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Leaching of Biocides Used in Façade Coatings under Laboratory Test Conditions

UTE SCHOKNECHT,*,†
JANA GRUYCHEVA,‡ HELENA MATHIES,†
HANNELORE BERGMANN,† AND
MICHAEL BURKHARDT§,∥

BAM Federal Institute for Materials Research and Testing, D-12200 Berlin, Germany, University of Chemical Technology and Metallurgy, BG-1756 Sofia, Bulgaria, and Department of Urban Water Management, EAWAG: Swiss Federal Institute of Aquatic Science and Technology, CH-8600 Dübendorf, Switzerland

The European Biocidal Products Directive 98/8/EC requires a risk assessment concerning possible effects of active ingredients on the environment. Biocides can be leached from treated materials exposed to outdoor use. These emissions have to be estimated and evaluated during the authorization procedure. Different immersion and irrigation tests were performed to investigate leaching of biocides from façade coatings. Several marketed formulations of textured coatings and paints spiked with a mixture of commonly used active ingredients (OIT, DCOIT, IPBC, carbendazim, isoproturon, diuron, terbutryn, and Irgarol 1051) were investigated. The emission process can be described by time-dependent functions that depend on the test conditions. The results of all test procedures confirm that leachability is related to water solubility and *n*-octanol–water partition coefficient of the active ingredients and that leaching of biocides from façade coatings is mainly a diffusion controlled process. Other factors like the composition of the product, availability and transport of water, concentration of active ingredients in the coatings, as well as UV-exposure of the coatings influence biocide emissions.

Introduction

Biocides are applied to protect materials and industrial processes from deterioration by organisms (1). Biocidal active substances are often used in renders and paints for exterior façade coatings to avoid growth of fungi and algae on the surfaces of buildings (1, 2). This applies especially to surfaces that get and stay wet either because of their chemical and physical structure or when effective insulation prevents drying of the surface, e.g., by external thermal insulation composite systems (ETICS). On wet surfaces, these biocides pass into the water and inhibit the growth of microorganisms. As a consequence, the biocides remain present in the runoff water and may reach the soil, surface water, or groundwater.

During the past decade, sources other than agricultural applications have been investigated to determine the cause of pesticides present in surface water and wastewater treatment plants. These investigations were initiated in response to observations that pesticides were found out of season for agricultural applications, when the use in agriculture had been forbidden for several years, or when the catchment area did not include an agricultural area (3–9). Environmental agencies initiated studies on the occurrence of biocides in surface water and wastewater and the possible impact of materials treated with biocides (10, 11).

The placing of biocidal products on the European market is regulated by the Biocidal Products Directive (BPD) 98/8/EC (12). The BPD requires a risk assessment concerning possible effects on the environment [see also the related Technical Guidance Document (TGD) (13)], which is based on the comparison of expected concentrations of active ingredients in the environment and ecotoxicity data of these substances. PEC (predicted environmental concentration) values must not exceed PNEC (predicted no effect concentration) values. Models for in-service situations are defined in Emission Scenario Documents (ESDs) (12) and serve as a basis for the calculation of PEC/PNEC ratios. The use of this concept is limited, since agreed test methods and interpretation procedures are lacking. Baines (14) demonstrates impressively that leaching data for active ingredients from preserved wood vary considerably between diverse test procedures. Different interpretations of these data result in divergent conclusions of the risk assessments.

Suitable and harmonized test procedures are required that allow the prediction of environmental concentrations. Products that are already on the market are examined within a rolling review program. This provides the opportunity to benefit from experience with previously known biocidal products for the development of risk assessment procedures in general, but also leaching tests in particular.

Materials treated with biocides that are exposed to water contact potentially release biocides. The release of active ingredients from treated materials is a process that is controlled by characteristics of the active ingredient and the material as well as the environmental conditions. Important parameters controlling the release of organic substances from materials into water are transport within the matrix (diffusion), water quality, coeluting substances, and degradation of the active ingredients (15).

Laboratory test methods are one approach to obtain data on the leachability of active ingredients from a certain matrix. Immersion tests that have been developed by OECD and CEN for the estimation of biocide emissions from treated wood into water (16–19) have already been evaluated (20, 21). The procedures are either based on permanent immersion or consist of wetting and drying cycles. Permanent immersion tests are commonly used to describe leaching of substances, e.g., from soil, sediment, waste, and construction materials. The procedures are simple and yield reproducible results. Many findings on leaching processes have been derived from these experiments (15, 22), and standardized methods are based on and developed using this approach. Short-term immersion tests are more laborious than permanent immersion tests. The experimental design is better adapted to service conditions than permanent immersion tests, since intermittent wetting and drying cycles allow transport of active ingredients to the surface of the coatings by evaporating water, although the immersion scheme has been developed to meet experimental requirements rather than environmental conditions.

* Corresponding author phone: +49 30 8104 1413; e-mail: ute.schoknecht@bam.de.
† BAM Federal Institute for Materials Research and Testing.
‡ University of Chemical Technology and Metallurgy.
§ EAWAG: Swiss Federal Institute of Aquatic Science and Technology.
∥ Current address: University of Applied Science, Institute of Environmental and Process Engineering UMTEC, CH-8640 Rapperswil, Switzerland.

TABLE 1. Description of the Test Formulations

code[a]	product	origin of the basic formulation without biocides	final concentration of the active ingredients (mg/kg)	amount of each active ingredient on the test specimens (mg/m^2)
R-A, R-B, R-C	render	commercial product	750	2250
R-B$_{500}$	render	commercial product	500	3500
R-B$_{variable}$	render	commercial product	250−2000[b]	1750−14 000
R-F	render	suggested formulation	750	2250
RP-A, RP-B, RP-C	render + paint	commercial product	750 (render) 1500 (paint)	3000
RP-F	render + paint	suggested formulation	750 (render) 1500 (paint)	3000

[a] Read the product codes as follows: 'R' and 'P' are renders and paints, respectively, that were provided without biocides by the producers A, B, and C and spiked with the biocide mixture for the leaching tests. The matrix for R-B$_{500}$ and R-B$_{variable}$ is the same as for the render R-B. R-F and RP-F are frame formulations that have been suggested for experiments with coatings. The compositions of R-F and the corresponding paint are given in the Supporting Information (Table SI-1). [b] Different concentrations for the active ingredients.

