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Development of a model to assess the environmental properties of common outdoor plasters and mortars

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Abstract

Construction products such as plasters and mortars are largely used on the outside of buildings. During the exposure of these products to precipitation and ambient air, the contact with rainwater can dissolve ingredients from the materials. The leached substances are then released into the environment via runoff. Since not every substance has an environmentally hazardous potential, the release of substances from construction products in contact with rainwater does not necessarily imply a negative impact on the environment. However, for some substances there remains a risk for the environment because of their eco-toxicity.

To analyze the release of relevant substances from building façades, the Fraunhofer Institute for Building Physics IBP has carried out systematic and extensive investigations on a large number of formulations of plasters and mortars that contained potentially environmentally relevant substances such as metals and biocides. Over a period of 10 years the investigations were carried out under real weather conditions as well as under constant physical conditions. However, investigations on a field scale are very complex and cannot always be carried out to estimate the leaching behavior of plasters and mortars and the release of substances to the environment by runoff. Models that depict the runoff process and the behavior in the environment would be helpful. However, there is currently no transfer model to conclude from the results of leaching tests on the actual influence on soil and groundwater.

The objective of the current work was to develop and validate a model capable to evaluate the environmental properties of outdoor plasters and mortars based on the extensive database from the long-term experiments from Fraunhofer IBP. To achieve this goal, a three-stage approach was chosen which led to a model with three levels.

In Level 1 a numerical model was developed in MATLAB on the basis of previous analytical models to calculate the collected stormwater runoff volumes from vertical test panels (VTP) during leaching outdoor tests (LOT). In the model, wind-driven rain (WDR) is considered to be the main mechanism for determining the amount of water impinging on the VTP, so it is a crucial factor in the modeling for the façade runoff. The new model makes it possible to simulate the runoff volumes from VTP that are covered with a wide variety of plasters and mortars. Using the new model, it was possible to relate the VTP runoff volumes obtained during an 18-month sampling period for LOTs performed at the Fraunhofer Institute for Building Physics IBP in Valley, Germany.

In Level 2 a leaching model was developed using the geochemical model PHREEQC with the Lawrence Livermore National Laboratory (LLNL) thermodynamic data base and coupled with MATLAB to optimize the runoff and weather parameters. The developed model was calibrated by comparing the data from laboratory Dynamic Surface Leaching Tests (DSLT) with simulation results up to an acceptable fit. The obtained parameters were then used in the LOTs simulations

for inorganic parameters in order to be validated. It was possible to relate the substance discharge from VTPs during an 18-month sampling period with the results obtained by the model. The developed model allows to predict the substance discharge from a wide variety of plasters and mortars under real weather conditions. Physical characteristics of the material (e.g., thickness, absorption capacity) play an important role in the leaching of substances in façades covered with plaster and mortar. It could be shown that vanadium, chromium and lead are relevant substances leached from most of the tested plasters and mortars during rain events due to the high magnitude of concentrations,

Finally, the evaluation of the environmental risk of stormwater runoff from façades covered with plasters and mortars takes place in Level 3 using a "Groundwater Risk Assessment" (GRA). For relevant inorganic substances which resulted from Level 2 modelling, it could be shown that vanadium, chromium and lead can lead to a significant alteration in the chemical status of groundwater. The evaluation showed that chromium is the only leached substance that invalidates the applicability of one of the materials for a particular scenario within the chosen frame conditions.

Level 2 was not performed for biocide leaching, because of lacking information. In order to have reliable input parameters for modeling Level 3 for biocides, a detailed evaluation of the long-term field-tests with model houses containing two different plaster compositions from Fraunhofer IBP was carried out.

The runoff concentrations as well as the influence of the façade orientation on the biocide release under real weather conditions was analyzed. The results of the analyzed rain events demonstrate that façade orientation plays an important role in the leaching loads of biocides. Biocide loads in the runoff decreased corresponding to the wind direction. The obtained results demonstrate that treatment facilities have to be installed at all building sides. The hydraulic and the substance load is highest at the weather side, which has a strong influence on the dimension and the lifetime of the treatment system.

