Chair of Hydrology

University of Freiburg

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Modelling of Biocide Emissions with ComleamD

Primary Supervisor: Prof. Dr. Jens Lange

Secondary Supervisor: Prof. Dr. Olaf Tietje

Master thesis under supervision of Prof. Dr. Jens Lange

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“In nature nothing exists alone.”

- Rachel Carson, Silent Spring

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Abstract

Biocides are used in paints and renders to mitigate the growth of algae and fungi on housing façades. With façades being exposed to weathering and wind driven rain, biocides and their transformation products are leached into the environment. To gain insight into the yet not well understood leaching processes of biocides and their transformation products field experiment data of three studies from Denmark, France and Germany regarding the biocide terbutryn were examined. It was shown that transformation products form a majority of overall emissions. However, knowledge of transformation products and their ecotoxicology is still scarce. Based on the findings of previous studies and in close collaboration with the founders of the biocide leaching modelling software COMLEAM, the extension ComleamD was tested and further developed. ComleamD offers the possibility of modelling parent compound emissions as well as transformation product formation and emissions. In a tiered approach three sequential emission scenarios including decay, diffusion and solar radiation were used to model the emission of terbutryn and its transformation products. The model was tested using field data of three examined studies. Based on goodness of fit values, it was shown that ComleamD is capable of modelling biocide and transformation product emission accurately, regarding quantity and temporal progression. The tiered approach showed an improvement in model performance along the sequential emission scenarios. Transferability to other biocides and the modelling of multiple biocides and their transformation products is possible. ComleamD is therefore emphasized as valuable tool for further biocide modelling and a holistic risk assessment including transformation products.

Keywords: Biocides, Terbutryn, Modelling, Transformation Products, COMLEAM, ComleamD, Leaching, Façades

Zusammenfassung

Biozide werden in Anstrichen und Putzen verwendet, um das Wachstum von Algen und Pilzen an Gebäudefassaden einzudämmen. Da Fassaden der Witterung und Schlagregen ausgesetzt sind, werden Biozide und ihre Transformationsprodukte in die Umwelt ausgewaschen. Um einen Einblick in die noch nicht gut verstandenen Auslaugungsprozesse von Bioziden und ihren Transformationsprodukte zu erhalten, wurden Daten von Feldversuchen aus drei Studien aus Dänemark, Frankreich und Deutschland in Hinsicht auf das Biozid Terbutryn untersucht. Es zeigte sich, dass Transformationsprodukte einen Großteil der Gesamtemissionen ausmachen. Das Wissen über Transformationsprodukte und ihre Ökotoxikologie ist jedoch gering. Auf Grundlage der Ergebnisse früherer Studien und in enger Zusammenarbeit mit den Entwicklern der Biozid-Auswaschungsmodellierungssoftware COMLEAM wurde die Erweiterung ComleamD getestet und weiterentwickelt. ComleamD bietet die Möglichkeit, sowohl die Emissionen von Ausgangsverbindungen als auch die Bildung und Emission von Transformationsprodukten zu modellieren. In einem mehrstufigen Ansatz wurden drei sequentielle Emissionsszenarien, einschließlich Zerfall, Diffusion und Sonneneinstrahlung, zur Modellierung der Emission von Terbutryn und seiner Transformationsprodukte verwendet. Das Modell wurde anhand von Felddaten aus drei untersuchten Studien getestet. Anhand der Anpassungsgüte wurde gezeigt, dass ComleamD in der Lage ist, die Emission von Bioziden und ihrer Transformationsprodukte hinsichtlich der Menge und des zeitlichen Verlaufs akkurat zu modellieren. Der mehrstufige Ansatz zeigte eine Verbesserung der Modellleistung entlang der sequentiellen Emissionsszenarien. Eine Übertragbarkeit auf andere Biozide und die Modellierung mehrerer Biozide und ihrer Transformationsprodukten ist möglich. ComleamD wird daher als wertvolles Werkzeug für die weitere Modellierung von Bioziden und einer ganzheitlichen Risikobewertung unter Einbeziehung von Transformationsprodukten hervorgehoben.

Stichwörter: Biozide, Terbutryn, Modellierung, Transformationsprodukte, COMLEAM, ComleamD, Auswaschung, Gebäudefassaden.

1. Introduction

Building façades are exposed to weathering. Wind driven rain and condensation lead to moisture in the façade and therefore a vulnerability to microbiological growth (Bollmann et al. 2014). Especially modern external thermal insulation composite systems (ETICS) offer good growing conditions due to the increased moisture as a result of insulation and therefore increased condensation (Breuer et al. 2012). Typically, ETICS are finished with an organic resin render as exterior layer further increasing microbiological activity in the façade (Bollmann et al. 2016). To inhibit the growth of microorganisms like algae, bacteria and fungi in façades biocides are added to construction materials like mortar, render and paints (Vega-Garcia et al. 2022). To be able to inhibit growth, the active substance has to be soluble to be able to operate in the dissolved phase, where microbiological growth occurs which makes the active substance susceptible to leaching by wind driven rain (Burkhardt et al. 2012). Therefore, leaching processes of active substances in paints and renders pose a potential threat to surface and groundwater bodies.

The Biocidal Products Regulation (BPR) of the European Union states that biocides are necessary to control organisms that are harmful to human health and to prevent damage to manufactured materials (European Union 2012). The BRP also states that use of biocidal products must not negatively affect human or animal health or have unacceptable effects on the environment. Also, the EU Water Framework Directive (WFD) of 2000 states that a good chemical status of the surface water and groundwater has to be ensured. Furthermore, point three of the EU regulation 305/2011 for the marketing of construction products states that the protection of health, the environment and workers has to be ensured (European Union 2011). The EU regulation on “Registration, Evaluation, Authorisation and Restriction of Chemicals” (REACH) from 2007 states that the risk of chemical substances towards human health and the environment has to be assessed and identified (European Union 2006).

The usual amount of biocides in paint and renders for exterior coatings varies between 0.1 to 1.5 % (Paulus 2005). This leads to an estimate of 3.9 million tons of biocides used for coatings in Europe in 2005 that can potentially leach in the environment (Burkhardt et al. 2007). It can be assumed that relevant emissions to the aquatic system exist for many biocides (Kahle and Nöh 2009). One widely used algaecide in exterior paints and renders is terbutryn (Paulus 2005).

Triazines like terbutryn (2-(t-butylamino)-4-(ethylamino)-6-(methylthio)s-triazine) have been banned in agricultural use in the EU since 2003 because of their toxicity to aquatic organisms, algae toxicity due to photosynthesis inhibition (Jurado et al. 2011) and danger to drinking water supplies due to their persistence in aquifers (Quednow and Püttmann 2007). Nevertheless, terbutryn and other biocides like carbendazim, diuron and octylisothiazolinone are still widely used in paints, renders and mortars to prevent the growth of fungi, algae and bacteria on housing façades (Vega-Garcia et al. 2022). Therefore, leaching of these biocides from façades poses a potential environmental threat.

Several studies have shown biocide concentrations in façade runoff (Bollmann et al. 2014; Bollmann et al. 2016; Bollmann et al. 2017; Burkhardt et al. 2009; Burkhardt et al. 2012; Hensen et al. 2018; Junginger et al. 2023; Linke et al. 2021; Schoknecht et al. 2016a; Schoknecht et al. 2016b; Vega-Garcia et al. 2020; Wicke et al. 2022). Most studies showed high biocide or transformation product (TP) concentrations in the façade runoff exceeding threshold values for drinking water and some even exceeding the German threshold values for surface water (Wicke et al. 2022). Also, biocides and their transformation products (TPs) used in paints and renders have been detected in surface waters (Quednow and Püttmann 2007) and in groundwater (Linke et al. 2021). In surface waters in Germany measurements of terbutryn even exceeded drinking water threshold values after dilution in two small river systems (Kahle and Nöh 2009).

Beside the potential threat of biocides themselves TPs can also have an effect on the environment and have to be taken into account (Kahle and Nöh 2009). Especially considering that TP emissions exceed parent compound emissions by up to eightfold (Schoknecht et al. 2016b). TPs are usually characterised by a higher mobility compared to parent compound (Kahle and Nöh 2009). Persistence and toxicity of metabolites are often unknown, and cumulative effect and combination effects can have a severe impact on the environment and human health. This was exemplified by the previously unknown TP dimethylsulfamid of the parent biocide tolylfluanid leading to the genesis of carcinogens when contaminated waters are ozonated for drinking water production (Kahle and Nöh 2009). Several recent studies emphasize the importance of TPs for overall risk assessment (Bollmann et al. 2016; Bollmann et al. 2017; Hensen et al. 2020; Junginger et al. 2022, 2023; Schoknecht et al. 2016a; Schoknecht et al. 2016b; Urbanczyk et al. 2019; Vega-Garcia et al. 2022; Wicke et al. 2022).

Therefore, measurements have to be taken to ensure that the use of biocides in housing façades does not negatively affect human health, the environment or the chemical quality of surface water and groundwater. On-site treatment of the façade runoff is a possible mitigation solution, however expensive and currently still not developed (Vega-Garcia et al. 2020). Prevention of pollution in the first place is therefore key to reduce emissions (Wicke et al. 2022). Furthermore, a comprehensive estimation of the leaching of biocides and their TPs is necessary in order to make policy decisions toward safe concentrations of biocides in paints, renders and mortars. The development of a comprehensive model can provide a valuable risk assessment tool and the possibility of determining biocide threshold values for paints and renders that ensure that emissions of active substances and their TPs only occur at concentrations and magnitudes that are negligible and have no effect on the environment.

1.1 Timeline of Research Publications

Studies on the emissions of biocides from building materials have been conducted for more than 40 years (Cockroft and Laidlaw 1978). However, most studies were focused on wood preservatives and leaching data were mostly only available for those wood preservatives (Schoknecht et al. 2003). Schoknecht et al. (2003) conducted a study on lab scale using test chambers to simulate weathering and leaching behaviour of different building materials and active components such as octylisothiazolinon, tolyfluanid, dichlofluanid, iodopropinylbutylcarbamat, propiconazole and permethrin. The studies of Schoknecht at the Federal Institute for Materials Research and Testing (BAM) of Germany laid the foundation for various recommendations and regulations.

Quednow and Püttmann (2007) monitored terbutryn concentrations of four small rivers in central Germany. Even though terbutryn has been banned from agricultural use since 2003 it was detected in every measurement and the mean concertation of two rivers even exceeded the German drinking water threshold value for single biocides (Quednow and Püttmann 2007). Highest concentrations were measured in the Weschnitz River with 5.6 µg/l exceeding the PNEC value of 0.034 µg/l. Quednow and Püttmann (2007) state that other sources than agriculture must explain terbutryn concentrations in winter, when usually no pesticides are being applied. Also, high terbutryn concentrations of sewage treatment plants effluents indicate an urban input path of biocides into rivers.

Burkhardt et al. (2007) states an increasing concern in contamination of surface and ground water by substances used in rural and urban areas. Furthermore, it is stated that “knowledge on the high diversity of substances applied in urban areas and their transport behaviour to receiving soil or waters bodies is still a new issue” (Burkhardt et al. 2007, p. 63). Burkhardt et al. (2007) studied the fate and behaviour of nine biocides used in building protection and established that building material properties have an impact on leaching behaviour.

Fenner et al. (2009) modelled the exposure of TPs of organic chemicals to the environment and specified data requirements for the modelling of TPs such as transformation schemes and formation fractions. As a result of monitoring studies and modelling it was stated that TPs need to be acknowledged as a crucial part of the pollution process (Fenner et al. 2009). Also Fenner et al. (2009) highlighted the importance of modelling, especially towards new and potentially relevant transformation products. However, the actual extent of TPs exposure remains uncertain due to small number of monitoring studies including TPs.

Burkhardt et al. (2009) evaluated the ecotoxicological effects, leaching and environmental risk assessment for surface waters caused by biocides in building façades. Among other biocides Burkhardt et al. (2009) determined a Predicted No Effect Concentrations (PNEC) for terbutryn of 34 ng/l.

Burkhardt et al. (2012) conducted a one year long field study with different biocides and render types where wind driven rain was correlated with runoff and leached biocide amount. Further, it was shown that the leaching varied depending on the render composition and structure. Degradation was accounted for a significant role in the overall mass balance (Burkhardt et al. 2012). Furthermore, it was shown that higher concentrations of the parent compound are to be expected in runoff from freshly painted façades, whereas over time the amount of TPs exceeds the parent compound emissions (Burkhardt et al. 2012).

In Denmark multiple WFD priority substances including terbutryn and irgarol were detected in freshwater, seawater and fish samples across the country (Vorkamp et al. 2014). The majority of substances was detected with high frequency and concentrations above annual average environmental quality standard (AA-EQS) but not above maximum average concentration environmental quality standard (MAC-EQS) (Vorkamp et al. 2014).

Styszko et al. (2015) showed that the material type has a significant impact on leaching behaviour. In a test with several biocides the differences of leaching behaviour of acrylate and silicone render were shown (Styszko et al. 2015). In a later study by Bollmann et al. (2016) it was also shown that the type of render affects the formation and leaching of TPs.

Following Burkhardt et al. (2012) several other long term field studies have been performed. Schoknecht et al. (2016a) showed different leaching behaviour of six test panels based on different locations and starting times. Wind driven rain is described as the driving leaching factor and differences between the emissions from repeated experiments indicate contribution of other meteorological parameters. Schoknecht et al. (2016a) also states that in standardized laboratory tests emissions surpass the data from field experiments and that test panels can be seen as conservative compared to real conditions. Furthermore, Schoknecht et al. (2016a) showed gaps in the mass balance of applied substances and measured concentrations in façade runoff concluding that TPs have to be taken into account to close the mass balance.

Bollmann et al. (2016) observed test panels with two different renders with different initial biocide amounts for one and a half year and measured parent compound and TPs concentrations as well as closing the mass balance with the measured TP concentrations. After the findings of

Bollmann et al. (2016) only a small amount (~ 4-5%) of the initially applied biocide is leached during the first 18 months of exposure. Hereby TPs accounted for approximately a quarter of total emissions and varied with different render compositions. Bollmann et al. (2016) also showed different leaching behaviour of acrylate and silicone renders. By examining the test specimen after the end of the experiment Bollmann et al. (2016) could close the mass balance and showed that TPs are an important contributor to total emissions. Additionally to initial concentration and render composition, the pigments in paints and renders influence the photo transformation of biocides as well as TPs ratios and consequently respective leaching of PC and TPs (Urbanczyk et al. 2019).

In a further study Bollmann et al. (2017) examined the degradation kinetics in soil for various biocides. Terbutryn was found to be persistent in the soil samples with a half-life of 231 days which differs greatly from estimated half-life times of terbutryn under laboratory conditions which range in an hourly timeframe of e.g. 11.9 hours under UV-light (Bollmann et al. 2016) or 202.3 hours (Junginger et al. 2022). A semi-field study by Junginger et al. (2023) suggest half-life times between 97 and 110 days under simulated sunlight. Therefore, the transferability of laboratory immersion test to real weather condition emission scenarios is limited.

Addressing the potential contamination of groundwater by biocides and their TPs, Hensen et al. (2018) examined concentrations of diuron, terbutryn, OIT and their TPs in an urban storm water infiltration system as well as concentrations in groundwater wells up- and downstream of the examined swale. Hensen et al. (2018) confirmed façades as pollution source and showed an increase of biocide concentrations in the groundwater downgradient of the storm water infiltration system. An additional sprinkling experiment on a fourteen year old façade showed that biocides and their TPs are released throughout the entire lifespan of a façade (Hensen et al. 2018).

Uhlig et al. (2019) applied regression approaches on long term biocide leaching data. Regarding the slope of emission curves, Uhlig et al. (2019) could determine which process at a given point in time controlled the leaching process. Furthermore, Uhlig et al. (2019) described the physical and chemical mechanisms determining the leaching and process. This conceptual model was later further adapted and expanded with TPs by Junginger et al. (2023).

A comprehensive field test was conducted by Vega-Garcia et al. (2020). Two test houses were constructed and observed under real weather conditions for 18 months, measuring runoff volumes and biocide concentrations of carbendazim, diuron, OIT and terbutryn for each rain event respectively to analyse the effect of façade orientation on biocide release, proving that highest emissions occur at the weather side. Nevertheless, measured concentrations in the runoff of all façades and expositions exceeded PNEC values.

Hensen et al. (2020) conducted a multistep approach to evaluate the ecotoxicological effects of transformation products of pesticides in aquatic systems. The study of six pesticides (boscalid, penconazole, diuron, terbutryn, octhilinone, and mecoprop) identified 45 TPs, with 94% of these TPs showing toxicological effects on environmental bacteria (Hensen et al. 2020), demonstrating that consideration of TPs is necessary for a realistic assessment of the environmental risk posed by biocides.

Linke et al. (2021) identified sources and pathways of diuron, OIT and terbutryn as well as their TPs in a small urban catchment. Even though construction had been finished 13 years previous to the study Linke et al. (2021) detected biocides and TPs, with one event even exceeding PNEC values, showing the long term environmental risk of biocides and their TPs and support findings of Hensen et al. (2018) of façades as long term contamination sources.

The observation of TPs emissions exceeding the parent compound emissions was made as well by Wicke et al. (2022) in some cases surpassing the parent compound concentration by factor ten. Similarly to previous studies, emissions in storm water runoff exceeded thresholds for surface water quality.

Junginger et al. (2023) measured terbutryn and TPs concentration in the façade runoff of test specimen and showed in accordance to previous studies that the key parameters controlling the formation and emission of TPs are runoff and solar radiation. Overall, the cumulative emissions of the TPs exceeded the terbutryn emissions by factor two. By determining a photo degradation half-time ($t_{1/2}$) of > 90 days for terbutryn under environmental conditions Junginger et al. (2023) provided a framework for the estimation of emissions of biocides and their TPs as well as stating that the disregard of TPs emissions can lead to an underestimation of overall biocide leaching. Overall, an increase of studies including TPs is noticeable. However, information on TPs and data of TPs especially from field experiments is still scare (Junginger et al. 2023).

2. Aim of this study

Several studies in recent research highlight the importance of including TPs in the modelling process (Bollmann et al. 2016; Bollmann et al. 2017; Hensen et al. 2018; Hensen et al. 2020; Junginger et al. 2022, 2023; Linke et al. 2021; Schoknecht et al. 2016a; Schoknecht et al. 2016b; Wicke et al. 2022). As early as 2009, a study by the Federal Ministry for the Environment, Nature Conservation, Nuclear Safety and Consumer Protection highlighted the importance of including TPs in the risk assessment of biocides (Kahle and Nöh 2009). Hensen et al. (2020) observed the formation of 45 TPs originating from six parent compounds and assessed a toxicological effect on environmental bacteria on 94% of the observed TPs. It is therefore crucial to include TPs in the risk assessment evaluation. However, there is currently no possibility of modelling substance specific emissions of biocides and their TPs.

Furthermore, long time field studies are time and cost intensive. The development of a model could provide monetary and temporal benefits in the risk assessment of biocides used in paints and renders. Also the possibility of predicting long term emissions is more practical in silico, since the expected life time of a housing façades is 50 years (Voigt et al. 2023).

For the purpose of modelling biocide emissions from construction materials the Construction Materials Leaching Model (COMLEAM) was developed at the University of Applied Sciences Rapperswil (Burkhardt et al. 2020). COMLEAM was used in recent studies to estimate parent compound and TPs emissions (Junginger et al. 2023; Vega-Garcia et al. 2022). However, a physically based model that incorporates the degradation process in the model is yet to be developed.

Therefore, in close collaboration with one of the founders of COMLEAM Prof. Dr. Olaf Tietje of the University of Applied Sciences Rapperswil, the recent extension Construction Material Leaching Model Development (ComleamD) was tested. With field data from leaching experiments including TPs provided from three different studies from Denmark, France and Germany, it was aimed to further develop ComleamD. A goal of this master thesis was to include the for emission and degradation relevant processes of diffusion and radiation in the modelling process by implementing a tiered approach of testing three emission scenarios. The sequential scenarios to be tested in ComleamD were:

1. Decay
2. Decay & Diffusion
3. Decay, Diffusion & Solar Radiation

It is hypothesised that the inclusion of these leaching processes considered relevant in the literature leads to an improvement of the model performance.

In summary the aim of this master thesis was to include TPs of biocides and the associated physical parameters of parent compound degradation as well as diffusion and solar radiation in the modelling process to provide a more complete tool for the risk assessment of biocides leaching from construction materials.

3. Materials and methods

3.1 Data

Basis for model testing and evaluation are three data sets from Bollmann et al. (2016), Schoknecht et al. (2016b) and Junginger et al. (2023). All three studies were conducted in a comparable way, which included the preparation of test specimen with paint or render and a long term exposition of the test specimen to outdoor weathering. For each rain event the façade runoff was captured, quantified and the eluate was analysed for terbutryn and its TPs.

Meteorological data including precipitation, wind speed and direction in 10 minute resolution was captured by nearby weather stations of the respective experiment setups. The meteorological data were converted to hourly data. Hereby the hourly sum of precipitation was used. For hourly wind speed the mean of the respective six values in 10 minute resolution was formed. Concerning the wind direction, the first value of the respective hour was chosen as wind direction for the whole hour due to the possible misinterpretation of mean or median values of e.g., wind directions of 5 and 355 degrees which would lead to an opposite wind direction of 180 degrees regarding mean or median values. Therefore, the assumption was made, that the first wind direction value of an hour is representative for the general wind direction of each hour. The wind data of each study are visualized as frequency of counts by wind direction and speed in *Figure 1*. Additionally, data on global radiation was provided for the experiment of Bollmann et al. (2016) in 10 minute resolution and aggregated to mean hourly radiation in W/m². The other studies lacked radiation data in appropriate resolution or radiation data were only partly available for the duration of the experiment.

The presentation and examination of emissions is generally carried out by viewing cumulative emissions and cumulative façade runoff (Tietje et al. 2018). Therefore, cumulative values of emissions were formed by transforming the measured concentrations and runoff volume into emissions in gram. For better comparability of parent compound and TP, emissions were presented as amount of substance in mol instead of mass of substance in gram (*Equation 1*) due to different molar masses. Further remarks on stoichiometry are made in 3.2 Assumptions.

$$n = \frac{\mathrm{m}}{\mathrm{M}} \tag{1}$$

With:

n = amount of substance [mol]
m = mass of substance [g]
M = molar mass of substance [g/mol]

Values below limit of detection were set to 0 according to the general recommendations regarding data handling by the final report of the work group on degradation kinetics of FOCUS (FOCUS 2006). Not measured data were interpolated linearly. This interpolation was evaluated to be necessary in order to obtain substance amount for every runoff event to not distort the cumulative substance amount. Interpolation was mainly carried out for the data obtained from Schoknecht et al. (2016b) because of partly lacking data of TP in the first six months of the experiment. For Bollmann et al. (2016) individual emission data values had to be interpolated because a storm destroyed the façade runoff containers. For Junginger et al. (2023) no interpolation due to missing data were necessary.

To obtain a general knowledge of the magnitude of the leaching and transformation processes data from three different studies (Bollmann et al. 2016; Junginger et al. 2023; Schoknecht et al. 2016b) that regarded terbutryn and its TP was evaluated. For better comparability across the different studies normalized emissions were formed by dividing the emissions of each study by its respective initially applied terbutryn amount. *Appendix Figure 4* shows the cumulative normalized emissions of the respective studies. An overview of the three studies and key parameters is given in *Table 1*. Detailed information on the experimental setup can be obtained from the respective study provided in the appendix.

Table 1, Overview of the observed studies.