TABLE 2. Active Ingredients That Were Investigated in the Laboratory Tests

active ingredient	substance class	CAS-No.	molecular mass	water solubility (mg/L)	log K_{OW}[a]
1,2-benzoisothiazolin-3-one (BIT)	heterocyclic N,S compound[b] (isothiazolinone)	2634-33-5	151.2	1000	0.64[c]
2-n-octyl-4-isothiazolin-3-one (OIT)		26530-20-1	213.3	480	2.45[b]
4,5-dichloro-2-n-octyl-4-isothiazolin-3-one (DCOIT)		64359-81-5	282.2	14	4.9[b]
3-iodopropynylbutylcarbamate (IPBC)	carbamate[b]	55406-53-6	281.1	168	2.81[d]
carbendazim	carbamate[b] (benzimidazole)	10605-21-7	191.2	8	1.6[b]
isoproturon	amide[b] (urea derivative)	34123-59-6	206.3	65	2.5[e]
diuron		330-54-1	233.1	35	2.85[e]
terbutryn	triazine	886-50-0	241.4	22	3.65[e]
Irgarol 1051 (cybutryn)		28159-98-0	254.2	7	2.8[c]

[a] Logarithm of the n-octanol−water partition coefficient. [b] According to ref 1. [c] Data from ref 10. [d] Data from ref 12 "Assessment Report for IPBC". [e] Data from ref 23.

The purpose of this study was to investigate whether these procedures can be adapted for laboratory tests with façade coatings. The study was completed by irrigation experiments under laboratory conditions.

Specimens were coated with the test products and exposed to (I) permanent immersion in water, (II) short-term immersion in water, and (III) irrigation. Since photolysis may be a process limiting the concentration of active ingredients at the surface of the coatings, the influence of UV irradiation was investigated by treating some of the specimens in an accelerated weathering machine prior to the leaching tests. The test program allowed investigations on both the leachability of different active ingredients and the differences between coatings. Parallel runs of different laboratory methods with specimens from the same batch enabled conclusions to be drawn on the influence of test parameters, as well as the suitability of these methods, to generate reliable data with reasonable effort.

Material and Methods

Renders, Paints, and Biocides. Textured coatings (also referred to as "renders") and façade paints used in ETICS as well as biocide stock formulations were provided by manufacturers. The products were based on styrene acrylates (renders) and silicon resin binders (paints) and did not contain any of the investigated biocides. A biocide mixture containing carbendazim, diuron, isoproturon, IPBC, terbutryn, Irgarol 1051, OIT, and DCOIT was added to these products as described in the Supporting Information. These active ingredients are commonly used to protect exterior façade renders and paints from algal and fungal growth. In addition, the biocide mixture included BIT, which is commonly used for in-can preservation at concentrations between 75 and 400 mg/kg (1). All active ingredients were dosed in the renders and paints at equal concentrations, except one render (R-B$_{variable}$) that was spiked with the biocides at different concentrations. The composition as well as the concentrations of the active ingredients therefore differed from normal commercial products that are optimized for efficacy. It was intended to ensure comparability of the results for active ingredients as well as the matrices rather than providing emission data for certain products. As a consequence, some biocides were added at concentrations that were higher than in commercial products, whereas others were added at lower concentrations. It is a common practice for the concentration of the biocides to be higher in the corresponding paint than in the render.

See Table 1 for a description of the test samples and Table 2 for data on the active ingredients that have been investigated in the laboratory tests.

Preparation of Specimens. The textured coatings were directly applied to polystyrene. A mineral rendering (a component of ETICS) was not applied, since it was intended to avoid impact of additional materials on the leaching test. Despite this deviation, the coatings were applied according to producers recommendations for handling of these products (i.e., number of layers, applied masses, drying periods) to ensure optimum conditions and avoid possible impact of aging of the coatings. Polystyrene proved to be inert in preliminary leaching tests, and the coatings adhered well to this material.

Polystyrene panels (Styropor, WKI Isoliertechnik GmbH, Berlin; thickness 16 mm) were cut into sections of 245 mm × 285 mm and coated with the test products. After application

TABLE 3. Maximum Concentrations of Active Ingredients in Eluates from Different Leaching Experiments[a]

| | maximum concentrations of active ingredients in the eluates (mg/L) | | | | | |
| | Lab-ST | | Lab-PI | | Lab-IR | |
active ingredient[b]	median	range	median	range	median	range
BIT	13.2	4.6–18.1	50.1	33.5–55.3	24.5	20.7–57.2
OIT	3.8	2.4–5.3	10.2	6.8–15.1	4.9	3.9–8.2
IPBC	1.2	0.5–1.7	4.4	4.1–6.7	2.3	1.3–3.1
isoproturon	3.4	2.5–5.2	12.2	8.5–15.7	3.8	3.2–7.9
diuron	2.3	1.3 – 4.4	6.7	4.4–8.0	3.3	2.7–5.7
terbutryn	0.9	0.3–1.1	2.7	1.3–3.6	1.2	0.6–2.1
DCOIT	0.2	0.1–0.3	0.5	0.5–0.6	0.3	0.2–0.5
carbendazim	0.3	0.1–0.6	3.8	3.2–4.7	0.4	0.3–0.6
Irgarol 1051	0.8	0.4–1.0	2.3	1.2–3.4	1.3	0.5–1.7

[a] Only the exposure to water differed between the three types of experiments. The specimens were prepared according to the same procedure and originated from the same batch for each product. Water quality and temperature, handling, and analysis of the leachates were the same in all experiments. [b] Active ingredients are listed in the order of decreasing water solubility (data originate from Lab-ST experiments with eight products and Lab-PI as well as Lab-IR experiments with four products; data for R-B$_{500}$ and R-B$_{variable}$ are not included).

of the renders (usually 3 kg/m^2) the specimens were allowed to dry at 20 ± 2 °C and 65 ± 5% relative humidity. The first layer of paint (250 g/m^2) was applied after 4 days of conditioning and a second layer (250 g/m^2) 3 days later in the case of coatings that consisted of render and paint. The resulting dry masses were about 2.5 kg/m^2 for renders and 2.9 kg/m^2 for mixed systems of render and paint. Edges were not sealed.