Based on this study a transport model was developed based on the data from the houses leaching field tests corresponding to Level 3. This transport model makes it possible to evaluate the environmental fate of the biocides within an unsaturated soil compartment until they reach a point of compliance. The organic parent compounds (PCs) evaluated within this model were carbendazim, diuron, octylisothiazolinone, and terbutryn. Ten transformation products (TPs), namely 2-aminobenzimidazole (2-AB), N'-[3,4-dichlorophenyl]-N,N-methylurea (DCMPU), 3,4-dichloroaniline (DCA), N'-3,4-dichlorophenylurea (DCPU), octylamine, octylmalonamic acid, 2-hydroxy-terbutryn (TB-OH), desbutyl-2-hydroxy-terbutryn (TB-OH-DesB), desethyl-terbutryn (M1), terbutryn-sulfoxide (TB-SO), were also evaluated within this study. The model was developed using Van Genuchten´s substance transport equation and general condition assumptions with reference to a Ground Water Risk Assessment. Factors such as soil type, percolation rate, soil organic carbon sorption coefficient, and the half-life of TPs were found to affect not only the PCs and TPs peak concentrations, but also the time-to-peak at the point of compliance and the time needed for the substances to leave the unsaturated soil compartment. It could be shown that by an additional topsoil layer with higher organic carbon content within the evaluated system, the final concentrations of biocides found at the point of compliance (OdB) can be decreased significantly. This highlights the impact of treatment measures when emitting runoff water from façades into environmental compartments for groundwater protection.

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1. General Introduction

1.1 Initial situation

Annex I of the European Construction Products Regulation (Regulation (EU) No. 305/2011 of March 9, 2011, in force since July 1, 2013) lists seven requirements that are placed on construction products and structures built from them. Requirement No. 3 concerns the areas of hygiene, health and environmental protection. In order for buildings to meet the legal requirements, building products must in turn have properties that are derived from the requirements for buildings. In addition to safety aspects and usability, the health of the building users and the impact on the environment must also be taken into account. As part of the CE (in conformity with European health, safety, and environmental protection standards) marking of mandated and harmonized product standards, a declaration of performance with regard to the environmental properties must also be submitted. For the investigation of the environmental properties of construction products in contact with water, CEN TC351 WG1 and WG5 developed the harmonized test methods to be used (DIN CEN/TS 16637-1 to -3). In the long-term immersion test for monolithic building products (DIN CEN/TS 16637-2), no drying phases are planned, which does not correspond to the reality of rain induced substance discharge from façade building materials. Intermittent immersion test according to the non-mandated standard DIN EN 16105 may appear to be the more suitable test method.

Both methods do not claim to represent the behavior of the construction products under real application conditions. Rather, they serve to make building products comparable in terms of their release of substances. Both standards do not include an assessment of the environmental effects of the released substances. The German Institute for Building Technology (DIBt) is responsible for establishing the connection between the protection of the environmental compartments soil and groundwater and the construction activity or the construction methods and building materials by applying the building regulations of the federal and state governments. There are general principles for evaluating the effects of building products on soil and groundwater (DIBt, 2011) which are the basis for an evaluation scheme for the effects of construction products in direct contact with groundwater (DIBt, 2011). A working group (AG) and a project group (PG) have been set up at the DIBt to deal with the issue of the environmental impact of irrigated components and possible modeling approaches. The database on which these two groups work turns out to be very sketchy in some cases.

1.2 Requirements and regulations

Construction products that fall within the scope of mandated product standards must provide information on their performance (declaration of performance) for the CE marking. Performance features resulting from the Construction Products Ordinance must be declared on the product packaging as part of the CE marking. According to basic work requirement 3 (hygiene, health and environmental protection), this also includes statements about the environmental behavior of construction products in contact with water. The reason for the evaluation of the leachability with water lies in the protection of the environmental compartments water and soil. Substances released from the building products through leaching must not lead to any deterioration in the condition of soils and water bodies. It follows that when developing an evaluation concept for released substance collectives, the various sovereign regulations for the protection of soil and water must be taken into account. For the modeling, approaches that have already been developed for other areas of application must also be considered; for example, it must be checked to what extent approaches from the leachate prognosis can be used for the assessment of runoff water from the building envelope.

