that was performed under controlled laboratory conditions. The experimental conditions were varied to investigate the combined influence of water contact and UV radiation on the leaching and transformation of biocides from film preservatives in paints. Test specimens were exposed to intermittent water contact according to the European standard EN 16105 [15], which was developed to determine the release of substances from coatings. UV radiation was applied in a weathering chamber using the same experimental parameters as in a previous study [16], since degradation of biocides was observed during the experimental period of about six weeks under these conditions. Three series of experiments were performed: (1) test specimens were exposed to water contact only, (2) test specimens were exposed to UV radiation only, and (3) test specimens were exposed to both water contact and UV radiation.

Selected for this study were two paint formulations, for which different patterns of transformation products due to UV radiation had been previously observed [16].

Eluates from the immersion cycles and extracts from the paint layers were analyzed for biocides and transformation products to observe the leaching of substances and their distribution in the remaining coating during the experimental period.

The results of this study demonstrate how the leaching of biocides from paints and the occurrence of selected transformation products in eluates and coatings are caused by exposure to water and/or UV radiation.

2. Materials & Methods

2.1. Paint Formulations

White and red styrene acrylate paints as used in a former study [16] were prepared and provided by the Dr. Robert-Murjahn-Institut GmbH (RMI), Ober-Ramstadt, Germany. The paints contained either titanium dioxide (TiO_2: white paint) or hematide (α-Fe_2O_3: red paint) and various film preservatives, i.e., diuron (CAS 330-53-1), terbutryn (CAS 886-50-0), octylisothiazolinone (OIT, CAS 26530-20-1), and carbendazim (CAS 10605-21-7), each active substance at a final concentration of 500 mg kg^{-1}. Terbutryn and diuron act as algicides, whereas carbendazim acts against fungi and yeasts, and 2-octyl-2H-isothiazol-3-one acts against fungi and bacteria [17]. The use of terbutryn, diuron, and OIT in film preservatives according to the BPR [11] is currently under evaluation by competent authorities. Carbendazim is already approved for film preservatives (PT 7) and for construction material preservatives (PT 10) under specific conditions that go into effect starting on 1 February 2022. It is defined as a substance for substitution, and products are not to be authorized for use in paints (PT 7) and plasters (PT 10) that are intended to be used outdoors [18]. The composition of the paints is given in Supplementary Material (Supplementary S1).

Preparation of test specimens

Two layers of paint (about 0.8 g wet paint for each layer) were manually applied on clean glass plates (5 cm $\times$ 5 cm). Initially, an area of 4 cm $\times$ 4 cm (16 cm^2) was framed by adhesive tape, and the paint was spread in the resulting cavity using a scraper. Additional layers of tape were added before applying the second paint layer. Afterward, the glass plates were allowed to dry for a minimum of two days. Fifty test specimens were prepared

for each paint, containing 0.56 ± 0.03 g weight of the dry white paint and 0.61 ± 0.04 g weight of the dry red paint per glass plate. The final amounts of each active substance were 239 ± 18 mg m^{-2} for the white paint and 258 ± 15 mg m^{-2} for the red paint. The test specimens were kept in a dark room at 21 ± 2 °C and $60 \pm 5\%$ relative humidity for five to ten days prior to UV exposure.

2.2. Exposure of Test Specimens to UV Radiation in a Weathering Chamber

The test specimens were exposed to UV radiation in a commercial UVTest® Fluorescent / UV Instrument (Atlas Materials Testing Technology, IL, USA) equipped with Atlas UVA-340 sunlamps generating a continuous spectrum (see Supplementary S2). The applied irradiation energy was 1.2 W m^{-2} at 340 nm, resulting in about 66 W m^{-2} for the applied UVA spectrum. The temperature inside the instrument was 40 °C. During UV exposure, the test specimens were kept dry. For this study, eleven out of nineteen time intervals from the schedule of the former experiment [16] were selected for sampling events, i.e., 0, 24, 72, 96, 168, 216, 384, 552, 720, 880, and 1056 h.

2.3. Exposure of Test Specimens to Water Contact

The test specimens had contact with water outside the setup for UV radiation, according to EN 16105 [15]—a standard procedure to investigate leaching from coatings by repeated immersion cycles. The test specimens were exposed to 2.5 mL cm^{-2} deionized water at 21 ± 2 °C for ten immersion cycles consisting of a first immersion event of 1 h followed by 4 h drying at 21 ± 2 °C and $60 \pm 5\%$ relative humidity and a second immersion event of 1 h.