The coated specimens were either used for irrigation experiments in their original dimensions or cut into pieces of 75 mm × 110 mm for immersion experiments. All specimens were allowed to dry for a minimum of 7 days. After that, a part of the specimens (two for each experiment) was exposed to UVA light in an accelerated weathering machine (QUV, Pausch Messtechnik) for 7 days with six cycles of 3 h irradiation and 1 h of darkness per day, resulting in an applied dosage of 22 J/m^2 (irradiance 48.6 W/m^2, i.e., 0.89 W/m^2 at 340 nm) prior to the leaching experiments. This procedure is based on an accelerated weathering protocol that is being discussed as part of the European Standard EN 152 for determining the protective effectiveness of a preservative treatment against blue stain in service (*24*). UV-A lamps produce a light spectrum similar to the conditions at noon during this procedure. The temperature within the QUV was 40–45 °C. In deviation from the original protocol, the specimens were not wetted during the UV exposure. Specimens that were not exposed to UV radiation were stored as described before. The leaching experiments were started directly after finishing UV exposure.

Test Procedures. Immersion procedures described in OECD documents (*16, 17*) were adopted for tests with façade coatings. A laboratory irrigation experiment was established to compare exposure by immersion and spraying.

Short-Term Immersion Tests (Lab-ST). Specimens with a coated surface area of 82.5 cm^2 were immersed in 200 mL of deionized water in separate polystyrene containers (183 mm × 136 mm × 60 mm) for 1 h, resulting in about 25 L of water per m^2 of coated surface area. The specimens floated on the water surface with the coated side downward. The leachates were collected in glass bottles, and the specimens were allowed to dry at 20 ± 2 °C and 65 ± 5% relative humidity for 4 h followed by a second immersion event of 1 h for each "immersion day". The two leachates per day were combined for each specimen and analyzed. The specimens were allowed to dry for a minimum of 42 h before the procedure was repeated for a total of nine immersion days.

Permanent Immersion Tests (Lab-PI). Specimens with a coated surface area of 82.5 cm^2 were permanently immersed in 200 mL of deionized water in containers as described for short-term immersions. The leachates were collected in glass bottles, replaced by deionized water, and analyzed after 0.25, 1, 2, 4, 8, 15, 22, and 29 days.

Irrigation Experiments (Lab-IR). Specimens with a coated surface area of 700 cm^2 were arranged on a 60° angled test assembly and irrigated with deionized water 10 times over 10 days. The water pressure and flow rate were controlled to provide water volumes of 2.5 L/m^2 within 2 min of irrigation per day.

Lab-ST experiments were carried out for all 10 products described in Table 1. Lab-ST experiments subsequent to UV radiation, Lab-PI, and Lab-IR experiments were run for six products (R-A, R-B$_{500}$, R-B$_{variable}$, R-F, RP-A, RP-F). All experiments were performed with two replicates at 20 ± 2 °C in air-conditioned test rooms with artificial lighting. Control experiments were performed with uncoated specimens. The volume and pH of the water samples and the mass of specimens were recorded for each sampling event. The difference of the masses before and after a leaching or irrigation event represents the water uptake of the specimens. Generally, the leachates were analyzed directly after sampling. Only a few samples had to be stored in glass bottles at 8 °C for, at most, 10 days before analysis. Control experiments confirmed that sorption of the active ingredients to the polystyrene containers can be neglected.

Analysis. A simultaneous liquid chromatography/mass spectrometry (LC/MS) method was developed that allows direct analysis of the leachates for nine biocides and a metabolite of terbutryn and Irgarol 1051 (for details, see Supporting Information).

Results

The concentrations of the biocides in the single leachates were related to time, i.e., either test duration or duration of water contact, to give a concentration profile for the experiment. Concentrations (mg/L) were converted into emission rates [mg/(m^2 d)] and cumulative losses (mg/m^2). The sum of all emissions of each substance was regarded as the total emission during the experiment either in mg/m^2 or in percentage of the initial amount of the active ingredient.

Concentrations. The maximum concentrations of the active ingredients in eluates of the different leaching experiments are summarized in Table 3. Maxima were usually determined for the first leachate in the Lab-ST experiments and for one of the initial irrigation events during the Lab-IR experiments. During Lab-PI tests, maximum concentrations were either observed for initial leaching periods or later when the duration of water contact increased. The concentrations
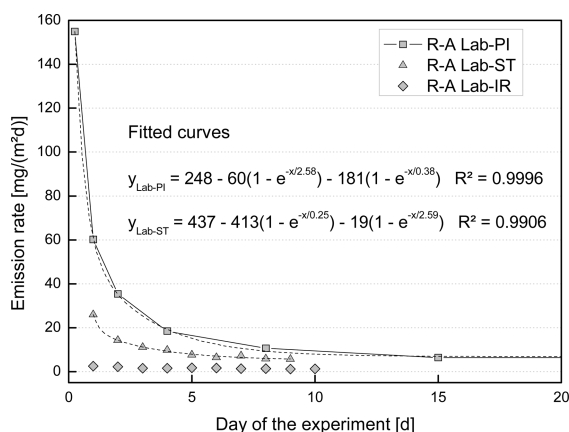
FIGURE 1. Emission rates of terbutryn from the render R-A from different laboratory tests. Data represent mean values of duplicate experiments. A continuous curve for Lab-PI experiments (dotted line) and single data points for the Lab-ST and Lab-IR experiments illustrate that the emission data were obtained from a permanent process and distinct leaching events, respectively. The emission rates calculated for certain sampling events of the permanent immersion tests represent integrated values for the previous leaching period. Equations and regression coefficients "R^2" apply to the fitted exponential functions (continuous lines) for Lab-PI and Lab-ST experiments. The data from the Lab-IR experiment could not be fitted with the selected exponential function.

of the biocides in the leachates decreased to about 25% of the maximum values during the Lab-ST experiments and to about 50% of the maximum values during Lab-PI and Lab-IR experiments.