Study	**Bollmann et al. 2016**	**Schoknecht et al. 2016**	**Junginger et al. 2023**
Location	Copenhagen, Denmark	Berlin, Germany	Schiltigheim, France
Time	08.2012 - 03.2014 580 days	04.2014 - 07.2017 1182 days	04.2021 - 10.2021 194 days
No. of measurements	43	198	27
Cum. Rainfall [mm]	1044	1875	611
Cum. Runoff [mm]	47.67 - 86.68	33.59 - 67.66	16.49
Runoff coefficient [%]	4.57 - 8.30	2.32 - 3.63	2.70
Runoff per day [ml]	83 - 150	52 - 57	85
Façade exposition	southwest	south south west	west
Max Wind speed [m/s]	30.17	5.40	14.50
Median Wind speed [m/s]	6.81	0.77	2.20
Variance Wind speed [m/s]	10.41	0.35	3.09
Initial Terbutryn conc. [mg/m²]	5100 (acrylate) 2400 (silicone)	198 (WC 9) 281 (WC 12)	875
Normalized Terbutryn emissions [%]	2.58 - 3.76	0.39 - 0.73	0.42
Normalized TP emissions [%]	2.00 - 4.97	3.39 – 5.35	0.67
Normalized emissions (Terbutryn + TPs) [%]	4.66 – 8.19	3.78 – 6.08	1.09
Ratio TPs / Terbutryn	0.53 - 1.54	7.31 – 8.59	1.61
Material	acrylate & silicone render	Wood coating on birch plywood (acrylate based and polymer dispersion)	Paint on silicone render
Encapsulated substance	No	yes	yes

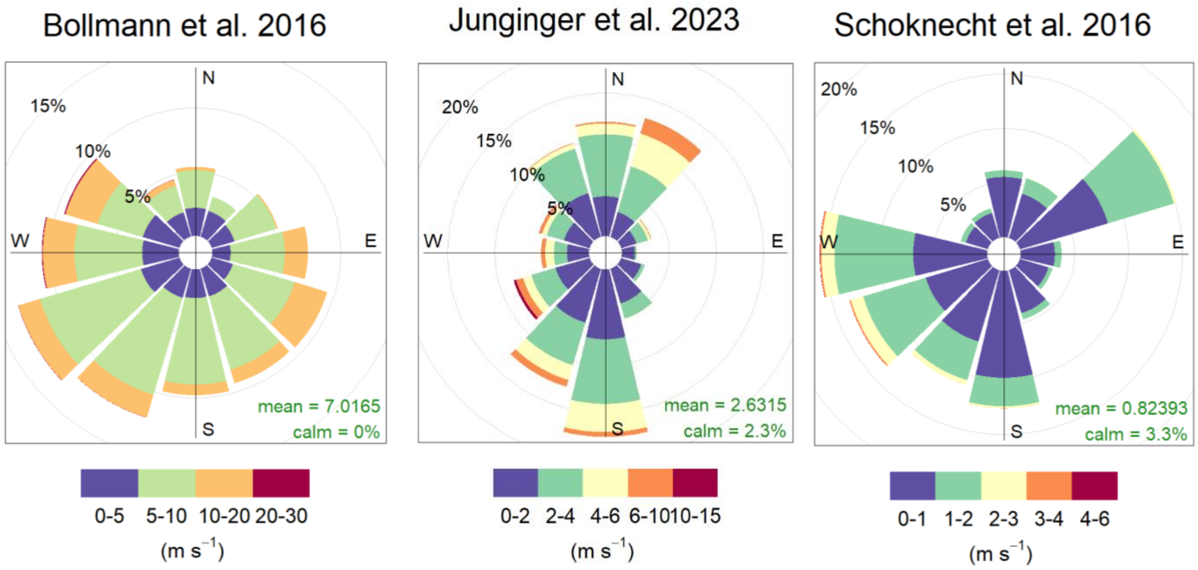


Figure 1, Overview of recorded wind speeds, directions and frequency of counts by wind direction for the respective studies.

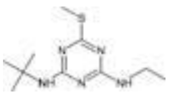
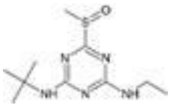
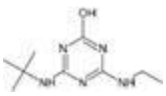
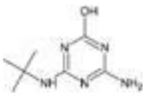
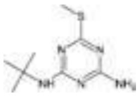
3.2 Assumptions

The dominating processes of leaching are heterogenic and dependent on chance (Tietje et al. 2018) due to for example high variability of wind driven rain, solar radiation or heterogenic distributed active substance in the façade. Furthermore, the relevant processes take place on different scales, whereas decay and transformation occur on a molecular scale, porosity on a microscopic scale, effective diffusion on a macroscopic scale and lastly leaching on the field scale (Tietje et al. 2018). Therefore, assumptions and simplifications must be made in order to be able to develop a satisfactory model of the relevant leaching processes.

3.2.1 Mol-based approach

In accordance with other studies regarding TPs a mol-based approach was chosen (Bollmann et al. 2016; Junginger et al. 2023; Schoknecht et al. 2016b). Because of different molecular masses of a terbutryn and its TPs a direct comparison in for example gram emitted substance per square meter could be misleading. Since all observed TPs have a triazin ring a mol-based approach is not causing any distortion in mass balance because based on stoichiometry the number of molecules stays the same as one parent compound molecule with a trazin ring degrades equally into one TP molecule with a triazin ring. A chemical overview of terbutryn and its TPs under consideration is given in *Table 2* where the uniformly triazin ring of terbutryn and its TPs is shown.

Table 2, Overview of the observed substances and their chemical properties. Based on Junginger et al. (2022).

Name	**Terbutryn**	**Terbutryn-Sulfoxide**	**2-Hydroxy-terbutryn**	**Desethyl-2-hydroxy-terbutryn**	**Desethyl-terbutryn**
Short name	Ter	TerSO / TB-SO	TerOH / TB-OH	TerDesEOH	TerDesE / M1
Chemical formula	$C_{10}H_{19}N_5S$	$C_{10}H_{19}N_5OS$	$C_9H_{17}N_5O$	$C_7H_{13}N_5O$	$C_8H_{15}N_5S$
IUPAC Name	2-N-tert-butyl-4-N-ethyl-6-methylsulfanyl-1,3,5-triazine-2,4-diamine	2-N-tert-butyl-4-N-ethyl-6-methylsulfinyl-1,3,5-triazine-2,4-diamine	6-(tert-butylamino)-4-(ethylamino)-1H-1,3,5-triazin-2-one	6-amino-4-(tert-butylamino)-1H-1,3,5-triazin-2-one	2-N-tert-butyl-6-methylsulfanyl-1,3,5-triazine-2,4-diamine
WS [mg/l]	17	7	906	8608	174
log K_{OW}	3.77	4.1	1.5	0.6	2.7
Molar mass [g/mol]	241.1361	257.1310	211.1433	183.1120	213.1048
CAS	886-50-0	82985-33-9	66753-07-9	66753-06-8	30125-65-6
Molecular structure					

3.2.2 Degradation

Terbutryn degrades under natural conditions in the range of sunlight wavelengths (Hensen et al. 2019). Other degradation processes like hydrolysis and biodegradation are assumed to be negligible when evaluating terbutryn degradation on façades (Bollmann et al. 2017; Junginger et al. 2022). Based on the findings of Junginger et al. (2022) hydrolysis is assumed to be insignificant at neutral pH levels and overall a minor contributor to overall degradation. Biodegradation was observed to a substantial extent (Junginger et al. 2022). However, biodegradation was observed in pond sediments and activated sludge and is therefore assumed to be insignificant in the degradation processes on the façade but should be taken into account when further evaluating overall environmental risk assessments.

Previous studies determined half-life times of terbutryn under laboratory and field conditions. Terbutryn was found to be persistent in soil samples with a half-life of 231 days (Bollmann et al. 2017) which differs greatly from estimated half-life times of terbutryn under laboratory conditions which range in hourly magnitudes of e.g. 11.9 hours under UV-light (Bollmann et al. 2016) or 202.3 hours (Junginger et al. 2022). Another laboratory study by Junginger et al. (2023) suggest half-life times between 97 and 110 days under simulated sunlight. This indicates that the transferability of laboratory immersion test to real weather condition emission scenarios is limited. Other studies suggest half-life times in soil ranging from 7 to 227 days depending on temperature and soil moisture (Lechón et al. 1997) or 180 to 240 days in water with river sediment under aerobic conditions (Muir and Yarechewski 1982). Under anaerobic conditions, Talja et al. (2008) observed half-life times of up to 650 days.

Given this variability of the half-life time of terbutryn, simulations with different decay rates were conducted to assess the effect of different half-life times on terbutryn and TPs emissions.

However, with limited data on half-life time in façades available, the approach of Junginger et al. (2023) determining half-life time under simulated sunlight and using a white paint with encapsulated terbutryn seemed to be most transferable to sunlight exposed test specimen under real life conditions. Therefore, a half-life time of 110 days was assumed for terbutryn. However, the real half-life time of terbutryn could be higher, since Junginger et al. (2023) used a constant midday solar radiation intensity contrary to varying diurnal and seasonal natural radiation intensities. Since data on TPs it scarce the half-life time of terbutryn was assumed for TPs as well.

3.2.3 Transformation Products

Bollmann et al. (2017) proposed a degradation pathway for terbutryn in soil and classified nine TPs. However, several of these detected TPs were not measured in the viewed studies. Other TPs were only measured in negligible concentrations or below the limit of detection. For instance, terbumeton accounted for approximately 1% of overall TP in measurements of Bollmann et al. (2016) and was hence viewed as insignificant to overall emissions. Similar magnitudes of terbumeton were measured in the experiment of Schoknecht et al. (2016b), accounting for 0.3 % of overall TP emissions. In the experiment of Junginger et al. (2023) terbumeton was not measured at all. Therefore, the main TPs which showed a significant share in overall emissions were determined to be terbutryn-sulfoxide (TerSO), 2-hydroxy-terbutryn (TerOH), desethyl-terbutryn (TerDesE) and desethyl-2-hydroxy-terbutryn (TerDesEOH). Given that Bollmann et al. (2016) closed the mass balance of terbutryn and its TPs at the end of the experiment, it can be assumed that the major part of emissions occurs from these TPs. The approach of considering these four TPs was also chosen in a recent study (Schoknecht and Mathies 2022). The considered TPs of terbutryn are shown in *Table 2.*

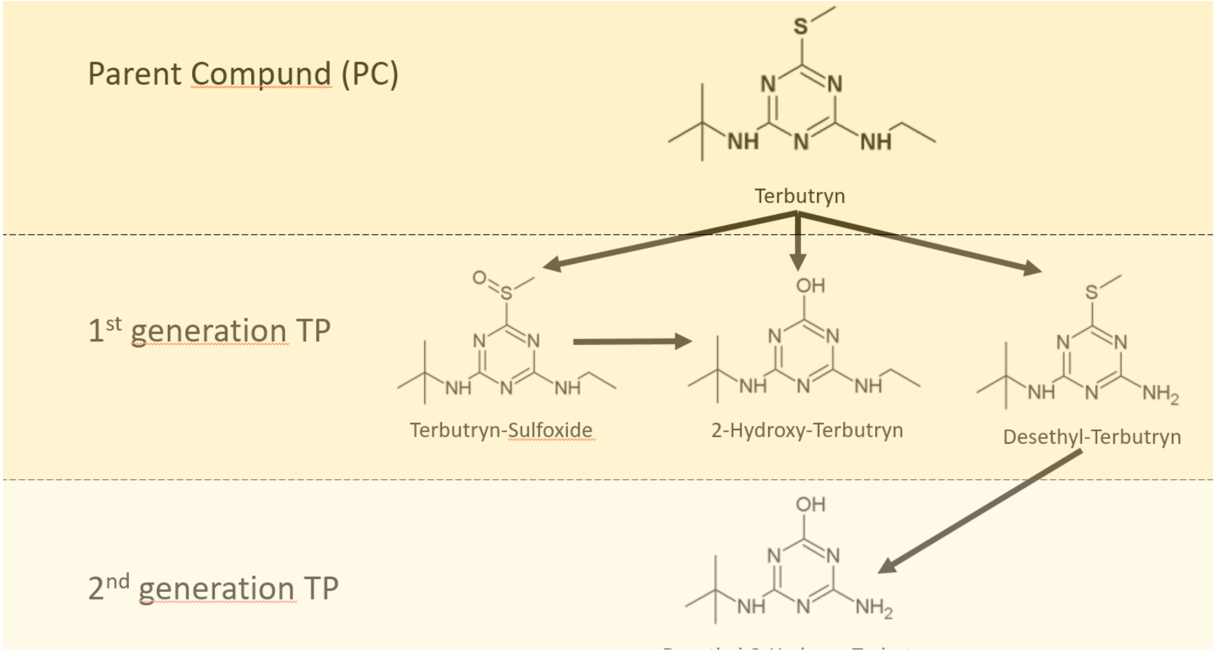


Figure 2, Proposed degradation pathway of terbutryn and its transformation products. Based on Junginger et al. (2022).

A more recent study of Junginger et al. (2022) suggested a slightly different degradation pathway of terbutryn compared to the findings of Bollmann et al. (2017) regarding photo degradation, hydrolysis and biodegradation. In this study the more recent degradation pathway of Junginger et al. (2022) was chosen as basis of terbutryn transformation and suggests a degradation of terbutryn into TerSO, TerOH and TerDesE. The 1st generation TP TerSO also degrades into the 1st generation TP TerOH. TerDesE further degrades into the 2nd generation TP TerDesEOH. A schematic illustration of the proposed degradation processes is shown in *Figure 2*.

3.2.4 Formation Fractions

In order to quantify the amount of respective TP formed out of initial parent compound amount formation fractions are needed. Generally, to determine the formation of TPs formation fractions are calculated as recommended by the FOCUS guidance on the calculation of persistence and degradation kinetic endpoints of metabolites (FOCUS 2006). The respective formation fraction of each TP is hereby described as:

$$f_{ij} = \frac{F_{ij}}{F_{iTotal}} \tag{2}$$

with:

f_{ij}: formation fraction of transformation product j from i
F_{ij}: flow from i to j
F_{iTotal}: total flow from i

However, regarding real life scenarios only eluate concentrations were measured and information about the distribution of terbutryn and its TP in the façade during the experiments are unknown. Because of the scarce availability of terbutryn and TP field data, mainly laboratory data of terbutryn degradation suitable for formation fraction calculation exists, as described earlier in section *Degradation 3.2.2*. Laboratory data were provided by Bollmann et al. (2016) and Junginger et al. (2023). An attempt was made to obtain formation fractions from the data of the laboratory photo degradation experiments. Crucial for the determination of formation fractions are genetic endpoints of the degradation process, as well as a clearly distinguishable formation phase, plateau and decline phase of the transformation product (FOCUS 2006). *Appendix Figure 3* compares the examined radiation experiments with an idealized degradation process defined by FOCUS (2006). Therefore, a clear distinction between formation phase, plateau and decline phase could not be made.

Furthermore, it has been shown that variables like for instance type of render composition (Bollmann et al. 2016), climate (Junginger et al. 2023), pigments (Schoknecht et al. 2021; Urbanczyk et al. 2019) and encapsulation (Junginger et al. 2023) have a profound impact on degradation and TP genesis. Additionally, the limited transferability of laboratory radiation experiments to real life conditions has to be taken into account. Therefore, it was assumed that a definitive value for the respective formation fractions could not be defined under the influence of described uncertainties and it is assumed that regarding the examined studies that formation fractions are individual for each experimental setup.

Nevertheless, the FOCUS guidance on the calculation of persistence and degradation kinetic endpoints of metabolites states that "the formation fraction can also be directly estimated as a free parameter in a fitting procedure" (FOCUS 2006, p. 23). Since per default the formation fractions range between 0 and 1 and the sum of all formation fractions equals 1, educated guesses were made regarding the share of each TP to overall emissions.

Therefore, estimates of formation fractions were made based on the distribution of the cumulative TP emissions and fitted iteratively to the data. In order to achieve better comparability of the other parameters, uniform formation fractions were chosen for all model runs, as shown in *Tables 3 and 4*.

3.2.5 Leaching Process

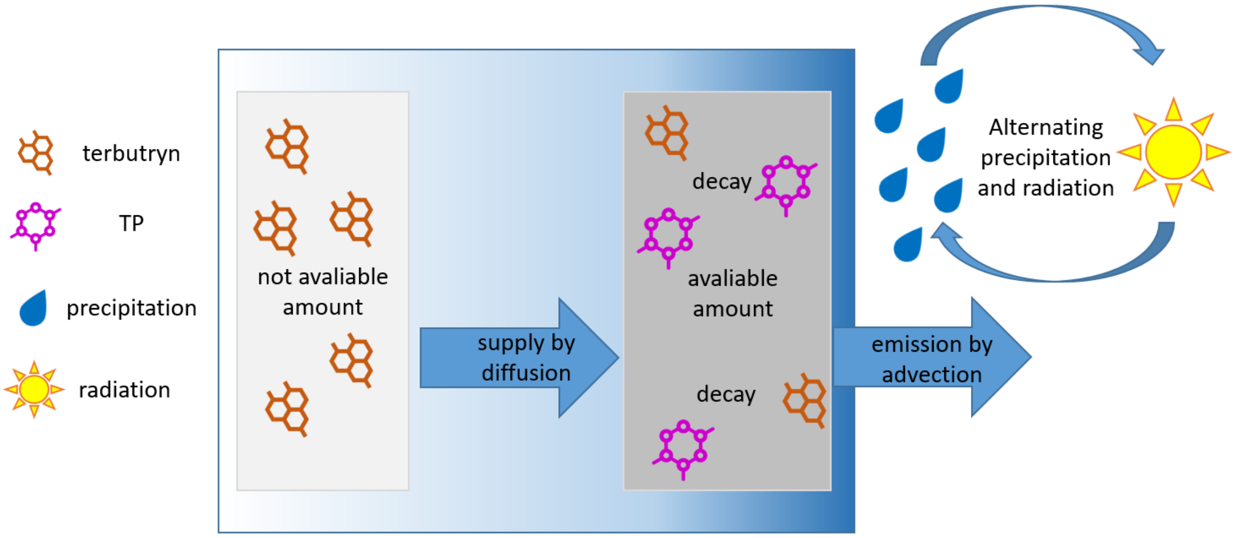


Figure 3, Schematic illustration of the assumed processes driving emissions from façades. Adapted from Junginger et al. (2023).

In accordance with previous studies (Bollmann et al. 2016; Burkhardt et al. 2012; Junginger et al. 2023; Schoknecht et al. 2016a; Schoknecht et al. 2016b), the predominant factors determining parent compound and TP emissions are assumed to be façade runoff and solar radiation. Photo degradation is the main cause of degradation (Junginger et al. 2023). Other degradation processes like hydrolysis and biodegradation are assumed to be negligible when evaluating terbutryn degradation on façades (Bollmann et al. 2017; Junginger et al. 2022) but should be taken into account when further assessing the environmental risk for soil, surface water and groundwater. Another factor driving biocide emissions from façades is assumed to be diffusion (Schoknecht et al. 2022), influenced by meteorological parameters (Schoknecht et al. 2016a; Schoknecht and Mathies 2022). Gradients in moisture and concentration cause a substance supply by diffusion from deeper render layers to the façade surface.

Figure 3 shows the assumed leaching process. WDR hits the façade surface and a proportion of the façade runoff penetrates into the render. The usually encapsulated active substance in deeper layers of the render is supplied to the façade surface by diffusion. Here, the active substance is exposed to radiation. Photo transformation occurs in the outer layer of the façade and the active substance decays into its TPs. The next WDR producing rain event emits the active substance and its TPs by advection. This alternating cycle of precipitation and radiation produces different emission loads, depending on initially applied substance amount, time passed since the last rain event, cumulative solar radiation, intensity of next WDR event and other meteorological parameters like temperature and humidity (Junginger et al. 2023). The emissions in the façade runoff are usually drained by a (storm water) sewage system or percolate trough soil into the groundwater. Heavy rain events can also cause an overload of the storm water sewage system leading to a direct emission into surface waters.

3.3 ComleamD Model

The modelling was conducted with ComleamD (COnstruction Material LEAching Model Development) which is a currently tested further development of Comleam. In contrast to its predecessor, ComleamD includes additional features and can take TPs into account and calculate the amount of TPs that are being leached from the façade as well as the remaining amount of TPs in the façade. The modelling process has been taking place in close cooperation and consultation with one of the founders of Comleam, Prof. Dr. Olaf Tietje who kindly provided and further modified the model.

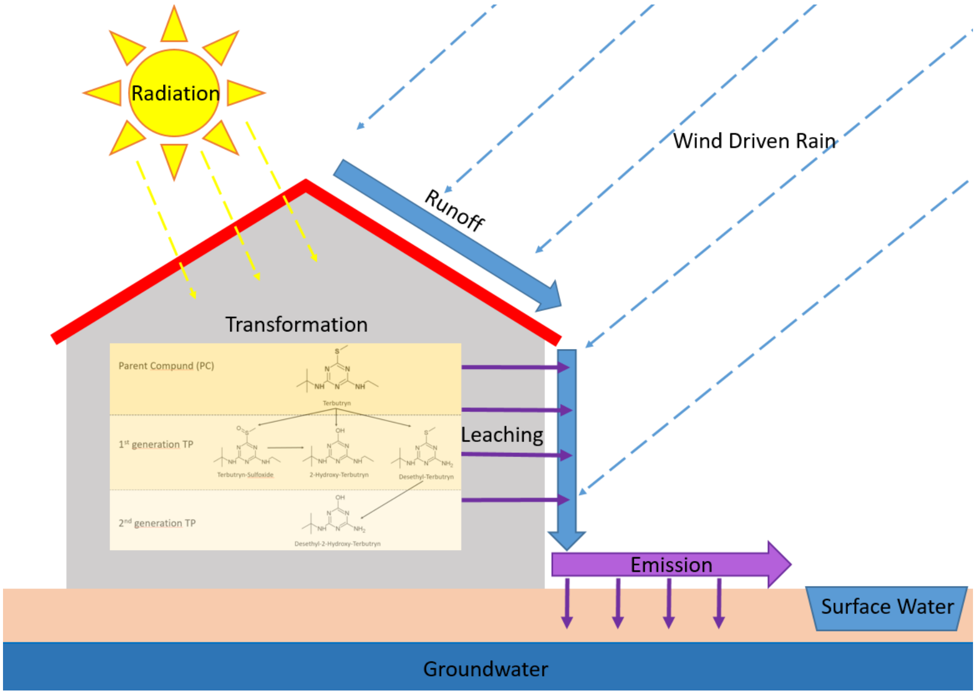


Figure 4, Schematic illustration of the in ComleamD considered processes driving the leaching of biocides and TPs.

Comleam was originally developed at the University of Applied Sciences Rapperswil to model the concentrations of biocides and other substances harmful to the environment in the runoff of horizontal and vertical building components exposed to weathering. A schematic illustration of the ComleamD model is shown in *Figure 4*. The water volume getting in contact with the component is derived from weather data by calculating wind driven rain (WDR). Initially applied substance amount and surface properties of the façade are provided in a geometry file. With a substance specific emission function the leaching of a substance is determined in dependence of façade runoff. Optionally, decay of a substance under consideration of solar radiation can be taken into account. A system of differential equations determines the water and substance flow from a component to the target compartment as well as the substance concentrations. The described input parameters of the model can be divided into four groups as shown in *Figure 5*. In the following an overview of ComleamD is given. Further information on the ComleamD model can be obtained from the ComleamD manual (Tietje 2023).

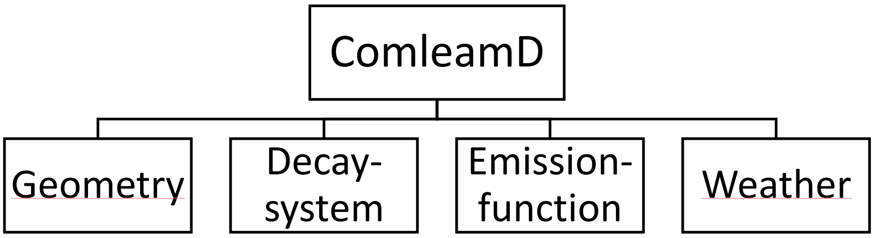


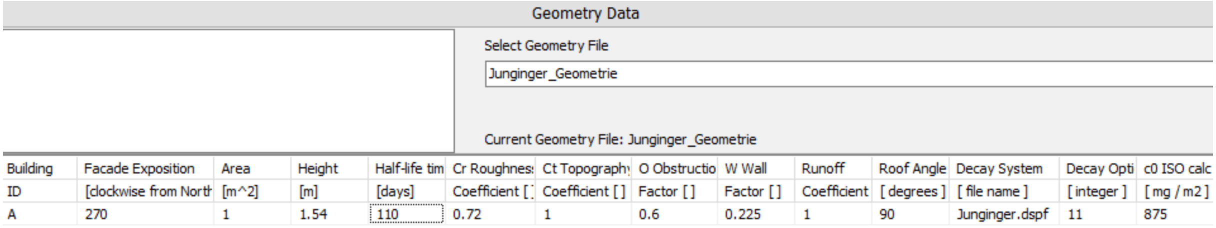
Figure 5, Schematic illustration of the ComleamD input parameters.

3.3.1 Geometry

The geometry data contains all information about the façade as well as the properties of the active substance.