2.4. Exposure Schemes

The two paints were investigated in separate experiments. The fifty test specimens for each paint were processed as follows: forty-four test specimens were arranged on sample holders for UV radiation. Twenty-two test specimens were exposed to UV radiation only (exposure scheme A). Two test specimens were successively removed from the setup at each sampling event for analysis. The remaining twenty-two test specimens were also exposed to UV radiation. In addition, these test specimens were removed from the UV radiation setup and exposed to water contact on the selected days of the sampling events before the next period of UV radiation, i.e., ten immersion cycles (exposure scheme B). Four test specimens were reversed in the sample holders so that the painted sides were not exposed to UV radiation, but to the same temperature and humidity as the other test specimens ("dark controls", "d", and "Ld"). Two "dark controls" were exposed to water contact at the end of the experiment ("Ld"). Two specimens were kept at 21 ± 2 °C and $60 \pm 5\%$ relative humidity in a dark room outside the UV radiation setup and were exposed to water contact only (exposure scheme C). UV radiation was interrupted during the immersion cycles to ensure the same duration of UV exposure for all test specimens. Two specimens were kept at 21 ± 2 °C and $60 \pm 5\%$ relative humidity in a dark room outside the UV radiation setup and were exposed to water contact only (exposure scheme A). The paint layers of these test specimens were extracted at the end of the experiment. See Figure 1 for an illustration of the exposure schemes.
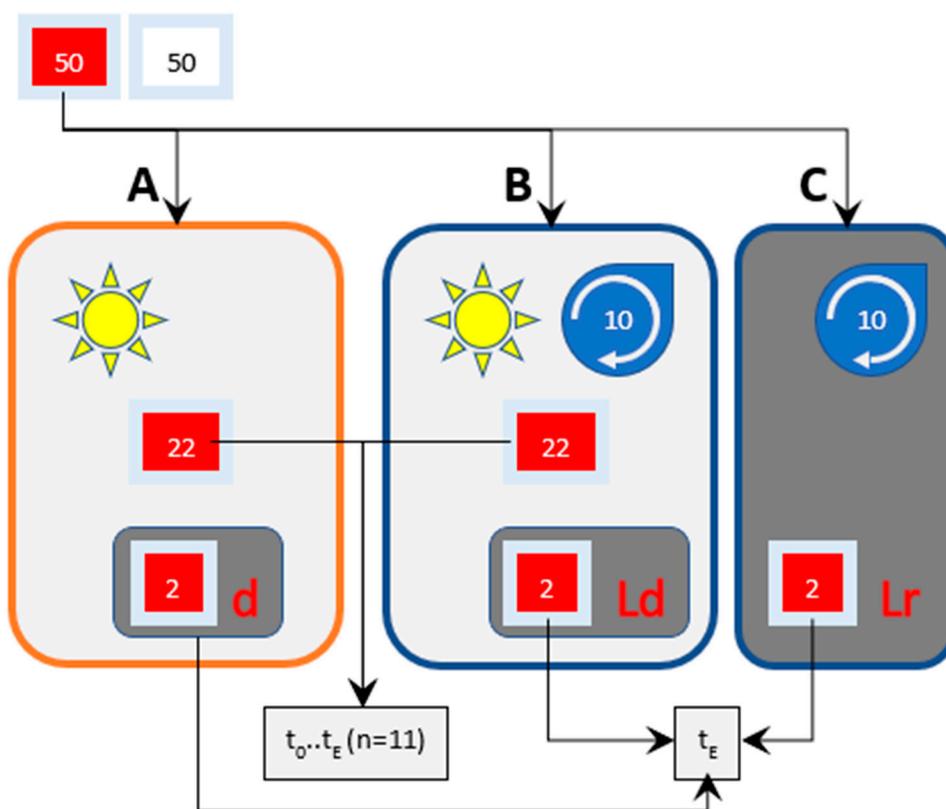
Figure 1. Illustration of exposure schemes (scheme only shown for red paint samples, white paint samples analog).

2.5. Sampling

The water samples from the two immersion events of each immersion cycle were combined, resulting in one eluate per sampling event. Two test specimens were successively taken after each immersion cycle for analysis of the paint layer.

The paint layers from each test specimen (duplicates for each sampling event) were almost completely removed from the glass plates with razor blades ($97 \pm 2\%$ of the original mass) and extracted with methanol (0.5 g of dry paint in 15 mL of methanol) in an ultrasonic bath for 1 h at 40 °C and 100% performance (SonorexSuper 10P, Bandelin, Berlin, Germany). The extracts were filtered through syringe filters (cellulose, 0.2 µm).

2.6. Analysis

Eluates and extracts from the paint layers were analyzed for biocides and transformation products by LC-MS analysis (liquid chromatography coupled to mass spectrometry). The samples were separated on a reversed-phase column using a gradient of acetic acid in water and acetonitrile. The analytes were quantified by means of the mass signals and external calibration using a single quadrupole mass spectrometer. See Supplementary S3 for details on the analytical method.

Several transformation products of terbutryn that proved to be important in the former study [16] and two demethylation products of diuron were quantified. Besides the four active substances, the following seven transformation products were quantified in eluates from the immersion cycles and extracts from the paint layers using calibration standards (see Supplementary S4 for information on the standard substances): 2-hydroxy terbutryn (TBOH, 4-(ethylamino)-6-[(2-methyl-2-propanyl)amino]-1,3,5-triazin-2(5H)-one, CAS 66753-07-9), desethyl-2-hydroxy-terbutryn (TBOH-DesE, 4-amino-6-[(2-methyl-2-propanyl)amino]-1,3,5-triazin-2(5H)-one, CAS 66753-06-89, desethyl terbutryn (TB-DesE, N-(2-methyl-2-propanyl)-6-(methylsulfanyl)-1,3,5-triazine-2,4-diamine CAS 30125-65-6), ter-

butryn sulfoxide (TBSO, N-ethyl-N'-(2-methyl-2-propanyl)-6-(methylsulfinyl)-1,3,5-triazine-2,4-diamine, CAS 82985-33-9), terbumeton [(4E)-4-(ethylimino)-6-methoxy-N-(2-methyl-2-propanyl)-1,4-dihydro-1,3,5-triazin-2-amine, CAS 33693-04-8], desmethyl-diuron (DCPMU, 1-(3,4-dichlorophenyl)-3-methyl urea, CAS 3567-62-2), and diuron-desdimethyl (DCPU, 3,4-dichlorophenylurea, CAS 2327-02-8). The extracts from the white paint were re-analyzed for additional transformation products of diuron, i.e., monuron (CAS 150-68-5) and dichloroaniline (CAS 95-76-1), after long-term storage for about 3 years at 8 °C.

2.7. Determination of Recovery Rates

Recovery rates for the analysis of active substances from dry paints were determined for paint formulations with known concentrations of active substances. Recovery rates of transformation products from dry paints were calculated by spiking biocide-free formulations of the red and white paint with known amounts of transformation products. The paint samples were applied on glass plates, and the extraction process was performed as described above. The recovery rates were considered when calculating results.

2.8. Screening for Potential Transformation Products Using Mass Spectroscopy Methods

Solutions of either terbutryn or one of the selected transformation products (TBOH, TBOH-DesE, TB-DesE, TBSO, terbumeton) in water (10 mg mL^{-1}) were prepared from stock solutions in methanol (1 mg mL^{-1}) and either exposed to UV radiation from UV lamps (254 nm or a spectrum with its maximum at 350 nm) or kept in the dark (control) under ambient conditions for 48 h. The solutions were qualitatively analyzed for the active substances and their transformation products by LC-MS using the methods on standards described in Supplementary S3. To identify further TPs where standards were not available, we analyzed the samples using high-resolution mass spectrometry (HRMS, Sciex TripleTOF) coupled to LC under conditions as described above. Here, we used a two-step process. First, we identified all peaks that showed at least five-fold intensity in radiated samples vs. control samples. Second, we grouped these peaks to obtain compound spectra, which were evaluated manually. Chemical formulas were assigned to compounds based on the exact mass (considering the measurement error of <2 ppm and limiting the allowed chemical elements to the ones contained in the irradiated precursor). Where unambiguous formulas could be assigned, MS/MS spectra were evaluated to obtain the molecular structure. The device was operated in IDA mode (independent data acquisition), i.e., MS/MS spectra were not confounded and were of mass precision <5 ppm. This approach allowed us to identify 17 compounds as listed in Supplementary S4.