The maximum concentrations in the eluates differed by a factor of about 3 between Lab-PI and Lab-ST experiments and about 1.5 between Lab-IR and Lab-ST experiments for the single active ingredients.

Emission Rates. The Lab-PI and Lab-ST experiments produced typical decreasing functions for emission rates over time that can be empirically approximated by the function $y = y_0 + A_1(1 - e^{-x/t_1}) + A_2(1 - e^{-x/t_2})$ (y, emission rates in mg/m^2 per immersion day; x, number of immersion days; A_1, t_1, A_2, and t_2, constants for each emission function). The emission rates for DCOIT varied within a certain range in some Lab-ST experiments and could not be fitted according to an exponential function. The emission of the active ingredients by irrigation either decreased or ranged within certain limits during the experiments (see Figure 1 for an example).

The maximum emission rates calculated from the concentrations of the active ingredients in the eluates are demonstrated in Table 4. The values differed by a factor of about 5 between the Lab-PI and Lab-ST experiments and 0.1 for the Lab-IR compared to the Lab-ST experiments.

Total Emissions. Total emissions ranged between 1 and 30% (60% for BIT) of the initial amount of the active ingredients for Lab-ST experiments, 3 and 50% (up to 100% for BIT) for Lab-PI experiments, and 0.1 and 5% (about 15% for BIT) for Lab-IR experiments, depending on the active ingredient and the test product. Total emissions obtained in Lab-ST experiments are summarized in Figure 2. The data for all experiments and ratios of total emissions between different experiments are given in Table SI-2 (Supporting Information). The correlation of total emissions of the single active ingredients in Lab-ST experiments is between 0.85 and 1.00 with Lab-IR experiments and between 0.57 and 0.98 with Lab-PI tests (see Table SI-3, Supporting Information).

Leaching Characteristics of Different Active Ingredients from Different Products. The total emissions roughly depend on the water solubility of the active ingredients and log K_{ow}

(see Supporting Information). In addition, biocide emissions were higher if renders were coated with a paint also containing biocides compared to the corresponding render without further coating. Data for different products were observed to be within certain ranges that were typical for the active ingredients. See Figure 2 for results of Lab-ST experiments. Lab-PI and Lab-IR experiments with R-A, R-F, RP-A, and RP-F yielded analogous patterns (not shown).

A detailed view of total emissions from single products results in different leaching patterns for the biocides in each product (see Figure 3 with data from Lab-ST experiments). Usually, biocides of the same chemical class tend to have similar ratios of leachability between products. However, the leachability of a certain biocide compared to the others can also vary between different products. Figure 4 demonstrates that the leachability of the biocides is similar for R-A and R-F in all experiments, but higher from RP-A and RP-F compared to R-F in Lab-ST and Lab-IR experiments, whereas Lab-PI tests tend to equalize the results for different products.

UV Exposure. UV exposure of the test specimens prior to the Lab-ST experiments caused lower concentrations of the active ingredients in the leachates, except for carbendazim (see Table SI-2, Supporting Information). The color of renders and paints changed from white to yellow during UV exposure, which indicates chemical changes of the components, e.g., IPBC.

2-(Methylthio)-4-(*tert*-butylamino)-6-amino-*s*-triazine (M1) is known to be a degradation product of the triazines Irgarol 1051 and terbutryn. This substance was identified retrospectively from the analytical data. M1 was only detected in leachates from test specimens that had been exposed to UV irradiation, but not in leachates from specimens that had been stored in the dark. The concentrations of M1 in the leachates ranged between 0.01 and 0.3 mg/L and yield similar emission curves with time as active ingredients. Emissions of terbutryn, Irgarol 1051, and M1 in Lab-ST experiments from specimens with and without UV exposure are illustrated for the products R-F and RP-F in Figure 5.

Discussion

Façade coatings are able to take up water during rain events. Water uptake is probably supported by the porous structure of renders, which also increases the surface area that is actually in contact with water.

The active ingredients that were added to the renders and paints were all detectable in the eluates of the different leaching tests. The test specimens caused an increase of pH in the test water (see Supporting Information). The active ingredients are expected to be stable at the observed pH values (pH 6−9), and analytical results should not be influenced by the pH stability of the substances.

The concentrations, emission rates, and total emissions of the active ingredients increased roughly with the water solubility and decreased with the *n*-octanol−water partition coefficient (K_{ow}) [Tables 3, 4, and SI-4 (Supporting Information) and Figures 2 and SI-2−SI-4 (Supporting Information)]. The wide ranges of the initial values do not represent differences between the products, since they are sensitive to small variations in the test conditions, e.g., the surface structure of the coatings. It has to be considered that the eluates from leaching tests not only contain biocides but also other constituents of the specimens, which can modify the solubility and distribution of the ingredients between leachates and coatings. Water solubility as well as log K_{ow} do not directly apply to the actual conditions in the leachates; therefore, these properties cannot be the only parameters used to explain the leachability of the biocides from a particular matrix. The leachability was most probably modi-