With the council resolution 85 / C 136/01 of May 7th, 1985 (EU, 1985) the so-called new approach to technical harmonization and standardization was initiated. The aim of this resolution is to standardize technical harmonization in the European Union (EU) on a new basis. This is limited exclusively to the harmonization of the essential product requirements. It uses the principle of 'reference to standards' and the principle of mutual recognition in order to overcome the technical obstacles that stand in the way of the free movement of goods (EU 1985). Based on this approach, the Construction Products Directive 89/106/EEC (CPD) (EU, 1988) came into force in 1988, which was replaced in 2013 by the European Construction Products Regulation EU/305/2011 (CPR) (EU, 2011-B). In contrast to the CPD, which had to be transposed into the national law of the member states, the wording of the CPR applies in all member states. Like the CPD in the past, the Construction Products Regulation does not place requirements on construction products, but on buildings (Art. 3 (1) and Annex I) (EU, 2011-B): "Buildings as a whole and in their parts must be suitable for their intended use, the health and safety of the people involved throughout the life cycle of the structures must be considered. Buildings must meet these basic requirements for buildings with normal maintenance over an economically reasonable period of time". "The essential characteristics of building products are defined in harmonized technical specifications in relation to the basic requirements for buildings" (Art. 3 (2)). It follows from this that the basic requirements for the structures can simultaneously lead to the definition of essential characteristics of the construction products. The basic requirement No. 3 for buildings (hygiene, health and environmental protection) is described as follows:

"The construction works must be designed and built in such a way that they will, throughout their life cycle, not be a threat to the hygiene or health and safety of workers, occupants or neighbors, nor have an exceedingly high impact, over their entire life cycle, on the environmental quality or on the climate during their construction, use and demolition, in particular as a result of any of the following:

(a) the giving-off of toxic gas;

(b) the emissions of dangerous substances, volatile organic compounds (VOC), greenhouse gases or dangerous particles into indoor or outdoor air;

(c) the emission of dangerous radiation;

(d) the release of dangerous substances into ground water, marine waters, surface waters or soil;

(e) the release of dangerous substances into drinking water or substances which have an otherwise negative impact on drinking water;

(f) faulty discharge of waste water, emission of flue gases or faulty disposal of solid or liquid waste;

(g) dampness in parts of the construction works or on surfaces within the construction works.“

In contrast to the CPD, which did not yet address sustainability, the requirements for the CPR were expanded to include BWR 7 ‘Sustainable use of natural resources’:

“The construction works must be designed, built and demolished in such a way that the use of natural resources is sustainable and in particular ensure the following:

(a) reuse or recyclability of the construction works, their materials and parts after demolition;

(b) durability of the construction works;

(c) use of environmentally compatible raw and secondary materials in the construction works."

The protection of the natural foundations of life is an important political task. Both the EU and national legislators enact regulations to limit harmful influences on the environmental compartments of water and soil. At the European level, the Water Framework Directive (EU, 2000) and the Groundwater Directive (EU, 2006-A) should be mentioned here, supplemented by product regulations such as the Biocidal Products and Plant Protection Products Regulations (EU, 2011-A).

The implementation of the Water Framework Directive (2000/60 / EC) (EU, 2000) should lead to an improvement in the water quality of ground and surface water as well as sovereign and marine waters. The aim is to promote sustainable water use and the long-term protection of existing resources. For this reason, a limited number of chemical substances have been classified as particularly worrying because of their widespread distribution and high concentrations in rivers, lakes and coastal waters. Their entry into the aquatic environment should be permanently reduced. These substances are called priority substances. For a sub-group of priority substances, the priority hazardous substances, due to their tendency to bioaccumulate, their persistence in the environment and their toxicity, stricter environmental targets apply. In particular, priority hazardous substances should be eliminated as far as possible (introductory reasoning, sentence 27 in EU, 2000) so that the concentrations of naturally occurring priority hazardous substances are close to the background values. The European Groundwater Directive (EU, 2006-A) contains a minimum list (Annex II, Part B) of parameters for which national threshold values are stated. These values are defined as the concentration level for a substance, at which no significant change will be imposed on the groundwater. This minimum list includes: arsenic, cadmium, lead, mercury, ammonium, chloride and sulphate as an indicator for the entry of salts that influence the electrical conductivity. The priority and priority hazardous substances are listed in Directive 2008/105 / EC (EU, 2008). This also includes substances that are or were usually used in building coatings or that can in principle be released from mineral plasters and mortars.

In 2006 the European Commission published the proposal for a directive to create a framework for soil protection (EU, 2006-B). The proposed directive includes, inter alia: Measures to limit the introduction of dangerous substances into the soil in order to avoid the accumulation of certain substances in the soil that impair soil functions and pose a risk to human health and the environment (EU, 2006-B, p. 6). The directive has not yet been adopted.

In Germany, the legal framework for the protection of soil and groundwater includes the regulations of the EU, which are directly applicable in the individual member states, as well as the EU directives, which have to be converted into national regulations. For example, the Water Framework Directive (EU, 2000) has been adopted into national legislation through the amendment of the Water Resources Act in 2002 (EU, 2000) and the water laws of the federal states.