A similar experiment was performed using diuron and its transformation products DCPMU, monuron, dichloroaniline, and 3-(3,4-dichlorophenyl)-1-formyl-1-methylurea (final concentration in water 100 mg mL^{-1}), identifying 16 TPs (Supplementary S4).

3. Results and Discussion

3.1. Leaching of Active Substances

The four biocides were leached from the paints in the experiment that was based on the EN 16105 standard [15]. As observed in earlier experiments [19], the leached amounts of terbutryn (1.1 to 2.4% of the original amount) and carbendazim (3.3 to 4.9% of the original amount) were in similar ranges and lower than emissions of diuron (9.2 to 12.5% of the original amount) and OIT (9.5 to 14.1% of the original amount). Emission of active ingredients was reduced when test specimens were additionally exposed to UV radiation (see Figure 2). This was expected for terbutryn, diuron, and OIT, as previous experiments [16] demonstrated photolytic degradation of these substances when dry test specimens were exposed to UV radiation. In contrast to terbutryn, diuron, and OIT, we expected emission curves to be more similar for carbendazim in experiments with and without UV radiation, since this substance was less sensitive to photolysis in experiments on water samples [20] and dry paints [16]. In our experiments, leaching of carbendazim was lower also in the UV-exposed samples in this experiment. It cannot be ruled out that

the combined exposure to water contact and UV radiation increased the transformation of carbendazim in the paints. Changes in the polymer matrix due to UV exposure can also be a reason for decreased leachability of carbendazim. However, structural changes within the polymer matrix and binding of the active substances in the matrix were not investigated during this study.
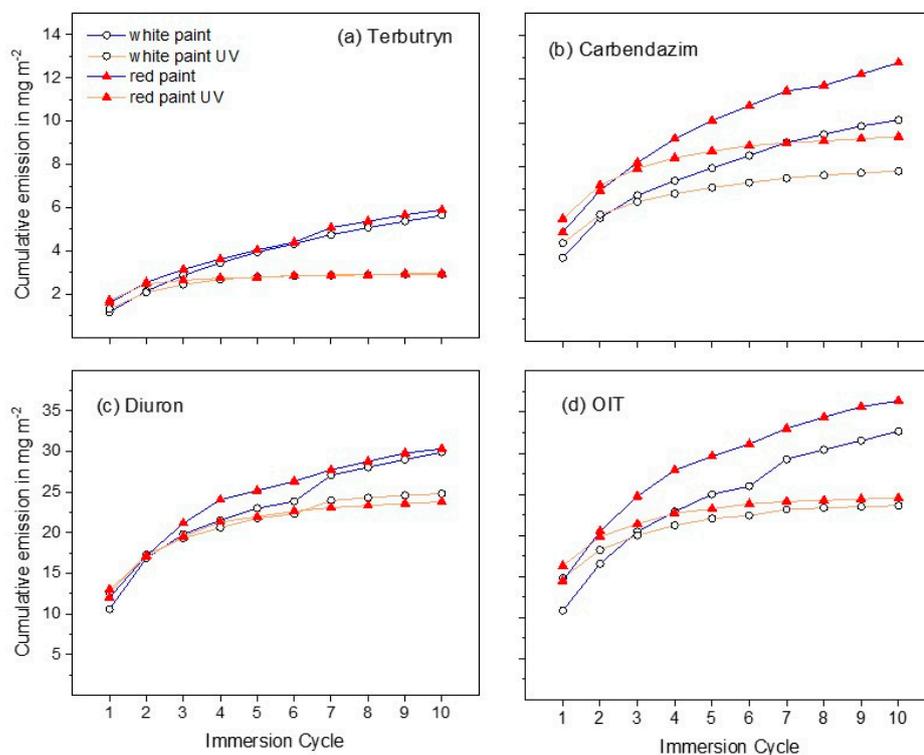

Figure 2. Cumulative emission curves for active substances from paint layers that were exposed either solely to water contact according to the immersion cycles as defined in EN 16105 [15] or to water contact combined with UV radiation. Each data point in the graphs represents a single experiment without repetition.

Former EN 16105 experiments on the leaching of active substances from coatings indicated very good repeatability of parallel experiments within one laboratory (relative standard deviations between 1 and 6%) [19]. Therefore, it is assumed that the curves from the different experiments can be compared, although the leaching tests were performed only once for each sampling event and exposure scheme.