A building ID identifies each building component. Hereby, different façades of a single building or multiple buildings can be described. The area of each component is provided in square meters as well as the height of each component in meters. Façade exposition is necessary to calculate WDR and must be provided in degrees from north. For example, a south exposed façade would be described by 180 degrees. Further necessary parameters for the WDR calculation are a roughness coefficient, a topography coefficient, an obstruction factor and a wall factor. The terrain roughness describes if and how much the wind speed is reduced by other buildings and ranges from e.g. 0.1 in densely populated areas with various buildings to 1 in a plain field. The topography factor describes whether or how much the component is being exposed to special weather due to its location near a hill or lake. The obstruction factor describes obstructions due to obstacles or other buildings. The wall factor considers the buildings height due to the impact of building height to WDR (Blocken et al. 2013). A runoff coefficient determines the amount of WDR hitting the surface that is converted into runoff. This coefficient therefore can take porosity, infiltration, evaporation and splash losses of WDR into the façade due to different render properties into account.

The geometry file also contains properties of the active substance. The half-life time of the substance is described and the decay system of the substance has to be provided (3.3.2 Decay System). Furthermore, the decay option has to be specified. ComleamD provides different decay options which include e.g., no decay, decay occurring continuous, decay occurring only between 6 am and 6 pm, decay only occurring during daytime while there is no precipitation and many other variations. The initial amount c_0 of substance within the façade is described in mg/m². An example of a geometry file is shown in *Figure 6*.



Geometry Data

Select Geometry File: Junginger_Geometrie

Current Geometry File: Junginger_Geometrie

Building	Facade Exposition	Area	Height	Half-life tim	Cr Roughnes:	Ct Topography	O Obstructio	W Wall	Runoff	Roof Angle	Decay System	Decay Opti	c0 ISO calc
ID	[clockwise from North	[m^2]	[m]	[days]	Coefficient []	Coefficient []	Factor []	Factor []	Coefficient	[degrees]	[file name]	[integer]	[mg / m2]
A	270	1	1.54	110	0.72	1	0.6	0.225	1	90	Junginger.dspf	11	875

Figure 6, Exemplary illustration of the geometry data and its parameters in ComleamD.

3.3.2 Decay System

The decay system describes the active substance and its TPs and simulates the leaching process. Data of the parent compound and its TPs like molecular mass, formation fractions, decay rate, mass coefficients relative to each substance and the substance specific parameters of the logarithmic emission function are stored in the decay system.

As previously described in *3.2.3 Transformation Products* the used decay system accounts for Terbutryn and the TPs TerSO, TerOH, TerDesE and TerDesEOH as well as the sink. A formation matrix F = ($f_{i,j}$) with i and j ranging from 1 to the n^{th} substance is containing the relation of each substance in the decay process (*Table 3*). The coefficients $f_{i,j}$ of the formation matrix range from -1 to 1 and describe how each substance decays into each other respective substance. The sum of all formation fractions equals 1. At the n^{th} position of the formation matrix is the sink with $f_{i,n} = 0$. Therefore, no input into the sink passes through. Due to stoichiometry, the sink closes the mass balance since calculations are made on a mol basis and every substance contains a single triazin ring.

Table 3, Formation matrix of terbutryn.

Formation Fractions	**Terbutryn**	**TerSO**	**TerOH**	**TerDesE**	**TerDesEOH**	**Sink**
Terbutryn	-1	0	0	0	0	0
TerSO	0.2	-1	0	0	0	0
TerOH	0.2	1	-1	0	0	0
TerDesE	0.6	0	0	-1	0	0
TerDesEOH	0	0	0	1	-1	0
Sink	0	0	1	0	1	0

For the calculation the decay rate k of each substance (*Equation 3*) and the formation fractions are needed. For each time step the emission of the respective substance is subtracted from the substance.

$$k = \frac{\ln(2)}{dt_{50}} \tag{3}$$

with:

k	decay rate
dt_{50}	half-life time

An hourly time step was chosen for the simulations. Emissions are calculated in dependence of façade runoff and are described in *Equations 5 to 8*. For each time step Δt a single first order decay is calculated. The mass balance of each time step is closed and calculated by the means of a differential equation system solved by an Euler algorithm. The differential equation system is shown in *Equation 4*.

$$\begin{aligned}
\mathrm{Ter} &= -k_a \cdot \mathrm{Ter} - E_{Ter} \\
\mathrm{TerSO} &= k_a \cdot \mathrm{Ter} \cdot f_{Ter,TerSO} - k_b \cdot \mathrm{TerSO} - E_{TerSO} \\
\mathrm{TerOH} &= k_a \cdot \mathrm{Ter} \cdot f_{Ter,TerOH} - k_b \cdot \mathrm{TerSO} \cdot f_{TerSO,TerOH} - k_c \cdot \mathrm{TerOH} - E_{TerOH} \\
\mathrm{TerDesE} &= k_a \cdot \mathrm{Ter} \cdot f_{Ter,TerDesE} - k_d \cdot \mathrm{TerDesE} - E_{TerDesE} \\
\mathrm{TerDesEOH} &= k_a \cdot \mathrm{TerDesE} \cdot f_{TerDesE,TerOH} - k_e \cdot \mathrm{TerDesEOH} - E_{TerDesEOH} \\
\mathrm{Sink} &= k_a \cdot \mathrm{Ter} \cdot f_{Ter,Sink} + k_b \cdot \mathrm{TerSO} \cdot f_{TerSO,Sink} + k_c \cdot \mathrm{TerOH} \cdot f_{TerOH,Sink} + \\
&\quad k_d \cdot \mathrm{TerDesE} \cdot f_{TerDesE,Sink} + k_e \cdot \mathrm{TerDesEOH} \cdot f_{TerDesEOH,Sink}
\end{aligned} \tag{4}$$

with

k_i	decay rate
$f_{i,j}$	formation fraction
E_i	Emission (further described in *Equation 12*)

3.2.2.1 Available and unavailable Terbutryn in Decay System

It is assumed that terbutryn from inner layers of the façade is transported by diffusion to the façade surface, as described in *3.2.5 Leaching Process*. To implement this transport a steady flow of unavailable terbutryn from the inner layer of the façade to the façade surface is assumed, where the terbutryn becomes available for decay. This was achieved by implementing the unavailable terbutryn as an additional substance in the decay system with a constant hypothetical decay rate that imitates the flow from unavailable terbutryn to for decay available terbutryn. The available terbutryn forms the basis of the decay system from which the TPs are calculated as shown in *Equation 4* and the extended decay system shown in *Table 4.* It was hypothesised that the delay of the leaching process at the beginning of the modelling phase could be represented.

Table 4, Formation matrix of terbutryn with non-available terbutryn.

Formation Fractions	Terbutryn NA	Terbutryn	TerSO	TerOH	TerDesE	TerDesEOH	Sink
Terbutryn NA	-1	0	0	0	0	0	0
Terbutryn	1	-1	0	0	0	0	0
TerSO	0	0.2	-1	0	0	0	0
TerOH	0	0.2	1	-1	0	0	0
TerDesE	0	0.6	0	0	-1	0	0
TerDesEOH	0	0	0	0	1	-1	0
Sink	0	0	0	1	0	1	0

3.3.3 Emission Function

Emission occurs by the contact of runoff water with the façade in the dissolved phase (Burkhardt et al. 2012). Based on lab and field studies, Tietje et al. (2018) assumed a functional relationship between runoff and emission. This simplified relationship of runoff and emission is described as:

$$E(q) = c_0 \cdot E_{rel}(q) \tag{5}$$

with:

$E(q)$	emission [mg/m²]
c_0	initial substance amount per m² of façade are [mg/m²]
$E_{rel}(q)$	relative emission function

Comleam provides a logarithmic, Langmuir, Michaelis-Menten, limitied growth and diffusion controlled function. The substance emission is calculated as a product of the initial substance concentrations and an emission function. According to a study conducted by the German Federal Environment Agency comparing the different emission functions, a logarithmic emission function showed the best fit out of six examined functions (e.g. limited growth, diffusion driven, Langmuir) (Tietje et al. 2018). Further remarks on the relevance of emission functions can be found in Tietje et al. (2018). The following logarithmic emission function from Tietje et al. (2018) was implemented in ComleamD:

$$E_{rel}(q) = \alpha_{char} \cdot l\,\mathrm{n}\left(1 + 1.72 \cdot \frac{q}{q_{char}}\right) \tag{6}$$

with:

$E_{log}(q)$	amount of substance emission per m² of the façade area [mg/m²]
q_{char}	characteristic runoff [l/m²]
α_{char}	characteristic substance proportion [-]

or simplified:

$$E_{log}(q) = a \cdot \ln(1 + b \cdot q) \tag{7}$$

with:

a	characteristic emission parameter 1 [mg/m²]
b	characteristic emission parameter 2 [l/m²]
q	façade runoff [l/m²]

In ComleamD a is replaced by the relative characteristic emission parameter a_{rel} which is the quotient of a and c_0. This transforms the emissions into a relative proportion of the initially applied amount and provides better comparability across different scenarios:

$$E_{log}(q) = a_{rel} \cdot \ln(1 + b \cdot q) \tag{8}$$

Even though the function is monotonically increasing and cumulative emissions could therefore potentially exceed the initially applied amount of active substance, Tietje et al. (2018) showed that with use of parameters relevant to practice this would require millions of years, exceeding the lifespan of façades significantly, while simultaneously providing the best fit during the lifetime of a façade compared to other emission functions.

3.3.4 Weather

Weather data in hourly resolution includes precipitation, mean hourly wind speed and the mean hourly wind direction as well as mean hourly radiation.

To determine the runoff of vertical surfaces wind driven rain (WDR) is calculated using the current precipitation, wind speed, angle between component exposure and wind direction and the location factor which considers the terrain roughness, topography, the obstruction due to other buildings and a wall factor considering the buildings height. *Equations 9* and *10* show the calculation of WDR according to DIN EN ISO 15927-3:2009-08:

$$WDR = \alpha \cdot P^{\beta} \cdot v \cdot \cos(\theta) \cdot \Delta t \tag{9}$$

with:

WDR	wind driven rain [mm/h]
α	location factor [-]
P	precipitation [mm/h]
β	precipitation exponent (= 0.88)
v	wind velocity [m/s]
θ	Angle between wind direction and exposition of the façade [°]

and

$$\alpha = C_r \cdot C_t \cdot O \cdot W \tag{10}$$

with:

C_r	Terrain roughness coefficient [-]
C_t	Topography factor [-]
O	Obstruction factor [-]
W	Wall factor [-]

In order to realise the effect of radiation on decay and TPs formation (Bollmann et al. 2016; Hensen et al. 2019; Junginger et al. 2022, 2023; Urbanczyk et al. 2019), a decay option proportional to global radiation was implemented. Hereby, decay is proportionally inhibited or increased depending on the quotient of momentarily global radiation to the mean global radiation of the simulation period. If global radiation is 0 W/m² no decay is occurring. A global radiation equal to the mean global radiation results into normal decay without inhibition or amplification. A global radiation twice as high as the mean global radiation results in decay twice as fast. Therefore, the diurnal and seasonal variability of global radiation is taken into account. The solar radiation factor is determined by *Equation 11*:

$$\acute{\iota} = \frac{w}{\overline{w}} \tag{11}$$

with:

$\acute{\iota}$	solar radiation factor [-]
w	solar radiation [W/m²]
$\overline{w}$	mean solar radiation [W/m²]

3.3.5 Mathematical Model

The mathematical Model of ComleamD is based on a solver for a system of ordinary differential equations. The input for each component and time step consists of initial conditions and the water runoff at the component. The input consists of the described geometry, weather, decay system and weather data. The temporal resolution is one hour. The output at the end of each time step is the emission of an active substance and its TPs from the façade, as well as a vector of state variables. The defined state variables are the amount of water within the interface compartment (y), the amount of substance within the interface compartment (z), the amount of water in the surface water compartment (Q) and the amount of substance in the surface water compartment (J).

ComleamD offers different solutions approaches to calculate the described state variables. In this thesis a decay calculation was chosen to assess the formation and emission of TPs. Furthermore, the decay system was supplement by an additional substance to simulate a steady supply of terbutryn from inner layers of the façade to the façade surface (*Section 3.2.2.1*). The differential equation system described in *Equation 4* forms the basis of the mathematical model and follows a 1st order decay.

The emission of each time step of the parent compound E1 and the transformation products E_2 to E_{n-1} reveal from the amount $z_{a,i}$ of the substances at the beginning of the time step and are calculated as described in *Equation 12*:

$$\Delta E_i = z_{a,i} \cdot \frac{E_{rel}(q_e) - E_{rel}(q_b)}{1 - E_{rel}(q_b)} \tag{12}$$

with:

$z_{a,i}$	substance amount at beginning of time step [mg/m²]
$E_{rel}(q_b)$	relative emissions at beginning of time step [-]
$E_{rel}(q_e)$	relative emissions at end of time step [-]

The relative emissions are calculated with the previously determined runoff resulting from WDR described in *Equation 14*. Emissions are normalized by using the relative emission parameter a_r, which is the quotient of a and c_0:

$$E(q_b) = a \cdot ln(1 + b \cdot q_b) \tag{13}$$

and

$$E_{rel}(q_b) = a_{rel} \cdot ln(1 + b \cdot q_b) \tag{14}$$

with:

a_{rel}	relative emission parameter [-]
q_b	runoff accumulated at the beginning of time step [mm]
q_e	runoff accumulated at the end of time step [mm]

Figure 7 illustrates the ComleamD model process. In the first time step the relative substance amount of the parent compound is equal to one and $z_{a,i}$ is equal to c0. The ComleamD core takes the information given in the decay system, which are the chemical properties, formation fractions, decay rates, and emission function parameters of parent compound and the described TPs as well as the initial active substance amount. For each time step Δt the decay and formation of the respective substances is calculated following a single first order decay. With mass of each substance $z_{a,i}$ for the respective time step calculated, emission of each substance E_i can be determined by *Equation 12* under consideration of previously determined WDR with *Equation 9* which also takes the geometry of the façade into account. Given the available amount of substances, the emission of each substance and the data from the decay system the Euler algorithm solves the differential equation system described in *Equation 4* and closes the mass balance of the time step. Given the flux amounts of façade runoff and substance amounts of parent compound and TPs the defined state variables y, z, Q and J can be determined at the interface compartment for each time step Δt and are written to an output file.

The output consists of the earlier described state variables and their products. Characteristic outputs considering emission are for example amount of substances per litre, remaining amount of substances, transformed amount of substances, relative remaining and transformed amounts and runoff volume. The output of ComleamD can be further integrated into soil transport models like the Pesticide Emission Assessment at Regional and Local Scales (PEARL) or hydraulic models like the Storm Water Management Model (SWMM) since runoff volumes and concentrations of active substance for each compartment are calculated.

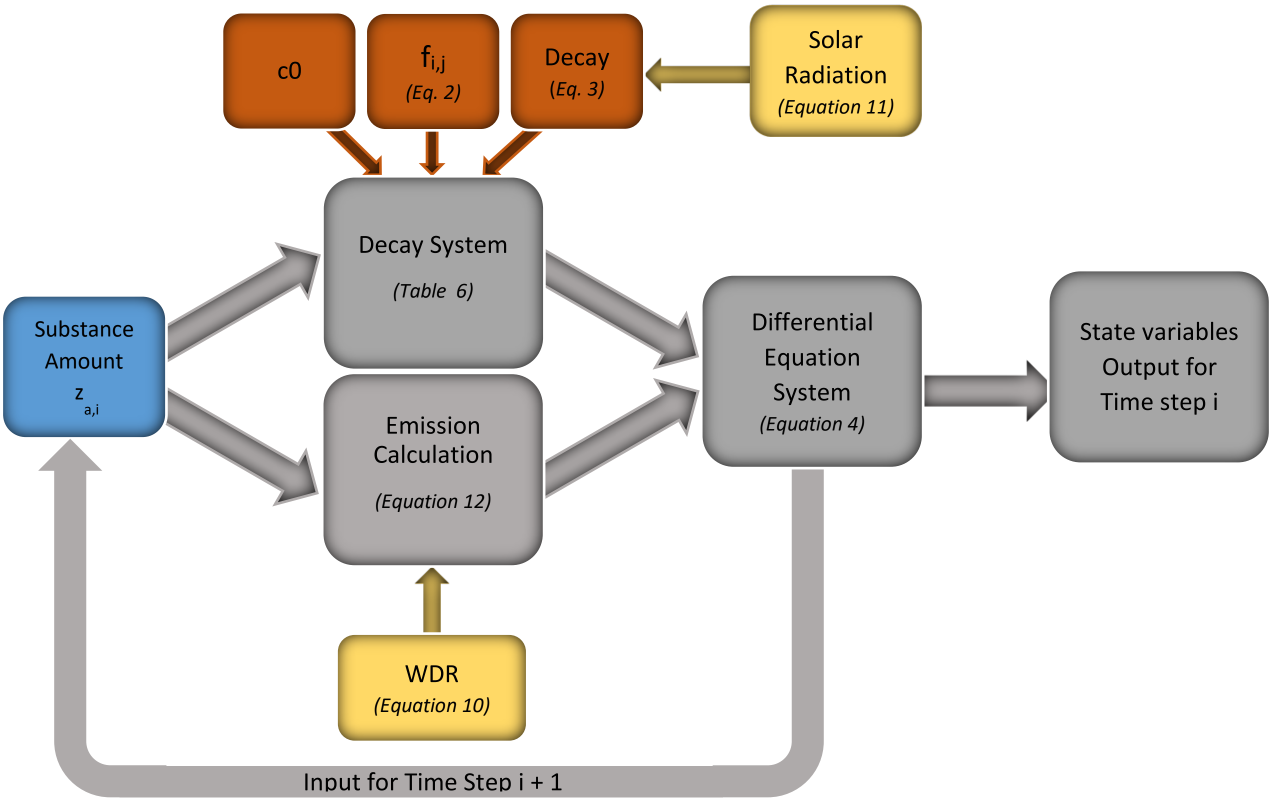


Figure 7, Flow chart of the ComleamD model progress for each respective time step.

3.4 Scenarios

ComleamD is an extension of Comleam and offers additional features. The main feature is the decay system that enables the modelling of substance degradation, TP formation and emission. Another feature is the implementation of solar radiation in the leaching model. With these additional features the following three sequential scenarios were created.

1. Decay
2. Decay & Diffusion
3. Decay, Diffusion & Radiation

In the first scenario only decay is taken into account. The parent compound degrades into the by the degradation matrix determined TPs and emission occurs according to the respective emission function of each substance. The second scenario adds the in *3.2.5 Leaching Process* described diffusion from inner layers of the façade to the surface of the façade to the modelling process. This was achieved by adding not available terbutryn with a pseudo decay rate mimicking the diffusion as described in *3.2.2.1 Available and unavailable Terbutryn in Decay System*. This is however only an approach to represent the complexity of diffusion processes in façades. Nevertheless, it was hypothesised that the delay in emissions caused by the decay of unavailable terbutryn in available terbutryn could lead to a more realistic emission scenario. The last and third scenario includes all previously described attributes and adds the impact of solar radiation on the decay process. Hourly solar radiation data are added to the weather data and the in *3.3.4 Weather* described solar radiation factor influences the decay process proportionally. Here, it was hypothesised that the impact of diurnal and seasonal solar radiation variability on the photo degradation driven decay could possibly further enhance model performance.

A sequential approach was chosen, in order to be able to quantify the potential improvement of model performance with each step representing more physical parameters of the leaching process until all assumed major contributors of the leaching process as describes in *3.2.5 Leaching Process* (*Figure 3*) are represented by the model.

3.5 Derivation of Emission Functions and Model Calibration

As described earlier determining an emission function is essential for modelling. In order to derive an emission function a logarithmic emission function in the form of *Equation 7* was fitted to the respective data. First a nonlinear regression model was fitted to the data in RStudio using the nls function of the stats package. Hereby, an iterative process determines nonlinear least-squares estimates of the parameters of a nonlinear model. Finding initial values for the convergence of the nonlinear model were challenging. Using the selfStart function of the stats package, initial values could be determined. However, the fitted parameters were unsatisfactory regarding goodness of fit values. Therefore, another fitting method based on the Levenberg-Marquardt Method was used.

This was done by means of the software FUNFIT, an algorithm written and provided by Prof. Dr. Olaf Tietje. The Levenberg-Marquardt Method is frequently used and a standard procedure of nonlinear least-square (nls) routines for nonlinear models (Press 2007). Briefly, an initial guess for the parameters is taken and then iteratively updated until a sufficient fit is achieved. This is determined by the sum of squares of the difference between the predicted and observed values.

The Levenberg-Marquardt Method combines the steepest descent method and the Hessian method and therefore also takes the curvature and gradient into account (Press 2007). This was considered as an advantage to the nls function of RStudio because of the desired extrapolation of the leaching data to project long term leaching behaviour.

To fit the data, the total cumulative emissions (terbutryn + TPs) were used as the independent variable on the ordinate and the cumulative runoff as the dependent variable on the abscissa. A satisfactory fit was quantified by a relative squared error (RSE) of less than five percent. The RSE was calculated as describes in *Equation 15*:

$$RSE = \frac{\sum_{i=1}^{n}(s_i - m_i)^2}{\sum_{i=1}^{n}(\overline{m} - m_i)^2} \tag{15}$$

with:

m_i measured data
$\overline{m}$ mean of measured data
s_i simulated data

The implementation of the determined parameters in the ComleamD-Modell produced data in the same order of magnitude as the measured data. However, a good fit could not be achieved especially for individual TPs. Therefore, further fitting was deemed necessary. The idea of further alternating the emission function parameters was assumed to be necessary due to the different K_{OW}-values. A low K_{OW}-value and therefore high water solubility should lead to higher mobility and consequently higher emissions. Comparing the K_{OW} values of terbutryn and its TPs (*Table 2*) differences can be observed. Generally, TPs tend to be more mobile than the parent compound. Since by the mathematical nature of the emission function (*Equation 7*) the a parameter proportionally affects the emission of a substance it was decided to alter this parameter according to K_{OW} value, water solubility and visual fit. The b parameter which is embedded in the logarithmic part of the function affects primarily the curvature of the logarithmic function and was assumed to be universal for all triazine substances of the respective study. Further remarks on the fitting of the emission function are made in 3.6 Model evaluation.

Initial model runs were conducted with the retrieved parameters of the emission functions (*Appendix Table 1*). However, this resulted in poor fitting visually and regarding r^2 and RMSE values which reinforced the assumption that all substances must have a different mobility and therefore differentiated leaching behaviour due to their chemical properties. Consequently, different *a* parameters of the emission function have to be defined for each substance. For this, the in ComleamD embedded derivative-free logarithmic parameter identification was used.

This further identification of the *a* parameter of each substance resulted in overall better model performance. In the last step of the model calibration the visual fit of the data was evaluated and adjusted iteratively and manually until *a* sufficient r^2 and RMSE value was achieved. It must be emphasised that all other model parameters such as formation fractions, decay rate and mass coefficients are uniform for all model runs and only the *a* parameter of the emission function was fitted individually and the *b* parameter of each study was universal for all substances of the respective study according to the initially determined emission function (*Appendix Table 1*).

3.6 Model evaluation

The functionality of the model was evaluated by using the coefficient of determination (r^2) and the relative Root Mean Squared Error (relative RMSE) as goodness of fit measurements. The coefficient of determination is common measure to assess the concordance between modelled and measured data and is defined by the quotient of the residual sum of squares SS_{res} and the total sum of squares SS_{tot} as shown as in *Equation 16 (Dormann 2013)*:

$$r^2 = 1 - \frac{SS_{res}}{SS_{tot}} \tag{16}$$

with:

r^2	coefficient of determination
SS_{res}	residual sum of squares
SS_{tot}	total sum of squares

The residual sum of squares is defined as shown in *Equation 17*:

$$SS_{res} = \sum_{i=1}^{n} (m_i - s_i)^2 \tag{17}$$

with:

m_i	measured data
s_i	simulated data

The total sum of squares is defined as shown in *Equation 18*:

$$SS_{tot} = \sum_{i=1}^{n} (m_i - \bar{m})^2 \tag{18}$$

with:

m_i	measured data
$\bar{m}$	mean of measured data

The relative RMSE was chosen because of the small magnitude of the data, the small RMSE could be misleading. Therefore the RMSE was relativized by putting it into proportion with the arithmetic mean of the observed normalized emission values as described in *Equation 19* and *Equation 20*:

$$RMSE = \sqrt{\frac{1}{n-1} \cdot \sum_{i=1}^{n} (s_i - m_i)^2} \tag{19}$$

with:

RMSE	root mean squared error
m_i	measured data
s_i	simulated data

$$relRMSE = \frac{\mathrm{RMSE}}{\bar{m}} \tag{20}$$

The measurements of the field data were assumed to be taken at 12:00 am and the respective modelled values were extracted from the simulation results at the same time and date to ensure comparability. The goodness of fit was categorized in good ($r^2 > 0.90$), fair ($0.80 > r^2 < 0.90$), acceptable ($0.70 > r^2 < 0.80$) and poor ($r^2 < 0.7$). Similar criteria were applied to the relative RMSE value with a good (rel. RMSE < 20%), fair (20% > rel. RMSE < 30%), acceptable (30% > rel. RMSE < 40%) and poor fit (rel. RMSE > 40%). In accordance with the FOCUS guidance on the calculation of persistence and degradation kinetic endpoints of metabolites, all fits were also evaluated visually (FOCUS 2006). It was emphasized to address the goodness of fit also visually, since r^2 and relative RMSE values not necessarily guarantee a good fit and the visual assessment of the complex temporal leaching behaviour in combination with goodness of fit values has to be taken into account (Anscombe 1973; Dormann 2013).