Further national regulations are

1. for soil as a protected asset:
    a. the Federal Soil Protection Act (BBodSchG, 1998)
    b. the Federal Soil Protection and Contaminated Sites Ordinance (BBodSchV, 1999),
2. for water as a protected asset:
    a. the Water Resources Act (WHG, 2009),
    b. the Groundwater Ordinance (GrwV, 2010),
    c. Surface Waters Ordinance (OGewV, 2011),
    d. the Drinking Water Ordinance (TrinkwV, 2016)
3. and across media:
    a. the Landfill Ordinance (DepV, 2009)
    b. the Recycling Management Act (KrWG, 2012) and

c. the Shell Ordinance (MantelV, 2021)

For the assessment of the soil-groundwater pathway within the application framework of the BBodSchG and the BBodSchV, a so-called ground water risk assessment (GRA) must be carried out. Based on the results obtained in the course of laboratory tests, test values are calculated in such way that can be compared with the insignificance threshold values (GFS). The relevant calculations can be made with the publicly available EXCEL workbook ALTEX-1D (ALTEX, 2010) which use as a base Van Genuchten's substances transport equation (Van Genuchten et al., 1982).

The insignificance thresholds values (GFS-values) (Table 1) are established by the Federal / State Working Group on Water. The GFS-values (µg/L), which were adopted in 2004 (LAWA, 2016), are currently used to assess local groundwater pollution. Table 1 shows the insignificance values (GFS-values) for selected organic and inorganic substances that are to be expected in the runoff of construction products. The GFS-values are concentration-based values derived from eco- and human toxicological tests. They are defined as the concentrations that do not cause any significant alteration of the chemical status of the groundwater or a "no-effect level" (LAWA, 2016). According to the "precautionary principle," the GFS-values are not quality targets or targets concentrations for groundwater. The GFS-values should make it possible to distinguish whether a spatially limited change in the chemical composition of the groundwater of anthropogenic origin is to be classified as minor or as a groundwater pollution (groundwater damage). "It forms the boundary between a slight change in the chemical composition of the groundwater and harmful pollution" (LAWA, 2016). The intended goal of the GFS-values is not only to maintain the groundwater in a state that it can still be used as drinking water for human consumption, but also to ensure that the aquatic ecosystem in the groundwater is functioning and biodiversity is preserved.

Due to the fact that the GFS-values act as target concentrations in the seepage water at a point of compliance, they can be used as a first reference to determine the relevant substances to be evaluated in our case. If the concentrations are lower than the GFS-values, these substances should not be relevant for the evaluation of the environmental characteristics of the plasters and mortars. Only substances with concentrations higher than the GFS-values will be determined as relevant substances.

Table 1: Selected insignificance threshold values (GFS-values) for assessing locally limited changes in groundwater (LAWA, 2016).

Element/Ion	**GFS-values [µg/L]**
B	180
V	4
Cr	3.4
Co	2
Ni	7
Cu	5.4
Zn	60
As	3.2
Se	3
Mo	35
Cd	0.3
Sb	5.0
Ba	175
Hg	0.1
Tl	0.2
Pb	1.2
Fluoride	900
Chloride	250 000
Sulfate	250 000
Diuron	0.1

1.3 Previous research

In the last 15 to 20 years a wide variety of investigations on the leaching of constituents have been carried out on representatives of many building product groups. While initially the focus was on the durability and quality retention of the building product, over the years the potential impact of the released ingredients on the environment became the focus of interest. Since mortars and plasters have complex formulations and - depending on the intended use - consist of a large number of components, ingredients on the exterior surface of buildings can in principle be mobilized by moisture and washed out of the façade by rainwater running off.

According to Schießl et al. (1995), the following transport processes are involved in leaching from mineral building materials:

1. If the façade surface is dry at the beginning of the rain event, the rainwater penetrates the building material through capillary suction. Here, water-soluble compounds that have crystallized out in the near-surface zones can be transported into the interior of the building material.
2. At the same time, substances on the surface are also washed off.
3. Only when it rains for a long time, leaching of substances due to diffusion processes take place (concentration gradient from the inside of the building material to the surface).

4. After the rain event has ended, the building material dries out again. As long as the water from the inside of the component reaches the surface, substances are also transported. After the water has been lost, they then crystallize out in zones close to the surface.