3.2. Terbutryn and Transformation Products in Eluates

Besides terburyn, several transformation products of this substance were detected in eluates from the immersion cycles using test specimens that were kept in a dark room at 21 ± 2 °C and 60 ± 5% relative humidity between the immersion cycles and using test specimens that were exposed to UV radiation (see Figure 3). TBSO, TB-DesE, and TBOH were observed in eluates from both exposure schemes, whereas TBOH-DesE was observed only in eluates from test specimens that were exposed to UV radiation. As a secondary transformation product formed from the primary transformation product TBOH, this substance occurred only during later periods of the experiment. Small amounts of TBSO (mainly in the white paint eluates), TB-DesE, and TBOH (in eluates from both paints) were also leached from test specimens that were exposed only to water contact (see also the emission curves of the transformation products presented as Supplementary S5). Terbumeton was not detected in the eluates.
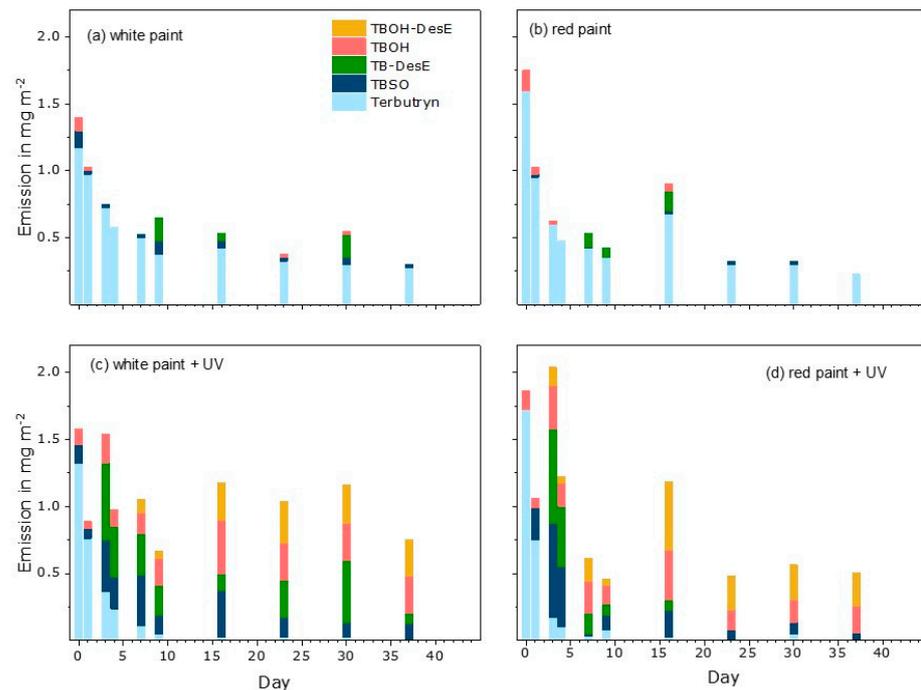
Figure 3. Emission of terbutryn and transformation products during immersion cycles. Upper row: test specimens were kept in a dark room at 21 ± 2 °C and 60 ± 5% relative humidity between the immersion cycles; lower row: test specimens were exposed to UV radiation at 40 °C between the immersion cycles. Each column represents a single experiment. The first data points for both experiments on either white or red paint layers can be considered independent repetitions and indicate the variability of results between test specimens.

The first data points of both exposure schemes represent test specimens that were immersed in water for a total of 2 h, but not exposed to UV radiation. The terbutryn concentrations in the eluates from the two test specimens from exposure scheme C and in the eluate from the twenty-two test specimens from exposure scheme B differed by 11% for the white paint and 7% for the red paint (ratio between results for scheme C and scheme B). The differences in the small amounts of TBOH were about 10% for both paints, and the difference in the small amount of TBSO that was detected in the white paint was 9%. These deviations allow us to follow trends within and between the different experimental series (see also emission curves in Supplementary S5).

The patterns of transformation products clearly differ for eluates from the two exposure schemes. UV radiation resulted in considerably lower amounts of terbutryn and greater amounts of transformation products in eluates. In eluates from the red paint, the amounts of the primary transformation products TBSO, TB-DesE, and TBOH decrease faster during the experiment with additional UV exposure than in eluates from the white paint. This observation probably indicates that transformation proceeds faster in this paint.

3.3. Diuron and Transformation Products in Eluates

Results for diuron and its transformation products are presented in Figure 4. Only the demethylation products DCPMU and DCPU were quantified as possible transformation products of diuron. Traces of DCPMU and DCPU were observed in the test specimens of the white and red paint at the beginning of the experiment, i.e., DCPMU and DCPU in the eluates do not necessarily indicate transformation during the first immersion cycle.
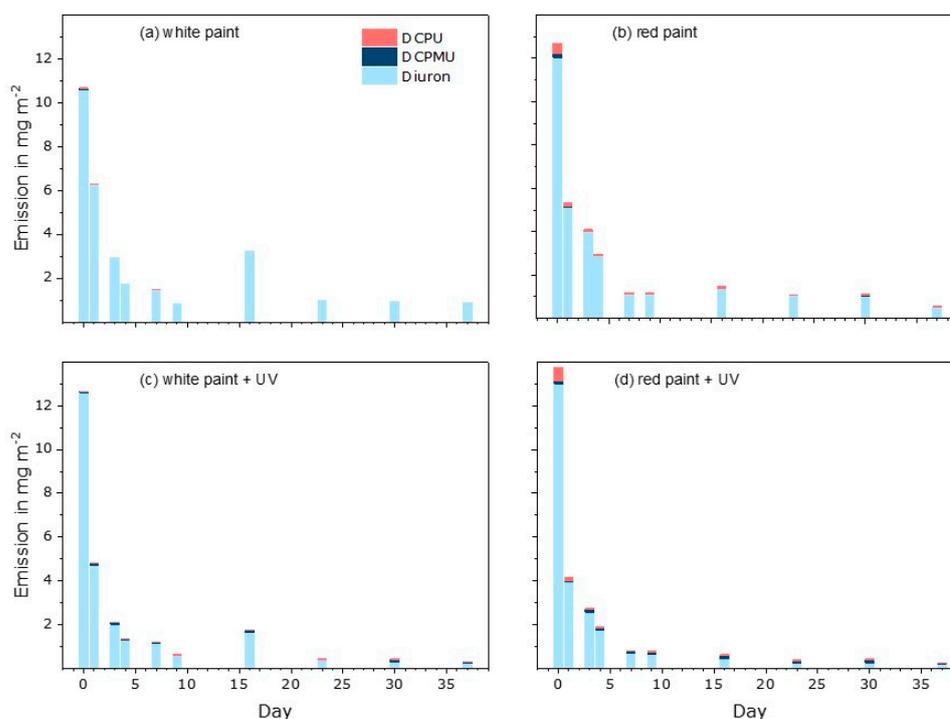

Figure 4. Emission of diuron and transformation products during immersion cycles. Upper row: test specimens were kept in a dark room at 21 ± 2 °C and 60 ± 5% relative humidity between the immersion cycles; lower row: test specimens were exposed to UV radiation at 40 °C between the immersion cycles. Each column represents a single experiment. The first data points for the two experiments on either white or red paint can be considered independent repetitions and indicate the variability of results between test specimens.

The first data points of both exposure schemes represent test specimens that were immersed in water for a total of 2 h, but not exposed to UV radiation. The diuron concentrations in the eluates from the two test specimens from exposure scheme C and in the eluate from the twenty-two test specimens from exposure scheme B differed by 16% for the white paint and 8% for the red paint (ratio between results for scheme C and scheme B). The differences in the small amounts of DCPU were about 20% for both paints, and the small amounts of DCPMU differed by 95% in the white paint and 40% in the red paint. These deviations seem to be high, but comparisons of trends within and between experimental series are still possible (see Supplementary S5).