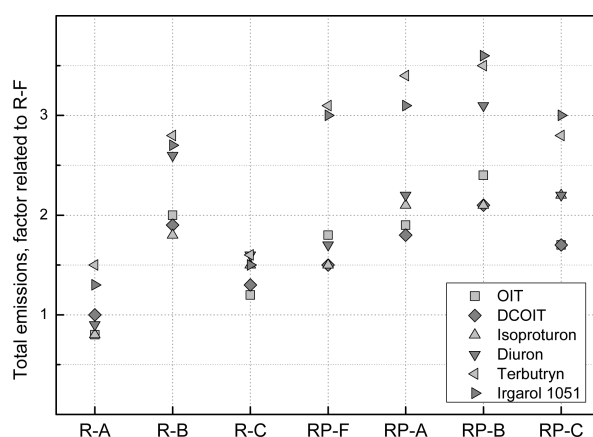| | maximum emission rates of active ingredients | | | | | |
| | Lab-ST mg/m^2 at 1 day of immersion | | Lab-PI mg/(m^2 d) | | Lab-IR mg/m^2 during one simulated rain event | |
active ingredient[b]	median	range	median	range	median	range
BIT	625	448−836	4651	3130−5041	58	56−155
OIT	178	111−254	919	634−1376	12	9−22
IPBC	57	23−82	244	164−332	6	3−7
isoproturon	173	114−239	965	735−1484	10	8−21
diuron	111	59−180	570	399−739	8	6−15
terbutryn	42	16−53	189	96−300	3	1−5
DCOIT	8	5−14	26	18−37	0.8	0.5−1
carbendazim	14	5−30	149	73−178	1	0.6−1.3
Irgarol 1051	40	17−47	196	97−270	3	1−4

[a] Only the exposure to water differed between the three types of experiments. The specimens were prepared according to the same procedure and originated from the same batch for each product. Water quality and temperature, handling, and analysis of the leachates were the same in all experiments. [b] Active ingredients are listed in the order of decreasing water solubility (data originate from Lab-ST experiments with eight products and Lab-PI as well as Lab-IR experiments with four products; data for R-B$_{500}$ and R-B$_{variable}$ are not included).
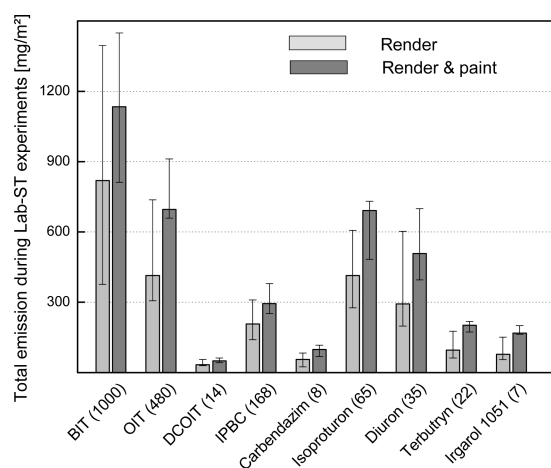
FIGURE 2. Total emissions of active ingredients in Lab-ST experiments with four renders (R-A, R-B, R-C, R-F) and four systems of render and paint (RP-A, RP-B, RP-C, RP-F). Columns represent median values; error bars indicate minimum and maximum values. Active ingredients are arranged according to decreasing water solubility within substance classes. Water solubility data of the active ingredients are given in brackets in mg/L. The original amounts of each active ingredient in the tests were 2250 mg/m^2 for renders and 3000 mg/m^2 for systems of render and paint. The data for the in-can preservative BIT were included in the figure to illustrate that highly water-soluble substances can easily leach, although this active ingredient is not intended to remain in the coating.

FIGURE 3. Total emissions of selected biocides from different products in Lab-ST experiments. The data for each biocide are given as factors of the results for the individual substances obtained for the render R-F.

fied by the chemical composition and/or physical structure of the coatings in all test procedures. Most likely, affinity of the organic substances to the matrix, dissolved organic carbon (DOC), surface structure, and porosity of the matrix are important factors in the case of façade coatings. Each product revealed characteristic leaching patterns for the investigated biocides (Figure 3). Since DOC can be a key parameter controlling the emission process, it is recommended to follow this parameter, especially when product formulations are optimized.

Emissions of biocides belonging to the same class, with similar water solubility, were in the same range, e.g., terbutryn compared to Irgarol 1051 and isoproturon compared to diuron. The emissions of the isothiazolinones OIT and DCOIT, with water solubility values of 480 and 14 mg/L, respectively, differed considerably. The emissions of the urea derivatives isoproturon and diuron were higher than expected from its water solubility values, whereas the results for DCOIT

were lower than expected. The data for carbendazim emissions were lower than expected from its log K_{OW} (see Supporting Information).

The concentration of the active ingredients is higher in the paints (1500 mg/kg) than in the render (750 mg/kg). The paints are situated on the surface of the render; therefore, the concentration of active ingredients on the surface—where water contact occurs—is higher for systems of render and paint compared to renders without further coats. Higher concentration of the active ingredients close to the surface caused higher emission. One cannot conclude from these experiments whether the active ingredients added to renders are retained by paints. However, the emissions of some active ingredients, i.e., BIT, OIT, isoproturon, and diuron, during permanent immersion (see Table SI-2, Supporting Information) were higher than the total amount of 750 mg/m^2 active ingredient in the paint layer. Therefore, a part of the resulting biocide must have originated from the render.