Conclusions from different studies correspond to parameters of influence on the leaching of irrigated construction materials during random rain events. These parameters are related to:

1. Material composition: the different substances contained in a building material can interact, which can cause bonding but also an increase in release. The content itself is not decisive for the release of substances (Hecht, 2005; Schiopu et al., 2007; Schoknecht et al., 2009).
2. Substance-dependent leaching: leaching rates depend on the physical and chemical properties of the substances and the construction material, especially the solubility of particular substances, which may depend on pH (Garrabrants et al., 2002; Nebel et al., 2010; Scherer, 2013; Vollpracht et al., 2010). For wetted building elements during random rain events, the pH of the material, not the leachate, is critical (Schoknecht et al., 2009). Wet-dry stress, temperature changes and contact with the gas phase can alter the matrices over time; for example, by carbonation, which leads to decreasing pH values. This influences long-term leaching (Garrabrants et al., 2002; Hecht, 2005; van Gerven et al., 2004).

Additionally, investigations for the assessment of product properties have been carried out according to standardized procedures with defined boundary conditions so that the values of different investigation sites and various investigations within one investigation site can be compared with one another (DAfStb, 2020; NEN 7375; DIN CEN/TS 16637-2 and DIN EN 16105). This is the only way to ensure a reliable basis for regulatory decisions. In Germany (DAfStb, 2020) and in the Netherlands (NEN 7375) established methods are available for the investigation of construction products in direct contact with groundwater, which provide the data basis for regulatory decisions. At the European level, a horizontal test standard for leaching from building products was developed on the basis of mandate M/366 of the European Commission (DIN CEN/TS 16637-2). At the same time, CEN/TC 139 WG10 published a non-mandated European standard (DIN EN 16105) in 2011 for testing the leaching behavior from pasty coatings. All of these standards only describe the production of the eluate, but not the analysis of the leached constituents in the eluate. Within the scope of mandate M/366, CEN/TC 351 WG 5 examines existing standards and standards developed for other product areas for their applicability when testing the leaching behavior of building materials. CEN/TC 351 WG 5 is working on analysis methods of hazardous substances in the materials and the determination of hazardous substance content in eluates and digestion solutions.

A good database for modeling comes from the Fraunhofer Institute for Building Physics IBP. To analyze the release of relevant substances from building façades, systematic and extensive investigations on a large number of formulations of plasters and mortars that contained potentially environmentally relevant substances such as metals and biocides on a field scale were carried out.

Over a period of 10 years the investigations were performed out under real weather conditions as well as under constant physical conditions.

Different research projects were performed at Fraunhofer IBP. Within the research project "Environmental properties of mineral mortars (IWM I) (2005 - 2009) the release of inorganic ingredients from façade building materials in contact with rain water was examined extensively. Within the scope of this project, one to three-layer mineral plasters and mortars were investigated with regard to the leaching of primarily inorganic substances (heavy metals and trace elements, inorganic anions) in a multi-year field experiment (Scherer, 2013). A wide range of worst-case recipes were used, which are not available on the market and which contained a maximum proportion of potentially ecologically harmful components. At the RWTH in Aachen, selected recipes from this research project were also subjected to a sprinkling test in the laboratory. At the same time, the first comparisons of laboratory sprinkling tests and standing tests with façade building materials were carried out in Aachen (Brameshuber et al., 2009; Nebel et al., 2010).

The research project “Environmental Properties of Mineral Mortars and Pasty Products” (IWM II) further developed the approach from IWM I. For this project, only single-layer test specimens were examined in order to be able to assign the influence of the individual components in the multilayer coatings. The research program included:

- mineral and pasty plasters,
- laboratory tests according to DIN EN 16105 and DIN CEN/TS 16637-2,
- an 18-month field test with vertical test panels (VTP with an area of 0.5 m² each)
- field investigations in test houses with external thermal insulation composite systems (ETICS) based on a mineral system and expanded polystyrene systems (EPS) to investigate the influence of the wind driven rain (WDR),
- detailed recording and evaluation of meteorological data, in particular exposure to torrential rain and its dependence on compass direction,
- and analysis of runoff volumes, sum-parameters like pH and electrical conductivity as well as inorganic (heavy metals, anions) and organic (biocides) substances in the eluates.

Selected test samples from the research project were made available to the ECN (Center for Energy Research of the Netherlands) in the Netherlands. At ECN the so-called pH-dependency test and parallel tests according to CEN/TS 16637-2 were carried out. Data from the outdoor exposure specimens was also transmitted to the ECN.

These data are an extensive and reliable database for further modeling.