DCPMU was leached from both paints after UV radiation, with slightly greater amounts from the red paint. It was almost not observed in eluates from test specimens that were exposed only to immersion cycles and stored in a dark room at 21 ± 2 °C and 60 ± 5% relative humidity between the immersion cycles. Leached amounts of DCPU were greater for the red paint that already contained some DCPU at the beginning of the experiment. Ratios between DCPU and Diuron in the eluates were rather constant in the range of 2 to 6% if test specimens were exposed to water only, but increased to about 16% during the experiment with UV exposure. This indicates that DCPU was formed due to UV radiation, whereas water contact caused leaching of the available substance. A small

amount of DCPU was leached from the white paint later during the experiment, probably as a secondary transformation product from DCPMU (see also the emission curves in Supplementary S5)

3.4. Terbutryn and Transformation Products in Paint Extracts

Terbutryn and the investigated transformation products were detected in extracts from white and red paint both after UV radiation only and after UV radiation in combination with immersion cycles (see Figure 5). Terbumeton was detected in small amounts in addition to substances that were already observed in eluates. The amounts that were leached from these small amounts of terbumeton that were available in the paint layers may have resulted in concentrations below LOD in the eluates. The distributions of terbutryn and transformation products were similar in test specimens before UV exposure (S) and in the "dark controls" in the UV radiation setup for both paints (dark). The contents of terbutryn and transformation products in extracts from "dark controls" that were leached by one immersion cycle at the end of the experiment (Ld) and from the test specimens that were leached by ten immersion cycles (Lr) were similar. This can be explained by the very small amounts of substances (less than 3% of the original content of terbutryn) that were leached during the ten immersion cycles which were less than the variability of the amount of paint per test specimen (8% for the white paint and 6% for the red paint).
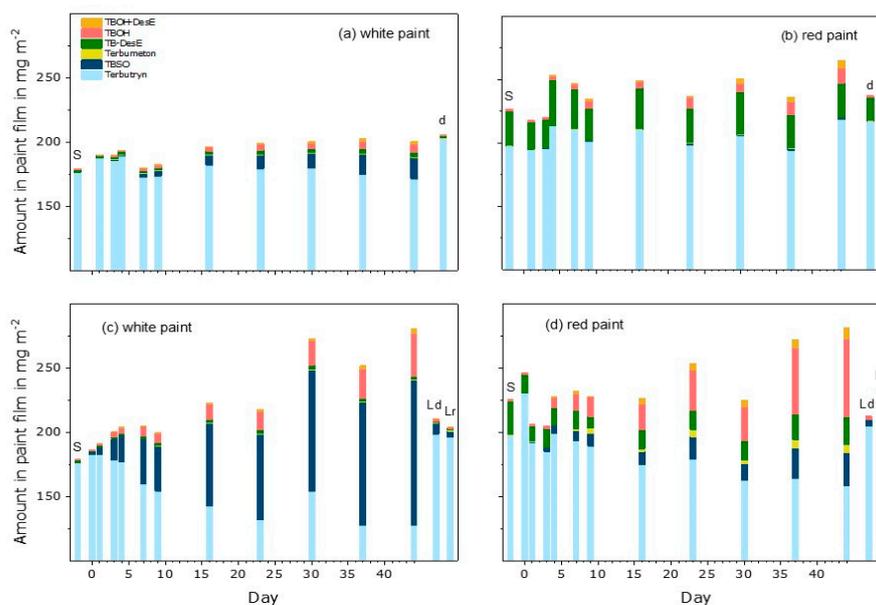

Figure 5. Amounts of terbutryn and transformation products detected in paint extracts. Upper row: test specimens were exposed to UV radiation at 40 °C; lower row: test specimens were exposed to UV radiation at 40 °C and water contact during immersion cycles. Extraction was performed after the immersion cycles. S: original amount detected in test specimens before start, d: test specimen was reversed in the sample holder, Ld: leaching test was performed with test specimens that were reversed in the sample holders (1 immersion cycle), Lr: leaching test was performed with test specimens that were stored at room temperature in the dark (10 immersion cycles). Each column represents mean values from two independently analyzed test specimens.

The graphs in Figure 5 illustrate that transformation is not only caused by UV radiation, but is also strongly supported by water contact, and that it differs between the investigated white and red paints (see also Supplementary S6). The patterns of transformation products and the amounts of terbutryn in the paint layers differ, if the test specimens are exposed to immersion cycles in addition to UV radiation.

Terbutryn content in the paint extracts was lower if the test specimens were exposed not only to UV radiation, but also to immersion cycles. This decrease is not necessarily

caused solely by leaching, but can also be caused by transformation reactions that depend on water contact. This is supported by the fact that the amount of terbutryn and its transformation products in eluates are lower than the difference in the remaining contents in the paints (see also Figures 2 and 3, Supplementary S5 and Supplementary S6). TBSO contents were greater in the white paint than in the red paint and increased with water contact in both paints, but especially in the white paint. Under the chosen test conditions, TBSO and TBOH tend to accumulate in the paints. This was especially pronounced for TBSO in the white paint (see Supplementary S6). Small amounts of terbumeton were observed mainly in the red paint after combined exposure to UV radiation and water contact. Results for TB-DesE from LC-MS analysis were affected by a matrix signal, so that the reported data probably overestimate the real values. The amounts of TB-DesE were greater in the extracts from the red paint, especially from test specimens that were exposed only to UV radiation, but were in similar ranges in the course of the experiments. Amounts of TBOH slightly increased during UV radiation in both paints, but to a greater extent when UV radiation was combined with immersion cycles. This increase was greater in the red paint than in the white paint. TBOH-DesE was detected only after at least four days of UV radiation. The amounts were increased if test specimens were exposed to immersion cycles in addition to UV radiation, and they were greater in the red paint than in the white paint. This is not necessarily caused by water contact (see also Figure 3 for the results in the eluates from test specimens without UV radiation), but probably depends on the availability of the primary transformation product TBOH.