Leaching of biocides from materials over a longer period of time requires both transfer of the active ingredients from the material into water (dissolution) and transport within the matrix. Water evaporates while the coatings are drying, and in this way it transports dissolved components to the surface of the coatings. Log−log graphs of cumulative emissions with duration of water contact indicate that leaching is mainly controlled by diffusion (see Supporting Information). Increased emissions as a function of the duration of water contact in the short term immersion tests,
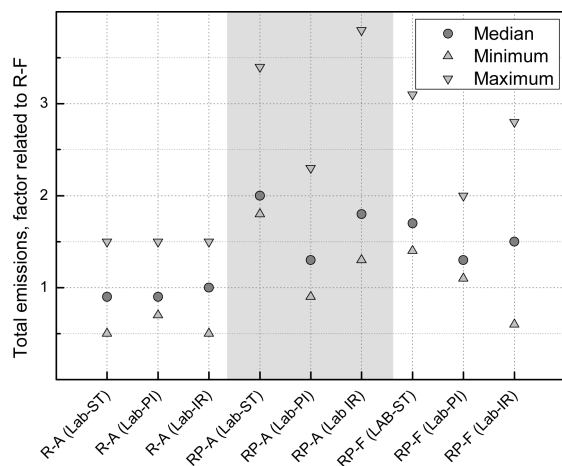
FIGURE 4. Ranges of total emissions of the investigated biocides (without BIT) in different experiments with the render R-A and the systems of render and paint RP-A and RP-F in relation to the results for the render R-F. The data are given as factors of the results obtained from the same test procedure with the render R-F. The ranges are described by median, minimum, and maximum values.
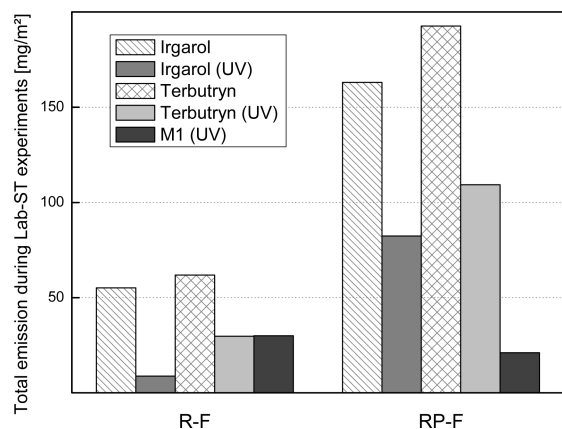
FIGURE 5. Emission of the degradation product M1 compared to emissions of Irgarol 1051 and terbutryn in Lab-ST experiments with specimens without and after UV exposure from the render R-F and the systems of render and paint RP-F.

i.e. intermitted wetting and drying, compared to permanent immersion (Figure SI-5, Supporting Information), are probably caused by the improved availability of the active ingredients at the surface of the coatings. However, consideration must also be given to the provisional supply of pure water.

Emissions mainly occur at the beginning of leaching periods. This was clearly shown by Burkhardt et al. (*25*), who analyzed active ingredients in subsequent water samples of the runoff water from façades that were exposed to irrigation in climate chambers. This is also supported by the observation that short-term immersion tests including nine times two immersion events of 1 h (i.e., 18 h of contact with water) caused only 4−7 times the emission of irrigation experiments with 10 rain events of 2 min (i.e., 20 min contact with water). The total amount of water applied during irrigation experiments was 25 L/m^2, whereas the same amount was available during each of the 18 immersion events.

The intensity of the UV radiation in the weathering machine (about 50 W/m^2) was lower than maximum values that façades can be exposed to by sunshine at noon under central European conditions. Bagda (*26*) reported maximum values between 800 and 900 W/m^2. However, the cumulative duration of UV irradiation in the weathering machine was

126 h. Obviously, UV irradiation affects the stability of active ingredients in coatings. UV-dependent degradation of triazines within the coatings is indicated by the detection of M1 in the eluates of UV exposed specimens. This substance was also detected in methanolic extracts of the coatings that have been exposed to UV irradiation without exposure to water, whereas it could not be detected in either eluates or extracts of coatings that had not been exposed to UV irradiation (data not shown). M1 does not seem to be the only degradation product of the triazines in coatings, since the amounts do not correspond to the differences between the triazine emissions from specimens that were either exposed to UV irradiation or stored in the dark (Figure 5). In any case, the influence of UV irradiation has to be considered for the assessment of long-term efficacy as well as expected environmental risks of biocides in façade coatings.

Photodegradation of Irgarol 1051 in water was already reported (*27, 28*). One of the degradation products is M1, which can also be formed by biodegradation. Evidence of Irgarol 1051 and M1 in marine sediments and coastal waters is attributed to the use of Irgarol 1051 as an antifouling agent. Irgarol 1051 and M1 were detected in surface water and sediment samples in Germany (*29*).

Irrigation experiments correspond best to the exposure conditions in practice. However, it is difficult to simulate the natural amount of rainfall within a certain period of time. Usually, nozzles require a relatively large amount of water (e.g., 2.5 L/m^2 within 2 min) to spray equally distributed water drops. It is impossible to harmonize irrigation tests without specifying the technical equipment. In addition, irrigation experiments are time-consuming. The amount of rain that was applied in the described test caused only low emissions of the active ingredients. This led to relatively poor repeatability and rates of emission against time that did not follow typical decreasing curves for some active ingredients.

Permanent immersion tests can be applied for façade coatings. However, façades are not commonly exposed to permanent water contact in practice, and this exposure seems to be unrealistic for coatings. The specimens were stable during permanent immersion, however, mass decline was observed at the end of the tests in a few cases.

Short-term immersion tests, including two immersion events of 1 h each per immersion day, were found to be adequate in terms of time and effort, concentrations of active ingredients in the eluates, and repeatability.

The highest concentrations of biocides in eluates were found under conditions of permanent contact with water, followed by those placed under conditions of contact with a small amount of water in the irrigation experiments.

Generally, permanent immersion with water resulted in approximately 2−4 times the amount released when compared with emissions released during short-term immersion tests (Table SI-2, Supporting Information). The immersion tests differed only in the exposure regime; design and age of the specimens and the test assemblies, water quality, temperature, handling, and analysis of the leachates were comparable. The ratio of the total emissions demonstrates that not only the duration of water contact (29 d, i.e., 696 h, of permanent immersion vs 18 h of short-term immersion) but also transport to the surface during the drying periods determines emissions.

The different test procedures led to the same conclusions on the relative leachability of the active ingredients in the coatings. The relationships of the total emissions between the test procedures were in a similar range for all active ingredients except for carbendazim (see Supporting Information). Short-term immersion and irrigation tests were more appropriate to distinguish different products concerning the

leachability of active ingredients than permanent immersion tests [see Table SI-3 (Supporting Information) and Figure 4].

These observations support the proposal to prefer short-term immersion compared to permanent immersion tests to investigate the leachability of biocides from coatings.