4. Results

4.1 Modelled Emissions

Varying between the observed studies, overall emissions (terbutryn + TPs) account for 1.08% to 6.36% of the initially applied active substance amount or the respective mass balance. Modelled emissions of all scenarios range in the same order of magnitude as measured emissions. The following explanations of modelled and measured emissions are given in relation to the respective initial substance amount and are therefore normalized to ensure comparability across the different studies. The fitted parameters of the emission function of each scenario and study can be obtained from *Appendix Table 1* and *Appendix Table 2*.

4.1.1 Decay

The results of the first emission scenario are shown in *Figure 8*. The model output shows an overall good visual fit to the measured data. Overall, a consistent disparity of modelled and measured emissions can be observed in the beginning of the experiments. Except for WC12 all other simulations show an overestimation of emissions in the beginning of the experiment.

For the data of Junginger et al. (2023) the model overestimates emissions in the beginning of the experiment and slightly underestimates the emissions at the end of the experiment. Final cumulative emissions are coherent. The modelled normalized terbutryn emission was 0.00437 compared to measured 0.00416. TerSO modelled reached a total modelled emission of 0.00567 compared to measured 0.00534. TerOH modelled yielded 0.00061 in contrast to measured 0.00062. TerDesE modelled came to 0.00079 and measured to 0.00074. Similar results can be observed for overall emissions and the sum of TPs with 0.01142 and 0.00706 for modelled and 0.01087 and 0.00671 for measured emissions respectively.

The modelled and measured data for Schoknecht et al. (2016b) shows an overall good fit as well. However, differences of leaching behaviour and modelled emissions can be observed comparing study WC9 and WC12. Overall emissions are underestimated by the model for the first half of the experiment for WC9 and overestimates in the second half. Contrary to that, WC12 emissions are overestimated in the beginning and underestimated in the end. For WC9, final modelled terbutryn emissions were 0.00181 compared to measured 0.00227. TerSO modelled returned a value of 0.00162 in comparison to measured 0.00176. TerOH modelled yielded 0.0381, measured 0.00389. TerDesE modelled produced 0.00194 in contrast to a measured value of 0.002260. TerDesEOH emissions showed a modelled value of 0.00980 compared to a measured value of 0.01163. For WC12, modelled terbutryn emissions were 0.00432 and measured emission were 0.00423. TerSO modelled resulted in 0.00767 cumulative emissions compared to measured 0.00782. TerOH values reached 0.009825 compared to measured values of 0.01028. TerDesE yielded 0.002530 for modelled and 0.00262 for measured emissions. TerDesEOH showed almost indifferent emissions with a modelled value of 0.00990 and a measured value of 0.01006. The modelled sum of emissions was 0.034271 compared to measured 0.035031. TPs showed a modelled value of 0.029952 at the end of the experiment and a measured value of 0.03080.

The test specimen of Bollmann et al. (2016) showed a relatively higher share of terbutryn emissions compared to the data of Junginger et al. (2022a) and Schoknecht et al. (2016b). The contribution of TPs to overall emissions is lower for both acrylate and silicone panels compared to the other studies. For A1, cumulative emission of terbutryn reached 0.018459 (modelled) and 0.025790 (measured). TerSO emissions modelled were 0.003914 and 0.003445 measured. Modelled TerOH yielded 0.00318, measured 0.00397. TerDesE modelled resulted in 0.00632 compared to 0.00794 measured. TerDesEOH differed from 0.00444 modelled to 0.00533 measured. Overall emissions varied from 0.03930 modelled to 0.04646 measured. Modelled TPs reached a share of 0.01784 compared to the measured share of 0.02068. S1 emissions for modelled overall emissions and TPs emissions were 0.06109 and 0.03573 respectively. The measured counterparts were 0.06341 and 0.03686. Regarding single substances terbutryn modelled contributed to 0.02536 compared to measured 0.02655. TerSO modelled reached a cumulative emission of 0.00665 in contrast to measured emissions of 0.00733. Modelled TerOH accounted for 0.00455 compared to measured 0.00460. Modelled TerDesE and TerDesEOH reached values of 0.01098 and 0.01354 respectively. The respective measured equivalents were 0.01041 and 0.01451.

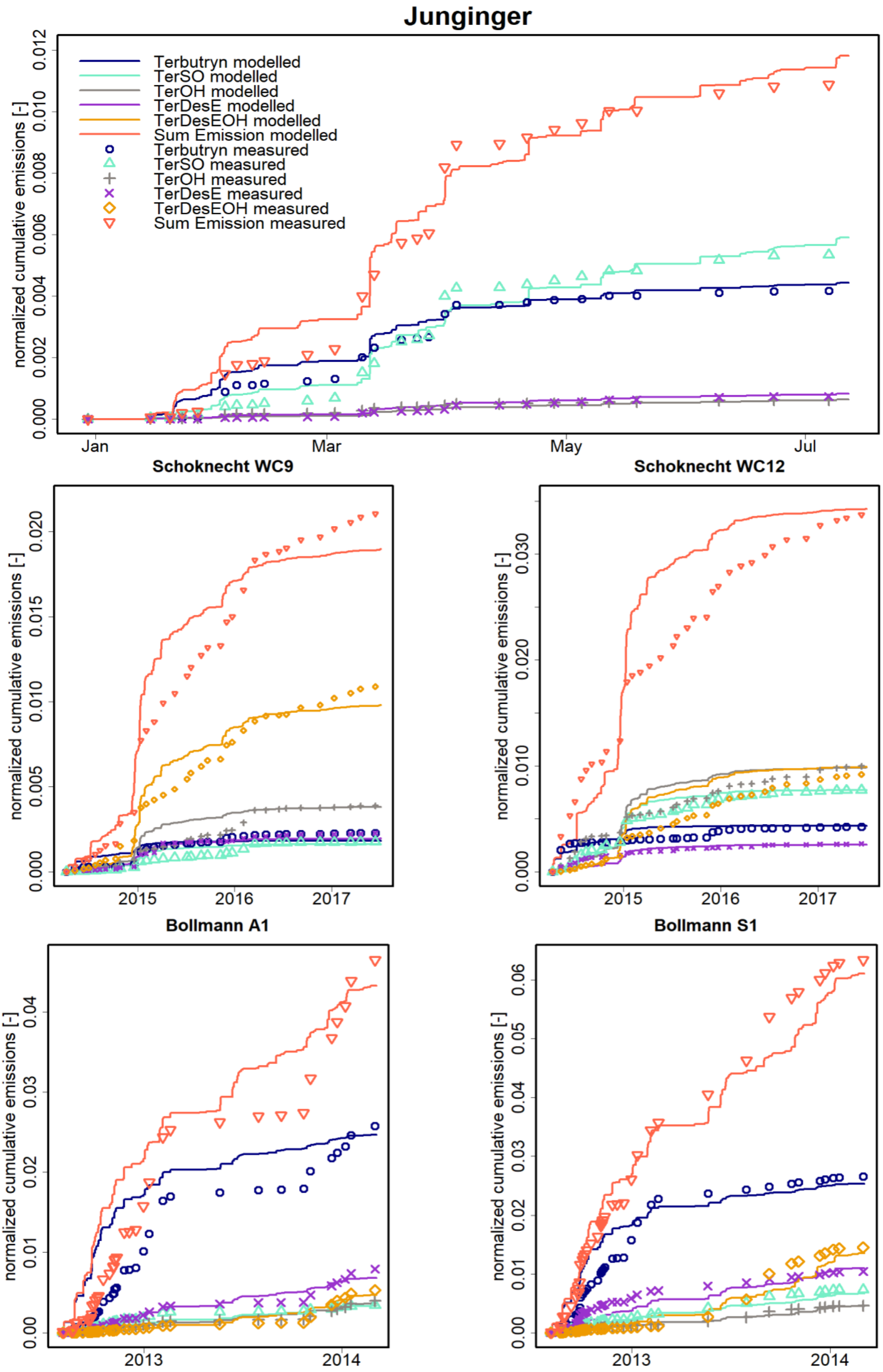
4.1.2 Decay and Diffusion

The effect of including of non-available terbutryn in the decay system to account for the diffusion process is shown in *Figure 9*. Visually, the integration of diffusion processes seems to improve the previous underestimating of especially terbutryn in the beginning of the respective experiments when comparing *Figure 8* to *Figure 9*. Particularly the temporal progression of cumulative emissions as well as terbutryn emissions for the Junginger, WC9, A1 and S1 test specimen are described more accurately by the model.

The modelled overall emissions (terbutryn + TPs) for the Junginger data including diffusion were 0.01141 to a measured value of 0.010874. Similar small differences can be observed for modelled TPs accounting for 0.00699 measured TPs accounting for 0.00671. Concordance of terbutryn can be observed with a modelled value of 0.00441 and measured value of 0.00416. TerSO modelled reached 0.00546 compared to 0.00534. TerOH modelled yielded 0.00076 in contrast to measured 0.00062. TerDesE also resulted in a modelled value of 0.00076 and a measured value of 0.00074.

The modelling of test specimen WC9 with diffusion of the study from Schoknecht et al. (2016b) resulted in enhanced overall emissions of 0.02218 compared to measured 0.021833. Modelled TPs showed a share of 0.019978 in contrast to measured TPs of 0.01956. Terbutryn modelled reached a contribution of 0.00221 compared to a measured value of 0.00228. TerSO modelled accounted for 0.00173 compared to measured 0.00176. The share of modelled TerOH was 0.00396 in comparison to measured 0.00389. Modelled values of TerDesE and TerDesEOH were 0.00256 and 0.01173 respectively with measured counterparts of 0.00226 and 0.01164. For WC12 with diffusion, modelled terbutryn emissions were 0.00382 and measured emission were 0.00423. TerSO modelled resulted in 0.00742 cumulative emissions compared to measured 0.00782. Modelled TerOH values reached 0.00934 compared to measured values of 0.01028. TerDesE yielded 0.00244 for modelled and 0.00262 for measured emissions. TerDesEOH showed lower emissions compared to the only decay scenario with a modelled value of 0.00810 and a measured value of 0.01007. The modelled sum of emissions was 0.03113 compared to measured 0.03503. TPs showed a modelled value of 0.02730 at the end of the experiment and a measured value of 0.03080.

For A1 with diffusion, cumulative emission of terbutryn were enhanced and reached 0.02395 (modelled) compared to 0.025790 (measured). TerSO emissions modelled were 0.00436 and 0.003445 measured. Modelled TerOH yielded 0.00388, measured 0.00397. TerDesE modelled resulted in 0.00762 compared to 0.00794 measured. TerDesEOH improved to 0.00534 compared to 0.00533 measured. Overall emissions varied from 0.04518 modelled to 0.04646 measured. Modelled TPs reached a share of 0.02122 compared to the measured share of 0.02068.


Junginger

Schoknecht WC9

Schoknecht WC12

Bollmann A1

Bollmann S1

Figure 8, Modelled and measured emission of terbutryn and TPs for respective studies for emission scenario one.

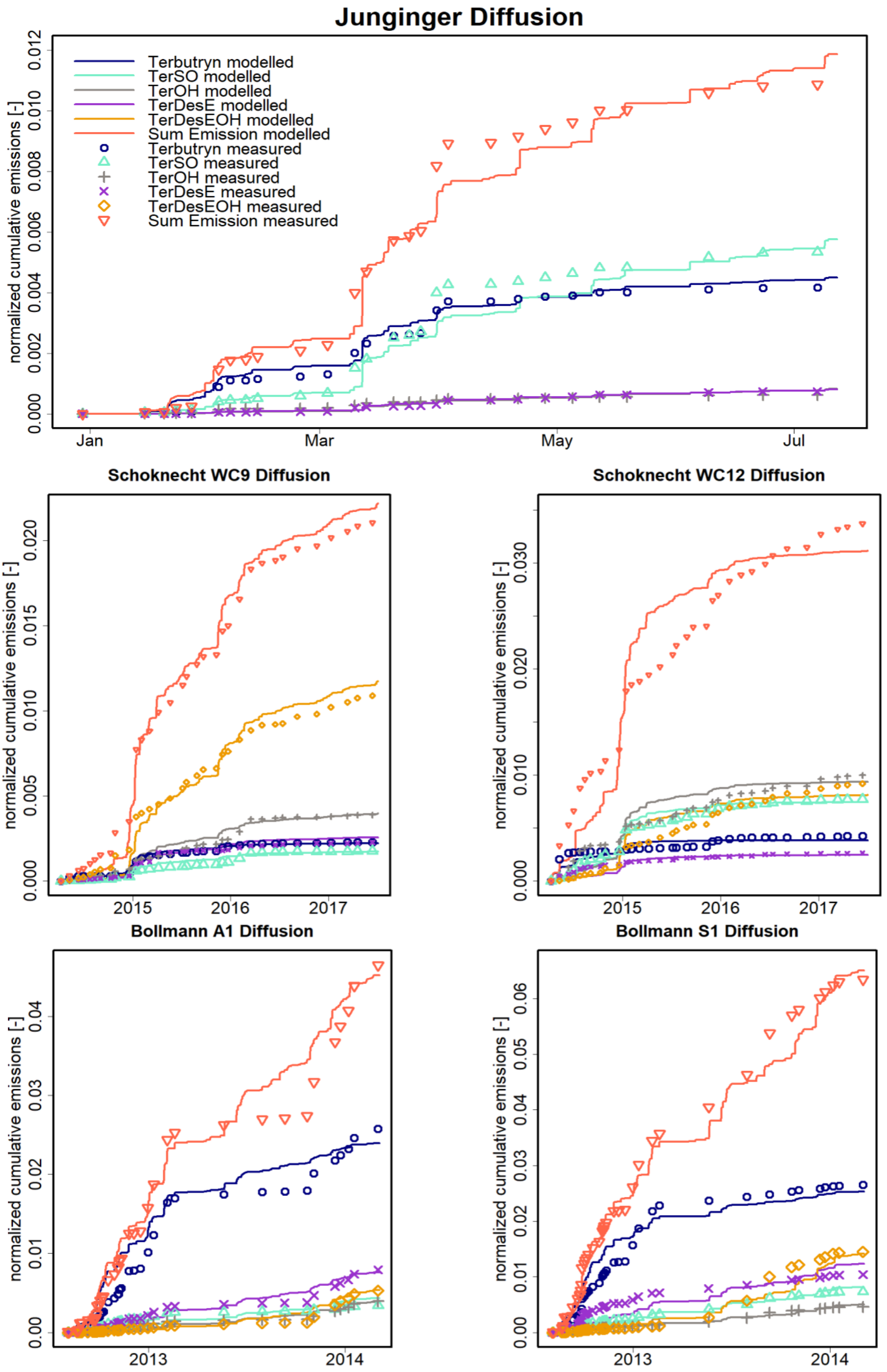


Figure 9, Modelled and measured emission of terbutryn and TPs for respective studies for emission scenario two.

S1 emissions with diffusion for modelled overall emissions and TPs emissions were 0.06502 and 0.03971 respectively. The measured counterparts were 0.06341 and 0.03686. Regarding single substances terbutryn modelled contributed to 0.02531 compared to measured 0.02655. TerSO modelled reached a cumulative emission of 0.00816 in contrast to measured emissions of 0.00733. Modelled TerOH accounted for 0.00501 compared to measured 0.00460. Modelled TerDesE and TerDesEOH reached values of 0.01235 and 0.01419 respectively. The respective measured equivalents were 0.01041 and 0.01451.

4.1.3 Decay, Diffusion and Solar Radiation

In the last scenario all physical parameters assumed to be relevant to leaching process were considered in the model. Visually, especially S1 shows a good fit of modelled and measured data. A1 underestimates emissions in the first half of the experiment but predicts the emissions in the second half of the experiment correctly (*Figure 10*).

For A1, cumulative emission of terbutryn reached 0.02615 (modelled) compared to 0.025790 (measured). TerSO emissions modelled were 0.00451 and 0.003445 measured. Modelled TerOH yielded 0.00418, measured 0.00397. TerDesE modelled resulted in 0.00769 compared to 0.00794 measured. TerDesEOH was 0.00494 modelled compared to 0.00533 measured. Overall emissions varied from 0.04749 modelled to 0.04646 measured. Modelled TPs reached a share of 0.021341 compared to the measured share of 0.02068.

S1 emissions for modelled overall emissions and TPs emissions were 0.06395 and 0.03846 respectively. The measured counterparts were 0.06341 and 0.03686. Regarding single substances terbutryn modelled was enhanced and contributed to 0.02548 compared to measured 0.02655. TerSO modelled was enhanced as well and reached a cumulative emission of 0.007924 in contrast to measured emissions of 0.00733. Modelled TerOH accounted for 0.00556 compared to measured 0.00460. Modelled TerDesE and TerDesEOH reached values of 0.01131 and 0.013658 respectively. The respective measured equivalents were 0.01041 and 0.01451.

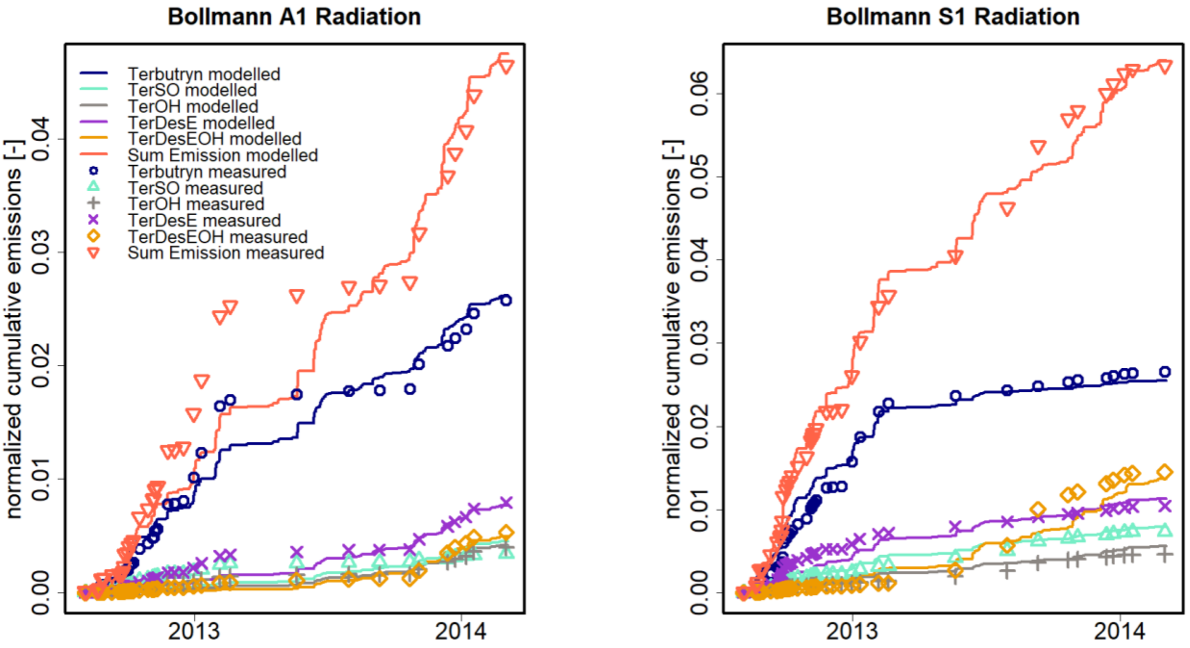


Figure 10, Modelled and measured emission of terbutryn and TPs for respective studies for emission scenario three.

4.2 Goodness of Fit

The goodness of fit was determined as described in *3.6 Model Evaluation* by calculating the r² and relative RMSE value for each substance and each scenario compared to the respective measurements. The results of r² and relative RMSE values are shown in *Figure 11*. Respective values of r² are given in *Appendix Table 3* and for the relative RMSE in *Appendix Table 4* For comparison of the goodness of fit of the different scenarios and substances *Figure 12 and Figure 13* were colour coded according to the in *3.6 Model Evaluation* determined categories.

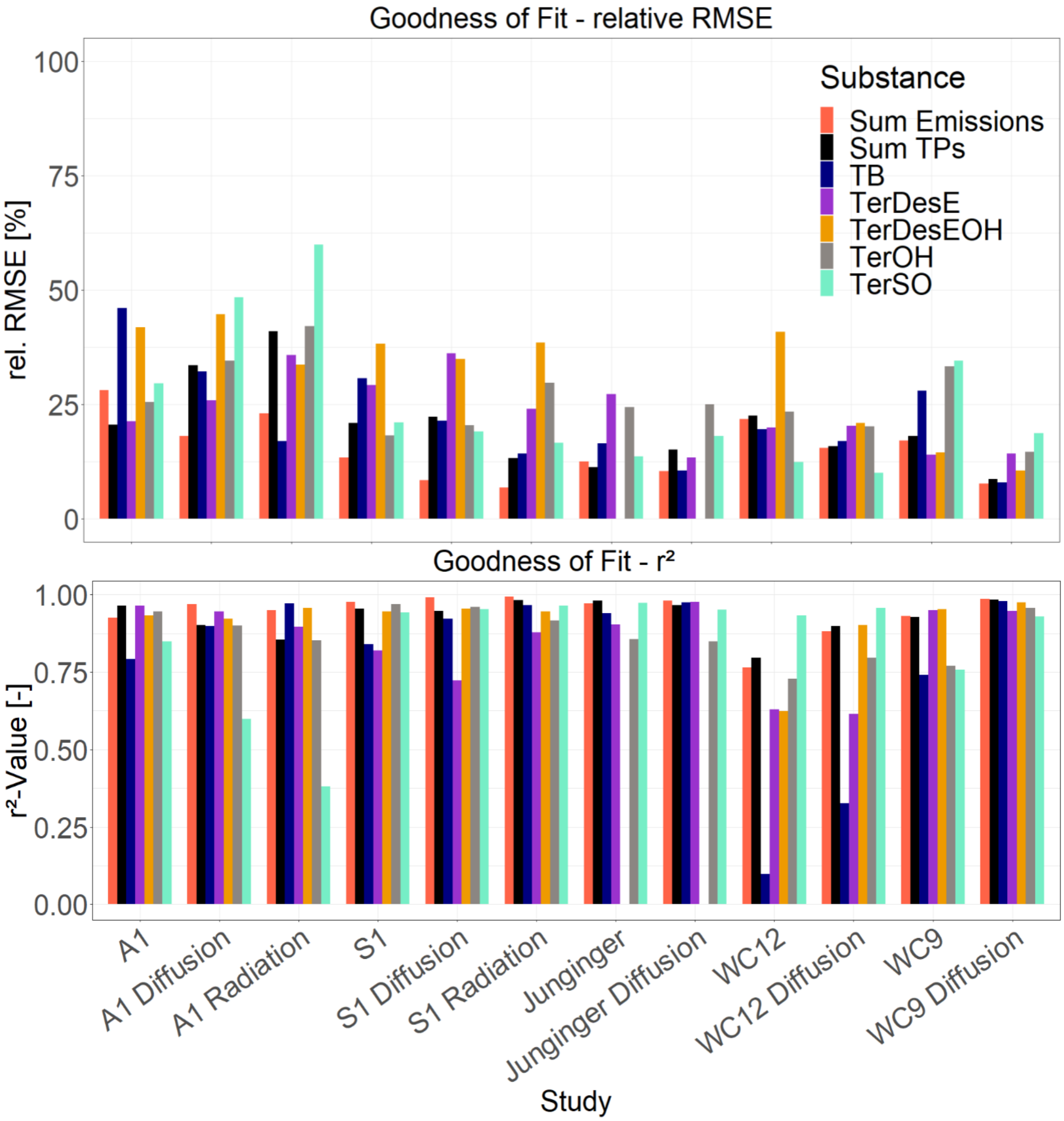


Figure 11, Goodness of fit values for different studies and emission scenarios for respective substances according to Equations 16 to 20.