Greater amounts of TBSO in the white paint than in the red paint were also observed for UV-exposed test specimens under the same experimental conditions [16]. Similar relative amounts of TBOH, TBOH-DesE, and terbumeton and the presence of TBOH-DesE only during later stages of the experiment were also observed in the previous study. However, smaller amounts of TB-DesE were detected in both paints in the former experiments. A certain amount of TB-DesE was probably already present in the red paint at the beginning of the current experiment (see data on test specimens before start "S" in Figure 5) and caused the observed differences between white and red paint.

A number of transformation products were detected by LC-MS and LC-HRMS in photolysis experiments in which we exposed aqueous solutions of terbutryn, TBOH, TBOH-DesE, TB-DesE, TBSO, and terbumeton (each as a single substance in water) to UV radiation at either 254 nm or to a spectrum with its maximum at 350 nm for 48 h. In addition to the investigated substances, detected mass signals correspond to terbutryn transformation products that were previously reported: desbutyl-terbutryn [1], desthiomethyl-terbutryn [9], desthiomethyl-desethyl-terbutryn [9], desthiomethyl-desbutyl-terbutryn [9], desbutyl-2-hydroxy-terbutryn [9], 2,4-diamino-1,3,5-triazin [21], 2-hydroxy-4,6-diamino-1,3,5-triazin [22], and terbutryn-TP-210 [1]. Desethyl-terbumeton is mentioned as a transformation product of terbumeton [23]. Furthermore, signals that correspond to the masses of desethyl-terbutryn sulfoxide and desbutyl-terbutryn sulfoxide were detected. The distribution of these substances differed between the two applied maxima of UV radiation. Not all signals could be assigned (unpublished data).

However, the transformation products that were selected for quantification in this study seem to include the main reactions of terbutryn, since the sum of all substances remains rather stable and approximately in the range of the original amount of terbutryn. The data presented in Figures 3 and 5 represent the detected amounts of the transformation products. The results for the transformation products were not recalculated in relation to the original amount of terbutryn. If large parts of terbutryn are transformed, this affects the calculated sum of all substances, since the molecules of most of the transformation products—except TBSO—are lighter than those of terbutryn (see Supplementary S4) and therefore lead to lower masses than the initial mass of terbutryn. The uncertainty of the measurement of transformation products is also influenced by the recovery rates, which had to be determined by a rather complex procedure. The results for the two test specimens that were analyzed in parallel for each sampling event were in similar ranges, i.e., the

results for each sample differed from the mean values in ranges between 1 and 5% for terbutryn, 5 and 11% for TBSO, 3 and 5% for terbumeton, 3 and 8% for TB-DesE, 2 and 7% for TBOH, and 7 and 11% for TBOH-DesE in the four experimental series (white and red paint, UV radiation only and UV radiation combined with immersion cycles).

The results of this study are summarized in Figure 6. TBSO, TB-DesE, and TBOH are generated by water contact as well as by UV radiation, whereas the reaction due to UV radiation is increased by occasional water contact. The secondary transformation product TBOH-DesE was observed only after UV radiation. Terbumeton was not observed in eluates from test specimens that were exposed only to water contact, but it was generated by exposure to UV radiation and was increased in the paint extracts after occasional water contact.
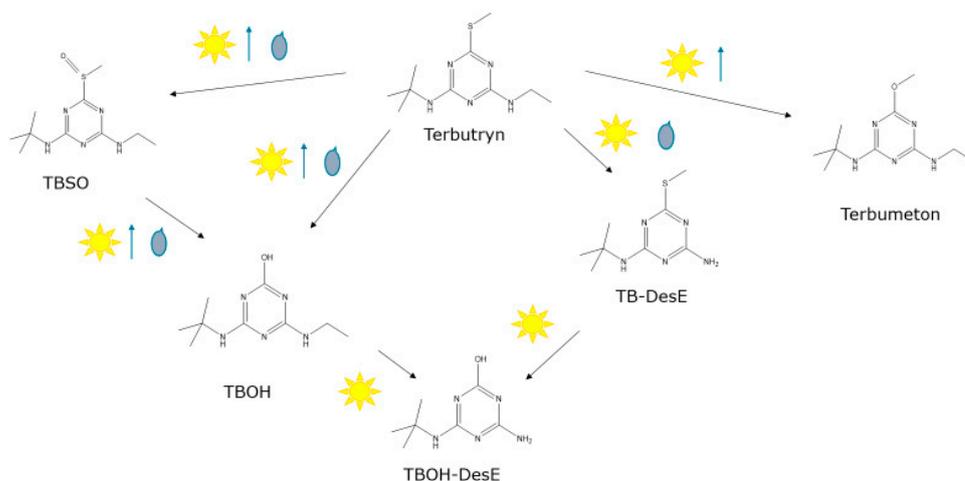

Figure 6. Transformation of terbutryn under different experimental conditions. The scheme is restricted to the transformation products that were observed during this study. It indicates whether reactions occurred due to water contact during immersion cycles (symbol: water drop), under UV radiation (symbol: sun), or if they increased if UV radiation was combined with immersion cycles (symbol: blue arrow).

Transformation of terbutryn depends not only on water contact and UV radiation. It can also be affected by the type of radiation and by the surrounding matrix. Terbutryn can also be metabolized by the enzymatic reactions of organisms [13]. Photodegradation of triazines, e.g., terbutryn, depends on the applied energy [24]. Different irradiation sources that cause either direct or indirect photolytic reactions produced different degradation rates of terbutryn in water [25]. Different patterns of transformation products were observed when the transformation of terbutryn was investigated either in water under laboratory conditions or in renders exposed to natural weathering. TBSO, TBOH, TB-DesE, and TBOH-DesE were the main transformation products in runoff from the renders, while desthiomethyl-terbutryn, TBOH, and TBSO were the main transformation products in the laboratory experiment on terbutryn in water. Terbutryn, TB-Des E, TBOH, TBOH-DesE, and a small amount of TBSO were detected in the render at the end of the experiment. Differences were observed between an acrylate-based and a silicone-based render [9]. Certain reactions of terbutryn were dominant in paints that contained titanium dioxide and iron oxide pigments [16]. Terbutryn sulfoxide was formed by biotic degradation in activated sludge [13].