Inorganic ingredients

Depending on the type of construction material used (permanent or temporary contact with water), the inorganic substances leached that can be potentially harmful to the environment are salts, heavy metals and trace elements. Using these construction materials without prior testing can lead to environmental and health risks, as the knowledge of the recipe is not sufficient in all cases. A study in Berlin has shown that the discharge of urban stormwater runoff into rivers can raise the concentration of some of these substances by a factor of ten (Wicke et al., 2022). The heavy metals chromium, nickel, copper, zinc and vanadium are named as potential substances emitted from façade renders and coatings coated mainly with concrete and other mineral materials (e.g., Persson et al., 2001, Schiopu et al., 2007; Weiler et al., 2019; Weiler et al., 2020a; Weiler et al., 2020b; Wicke et al., 2016; Wicke et al., 2022; Vollpracht et al., 2010).

For construction products that are installed directly in the groundwater, such as concrete, a national evaluation concept for the environmental properties based on the "stand test" (56-day long-term leaching test according to the then valid guidelines of the “Deutsche Ausschuss für Stahlbeton DafStB” (actual version DafStB, 2020)) was published (Hohberg, 2003). After the publication of revised GFS-values in 2004, this evaluation concept was updated by Brameshuber et al. (2004) (see also (DIBt, 2011)). This concept earmarks leaching tests for different materials in different application scenarios. The DIBt concept applied for construction elements in direct contact to soil, not to irrigated construction elements such as façades and roofs (Vollpracht et al., 2010 and Weiler et al., 2019). The relevance of runoff emissions from façades and roofs have been shown in different studies (e.g., Clara et al., 2014, Gasperi et al., 2014; Scherer, 2013; Wicke et al., 2016) and has been discussed by an expert group of the DIBt and in different studies (Dijkstra et al., 2005 and Vollpracht et al., 2010). A similar test procedure, which follows a different assessment system, exists in the Netherlands (NEN 7375). As part of the work of CEN/TC 351 WG 1 (creation of horizontal test methods that provide uniform data for assessing the environmental compatibility of construction products), the European leaching test (DIN CEN/TS 16637-2), a synthesis of German and Dutch standard tests, was validated with regard to its robustness (Rickert et al., 2011). This laboratory procedure does not dictate a fixed volume to surface ratios or the geometry of the test specimens. It is left to the product TCs (Technical Committees) to define suitable parameters for the product groups they represent within the framework of European standardization.

Substance release from intermittently irrigated façades are difficult to predict and therefore also to asses due to the permanent wet-dry stress, which influences a deviating leaching behavior of the materials (Hecht, 2005; Schoknecht et al, 2009). During the dry periods, faster capillary transport is presented increasing the availability of substances for leaching and their wash-off during the next effective rain event (Hecht, 2005). Substance characteristics, contact time with water of the material and the rainwater volume applied to the façades also influence the amount of the released substances (e.g., Garrabrants et al., 2002; Hendriks et al., 1997; Vollpracht et al., 2010 and Weiler et al., 2020a). Changing release patterns compared to those of permanently wet components have been also observed (Scherer, 2013 and Weiler et al., 2020a). As stated by Weiler et al. (2020b), it is necessary to determine and verify the relevant influencing factors on leaching through intermittent water contact and other environmental factors on the respective material in order to obtain a wider database by the use of time saving testing methods and to define reasonable release limits. Schoknecht et al. (2022) developed a target concept capable of integrating knowledge of emission sources, leaching processes, transport pathways and effects on the receiving compartments in order to serve as a basis for an environmental risk assessment for construction products.

Organic ingredients

As well as for mineral materials, façade coatings containing organic substances can be potentially harmful for the environment. The leached organic substances from these construction materials represent a risk to the environmental compartments (e.g. unsaturated soil, ground- and/or surface waters). Organic substances such as unreacted monomers, additives, impurities, degradation products and biocides can be found in façade runoffs (e.g., Bollmann et al., 2016; Burkhardt et al., 2011; Schoknecht et al., 2009; Schoknecht et al., 2016; Schwerd, 2011; Schwerd et al., 2015; Styszko et al., 2016; Uhlig et al., 2019). A precise allocation of the leached substance to its sources is certainly difficult as concentrations are often measured in the runoffs which can be subjected to probe contamination (Weiler et al., 2020a). Nevertheless, possible sources can be identified by comparing with different catchment samples.