Lowest r² was determined for modelled terbutryn of WC12 with 0.10. The highest r² value was observed for S1 Radiation with 0.99. The substance matched most accurately by the model according to r² values was the sum of emissions with a mean r² value of 0.94. The mean r² value across all studies and substances was 0.88. The median r² value across all studies and substances was 0.94. 77% of r² values were above 0.90.

For the Junginger data r² increased or stayed the same for all substances expect for TerOH which decreased from an r² value of 0.88 to 0.80 when applying the diffusion scenario compared to the decay scenario. The mean of all r² values of the Junginger data increased from 0.93 to 0.94 when comparing decay with decay and diffusion scenario. This supports the previously discussed improved visual fit.

Regarding the Schoknecht WC9 data a significant improvement of all r² values can be observed when comparing the diffusion and decay scenario with the decay scenario. For example the goodness of fit for terbutryn, TerSO TerOH each increased by more than 0.20 for WC9 when including diffusion in the modelling process. Similar results are achieved for WC12, but with a decrease of the r² value of TerDesE from 0.63 to 0.61. All other r² values increased. This is represented by an increase of the mean r² of all substances from 0.86 to 0.96 for WC9 and from 0.65 to 0.76 for WC12.

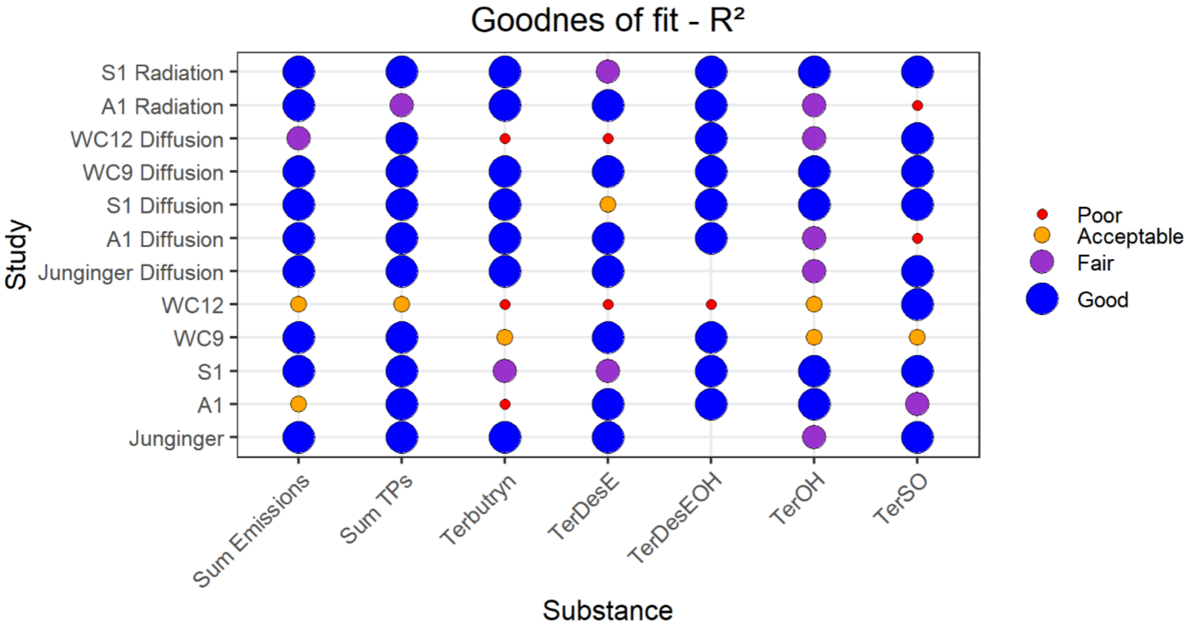


Figure 12, Color coded representation of r² values according to in 3.6 Model Evaluation determined categories: Good/blue r² > 0.90), fair/violet (0.80 > r² < 0.90), acceptable/orange (0.70 > r² < 0.80) and poor/red (r² < 0.7).

For the Bollmann A1 data model performance decreases with more complex model scenarios. Only Terbutryn r² values increase with each scenario. TerSO fit is decreased by more than half when comparing the decay scenario with the radiation scenario. The goodness of fit also decreases for TerDesE and the overall sum of TPs. The sum of emissions was increased by implementing the diffusion scenario but decreased when taking solar radiation into account. Regarding the mean r² of all substances for A1 the fitting value decreases from 0.91 in the decay scenario over 0.87 in the diffusion scenario to 0.83 in the radiation scenario. Contrary to that the measured data of S1 could be represented better with a more complex model scenario. For S1, all r² values increased or remained the same except for TerOH with an r² decrease from 0.97 to 0.92 which still represents a high concordance. This is also represented by the mean r² values of all substance for the different scenarios increasing from 0.92 when only accounting for decay to 0.95 when accounting for decay, diffusion and radiation.

Regarding the relative RMSE, the poorest model performance was determined for TerSO values of A1 Radiation with a value of 59.94%. Contrary, the best model fit according to relative

RMSE was achieved by the modelled overall emissions of S1 Radiation with a value of 6.87%. The mean relative RMSE across all studies and scenarios was 23.17%. The median relative RMSE resulted in 20.76%. 44% of all relative RMSE values were below 20%. 74% of relative RMSE values were below 30%. The comparison of modelled and measured data for the two scenarios applied to the Junginger data showed a decrease of the relative RMSE for terbutryn, TerSO, TerDesE and the overall sum of emissions. Differences of modelled and measured values increased for TerOH and the sum of TPs when comparing the decay with the decay and diffusion scenario. However, the mean relative RSME of all substances decreased from 17.57% to 15.43%. Regarding the Schoknecht data of test specimen WC9 a decrease of the relative RMSE for all substances can be observed expect for TerDesE which remained on a similar level. Therefore, mean relative RMSE of all substances nearly halved from 22.77% to 11.78%. The same results of individual substances can be observed for WC12, however less pronounced with a decrease of the mean relative RMSE of all substances from 22.90% to 17.10%.

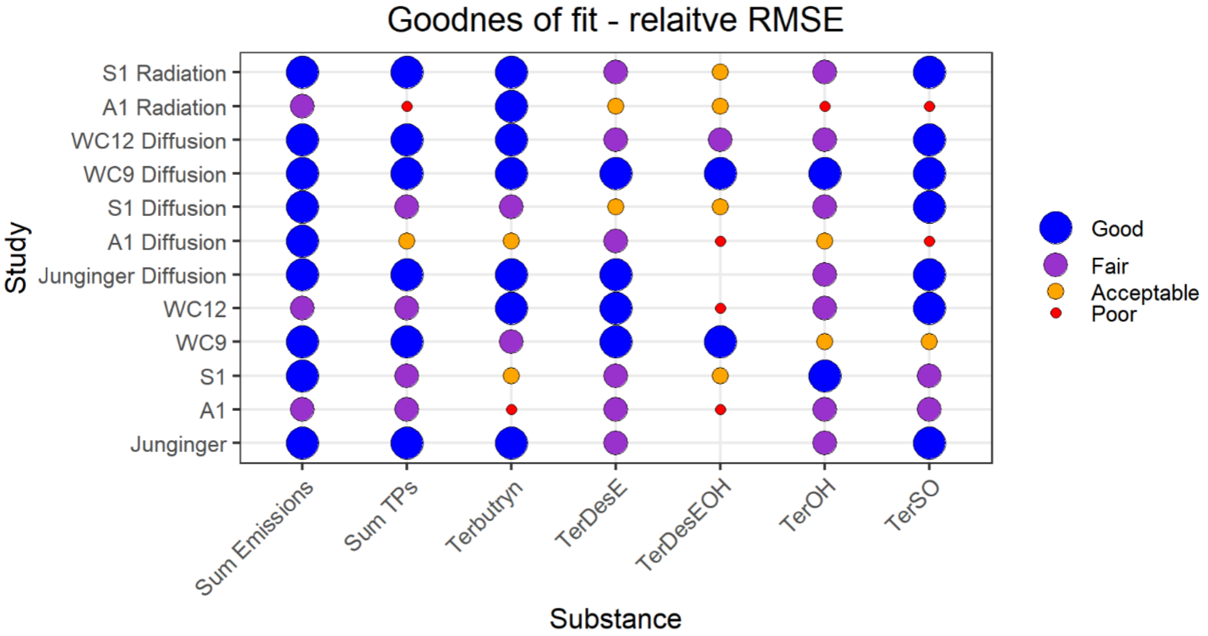


Figure 13, Color coded representation of relative RMSE values according to in 3.6 Model Evaluation determined categories: good/blue (RMSE < 20%), fair/violet (20% > RMSE < 30%), acceptable/orange (30% > RMSE < 40%) and poor/red fit (RMSE > 40%).

The acrylate render test specimen of the experiments conducted by Bollmann et al. (2016) showed the highest discrepancy of modelled and measured values according to the relative RMSE. For A1, similar to the r² values the relative RMSE decreased as well along the different scenarios regarding terbutryn. Accuracy decreased for TerSO, TerOH and the sum of TPs. Especially TerSO values of the radiation scenario showed a high relative RMSE. Therefore the mean relative RMSE increased from 30.32% in the decay scenario to 33.90% in the decay and diffusion scenario and to 36.05% in the scenario including decay, diffusion and radiation. Similar to the r² value the relative RMSE values the silicone render test specimen showed a better model fit with the more complex scenarios. Terbutryn, TerSO and the sum of emissions improve accuracy with each model scenario. On the other hand the relative RMSE o TerOH increases while TerDesE shows a worse performance when accounting for diffusion but achieves an overall better fit when including radiation in the model. TerDesEOH remain on a similar level in each scenario. For the sum of overall emissions S1 Radiation shows the overall lowest relative RMSE of 6.87% and an also low value of the sum of TPs. Across all substances the mean relative RMSE decreases from 24.54% to 20.46% from scenario one to scenario three.

4.3 Effect of Decay Rate on Emissions

The Junginger emission data were simulated with different decay rates of terbutryn. Hereby decay rates were used that are in the range of decay rates determined by previously conducted studies (Bollmann et al. 2017; Junginger et al. 2022, 2023; Lechón et al. 1997; Muir and Yarechewski 1982). All other model parameters remained unchanged. The effect of different decay rates to the remaining substance in the façade and emissions from the façades is shown in *Figure 14*. The effect of the decay rate on the formation of the different TPs is shown in *Appendix Figure 7*.

A short decay rate leads to faster depletion of the substance in the façade, quicker formation of TPs and a plateau of cumulative emissions. In the simulation with a dt_{50} of ten days terbutryn degrades so fast that practically no emission occurs after two months. Contrary, higher decay rates lead to slower depletion and a continuous incline of cumulative emission after 194 days of weathering. However, a lower half-life time can lead to higher overall emissions. Highest total emissions (TB + TP) were observed in the simulation with a dt_{50} of 110 days and seconds highest emissions with a decay rate of 50 days. Third highest total emission occurred with a dt_{50} of 231 days. Lowest emission was observed at a dt_{50} of ten days.

Terbutryn and TPs were both almost completely depleted after 194 days with a dt_{50} of ten days with 0.01% of the initial amount of substance remaining. With a half-life time of 50 days 43.90% of substance remained after the duration of the experiment. The in the main simulation used dt_{50} of 110 days resulted in 82.08% remaining substance. At the end of the simulation with a dt_{50} of 231 days 94.64% of the initially applied amount remained in the façade. Also the differences in the terbutryn/TPs ratio changes with different half-life times and steadily increases with a higher dt_{50}. TPs predominate at a dt_{50} of ten days with a terbutryn/TPs ratio of 0.01. The ratio decreases to 0.18 at a dt_{50} of 50 days. At a dt_{50} of 110 days terbutryn and TPs are in a ratio of 0.55. With a greater half-life time of 231 days terbutryn prevails with a ratio of 1.41.

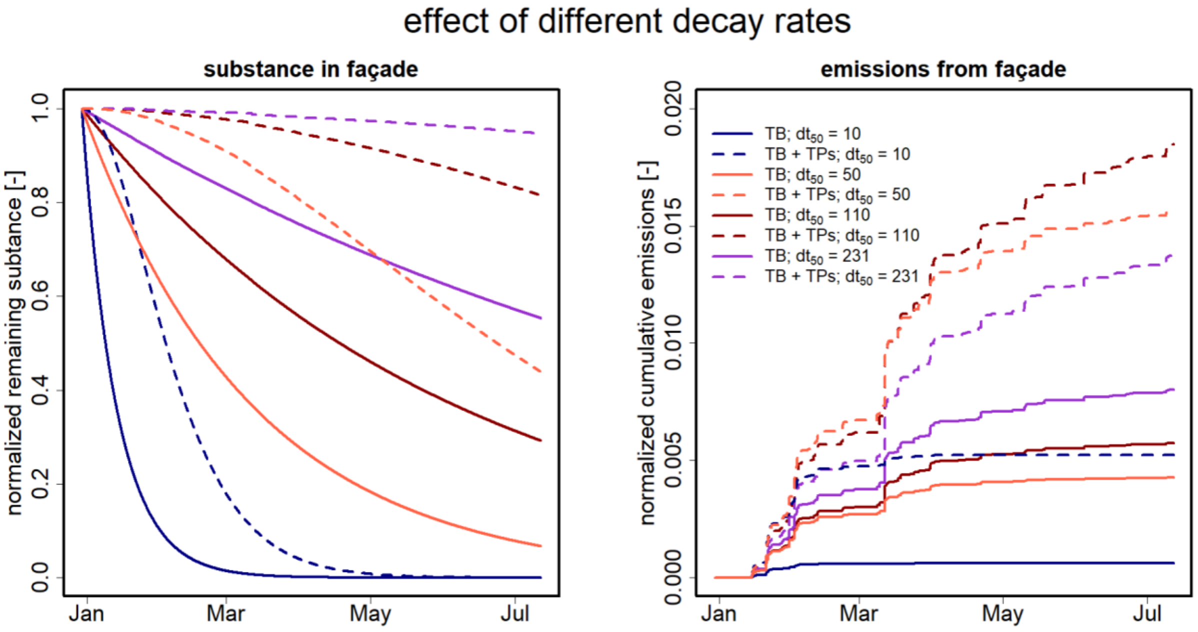


Figure 14, Effect of different decay rates on substance in façade and emissions from façade.

4.4 Effect of Solar Radiation

Solar radiation drives the photo degradation of terbutryn and therefore the for emission available substance and TPs (Junginger et al. 2022, 2023; Urbanczyk et al. 2019; Bollmann et al. 2016; Hensen et al. 2019). In order to implement the diurnal and seasonal variability of solar radiation (*Appendix Figure 2*) a solar radiation factor was added to enhance or inhibit the decay of a substance relative to the mean solar radiation.

Solar radiation data in hourly resolution was only available for the study of Bollmann et al. (2016). Therefore, the model extension with solar radiation could only be observed on this specific data. *Figure 15* shows the effect of radiation on the remaining substance in the façade. All parameters of the model are identical except the addition of the decay being affected by the solar radiation factor. Without taking solar radiation into account the decay and formation of terbutryn and its TPs follows solely a single first order decay. The exponential decay occurs uniform. The terbutryn substance amount is being reduced and TPs form and decay steadily as well. With consideration of the solar radiation factor a seasonal variability of terbutryn degradation and TP formation can be observed (*Figure 15*). In the beginning of the experiment in August 2012 higher radiation values lead to a faster decay compared to the original model data. The decay of terbutryn is then inhibited during the 2012/13 winter period and accelerated again in the following summer. The same inhibition and acceleration of decay and formation can also be observed regarding the TP and the sink in which the TP are degrading into.

This seasonal shift can also be observed regarding the emissions. Comparing *Figure 9* and *Figure 10* a visually better fit of the terbutryn emissions, especially in the beginning and end of the field experiment can be observed. r^2 values of terbutryn increased from 0.90 to 0.97 for A1 and from 0.92 to 0.97 for S1 when additionally applying the solar radiation factor to the decay system. The relative RMSE is nearly halved from 32.15% to 17.02% for A1 and decreased from 21.43% to 14.29% for S1. The sum of emissions remained similar with a change of the r^2 value from 0.97 to 0.95 for A1 and from 0.99 to 0.99 for S1. Relative RMSE increased from 18.02% to 23.04% for A1 and decreased from 8.37% to 6.87% for S1. The change of r^2 and relative RMSE values of the individual TPs is shown in *Figure 12* and *Figure 13*.

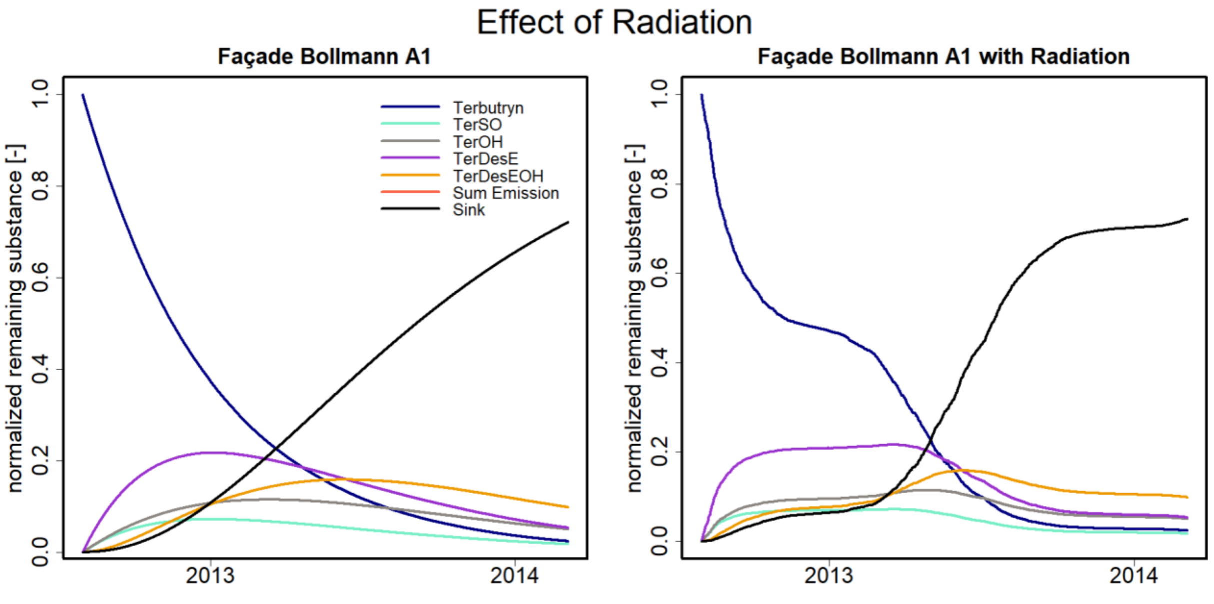


Figure 15, Effect of solar radiation factor on normalized remaining substance.

4.5 Extrapolation of Emission Function

In order to estimate the long term leaching behaviour, the derived emission function parameters (*Appendix Table 1*) were used to extrapolate the cumulative emissions over the typical life time of a façade. 1000 mm of façade runoff corresponds to a time span of approximately 25-50 years depending on the examined test specimen with different annual rainfall and runoff coefficient due to façade surface properties. This time span represents the average lifetime of a housing façade (Voigt et al. 2023). The cumulative emissions of the respective extrapolated emission functions are shown in *Figure 16*.

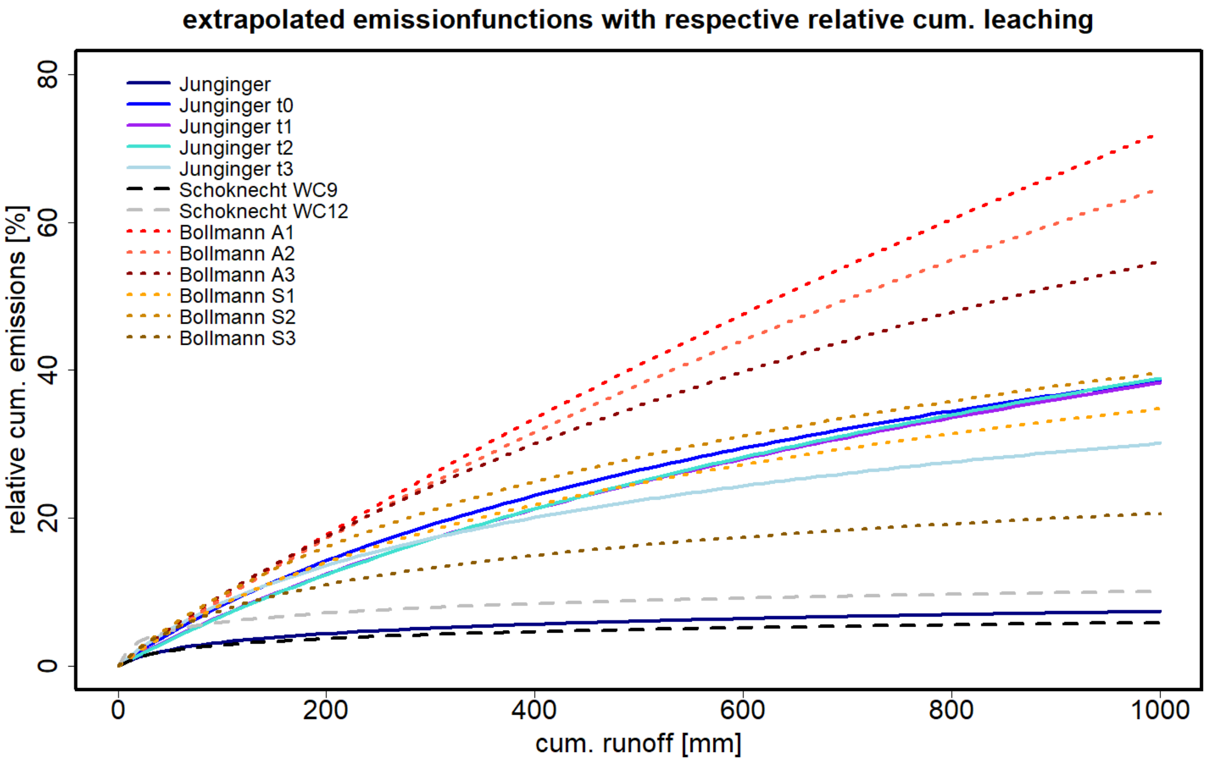


Figure 16, Extrapolated emission functions with respective relative cumulative emissions. Represented by the logarithmic emission function described in Equation 8 and respective parameters from Appendix Table 1.

The overall share of leached initially applied active substance varies between 6% and 72% after 1000mm of façade runoff. The highest extrapolated relative cumulative emissions occurred with the emission function parameters retrieved from the acrylate test specimen of Bollmann et al. (2016). Lowest emissions were observed for WC9 of Schoknecht et al. (2016b). In the experiment of Junginger et al. (2023) four façade samples were taken at different times during the experiment and examined in immersion test with intermittent water contact corresponding to a façade runoff of 10 to 25 years (Junginger et al. 2023). Hereby, the emissions of the immersion test excel the emissions of the façade of the field experiment by a multiple. The extrapolated cumulative emissions of Junginger et al. (2023) and Schoknecht et al. (2016b) range in a different order of magnitude compared to the acrylate and silicone render test specimen of Bollmann et al. (2016). Furthermore, the leaching process of Junginger et al. (2023) and Schoknecht et al. (2016b) appears to have reached a plateau whereas the cumulative emissions of both acrylate and silicone renders of Bollmann et al. (2016) increase continuously after 1000mm of façade runoff. It must be taken into account, that the emission parameters were retrieved from cumulative façade runoff ranging from 16mm to 121mm and relative cumulative emissions ranging from 1.08% to 8.19% and extrapolation was therefore carried out by up to a factor of ten.

4.6 Relationship of Emission Function Parameters

The emission function parameters of the three different studies range in different orders of magnitude (*Appendix Table 2, Appendix Figure 9 & 10*). Viewing the emission function parameters and the initially applied active substance amount, it was hypothesized that a possible functional relationship of these parameters could be determined. *Figure 17* shows the relationship of logarithmic emission function parameters and respective initially applied substance amount *c0*. For the Schoknecht data WC9 and WC12 with different initial concentrations are displayed. For the acrylate and silicone render of Bollmann, three test specimen each with the same initial concertation were observed. Within the different test specimen with identical initial concentration and experiment conditions, different parameters of the emission function were retrieved, however ranging within the same order of magnitude. A linear regression was carried out for the logarithmic *a* and *b* parameters in relation to the initial concentration. For the *a* parameter the correlation was determined by a r² value of 0.93 and a r² value for 0.87 for the *b* parameter. The regression line of the *a* parameter is described by $y = 0.610 \cdot x - 2.3256$ and for the *b* parameter by $y = 0.4073 \cdot x - 0.9128$.