3.5. Diuron and Transformation Products in Paint Extracts

The amount of diuron in the test specimens decreased during the experiments due to UV radiation (see Figure 7). This was already observed under the same experimental conditions in the previous study [16]. In the previous study, the remaining concentrations of diuron were slightly lower in the white paint than in the red paint. The current study could not confirm this, because analytical data for diuron in extracts from the red paint were inconsistent. Therefore, comparing this observation from both studies is not justified.
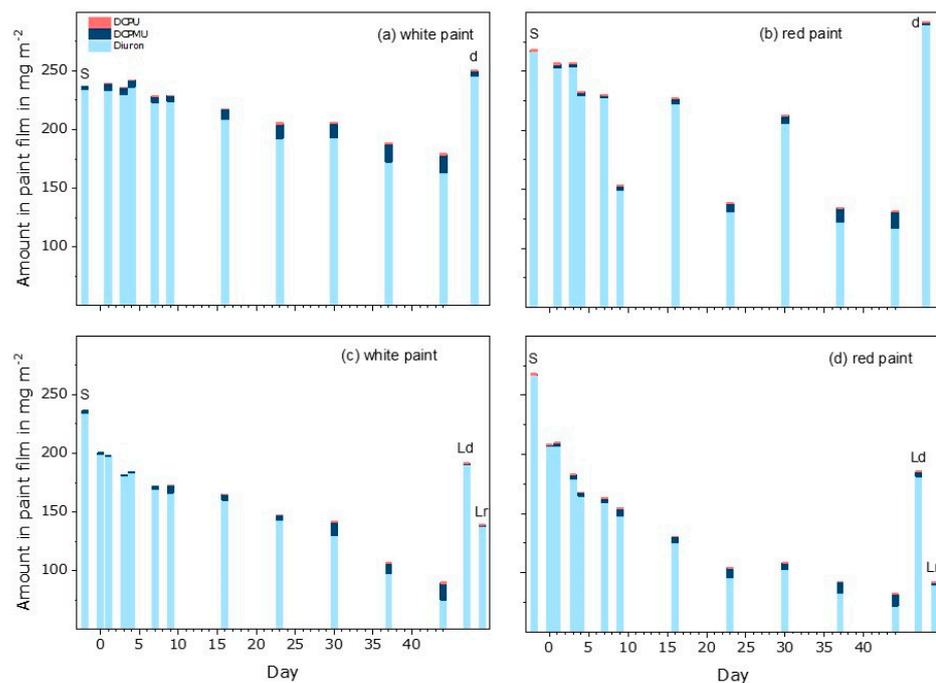
Figure 7. Amounts of diuron and transformation products detected in paint extracts. Upper row: test specimens were exposed to UV radiation at 40 °C; lower row: test specimens were exposed to UV radiation at 40 °C and water contact during immersion cycles. Extraction was performed after the immersion cycles. S: original amount detected in test specimens before start, d: test specimen was reversed in the sample holder, Ld: leaching test was performed with test specimens that were reversed in the sample holders (1 immersion cycle), Lr: leaching test was performed with test specimens that were stored at room temperature in the dark (10 immersion cycles). Each column represents mean values from two independently analyzed test specimens. Inconsistent data for diuron between 9 and 30 days for the red paint after UV radiation (upper row) are probably explained by outliers.

The amounts of diuron in the paint extracts were lower if the test specimens were additionally exposed to immersion cycles. As for terbutryn, the differences between the diuron content of the test specimens were greater than the amount of diuron and the two demethylation products in the leachates—at least for the white paint. The inconsistent data on diuron from one experiment on the red paint (see also Figures 2 and 4, Supplementary S5 and S6) prohibit drawing conclusions here. It can be assumed that this difference is explained not only by leaching, but also by transformation.

DCPMU content increased in the test specimens during all four experiments with slightly greater amounts in the white paint that was exposed to UV radiation. As mentioned earlier, DCPU was already present in the red paint before the experiment started. This content decreased during the first four days of the experiments with this paint. After that, the contents remained in a similar range. The amounts were slightly lower in the test specimens that were exposed to immersion cycles. This is consistent with the amounts of DCPU that were found in eluates at the beginning of the experiments with immersion cycles (see Figure 4 and Supplementary S5). The amounts of DCPU in the white paint

increased only after 16 days of UV exposure, and only after 23 days of UV exposure in combination with immersion cycles. This is probably caused by the formation of this secondary transformation product from its precursor DCPMU.

Moreover, for diuron and its transformation products, the results for the duplicate test specimens were in similar ranges, i.e., the results for each sample differed from the mean values in ranges between 2 and 5% for diuron, between 5 and 13% for DCPMU, and between 1 and 3% (31% in one series) for DCPU in the four experimental series.

In addition to DCPMU and DCPU, numerous signals were observed in aqueous solutions of diuron, DCPMU, monuron, dichloroaniline, and 3-(3,4-dichlorophenyl)-1-formyl-1-methylurea that were exposed to UV radiation at either 254 nm or to a spectrum with its maximum at 350 nm for 48 h both by LC-MS and LC-HRMS analysis. In addition to the investigated substances, detected mass signals correspond to substances that were already reported or can be assumed as transformation products of diuron, i.e., 3-(4-chloro-3-hydroxyphenyl)-1,1-dimethylurea, 3-(3-chloro-4-hydroxyphenyl)-1,1-dimethylurea [1,26–29], 1-(3-chloro-4-hydroxyphenyl)-3-methylurea [30], 3,4-dichlorophenyl isocyanate [29], 3-(3-hydroxyphenyl)-1,1-dimethylurea (fenuron), and 3-(3-hydroxyphenyl-1,1-dimethylurea (hydroxyfenuron). The formation of different dimers from fenuron and monuron [26] was also indicated by the observed mass signals. Different distributions of substances were observed for the two maxima of applied UV radiation. Several signals could not be assigned to an assumed structure. Monuron and 3-(4-chloro-3-hydroxyphenyl)-1,1-dimethylurea or 3-(3-chloro-4-hydroxyphenyl)-1,1-dimethylurea (hydroxyfenuron) was derived from diuron under these experimental conditions (unpublished data).

However, the sum of the amounts of diuron, DCPMU, and DCPU decreased considerably during the experiments and can be explained only partly by leaching during the immersion cycles.