Laboratory tests can be designed as relatively simple and short procedures under controlled test conditions. Such experiments can provide information on the leaching process itself, and variations of single test parameters allow the investigation of specified factors. Certain parameters have to be standardized to ensure reproducibility of the tests. It has been demonstrated in previous leaching experiments, with preservative-treated wood, that the ratio between emitting surface area and water volume, as well as the sampling scheme, have to be defined. The emissions of active ingredients from wood do not differ between leaching experiments if the test water has a pH of either 5 or 7. The actual pH of the eluates is determined by the treated wood itself (20, 21, 30). This applies also to façade coatings. Moisture content and water transport within wood are regarded as crucial factors regulating the emission of active ingredients from wood into water. Lebow and Lebow (31) related emissions of copper, chromium, and arsenic from treated wood to different moisture contents of wood in different laboratory tests as well as under service conditions. The availability and transport of water within the façade coatings is also crucial for the leaching process from these products.

Product development benefits from the reproducibility of laboratory tests. Data as presented in Table SI-2 (Supporting Information) and Figures 1 and 3 do not only describe the leachability of active ingredients depending on the products composition but also identify favored active ingredients for a certain product formulation.

It remains problematical to use laboratory leaching data for active ingredients from materials to predict environmental concentrations. Simple laboratory tests cannot reflect all variable parameters that determine the duration of water contact, water uptake and water transport within materials, the amount of water that drips off from a surface, and the stability of the active ingredients under actual service conditions. Experiences from laboratory tests must be compared with experiences under actual conditions of use, to enable the application of laboratory test results for risk assessments. Lindner (32) compared diuron emissions from test specimens that were coated with an aqueous masonry emulsion paint based on an acrylic polymer and exposed to either outdoor weathering for 2 years or leaching in a laboratory test under tap water for 50 h. He observed a consistent ratio between both tests in terms of the diuron remaining in the paint over time.

The emission functions depend strongly on the experimental conditions and cannot be directly applied to service conditions (see Figures 1 and SI-6, Supporting Information). It has to be kept in mind that leaching under service conditions does not follow a steady leaching function because of changing conditions during the seasons, whereas laboratory data obtained under constant conditions do. Concentrations of biocides in eluates from laboratory tests are assumed to be relatively high compared to runoff from façades, since dilution and degradation are not regarded or even avoided. Concentrations of active ingredients reported for surface waters relating to other sources than agricultural use were found to be 0.05 μg/L up to maximum values of 0.1 μg/L for diuron in a medium size river in Switzerland (5); 0.01−0.1 μg/L for Irgarol 1051 in a small river in Switzerland (9); above 0.1 μg/L for terbutryn, Irgarol 1051, the triazine metabolite M1, and carbendazim in a sewer system of an urban area near Zürich (6); and 0.2−0.8 μg/L of terbutryn, in exceptional cases about 5 μg/L, in two small rivers in Germany (7).

Attempts have been made to predict environmental concentrations of active ingredients on the basis of laboratory data (8). This is encouraged by the fact that leachability is an intrinsic property of a substance in a certain matrix that can be described by leaching functions, depending on the test conditions.

Data originating from standardized leaching tests are necessary to develop harmonized risk assessment procedures. Furthermore, experiences from actual service situations are required in order to estimate the service lifetime being represented in laboratory testing to improve the reliability of predictions of environmental concentrations. The results reported here encourage the use of relatively simple test procedures like the described short-term immersion test. Whereas comparisons of slightly modified formulations can be a meaningful tool for product development, it should be possible to define models for certain types of coatings that can serve for risk assessments. Similar chemical composition and water transport within these matrices seem to be crucial properties for these models.

Acknowledgments

Supporting Information Available

Details on the preparation of the test products and on the analytical method as well as the complete data set for total emissions, correlation between diffent tests, data on pH-values of the leachates, the influence of water uptake of the coatings, water solubility and log K_{OW}, and concentration of the active ingredients on the emission; graphs describing the leaching process; and a discussion of the data for carbendazim. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Paulus, W., Ed. *Directory of Microbicides for the Protection of Materials—A Handbook*; Springer Netherlands: Dordrecht, 2005.

(2) Bagda, E.; Brenner, T.; Diel, K.-H.; Lindner, W.; Schied, G.; Warscheid, T.; Wunder T. *Biozide in Bautenbeschichtungen*; Expert-Verlag: Renningen, 2000.

(3) Bucheli, T. D.; Müller, S. R.; Voegelin, A.; Schwarzenbach, R. P. Bituminous roof sealing membranes as major sources of the herbicide (R,S)-mecoprop in roof runoff waters: Potential contamination of groundwater and surface waters. *Environ. Sci. Technol.* **1998**, *32*, 3465–3471.

(4) Skark, C.; Zullei-Seibert, N.; Willme, U.; Gatzemann, U.; Schlett, C. Contribution of non-agricultural pesticides to pesticide load in surface water. *Pest Manage. Sci.* **2004**, *60*, 525–530.

(5) Kupper, T.; Chèvre, N.; Burkhardt, M.; Rossi, L.; de Alencastro, F.; Boller, M. Release of biocidal products into aquatic systems: Determination and evaluation of sources, pathways and fate in urbanised areas. SETAC Conference, Cambridge, 2005; available at http://www.sea.eawag.ch/inhalt/sites/Publikationsliste/pdf/Artikel_Kupper_SETAC Cambridge_2005.pdf.

(6) Burkhardt, M.; Kupper, T.; Hean, S.; Haag, R.; Schmid, P.; Kohler, M.; Boller, M. Biocides used in building materials and their leaching behaviour to sewer systems. *Water Sci. Technol.* **2007**, *56* (12)), 63–67.

(7) Quednow, K.; Püttmann, W. Monitoring terbutryn pollution in small rivers of Hesse, Germany. *J. Environ. Monit.* **2007**, *9*, 1337–1343.

(8) Jungnickel, C.; Stock, F.; Brandsch, T.; Ranke, J. Risk assessment of biocides in roof paint. *Environ. Sci. Pollut. Res.* **2008**, *15* (3)), 258–265.

(9) Steinmann, P.; Niederhauser, P. *Pestiziduntersuchungen bei den Hauptmessstellen Furtbach Würenlos und Glatt vor Rhein im Jahr 2007*; Baudirektion Kanton Zürich, AWEL (Amt für Abfall, Wasser, Energie und Luft): Zurich, 2008, pp 63.