Generally, it appears that with increasing initial substance amount the logarithmic *a* parameter value increases, whereas the logarithmic *b* parameter value decreases. However, with the small sample quantity the exhibited results are not significant and have to be interpreted with care.

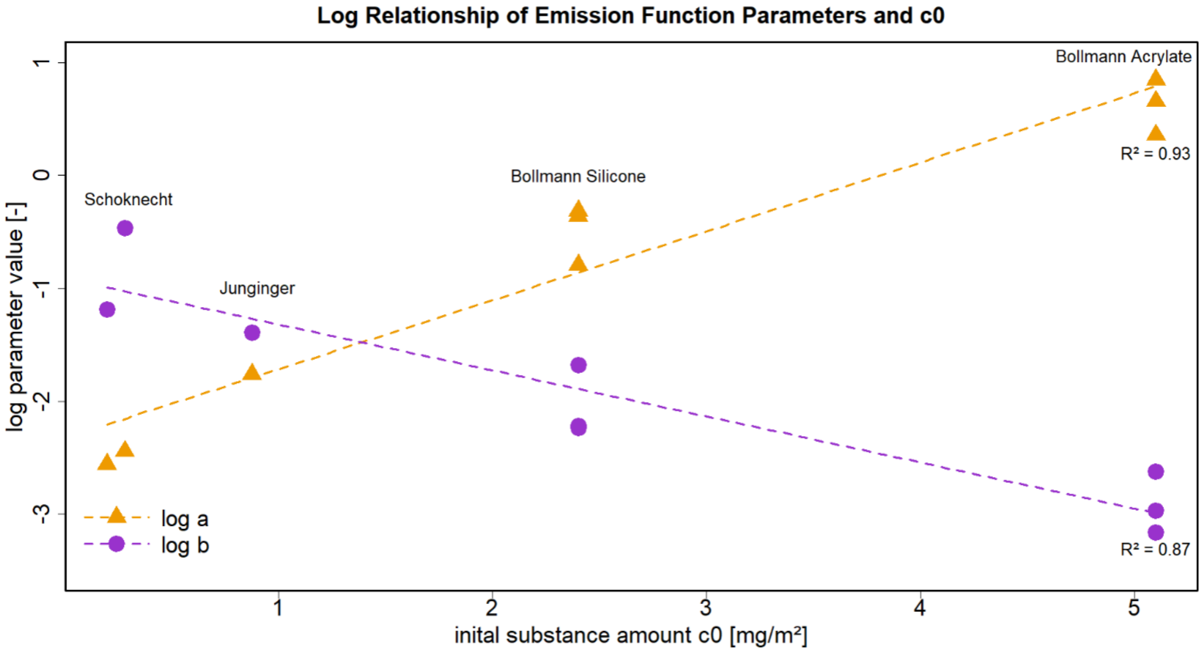


Figure 17, Relationship of initial substance amount and logarithmic emission function parameter values.

5. Discussion

5.1 Uncertainties

The leaching of biocides from façades is a complex interaction of various parameters and variables (Bollmann et al. 2016; Bollmann et al. 2017; Burkhardt et al. 2009; Burkhardt et al. 2012; Cockroft and Laidlaw 1978; Junginger et al. 2023; Schoknecht et al. 2016a; Schoknecht et al. 2016b; Schoknecht et al. 2022; Schoknecht and Mathies 2022; Urbanczyk et al. 2019; Vega-Garcia et al. 2020; Vega-Garcia et al. 2022; Wicke et al. 2022). In order to be able to model these complex interactions various assumptions were made as describes in *3.2 Assumptions*. Therefore, the modelling of biocide emissions from façades is challenged by a number of uncertainties.

First of all, the key cause of emissions is the façade runoff originating from wind driven rain (Bollmann et al. 2016; Burkhardt et al. 2009; Junginger et al. 2023; Schoknecht et al. 2016b; Vega-Garcia et al. 2020). The façade runoff controls the emission process since without solution and advection of biocides and their TPs by water no emission can occur. This leads to the first and probably biggest uncertainty of biocide emission modelling caused by WDR. WDR itself has been a subject of study for almost a century (Blocken et al. 2013) and is still undergoing recent research due to its complexity (Gholamalipour et al. 2022) and wide range of influencing parameters (Blocken et al. 2013). To begin with, the fundamental parameters of WDR calculation are precipitation, wind speed and wind direction which are subject to measurements errors. This error is further enhanced by the usual and also in this study performed aggregation or selection of wind speeds and directions exceeding the initial measurement resolution. Especially, the hourly resolution of wind direction leads to an uncertainty in the WDR calculation. Also, weather events below the measurement resolution like gusts cannot be taken into account as well as complex turbulent winds. Therefore, the input parameters of the WDR calculation are susceptible to error. Regarding the calculation of WDR (Equation 9) other parameters beside measurements of precipitation, wind speed and wind direction influence WDR. Topography, surrounding buildings (e.g. leading to wind channels in urban areas), topography, roughness of the surrounding terrain and the size of the façade itself influence the amount of WDR that results in façade runoff (Blocken et al. 2013; DIN EN ISO 15927-3:2009-08; Gholamalipour et al. 2022). On the other hand, these factors in the geometry file in ComleamD also allow to adapt façade runoff and to account for the different surface attributes and surroundings.

The combination of the previously discussed uncertainties is shown in the measured cumulative façade runoff of the triplet experiments for acrylate and silicone render of Bollmann et al. (2016). The different render compositions consisting of acrylate or silicone produced varying façade runoff amounts while being exposed to the same weathering conditions. Further, the respective three test specimen with identic acrylate and silicone render compositions produced varying amounts of façade runoff while being exposed to the same weathering and being positioned next to one another. As described previously in *Table 1* overall runoff coefficients across the different studies and test specimen ranged from 2.32% to 8.30%. This shows that render and paint properties have a profound impact on façade runoff. Since the façade runoff is a linear parameter of the logarithmic emission function this uncertainty alone could lead to an over or underestimation of emissions by almost 6%, neglecting initial error of measurements of the meteorological parameters discussed earlier.

It can therefore be argued that WDR as one of the main inputs of the ComleamD model is susceptible to a consequential error of the previously described input variables. Nevertheless, it was shown that an adjustment of the available parameters in ComleamD can compensate for this uncertainty. However, the previously mentioned uncertainty of the input variable of WDR has to be taken into account.

Another uncertainty poses the degradation of terbutryn. As mentioned previously in *3.2.2 Degradation* several half-life times of terbutryn have been determined under natural and laboratory conditions (Bollmann et al. 2016; Bollmann et al. 2017; Junginger et al. 2022, 2023; Lechón et al. 1997; Muir and Yarechewski 1982; Talja et al. 2008). Since the emission is based on the available amount in the façade the decay rate has a profound impact on emissions. Assumed and not determined half-life times therefore pose an uncertainty to overall emissions. In this study a half-life of 110 days determined by Junginger et al. (2023) was used for terbutryn and it TPs. However, the used half-life time was obtained under laboratory conditions and real half-life time under natural conditions could be higher, since a constant radiation of midday intensity was used in the experiment (Junginger et al. 2023). Furthermore, photo degradation only occurs on the outer layer of the façade (ca. 100 µm) where solar radiation can penetrate and reach the terbutryn molecules (Junginger et al. 2023; Uhlig et al. 2019). These micro scale processes are not accounted for in the ComleamD model. However, an approximation of this process was implemented by the addition of unavailable terbutryn and therefore only making a reduced share of the initial terbutryn amount available for degradation. Nevertheless, this cannot represent the complex physical process of photo degradation. A further uncertainty is the lacking knowledge of degradation behaviour of TPs. It is unclear how fast and trough which processes TPs further degrade into other TPs or if they are being mineralized.

The lacking knowledge on TPs is another uncertainty of biocide modelling. If the state variables of degradation of a parent compound and its TPs is known, it is also crucial to know the degradation pathway in order to correctly determine parent compound and TP relation and corresponding amounts. In recent literature three degradation pathways of terbutryn are described (Bollmann et al. 2016; Junginger et al. 2022; Schoknecht and Mathies 2022). All proposed degradation pathways assume a degradation of terbutryn into TerSO, TerOH and TerDesEOH. Nonetheless, Schoknecht et al. (2022) and Bollmann et al. (2016) both propose an additionally degradation of TerOH into TerDesEOH. Also Bollmann et al. (2016) proposes further degradation into five additional TPs. Since the decay system and associated formation fractions are based on the degradation pathway different assumptions of the way a parent compound decays in its TPs poses an uncertainty in the modelling process. In retrospective the additional degradation of TerOH into TerDesEOH proposed by Bollmann et al. (2016), Schoknecht and Mathies (2022) and Schoknecht et al. (2022) could provide a solution to the systematic over- and underestimation of TerDesEOH in the modelling process.

A more general problem regarding degradation is the determination of formation fractions. As mentioned earlier in *3.2.4 Formation Fractions* the formation fractions could not be determined according to the FOCUS guidance on the calculation of persistence and degradation kinetic endpoints of metabolites and were estimated on basis of the share of TPs to overall emissions. This bears an uncertainty since due to different mobility the actual share of the respective TP in the façade could be higher and emission function parameters were fitted incorrectly to compensate for the initial error in respective TP share in the façade. In order to obtain formation fractions under real life conditions a sacrificial testing method following the example of Junginger et al. (2023) but with sacrificial measurements of the façade for every rain event could provide a continuous mass balance and capability of determining formation fractions. Alternative, a replicate of the laboratory experiment conducted by Junginger et al. (2023) with a longer exposure time to artificial sunlight to ensure the observation of formation phase, plateau and decline phase of terbutryn and its TPs could provide reliable formation fractions. This could also provide a possibility to determine the half-time of TPs.

Lastly, the combination of the previously described aspects are reflected in the leaching process which itself is based on a complex set of additional factors. Previous studies described the leaching process in detail (Junginger et al. 2023; Schoknecht et al. 2016b; Uhlig et al. 2019). Furthermore, key drivers of the hygrothermal façade properties like humidity, temperature and render materials and properties are not taken into account. All these uncertainties are compensated by the *a* and *b* parameter of the respective logarithmic emission function.

An uncertainty caused by the discussed assumptions and simplifications has therefore to be taken into account for when evaluating the results of biocide modelling with ComleamD.

5.2 Modelled Emissions & Goodness of Fit

The majority of modelled emission could achieve concordance with the measured emissions. This could be determined by a majority of r^2 values above 0.90, relative RMSE values below 30% and an appropriate visualisation of the measured data by the model. Between the results of the modelled emissions and the goodness of fit of the different scenarios and substances, differences were noticeable. In the following, it was tried to explain these differences and compare them with the tiered approach defined earlier in the aim of this study.

The first emission scenario taking only decay into account already describes the leaching behaviour adequately. However, the goodness of fit values are lowest across the examined emission scenarios. Regarding the visual fit of the sum of emissions in *Figure 8* an overestimation of emissions for all studies in the beginning of the experiment can be observed. It is hypothesized, that without consideration of diffusion emissions are overestimated, since the model calculates emissions immediately based on all substance, without respecting that only a fraction of the respective substances is available for leaching at the surface of the façade (Junginger et al. 2023; Uhlig et al. 2019). Since it was tried to achieve the best goodness of fit values possible, the later observed underestimation in the middle of the experiment course and overestimation at the end of the experiment course could be caused by the attempt of fitting the emission function parameters to a model that is not suited to display the correct leaching behaviour. This pattern of over and underestimation can be observed uniform across all studies, indicating an error of the model structure. In conclusion, it is assumed that the decay scenario can represent the generally leaching behaviour of terbutryn and its TPs but with restrictions regarding the temporal distribution of emissions.

In the second scenario the implication of diffusion in the modelling process was hypothesized to respond to the aforesaid error. The implication of not all parent compound substance being available for degradation improved model performance across all examined studies. However, the implied diffusion is based on the decay system with not available terbutryn degrading into available terbutryn which then further degrades into the TPs according to the degradation pathways and the in the formation matrix determined formation fractions. The diffusion of biocides from porous renders is a complex physiochemical process described in studies on its own (Styszko et al. 2015; Styszko and Kupiec 2018; Wangler et al. 2012). The simplification of representing the complexity of biocide diffusion in façades with a single first order decay is to be assessed critically. With a single first order decay the diffusion of not available parent compound occurs at a constant rate regardless of emitted substance, moisture, temperature and render properties. Therefore, a more accurate diffusion model is desirable. A combination of the in ComleamD already existing partly available substance approach and the decay system is emphasized. Here, the substance at the outer end of the façade decreases due to emission and decay but increases due to supply from the inner part of the façade. With this two compartment model a more sophisticated representation of the diffusion process would be possible, based on a supply rate according to an equilibrium state between the inner and outer façade compartment. However, a combination of the decay system and the supply approach is yet to be implemented.

The third scenario including decay, diffusion and solar radiation produced the model scenario with the highest goodness of fit values and also the visually most accurate representation of the temporal course of emissions of the respective substances. The approach of controlling the decay rate by a solar radiation factor depending on the quotient of current solar radiation and mean solar radiation provides a simple way of including the diurnal and seasonal variability of photo transformation. Even with no radiation data available, the seasonal variability could be described with a hypothetical solar radiation factor following a sinus function across the year. It is emphasized to include this third tier in the modelling of TPs, since the effect of varying solar radiation under natural conditions was shown by Minelgaite et al. (2017).

The best fit according to r^2 values and relative RMSE was achieved by S1 Radiation, whereas the worst fit was achieved by A1 Radiation. For all examined studies expect A1 an improvement of model performance could be observed along the different emission scenarios. This shows that the incorporation of diffusion and radiation in the modelling process can enhance model performance. It should be highlighted that already the simplest tier scenario regarding only decay correctly represented the temporal course of the emissions of the individual substances.

The poorest performance of all scenarios can be observed for A1. It is assumed that due to the nature of emission from this test specimen, with the by far highest initial terbutryn concentration and no encapsulation of the active substance the logarithmic emission function is unfit to describe its leaching behaviour for the observed time frame. When examining *Appendix Figure 4* the linear relation of cumulative emissions and cumulative runoff compared to the logarithmic behaviour of the other observed field experiments becomes clear. A further distortion of the modelled and measured values could be caused by the proportional effect of solar radiation on decay if the initial data is unfit to be displayed by a logarithmic emission function. However, the sum of emissions and the individual TPs were still described accurately. The distortion and resulting low goodness of fit values were mainly caused by an underestimation of terbutryn from winter to summer in 2013. Therefore, an adequate model performance can be attributed for the third emission scenario for A1.

Regarding the results of all emission scenarios and observed studies the emissions of TerDesEOH yielded among the highest relative RMSE. When examining *Figure 8* to *10* an overestimation of TerDesEOH in the beginning and an underestimation of TerDesEOH at the end of the experiment course is noticeable. This, coupled with relatively high relative RMSE values across all scenarios and studies indicates a systematic error since a trend of residuals is recognisable. It is hypothesized that this may be caused by a wrong assumption of the degradation pathway. As discussed previously, several proposed degradation pathways of terbutryn exist (Bollmann et al. 2016; Junginger et al. 2022; Schoknecht and Mathies 2022). The in this study assumed degradation pathway does not include a degradation of TerOH into TerDesEOH as supposed in other studies.

Also, a wrong distribution of formation fractions could cause this distortion, since formation fractions could only be estimated and were uniform for all scenarios and studies. Further studies testing the different proposed degradation pathways could provide clearance on the degradation pathways of terbutryn in housing façades under natural conditions.

With limited data and A1 being deemed unfit, yet S1 Radiation producing the best results, it is hypothesised that generally the third tier scenario is assumed to achieve the best model performance. However, further testing and validation with field experiments is needed to prove this hypothesis. Especially, the implementation of a model taken the diffusion process into account could further enhance model performance. The testing of ComleamD and the in this study presented results are considered a starting point for further research.

5.3 Effect of Decay Rates on Emissions

The decay rate or half-life time of an active substance and its TPs has a substantial effect on the timespan and amount of emissions from a façade as shown in *Figure 14*. Therefore, choosing the right half-life time of an active substance is crucial in order to be able to model realistic emissions. Emission rates in form of the parameters of the emission function remain constant. However, with changing available substance in the façade due to different decay rates the emission of the substance changes as well, even though the emission function parameters remain the same. This effect is further enhanced by the different mobility of TPs due to their chemical properties. This combination of effects is shown in the results in *Figure 14* where the highest emissions occur at a half-life time of 110 days, second highest emission at a half-life time of 50 day, third highest at a half-life time of 231 days and the lowest emission occurs at a half-life time of 10 days. If compared to *Appendix Figure 7* it becomes clear that for the half-life time of 110 days, the most substance is available for emission and that the available substance consists of a great share of more mobile TPs. Contrary to that are the emission of the very high and very low half-life times of 10 days and 231 days. With the very low half-life time of 10 days TPs form and degrade themselves so rapidly that after a short period of time no emission occurs anymore at all. With the great half-life time of 231 days only a small share of TPs has formed, and overall emissions are lower due to the lower mobility of terbutryn compared to its TPs. Generally short half-life times of active substances are desirable, since fast degradation is assumed to reduce environmental impact (Kahle and Nöh 2009). The results of the comparison of emission amount of different half-life times confirms this only partly. However, a short half-life time can lead to an overall higher peak of the sum of emissions since TPs are produced more rapidly and become available for emission. With limited data on TPs ecotoxicity, the environmental risk could be even higher but usually TPs tend to be less toxic than the parent compound (Wicke et al. 2022).

As stated before in *3.2.2 Degradation* several half-life times for terbutryn have been determined under various conditions. Data on TPs is scarce and half-life times are not documented. The available data on terbutryn photo degradation conducted by Bollmann et al. (2016) and Junginger et al. (2023) does not provide the possibility of determining decay rates of TPs as "for metabolites, the formation phase, plateau or maximum concentration, and decline phase should be clearly established" (FOCUS 2006, p. 69). Therefore, further research regarding TPs and their half-life times is needed to properly model TP emissions. It is empathised that a laboratory test following the example of Junginger et al. (2023) under simulated sunlight but with a longer exposure time could provide the data to determine TPs half-life time and formation fractions according to the FOCUS guidance on the calculation of persistence and degradation kinetic endpoints of metabolites since as shown in *Appendix Figure 3* TPs are still in the formation phase. The importance of using simulated sunlight for the observation of terbutryn degradation is highlighted by the fact that conducted experiments under ultra-violet light produced a high share of TPs that were below limit of detection under field conditions (Bollmann et al. 2016). This is underlined by the findings of Minelgaite et al. (2017) observing mitigated decay under natural conditions compared to laboratory experiments with UV-light.

In this study only the decay of terbutryn and its TPs on the façade were considered. The different decay rates of terbutryn under varying conditions were discussed in 3.2.2 Degradation. The varying decay rates of biocides under different conditions are highlighted in previous studies (Fenner et al. 2013). Therefore, for further environmental risk assessment or the modelling of the further fate of terbutryn and its TPs changing decay rates in soil, pond sediments, activated sludge, surface water and ground water as well as under aerobic and anaerobic conditions have to be taken into account.

5.4 Effect of Solar Radiation on Emissions

The impact of solar radiation on degradation of terbutryn was shown in previous studies (Hensen et al. 2019; Junginger et al. 2022, 2023; Urbanczyk et al. 2019). It was assumed that the photo degradation is the main driver of terbutryn degradation in housing façades and an incorporation of measured global radiation would positively affect model performance in terms of enhanced r² and relative RMSE values.

The solar radiation factor only influences the decay by enhancing or inhibiting the decay process of all substances of the decay system according to the solar radiation in each time step relative to the mean solar radiation. Therefore, no physical modelling of the photo degradation process was conducted but mere a simplification that affects the rate of degradation. Consequently, uncertainties caused by factors of the decay process are transferred to the results of model results including solar radiation. Nevertheless, it was shown that diurnal and seasonal variability can be included in the modelling process (*Figure 10* and *Appendix Figure 2* and *Appendix Figure 8*).

In terms of model performance regarding r² and relative RMSE values the effect of solar radiation are ambivalent. Terbutryn emissions yielded good fits for both observed renders from the study conducted by Bollmann et al. (2016). Visually, the model results of A1 Radiation and S1 Radiation show a more temporally adjusted progression of emissions. However, the inclusion of solar radiation led to worse model performance for the acrylate render. The relatively low compliance of all A1 scenarios was previously discussed in *5.2 Goodness of Fit* and was mainly attributed to the linear emission behaviour. It is hypothesised that the application of the solar radiation factor to the linear emission behaviour decreased model performance since the initial error of choosing an unfit form of emission function is enhanced. Contrary to that the highest r² and relative RMSE values were achieved by the S1 Radiation. It is hypothesised that the initially good fit of the S1 data were further enhanced by including the seasonal impact of the solar radiation factor since the improvement of r² values can be associated with the reduction of emissions in the winter of 2012/13 and the increase of emissions during the summer of 2013. This leads to a solution of the temporal under- and over estimation of the first and second emission scenario compared to the third scenario which includes the solar radiation factor.

Since only solar radiation data for one field experiment was available further testing is needed to make well-founded statements. A challenge of implementing solar radiation is the availability and spatial distribution of solar radiation data. For instance in Germany only half of the 181 official weather stations record solar radiation (Deutscher Wetterdienst 2023).

Overall, solar radiation is an important part of the leaching process. Regression analyses by Junginger et al. (2023) showed that it is significant to overall emissions and the ratio of TPs and parent compound. This is underlined by the findings of a previous study observing the cease of photo degradation in winter months for three biocides under natural conditions (Minelgaite et al. 2017). The conducted implementation of a solar radiation constant in ComleamD can enhance model performance and lead to an improved temporal progression of modelled emissions. On the other hand, a deterioration of model performance is possible as well. It is emphasised that the use of a solar radiation factor can generally improve model performance.

5.5 Extrapolation of Emission Function

Several field experiment ranging from one to two years show that in that time only 1-5% of the initial biocide concentrations is emitted (Bollmann et al. 2016). The in this study observed sum of emissions (Terbutryn + TPs) ranged from 1-8% over a time span of half a year to three years. Since housing façades are exposed to weathering throughout their entire service life of up to 50 years (Voigt et al. 2023) it is of interest for long term risk assessment to estimate the emissions and the share of initially applied substance and their TPs that is leached throughout the entire lifetime of a façade. Therefore, an extrapolation of 1000 mm of façade runoff was carried out which corresponds to 25 - 50 years depending on runoff coefficient of the façade. As shown in *4.5 Extrapolation of Emission Function*, the cumulative emissions of the respective extrapolated fitted emission functions vary between 6% and 80% of the initially applied active substance. This raises the question of what the cause of this difference in the comparable experimental setups is.

Highest emissions after 1000 mm of façade runoff were observed for the acrylate and silicone render test specimen of Bollmann et al. (2016) where acrylate render leads to increased relative emissions compared to silicone render caused by different surface material properties (Styszko and Kupiec 2018). In the experimental setup of Junginger et al. (2023) also silicone render was used for the test specimen. However, emissions after 1000 mm of façade runoff only accounted for 6% of initially applied substance compared to the up to 40% of the silicone render of Bollmann et al. (2016). A possible explanation of this disparity is the encapsulation of active substance. For the Junginger test specimen a paint with encapsulated terbutryn was applied to the render whereas the render of the Bollmann test specimen was mixed with unencapsulated substance. A similar share of cumulative leaching relative to initially applied substance can also be observed for the wood preservatives of Schoknecht et al. (2016b) that also used a paint formula with encapsulated terbutryn. It is therefore hypothesised that encapsulation contributes to a reduction of long term emissions from housing façades.

Another point raised by the extrapolation is what happens with the façade after its service life expires. If encapsulated mixtures inhibit emission as observed in the render mixture used by Junginger et al. (2023) or the wood coatings of Schoknecht et al. (2016b) the majority of active substance remains in the façade. The possibility of biocide loads in construction material waste should therefore be taken into account regarding recycling and disposal of construction materials.