Studies of transformation products of diuron in runoff from construction products have considered mainly DCPMU and DCPU. So far, the occurrence of 3-(4-chloro-3-hydroxyphenyl)-1,1-dimethylurea, 3-(3-chloro-4-hydroxyphenyl)-1,1-dimethylurea in runoff [1] and in eluates from façade coatings [22] was also reported. Repeated analysis of the extracts from the white paint after long-term storage indicated that dichloroaniline and monuron were also formed during the experiments. The formation of dichloroaniline was apparently supported by water contact during the immersion cycles. In addition, small amounts of monuron were identified in the samples. The amounts of monuron were greater in the samples that were exposed only to UV radiation, whereas these small amounts of monuron were probably effectively leached during the immersion cycles. Comparison of the results for diuron, DCPMU, and DCPU from the analysis directly after the experiment and of methanolic extracts after long-term storage indicates that data for the later analysis are still reliable. Only the very small amounts of DCPU were not observed during the repeated analysis (see Supplementary S6).

The results on diuron during this study are summarized in Figure 8. The reasons for different observations in the different experimental procedures were not investigated. It can be assumed that the occurrence of substances is influenced by different stabilities and further reactions under the actual experimental conditions.
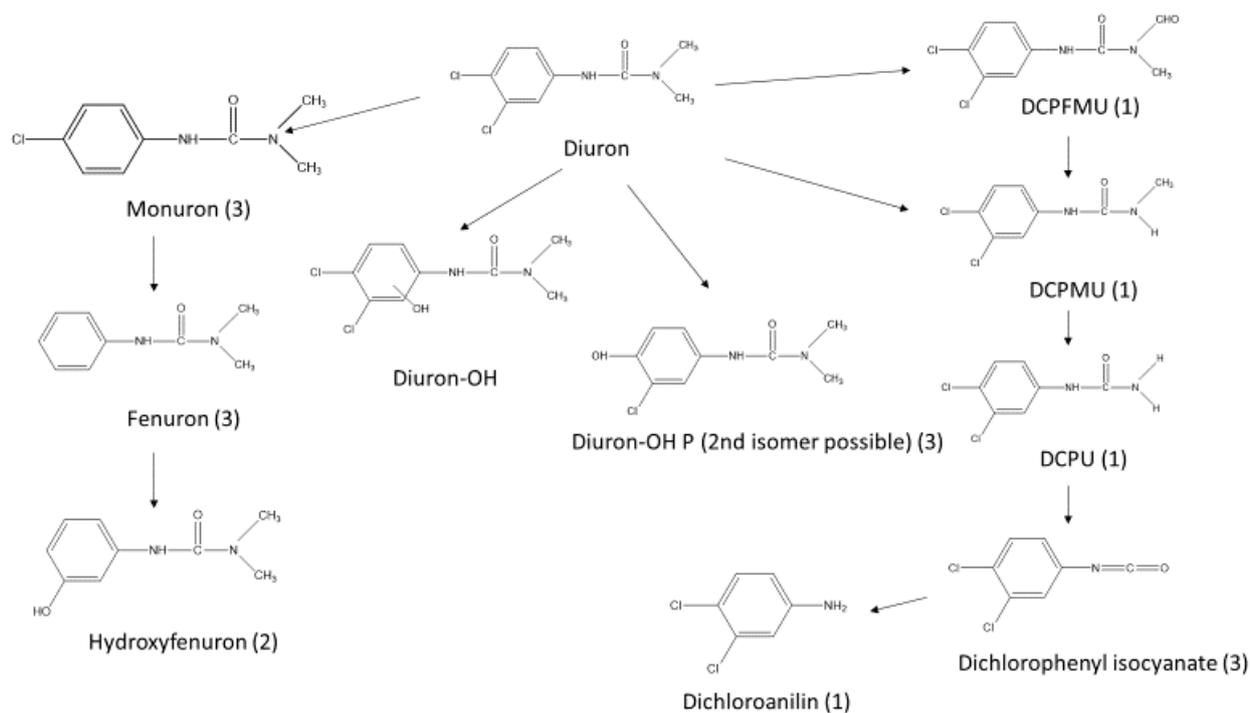
Figure 8. Possible transformation of diuron. (1) Substances were observed during the experiments on paints and confirmed by analysis of reference standards; (2) substances were indicated by the mass signals observed in samples from the photolysis experiments of substances in water; and (3) substances were detected in both experiments.

4. Conclusions

Laboratory experiments proved to be a useful approach to distinguish the effects of different weather parameters on the transformation of biocidally active substances in paints.

The results of this study demonstrate that different patterns of biocides and transformation products in coatings occur under the varying influence of water contact and UV radiation. The ratio between transformation products can also vary with pigments as was demonstrated for terbutryn. This is certainly the case not only under laboratory conditions, but also in stormwater from buildings that are exposed to natural weathering. Water contact and UV radiation are expected to be the main drivers that determine substance patterns also in runoff from constructions under real conditions. The concentrations of substances in eluates and runoff result from both transport and transformation processes. These processes run in parallel, with different optimum conditions. In addition, the processes depend on time, e.g., time for the diffusion of substances within wet materials and time for various hydrolytic and photolytic reactions. Changes in the composition of substances due to one process affect the other processes.

Under the applied laboratory conditions, the test specimens were constantly exposed to a high level of radiation energy for several weeks at a temperature above the mean temperatures of building surfaces. Water contact of the test specimens during the immersion cycles was more intense than natural precipitation. Therefore, the observed leaching and transformation processes will probably take more time under real weathering conditions, and the results from the laboratory experiments cannot be directly transferred to real conditions. Furthermore, not only quantitative, but also qualitative variations in the applied radiation energy influence the reactions of biocides and polymer matrix components. Nevertheless, the results of this study indicate the transformation products that can be released from coatings on buildings also under real weathering conditions.

The results of this study point out that the results from environmental monitoring data are snapshots. The observed concentrations of active substances and transformation

products depend on actual exposure conditions during the previous time period and do not allow us to describe emission processes and predict further emissions when the sampling frequency is not very high.

After intense exposure to UV radiation, the concentration of terbutryn was much lower than the concentrations of certain transformation products. Therefore, after long periods of UV radiation, terbutryn in a construction product can be noticed by its transformation products in runoff.

The results on diuron and its transformation products indicate that not only the demethylation products but also other degradation products that originate from these demethylation products, as well as monuron, which is formed by the dechlorination of diuron, can contribute to closing gaps in mass balances for the environmental fate of diuron from coatings.

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