During the years, the main interest of research changed from the durability of a building product (e.g. the protective effect of a biocide) to its environmental compatibility (Breuer et al., 2012; Schwerd, 2011; Schwerd et al., 2017). It was found that only a small proportion (max. 13%) of the biocides originally used (e.g., diuron (DR), octylisothiazolinone (OIT), carbendazim (CD) and terbutryn (TB)) are leached out of façade coatings within the first 18 months of use by rainwater runoff. The maximum concentrations in the runoff water were recorded at the beginning of outdoor weathering and can reach up to approx. 18 mg/L in individual cases. Burkhardt et al. (2009) showed critical biocide concentrations in the façade runoff with newly constructed building façades. Nowadays, the discharge of biocides from façades is reduced by encapsulating the active ingredients within microcapsules (Schwerd et al., 2015; Burkhardt et al., 2011).

The balancing of the active ingredients used and the residual contents in the coatings sometimes shows large gaps in the balance, which indicates further mechanisms running parallel to the leaching that influence the active ingredient contents (Schwerd, 2011; Schoknecht et al., 2016). Leaching of biocides from external thermal insulation composite systems (ETICS) does not only depend on the availability of water, but is also controlled by transport processes within the materials and the stability of the observed substances (Schoknecht et al., 2016). The leaching mechanism occurs as follows: 1) water which is adsorbed at the surface of the façade is transported to deeper layers, 2) biocides are dissolved from particles or microcapsules, 3) the biocide is transported via diffusion (driven by concentration gradient, dependent on temperature, etc.), 4) some biocides are degraded via photolysis or hydrolysis, leading to a reduction of some biocide concentrations, and 5) the biocide is transferred to the water on the surface of the coating where evaporation and water up-take occurs (Blocken et al., 2012; Schoknecht et al., 2009; Styszko et al., 2016; Uhlig et al., 2019). Wangler et al., (2012) further found out that a temperature increase results in an increased emission rate. According to Bollmann et al. (2016), the formation of transformation products under the influence of UV was identified as a key mechanism for the active ingredient TB and the balance gap was closed.

The maximum concentrations of biocides in the stormwater runoff of façade coatings tend to be higher in the early lifetime of the coatings, reaching fairly constant concentration levels later on, generally in the range of hundreds of µg/L to mg/L (Burkhardt et al., 2009; Burkhardt et al., 2012; Bollmann et al., 2014). Uhlig et al. (2019) argued that the leaching is not fairly constant, instead there exist phases of higher leaching events far beyond the initial exponential decay. These events reveal changes in the slope after several years of field exposure making difficult to identify and model the governing leaching processes.

In 2011, CEN/TC 139 WG 10 published DIN EN 16105, a standard for the investigation of leaching from façade coatings with a fixed volume-to-surface ratio and drying phases when changing the eluent. Comparative studies of the release of biocides in the field and in the laboratory were covered by Schoknecht et al. (2016).

Wicke et al. (2016) used Berlin as an example, they showed that depending on the examined catchment area, a wide variety of substances occur in the rainwater runoff, sometimes in considerable concentrations and loads. Connected directly to construction products and viewed as relevant were the biocides CD, DR and TB (Wicke et al., 2022).

Paijens et al. (2019) argued that biocides are still poorly regulated and monitored in the aquatic environment, although they are widely used in urban areas. Further studies on biocide concentrations in aquatic environment for full risk assessment were also recommended in a joint workshop by NORMAN network and the German Federal Environment Agency (Pohl et al., 2015). Although biocidal chemicals are widely researched, the environmental fate of transformation products (TPs) is not well understood. Although there are plentiful publications on monitoring emerging contaminants (ECs), the majority does not address the regulating of transformation products of parent compounds (PCs) (Lambropoulou et al., 2014). Meanwhile, these transformation products can be highly volatile and toxic. TPs that are biologically active and resistant to biodegradation are particularly concerning in this context (Picó & Barceló, 2015).

Linke et al. (2021) investigate the leaching of biocides used in façade coatings to identify individual sources and entry pathways in a small-scale urban area. Within the monitoring sources, runoff samples taken from façades, rainwater pipes, drainage and stormwater infiltration systems (SIS) were analyzed. Biocide concentrations found in their samples were above PNEC for surface water. Biocide concentrations were found and identified in façade runoff, runoff from roof downpipes, drainage pipes and SIS soil infiltrated drainage pipes.

Bork et al. (2021) investigated the mobility of biocides in SIS by observing the influence of molecular, chemical and structure properties of integrated the soil layers. It was stated that these properties change over time and thus possibly also the relevance of preferential flow paths, e.g. due to ongoing biological activity. The study showed that despite similar soil texture and chemical properties, retention of tracers and biocides differed distinctly between SIS due to the increase of macropores number related to biological activity and aging of the SIS.