The extrapolated emissions from immersion tests of Junginger et al. (2023) are up to six times higher than the extrapolated emissions from the field experiment. Similar to the findings of previous studies, the results obtained from laboratory immersion tests can be seen as conservative compared to real life scenarios (Schoknecht et al. 2016a). Since emissions occur predominantly in the first half year (Bollmann et al. 2016; Breuer et al. 2012; Burkhardt et al. 2012) the slope of cumulative emissions can be assumed to be highest in the early stages of exposure. Therefore, the fitting of emission functions to a cumulative runoff corresponding to one to five years is assumed to yield higher emissions when extrapolated compared to the extrapolation of an emission function obtained from fitting to a cumulative runoff of 10 years. With the findings of this and previous studies it is therefore hypothesised that an overestimation of extrapolated emissions can be assumed.

However, with a multitude of processes involved in the leaching of biocides from façades and the initial fitting of emission functions being carried out by up to 60 times lower façade runoff the interpretation of extrapolated relative emissions is limited. In future, the comparison of long-term emissions obtained from extrapolated emissions functions with emissions from long-term field studies could provide insights on the validity of extrapolation of emission functions.

5.6 Relationship of Emission Function Parameters

It was assumed that a functional relation of the emission function parameter and the mobility of the respective substances exists. By the nature of the logarithmic emission function the *a* parameter mainly controls the leached amount due to its proportional dependency. It was therefore hypothesized that compared to terbutryn more mobile substances like the TPs TerOH and TerDesEOH with higher water solubility and lower log K_{OW} values should be described by a bigger *a* parameter value.

Junginger et al. (2023) described that TPs are likely to be retained more than terbutryn on the façade surface and are more likely to be released after large amount of façade runoff. Also, Junginger et al. (2023) argued that diminished release of TPs of façade could be caused by physiochemical properties of the façade and the TPs. This is underlined by the in this study observed difference in measured TP shares in overall emissions across the three studies (*Table 1* and *Appendix Figure 4*).

However, with lower amounts of TPs compared to terbutryn it is expectable that the *a* parameter as driver of emission amount is lower since overall share of substance in the façade is initially terbutryn which then degrades in the model to TPs. The a-parameter therefore takes multiple other parameters beside mobility based on chemical properties into account. Therefore, the transferability of emission function parameters in between different scenarios is limited.

Nevertheless, an attempt was made to establish a functional relationship between the initially applied active substance amount *c0* and the *a* and *b* parameter of the emission function for the sum of emission (Terbutryn + TPs). The regression of logarithmic emission function parameters yielded high r^2 values for both regressions (a: $r^2 = 0.93$; b: $r^2 = 0.87$) indicating a correlation. As already mentioned previously the interpretation of the regression is limited regarding the sample quantity of $n = 18$ from three different studies. However, this attempt is emphasized to be a starting point in future analysis of the relationship of render composition and emission function parameters.

As described in *5.1 Uncertainties* a multitude of factors affect the leaching process. All of these uncertainties and also factors that are not taken into account by the model, as for example temperature, humidity and the physical diffusion process are included in the emission function parameters. A generalisation of the emission function is therefore challenging since the observed leaching behaviours of similar field studies differ greatly and an universal emission function for risk assessment could therefore not be determined. However, with further research and the determination of a predominant render type and initially applied substance amount an universal emission function could be defined for risk assessment.

5.7 Sink

The sink of the ComleamD model accounts for all substances that degrade from the TPs. Since information on TPs is still scarce (Junginger et al. 2023) it was assumed that TPs degrade as well by photo degradation. As described previously in *3.2.2 Degradation* the half-life time of terbutryn was assumed for the TPs as well. In the assumed degradation pathway, TerOH and TerDesEOH form the end of the decay system and therefore enter the sink after being degraded. It is unknown in what substances these TPs further degrade or if the triazine ring is degraded as well and the TPs are mineralized after this step of the degradation pathway. In this study it was assumed that the degradation pathway ends with TerOH and TerDesEOH and that no emission from the sink occurs. With the findings of Bollmann et al. (2016) where the mass balance of terbutryn and its TPs was closed by examining the remaining substance amounts in the façade at the end of the experiment it can be assumed that the majority of the relevant TPs of terbutryn are accounted for.

However, with the used half-life time of 110 days the proportion remaining terbutryn and TPs in relation to unknown substance differs greatly compared to the findings of Bollmann et al. (2016). Since it was shown in previous studies that emission still occurs 13 years after the end of construction (Hensen et al. 2018), the amount of active substance remaining in the façade cannot be almost completely diminished as observed in *Appendix Figures 5, 6 & 8.* Junginger et al. (2023) argued that the half-life time of terbutryn might be higher under real life conditions. In combination with the assumption of the diffusion of active substance from inner layers of the façade (Schoknecht et al. 2022; Styszko et al. 2015; Styszko and Kupiec 2018) and photo degradation only occurring at the surface of the façade (Junginger et al. 2023; Uhlig et al. 2019). It can be assumed that the real half-life time of terbutryn must be higher since only a fraction of the substance is actually susceptible to decay. The high share of sink which represents fully degraded initial terbutryn at modelled time frames of half a year to three years underlines this assumption. It can therefore be hypothesized that the sink could be an indicator of the validity of the decay rate of terbutryn if comparison to real life scenarios like the measurement of remaining substance in the façade conducted by Bollmann et al. (2016) is possible. In conclusion it is therefore emphasized to obtain sacrificial samples of the façade during and at the end of the experiment following the example of Junginger et al. (2023) to validate the degradation and formation processes taking place under real life conditions and to close the mass balance during and at the end of the experiment.

5.8 Laboratory Tests as Data Source

Key for accurate modelling of emissions is suitable data, since the emission function parameters are fitted individually for each experimental setup and are specific for render and paint properties. As shown in this study the parameters of the emission function range over several orders of magnitude when comparing different studies and different types of renders, paints, initial concentrations and type of encapsulation of the active substance. However, the acquisition of field data is time and cost intensive and long term field studies cannot be executed for every render and substance composition.

The cost and time effective generation of laboratory data could therefore provide a basis for emission function parameter identification. In addition, standardised leaching tests have already been called for in earlier studies by the Federal Institute for Materials Research and Testing (BAM) (Schoknecht et al. 2016a). Immersion tests with intermittent water contact were carried out by Schoknecht et al. (2016a) and Junginger et al. (2023) according to guideline DIN EN 16105:2011-12. Both laboratory tests generated higher emissions compared to the field tests. Therefore, laboratory tests can be seen as conservative compared to field experiments and represent a worst case scenario (Junginger et al. 2023; Schoknecht et al. 2016a). Furthermore, the introduction of a harmonised and universal test with a combined approach of laboratory leaching tests and ecotoxicological risk assessment of immersion samples after the example of Vermeirssen et al. (2018) could provide a comprehensive data source for further modelling.

It can also be argued that previously conducted field experiments only measuring an active substance without taken TPs into account are not suitable for a holistic risk assessment since Junginger et al. (2023) showed that disregarding TPs leads to an underestimation of overall emissions. This reduces the number of suitable field studies for emission function parameter identification significantly and empathises the need of emission data which could be met by standardized laboratory tests. With more leaching data from common renders and paints an universal emission function or different scenarios could be created in order to estimate emissions of parent compound and TPs on the scale of whole cities or basins.

6. Conclusion

Biocide emissions from housing façades pose a potential threat to the environment. Evaluating data of field experiments from three studies, it was shown that the majority of emissions are TPs. Therefore, TPs have to be taken into account to adequately evaluate the potential risk of biocide emissions from housing façades. With the in this study tested and further developed ComleamD model it was possible to accurately model the emissions of the biocide terbutryn and its TPs for three field experiments in France, Denmark and Germany. It was shown that ComleamD is capable to portray the highly variable share and amount of TPs caused by various factors such as weather, surface material, render composition, encapsulation and initial active substance amount.

The tiered approach of this study displayed the impact of decay, diffusion and solar radiation on terbutryn and TPs emissions. It was shown that the decay rate has an impact on emission quantity and quality regarding parent compound and TP ratio. Contrary to usually desired low half-life times of biocides, it was shown that a lower half-life time does not necessarily lead to reduced overall emissions. The control of the decay rate by a solar radiation factor presented an adjustment of the seasonal variability of photo degradation. The representation of diffusion by single first order decay of unavailable terbutryn into available terbutryn proved to be unsatisfactory. It is therefore emphasized to represent diffusion with a two compartment model, controlling the diffusion based on a supply rate between available and non-available parent compound substance influenced by hygrothermal state variables and combine it with the existing and in this study tested decay system.

Information on TPs is still scarce and essential data regarding ecotoxicity, accumulation, formation fractions and decay rates are still unknown. Therefore, further research on TPs is emphasized. To obtain a better understanding of the leaching process it is suggested to include measurements of not only the leaching but also the façade itself in order to close the mass balance throughout leaching experiments. Also, laboratory tests with intermittent water contact and radiation by simulated sunlight could provide further insights in the leaching process. Harmonized laboratory tests could provide the possibility of determining emission function parameters for risk assessment. The derivation of universal emission function parameters was not possible due to the disparity of parameters fitted for the respective studies and emission scenarios. This highlights the importance of reliable and harmonized laboratory tests to determine render and substance specific emission function parameters. With more data available, the in this study hypothesised logarithmic relationship of emission function parameters and initial active substance amount could be further investigated.

In conclusion, ComleamD provides the possibility to model the emissions of terbutryn and its TPs from housing façades. A transferability to other biocides and combination of multiple parent compounds and TPs is possible. The in this study presented results are emphasized to be a starting point for further research to develop ComleamD into a valuable tool for the risk assessment of biocides in construction materials.

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Appendix

Data Sources

Field Data

The examined field data and respective meteorological data were kindly provided by Dr. Ulla Bollmann from the Geological Survey of Denmark and Greenland · Department of Geochemistry, Dr. Tobias Junginger from University of Strasbourg - Earth and Environment Strasbourg (UMR 7063) and Dr. Ute Schoknecht of the Bundesanstalt für Materialforschung und -prüfung (BAM). Experimental setup and substance analysis methods can be obtained from the respective studies. The respective studies are listed below.

Bollmann, Ulla E.; Minelgaite, Greta; Schlüsener, Michael; Ternes, Thomas; Vollertsen, Jes; Bester, Kai (2016): Leaching of Terbutryn and Its Photodegradation Products from Artificial Walls under Natural Weather Conditions. In *Environmental science & technology* 50 (8), pp. 4289–4295. DOI: 10.1021/acs.est.5b05825.

Junginger, Tobias; Payraudeau, Sylvain; Imfeld, Gwenaël (2022): Emissions of the urban biocide terbutryn from façades: the contribution of transformation products. Unpublished.

Schoknecht, Ute; Wegner, Robby; Uhlig, Steffen (2016b): Emissions of material preservatives into the environment – realistic estimation of environmental risks through the improved characterisation of the leaching of biocides from treated materials used outdoors. Edited by Umweltbundesamt. Federal Ministry for the Environment, Nature Conservation, Building and Nuclear Safety (Texte | 22/2016). Available online at https://www.umweltbundesamt.de/publikationen/emissions-of-material-preservatives-into-the, checked on 3/2/2023.

Software

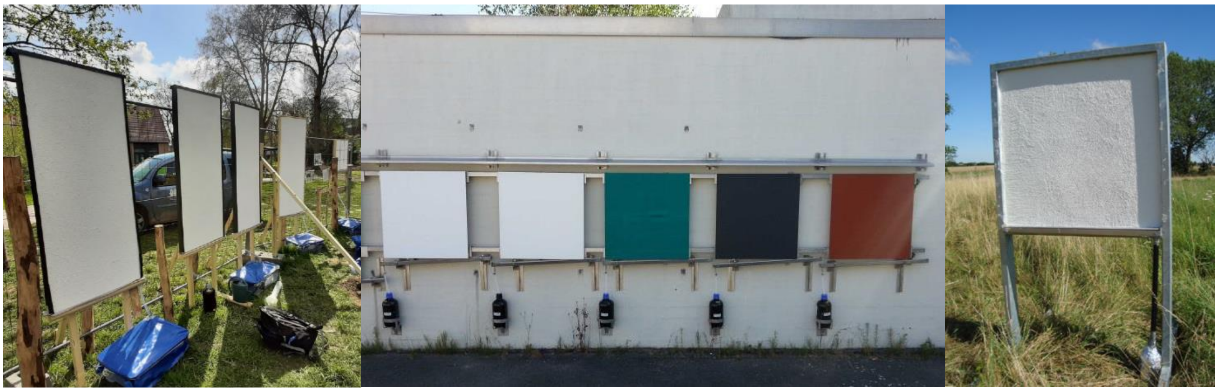
ComleamD

Olaf Tietje (2023). ComleamD - Construction Material Leaching Model. Development Version. Systaim GmbH, Zürich.

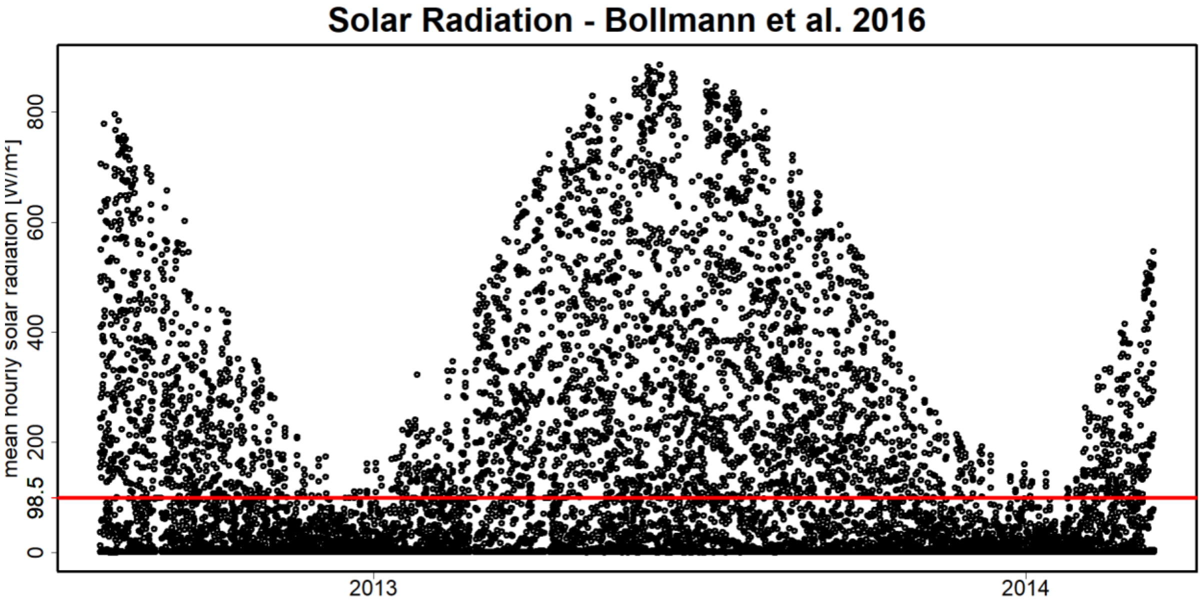
RStudio

Posit team (2022). RStudio: Integrated Development Environment for R. Posit Software, PBC, Boston, MA. URL http://www.posit.co/.

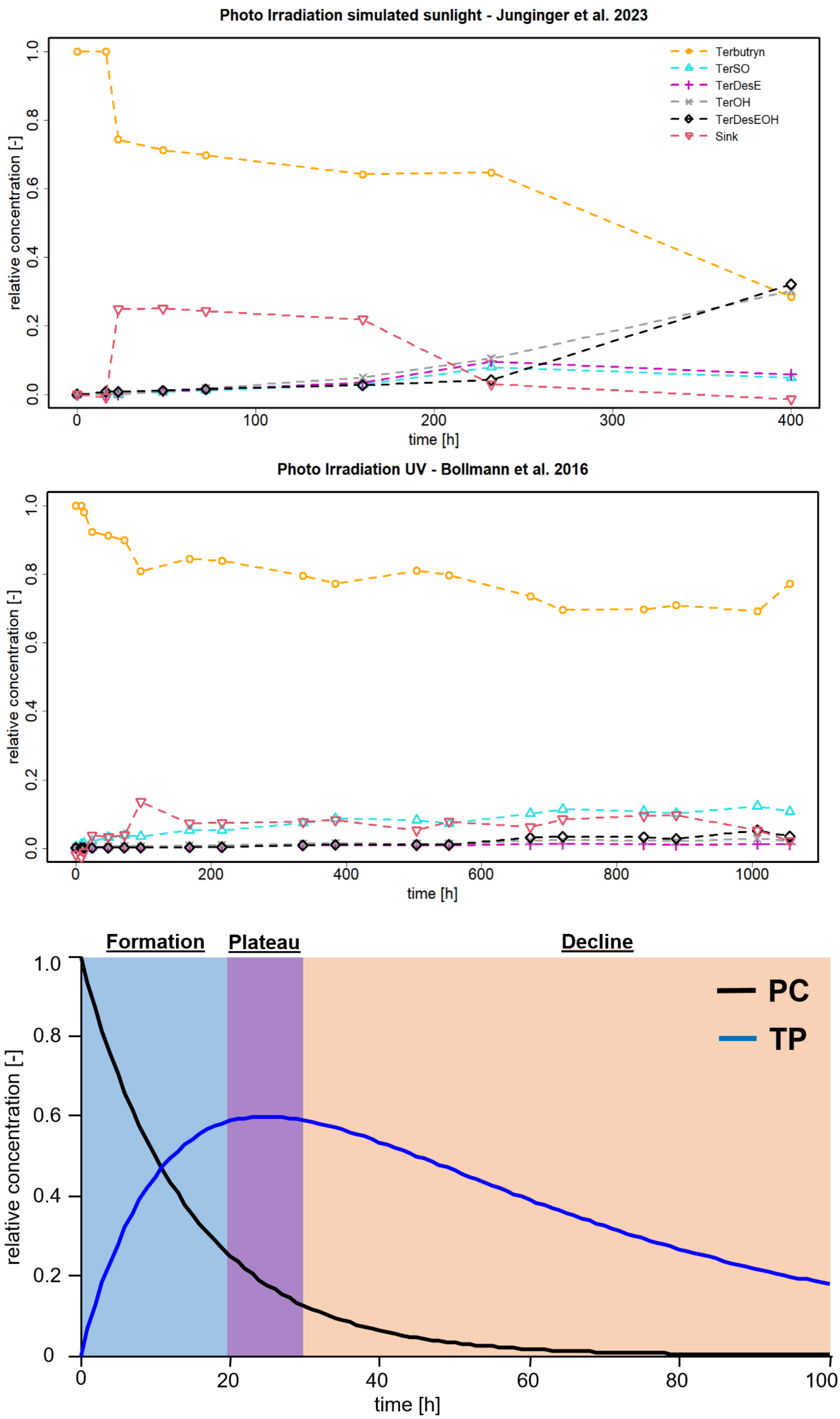
Figures



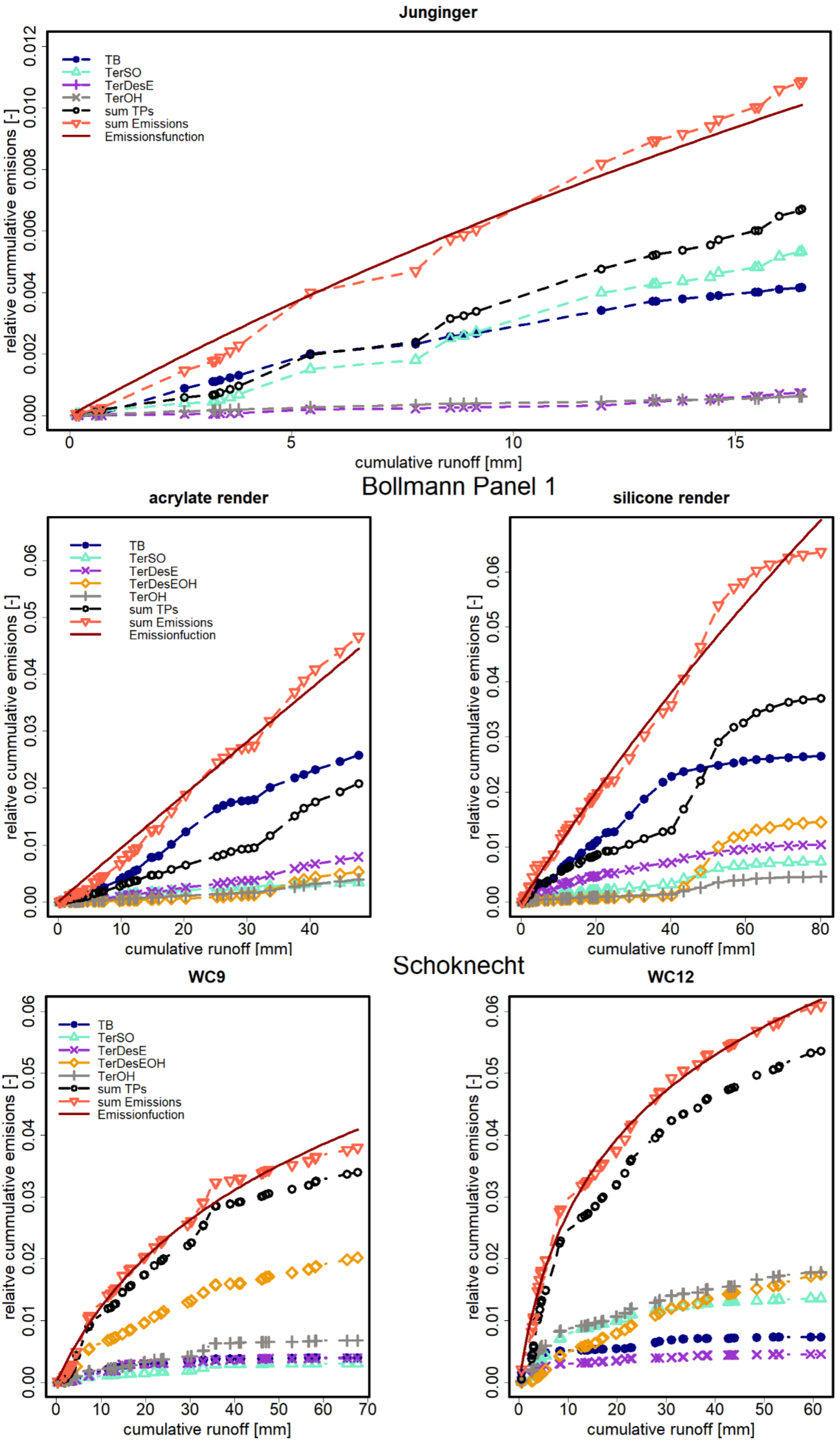
Appendix, Figure 1, Experimental setup of the examined studies. From left to right: Junginger et al. 2023, Schokencht et al. 2016 (only white panels), Bollmann et al. 2016.



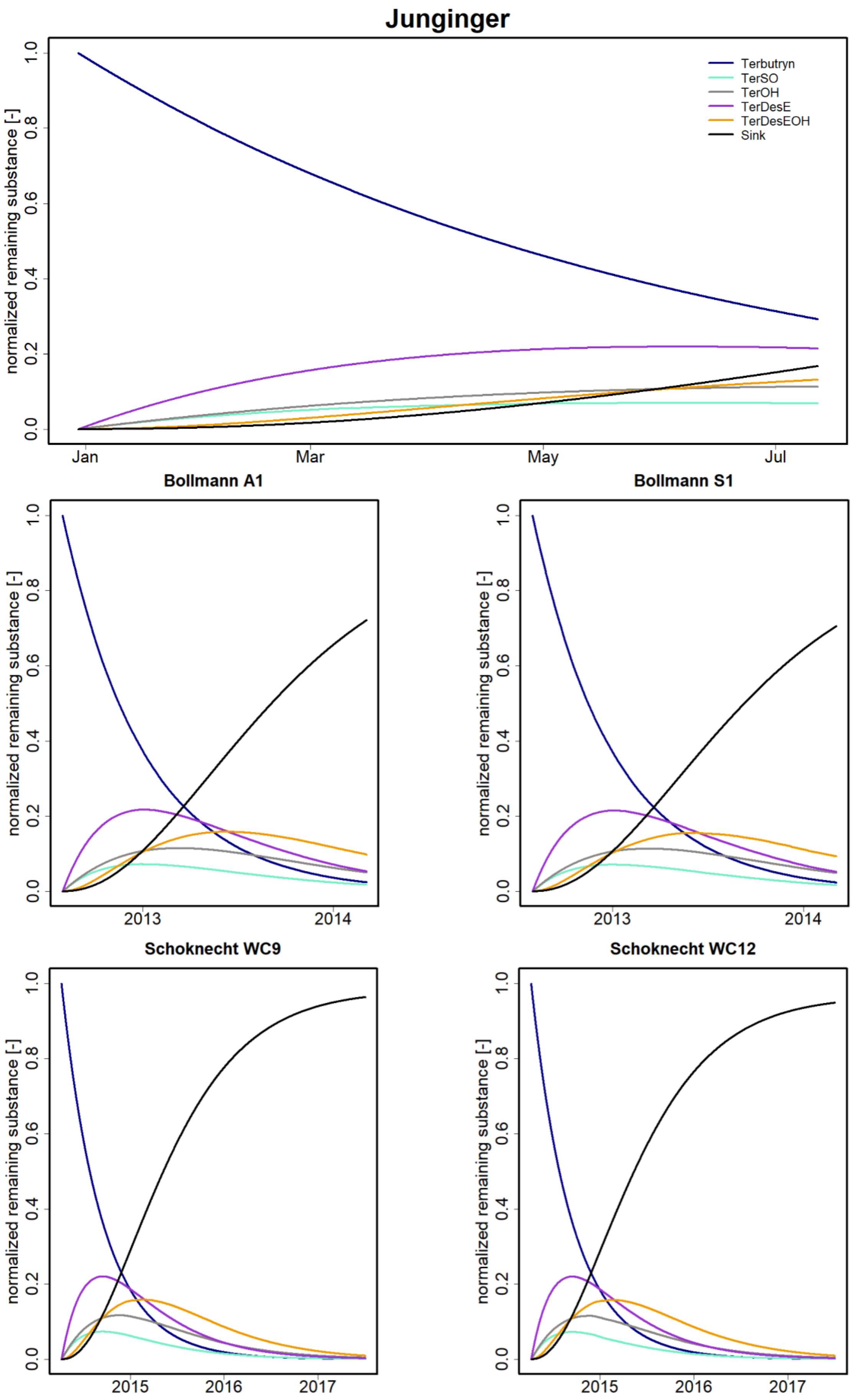
Appendix, Figure 2, Measured hourly solar radiation of weather station next to test specimen of Bollmann et al. (2016) with mean solar radiation as horizontal red line.