(10) Bürgi, D.; Knechtenhofer, L.; Meier, I. Projekt BIOMIK, Teilprojekt 1: Biozide als Mikroverunreinigungen in Abwasser und Gewässern. 2007; available at http://www.bafu.admin.ch/gewaesserschutz/03716/06387/index.html?lang=de.

(11) Kahle, M.; Nöh, I. Biozide in Gewässern, Eintragspfade und Informationen zur Belastungssituation und deren Auswirkungen. UBA-Texte, 2009; available at http://www.umweltbundesamt.de.

(12) Directive 98/8/EC of the European Parliament and of the Council of 16th February 1998 Concerning the Placing of Biocidal Products on the Market. Available at http://ecb.jrc.ec.europa.eu/biocides/.

(13) Technical Guidance Document in support of Commission Directive 93/67/EEC on Risk Assessment for new notified substances, Commission Regulation (EC) No 1488/94 on Risk Assessment for Existing Substances and Directive 98/8/EC of the European Parliament and of the Council Concerning the Placing of Biocidal Products on the Market. Available at http://ecb.jrc.ec.europa.eu/tgd/.

(14) Baines, E. F. *Emission Rates of Active Substances from Preserved Wood in Use Class 3*; International Research Group on Wood Preservation, 2008, IRG/WP 08-50256, pp 18.

(15) Van der Sloot, H. A.; Dijkstra, J. J. Development of horizontally standardized leaching tests for construction materials: A material based or release based approach?—Identical leaching mechanisms for different materials; ECN-C-06-060, 2004; available at http://www.ecn.nl/publications.

(16) OECD guideline 313 (October 2007): Estimation of Emissions from Preservative-Treated Wood to the Environment: Laboratory Method for Wooden Commodities That Are Not Covered and Are in Contact with Fresh Water or Seawater. Available at http://www.oecd.org/dataoecd/26/19/39584884.pdf.

(17) OECD guidance for industry data submissions on the estimation of emissions from wood preservative-treated wood to the environment: For wood held in storage after treatment and for wooden commodities that are not covered and are not in contact with ground (July 2009). Series on Testing and Assessment No. 107. Available at http://www.oecd.org/dataoecd/42/31/43411595.pdf.

(18) CEN/TS 15119—1:2008: Durability of wood and wood-based products—Determination of emissions from preservative treated wood to the environment—Part 1: Wood held in storage yard after treatment and wooden commodities exposed in use class 3 (not covered, not in contact with the ground)—Laboratory method.

(19) CEN/TS 15119—2:2008: Durability of wood and wood-based products—Determination of emissions from preservative treated wood to the environment—Part 2: Wooden commodities exposed in use class 4 or 5 (in contact with the ground, fresh water or sea water)—Laboratory method.

(20) Schoknecht, U.; Mathies, H.; Wegner, R.; Melcher, E.; Seidel, B.; Kussatz, C.; Maletzki, D. The influence of test parameters on the emission of biocides from preservative-treated wood in leaching tests. Report, UFO-Plan 203 67 441; 2004; pp 161.

(21) Schoknecht, U.; Mathies, H.; Morsing, N.; Lindegaard, B.; van der Sloot, H.; van Zomeren, A.; Deroubaix, G.; Legay, S.; Tadeo, J. L., García-Valcárcel, A. I.; Gigliotti, G.; Zadra, C.; Hajšlová, J.; Tomaniová, M.; Wegner, R.; Bornkessel, C.; Fürhapper, C. Inter-laboratory evaluation of laboratory test methods to estimate the leaching from treated wood; Report (EU Grant Agreement No. 04/375757/C4); 2005; pp 211.

(22) Van der Sloot, H. A.; Heasman, L.; Quevauviller, Ph. *Harmonization of leaching/extraction tests. Studies in environmental science 70*; Elsevier: Amsterdam, 1997.

(23) Tomlin, C., Ed. *The Pesticide Manual*; British Crop Protection Council: Farnham, 1996.

(24) EN 152—1:1988: Test methods for wood preservatives; laboratory method for determining the protective effectiveness of a preservative treatment against blue stain in service; part 1: Brushing procedure; 1988.

(25) Burkhardt, M.; Junghans, M.; Zuleeg, S.; Schoknecht, U.; Lamani, X.; Bester, K.; Vonbank, R.; Simmler, H.; Boller, M. Biozide in Gebäudefassaden—Ökotoxikologische effekte, auswaschung und Belastungsabschätzung für Gewässer. *Umweltwiss. Schadst. Forsch.* **2009**, *21* (1)), 36–47.

(26) Bagda, E. Beschichtungen im Wetter. *Farbe Lack* **1985**, *91* (7)), 595–599.

(27) Okamura, H.; Aoyama, I.; Liu, D.; Maguire, J.; Pacepavicius, G. J.; Lau, Y. L. Photodegradation of Irgarol 1051 in water. *J. Environ. Sci. Health* **1999**, *B34* (2), 225–238.

(28) Okamura, H.; Sugiyama, Y. Photosensitized degradation of Irgarol 1051 in water. *Chemosphere* **2004**, *57*, 739–743.

(29) Schmidt, R.; Berghahn, R.; Feibicke, M.; Mailahn, W.; Meinicke, S.; Mohr, S. Field, fate and effect studies on the biocide *N-tert*-butyl-*N'*-cyclopropyl-6-methylthio-1,3,5-triazine-2,4-diamine—Irgarol (CAS No 28159-98-0). Umweltbundesamt Report; May 2007, pp 140.

(30) Schoknecht, U.; Wegner, R.; Horn, W.; Jann, O. Emission of biocides from treated materials—Test procedures for water and air. *Environ. Sci. Pollut. Res.* **2003**, *10* (3), 154–161.

(31) Lebow, S.; Lebow, P. *The role of moisture content in above-ground leaching*; International Research Group on Wood Preservation, 2007; IRG/WP 07-50245, pp15.

(32) Lindner, W. Studies on film preservatives: Retention of DCMU on outdoor paints. *Biofouling* **1997**, *11* (3), 179–189.