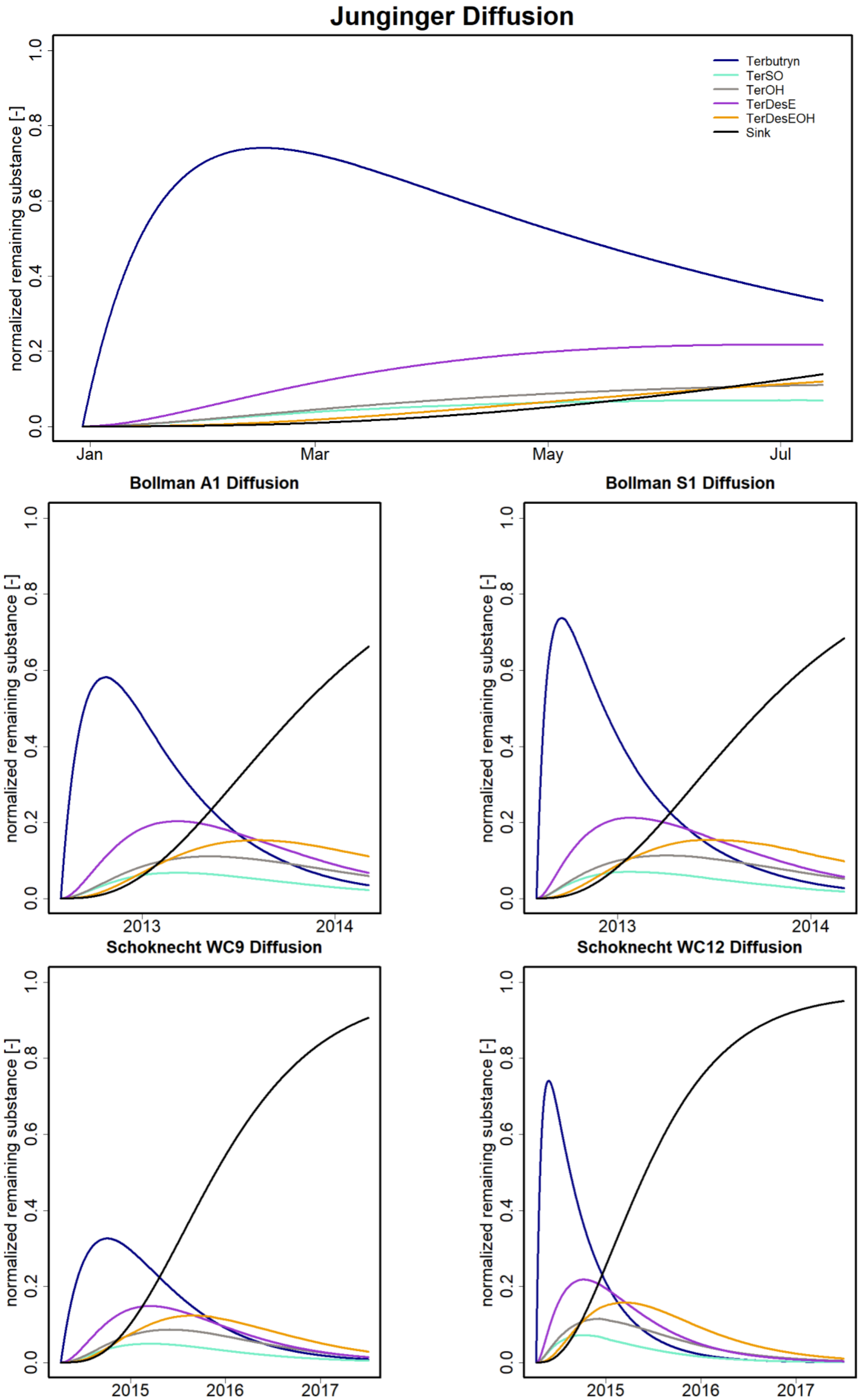
Appendix, Figure 3, Laboratory test data of photo degradation experiments of terbutryn conducted by Junginger et al. (2023) and Bollmann et al. (2016) compared to idealized degradation process described by FOCUS guidance on the calculation of persistence and degradation kinetic endpoints of metabolites (FOCUS 2006).



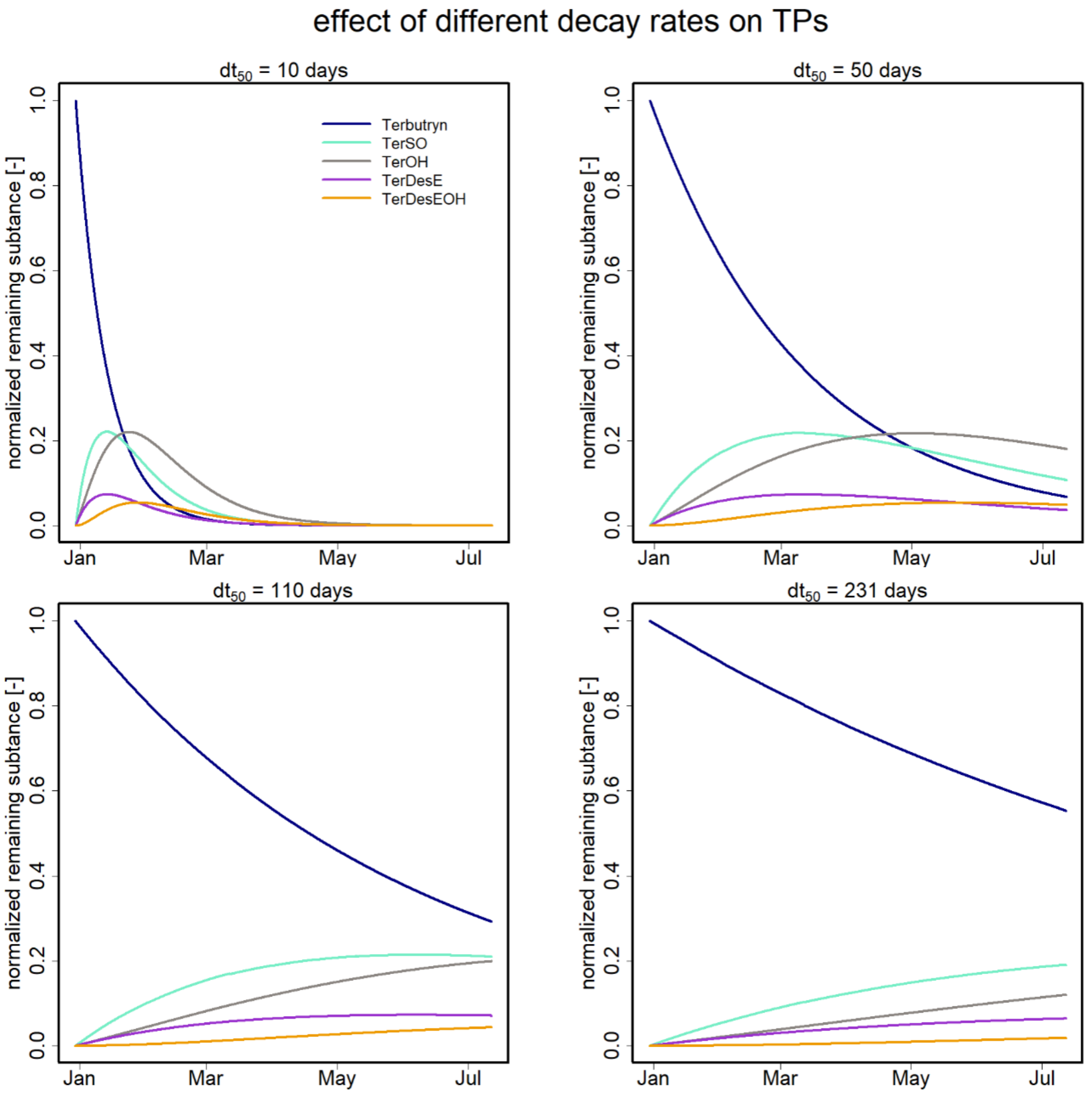
*Appendix, Figure 4, Cumulative emissions of terbutryn, transformation products and sum of the emissions of the respective studies, and in each case fitted emission function E(q) = a * ln(1 + b * q) with parameters from Appendix Table 1.*



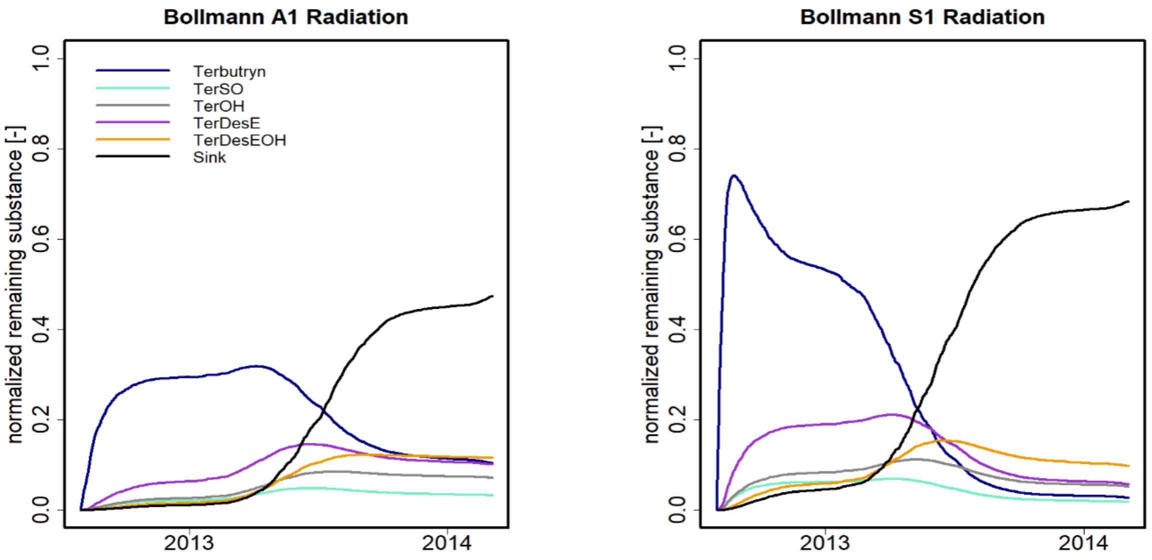
Appendix, Figure 5, Modelled and measured remaining substance of terbutryn and TPs for respective studies for emission scenario one.



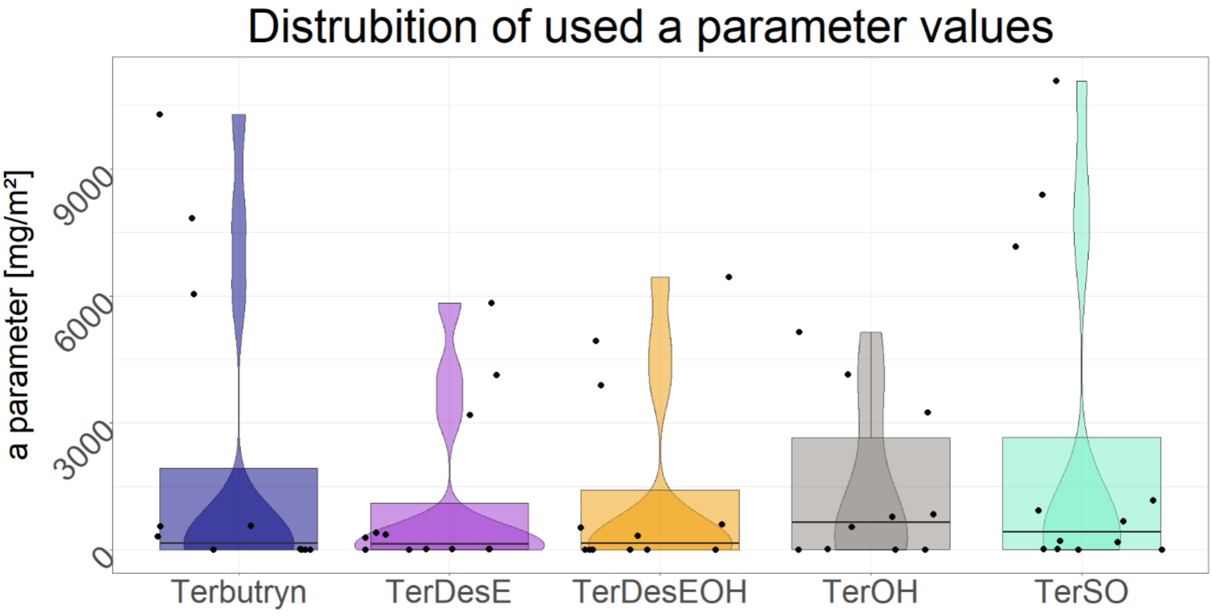
Appendix, Figure 6, Modelled and measured remaining substance of terbutryn and TPs for respective studies for emission scenario two.



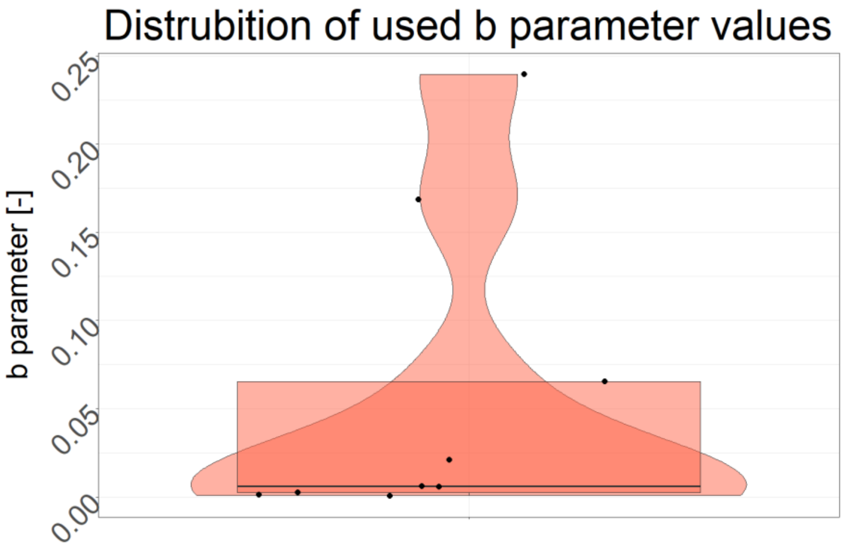
Appendix, Figure 8, Effect of different decay rates on normalized remaining substance for emission scenario one for data of Junginger et al. (2023).



Appendix, Figure 7, Modelled and measured remaining substance of terbutryn and TPs for respective studies for emission scenario three.



Appendix, Figure 9, Violin and Boxplot distribution of used a parameter values across different studies and emission scenarios.



Appendix, Figure 10, Violin and Boxplot distribution of used b parameter values across different studies and emission scenarios.

Tables

Appendix, Table 1, Initially fitted emission function parameters of sum of emissions (terbutryn + TPs)

Study	a [mmol]	a [mol]	a [mg/m²]	b [-]	rel. RSE [%]
Junginger					
Field Data	0.071582	7.16E-05	17.26105	0.040493	4.65
Immersion t0	0.85555	0.000856	206.3039	0.004148	1.47
Immersion t1	1.100651	0.001101	265.4067	0.002533	2.61
Immersion t2	1.177902	0.001178	284.0348	0.002312	1.34
Immersion t3	0.46842	0.000468	112.9529	0.009329	3.43
Schoknecht					
WC9	0.011451	1.15E-05	2.761235	0.065388	3.81
WC12	0.014955	1.5E-05	3.642026	0.341632	2.03
Bollmann					
A1	29.20468	0.029205	7042.302	0.000686	3.76
A2	18.77893	0.018779	4528.277	0.00107	1.57
A3	9.455411	0.009455	2280.041	0.002396	1.47
S1	1.804397	0.001804	435.1053	0.005819	3.27
S2	2.021859	0.002022	487.5432	0.006041	2.43
S3	0.663926	0.000664	160.0966	0.021008	1.8

Appendix, Table 2, Individually fitted a-parameter of the emission function for respective substances, studies and emission scenarios.

Study	a TB	a TerSO	a TerOH	a TerDesE	a TerDesEOH
	[mg/m²]	[mg/m²]	[mg/m²]	[mg/m²]	[mg/m²]
Junginger	12.2351	180.9437	15.6346	8.6646	NA
Junginger Diffusion	12.451	212.9196	24.8752	10.3417	NA
WC9	1.3133	5.6198	6.7636	2.2561	11.7234
WC12	1.9012	20.1	14.1	2.2823	10.2231
WC9 Diffusion	1.5659	6.5436	8.2066	3.2601	17.3183
WC12 Diffusion	1.8904	19.4225	13.4394	2.1991	8.4289
A1	6036.0811	7159.8992	3188.2692	3889.951	3244.5945
S1	567.492	932.8646	363.766	521.776	782.2735
A1 Diffusion	7829.6278	8379.0052	4130.4039	4937.4746	4137.4746
S1 Diffusion	563.5389	1171.7338	413.7442	606.7129	837.8344
A1 Radiation	10279.6352	11079.0052	5830.4039	6437.4746	5137.4746
S1 Radiation	313.5389	671.7338	283.7442	326.7129	537.8344

Appendix, Table 3, r² values of respective modelled substances across different studies and emission scenarios.

Study	TB [-]	TerSO [-]	TerOH [-]	TerDesE [-]	TerDesEOH [-]	Sum Emissions [-]	Sum TPs [-]
Junginger	0.94	0.97	0.88	0.91	NA	0.97	0.98
Junginger Diffusion	0.97	0.97	0.80	0.94	NA	0.98	0.97
WC9	0.74	0.76	0.77	0.95	0.95	0.93	0.93
WC12	0.10	0.93	0.73	0.63	0.62	0.77	0.79
WC9 Diffusion	0.98	0.93	0.96	0.95	0.98	0.99	0.98
WC12 Diffusion	0.33	0.96	0.80	0.61	0.90	0.88	0.90
A1	0.79	0.85	0.95	0.96	0.93	0.93	0.97
S1	0.84	0.94	0.97	0.82	0.95	0.98	0.95
A1 Diffusion	0.90	0.60	0.86	0.95	0.91	0.97	0.91
S1 Diffusion	0.92	0.95	0.96	0.72	0.95	0.99	0.95
A1 Radiation	0.97	0.38	0.85	0.90	0.96	0.95	0.85
S1 Radiation	0.97	0.96	0.92	0.88	0.94	0.99	0.98

Appendix, Table 4, Relative RMSE values of respective modelled substances across different studies and emission scenarios.

Study	TB [%]	TerSO [%]	TerOH [%]	TerDesE [%]	TerDesEOH [%]	Sum Emission [%]	Sum TPs [%]
Junginger	16.41	13.60	24.39	27.27	NA	12.47	11.26
Junginger Diffusion	10.57	18.09	25.01	13.40	NA	10.41	15.08
WC9	27.93	34.54	33.27	13.98	14.52	17.11	18.07
WC12	19.61	12.35	23.35	19.91	40.83	21.73	22.49
WC9 Diffusion	7.91	18.76	14.65	14.26	10.52	7.66	8.69
WC12 Diffusion	16.95	10.00	20.20	20.32	20.95	15.48	15.83
A1	46.05	29.64	25.53	21.24	41.82	28.09	20.57
S1	30.76	21.09	18.16	29.22	38.22	13.36	20.96
A1 Diffusion	32.15	48.34	34.60	25.90	44.71	18.02	33.58
S1 Diffusion	21.43	19.12	20.40	36.18	34.93	8.37	22.35
A1 Radiation	17.02	59.94	42.02	35.73	33.67	23.04	40.95
S1 Radiation	14.29	16.65	29.72	23.99	38.50	6.87	13.21

List of Symbols

Symbol	**Unit**	**Meaning**
a	[mg/m²]	Characteristic emission parameter 1
a_{rel}	[-]	Relative emission parameter
b	[l/m²]	Characteristic emission parameter 2
c0	[mg/m²]	Initial active substance amount
C_r	[-]	Terrain roughness coefficient
C_t	[-]	Topography factor
E(q)	[mg/m²]	Emission
E_i	[mol/m²]	Emission of substance i
$E_{rel}(q_b)$	[-]	Relative emission at beginning of time step
$E_{rel}(q_e)$	[-]	Relative emissions at end of time step
$f_{i,j}$	[-]	Formation fraction
F_{ij}	[mol]	Flow from i to j
F_{iTotal}	[mol]	Total flow from i
k	[-]	Decay rate
M	[g/mol]	Molar mass of substance
m	[g]	Mass of substance
$\bar{m}$	[mol]	Mean of measured data
m_i	[-]	Normalized measured data
n	[mol]	Amount of substance
O	[-]	Obstruction factor
P	[mm/h]	Precipitation
q	[l/m²]	Façade runoff
q_b	[mm]	Runoff accumulated at the beginning of time step
q_{char}	[l/m²]	Characteristic runoff
q_e	[mm]	Runoff accumulated at the end of time step
r^2	[-]	Coefficient of determination
RMSE	[-]	Root mean squared error
s_i	[-]	Normalized simulated data
SS_{res}	[-]	Residual sum of squares
SS_{tot}	[-]	Total sum of squares
v	[m/s]	Wind velocity

w	[W/m^2]	Solar radiation
$\overline{w}$	[W/m^2]	Mean solar radiation
W	[-]	Wall factor
$z_{a,i}$	[mg/m^2]	Substance amount at beginning of time step
α	[-]	Location factor
α_{char}	[-]	Characteristic substance proportion
β	[-]	Precipitation exponent
θ	[°]	Angle between wind direction and exposition of the façade
ί	[-]	Solar radiation factor

Abbreviations

BPR	Biocidal Products Regulation
COMLEAM(D)	Construction Material Leaching Model (Development)
dt_{50}	Half-life time
ETICS	external thermal insulation composite systems
FOCUS	Forum for the coordination of pesticide fate models and their use
K_{OW}	Octanol-water partition coefficient
OIT	Octylisothiazolinone
relRMSE	Relative root mean squared error
RMSE	Root mean squared error
RSE	Root squared error
TB	Terbutryn
TerDesE	Desethyl-terbutryn
TerDesEOH	Desethyl-2-hydroxy-terbutryn
TerOH	Terbutryn-2-hydroxy
TerSO	Terbutryn-sulfoxide
TP	Transformation Product
WDR	Wind driven rain
WFD	Water Framework Directive

Declaration of Honour

I hereby declare that the thesis was written independently and only with the use of the indicated aids.

Place, Date

Signature

Ehrenwörtliche Erklärung

Hiermit erkläre ich, dass die Arbeit selbständig und nur unter Verwendung der angegebenen Hilfsmittel angefertigt wurde.

Ort, Datum

Unterschrift