To gain information on the leaching of biocides from ETICS coatings a variety of studies have been carried out at the laboratory scale (e.g., Bollmann et al., 2016; Burkhardt et al., 2007; Schoknecht et al., 2009; Wangler et al., 2012; Styszko et al., 2016) or under field conditions (e.g. Burkhardt et al., 2011; Burkhardt et al., 2012; Schwerd et al., 2015; Wangler et al., 2012; Wittmer et al., 2011a), focused on biocides from organic façade coatings (plasters and paints). Models to examine the biocide leaching process have been developed (e.g., Wittmer et al., 2011b; Coutu et al., 2012). Standard test methods at the laboratory scale are one approach to obtain data on the leachability of biocides form façade coatings (e.g., DIN EN 16105; CEN/TS 16637-1 and -2)). The procedures are based on long-term immersion in eluent or consist of wetting cycles and drying phases where the eluent is regularly renewed. While in laboratory experiments the production of a test specimen and its experimental procedure are defined, in outdoor tests, specimens of different kinds concerning geometry, size and setup are subjected to real weather influences like WDR that affect the surface of an exposed coating. Temperature and UV irradiation can influence organic substances through transformation and degradation processes (Bollmann et al., 2016 and 2017; Schoknecht et al., 2009).

Models for substance release and transport

Some models are able to predict the amount of substances released from façades under real outdoor conditions (e.g., Burkhardt et al., 2018; Coutu et al., 2012; Jungnickel et al., 2004; Styszko et al., 2018; Walser et al., 2008; Wangler et al., 2012; Wittmer et al., 2011b; Uhlig et al., 2019). Most of these models, for example the model presented by Burkhardt et al., (2018) using the software COMLEAM, focus on the leaching of biocides and not on metals or anions. The models use predefined emission functions to determine the amount of substance leached through input parameters (e.g. type of material, substance characteristics, geometry of the façade, and weather factors). These functions can be also derived by the user and are obtained from the results obtained in experimental studies, making them suitable for certain materials in some cases. If the simulated materials are not available in the database of the models, are new or are under development, the user is limited to the predefined material emission functions these programs (e.g. COMLEAM and LeachXS) offer or must obtain their own functions from experimental studies.

Adequate modeling of emission processes is required to predict emission values in the framework of a risk assessment of biocidal products (Uhlig et al., 2019). Authors have proposed different criteria for determining which mechanism controls the leaching process at a given point of time by analyzing the slope of emission curves (Schoknecht et al., 2016; Uhlig et al., 2019). A numerous amount of parameters were included within these modeling approaches, e.g., temperature, relative humidity and global radiations, to provide a new framework for interpreting and modeling outdoor biocide emission curves. Tietje et al. (2018) applied different mathematical functions to fit emission curves for the release of TB from façade renders on the basis of retrieved experimental data from field tests. The functions obtained by Tietje et al. (2018) include different physico-chemical processes, such as diffusion and desorption. Styszko et al. (2018) developed a diffusion-based transport model that takes into consideration biocide redistribution within renders during dry periods. Results from this model are in the range of results retrieved in laboratory tests. Wangler et al. (2012) applied a diffusion-based model for renders that were in permanent contact with water and for experiments that included dry periods. The model does not include processes often presented in outdoor situations such as changes in temperature and biocide degradation. Wittmer et al. (2011b) assumed in their exponential function model that biocide leaching from façades results from fast diffusion processes and slow diffusion processes. This model was applied to leaching data from cyclic exposure of test specimens in a weathering chamber.

It is therefore important that a comprehensive model starts from the composition of the façade materials in order to predict the leaching of substances. The physical (transport) or chemical (equilibrium or kinetic reactions) mechanisms that occur inside and outside the material compartments during the outdoor exposure have to be included. This is already the case for the model presented by Schiopu et al. (2007, 2008) and Tiruta-Barna (2008), which has been developed for the release of metals and anions from concrete. With this, it is not necessary to carry out new experimental studies or couple the unknown emission function of a new material with the emission functions offered by the database of a program to model the leaching of substances during outdoor exposure conditions.

There are also software packages for the approval of pesticides (e.g. FOCUS Pelmo) available for the simulation of behavior and transport of pesticides in soil to groundwater. FOCUS is the acronym for "FOrum for Co-ordination of pesticide fate models and their USe". The simulation programs of the FOCUS series can be obtained from the European Soil Data Center (ESDAC), a facility of the Joint Research Center (JRC) of the European Commission (JRC, 2021). They were criticized for allegedly underestimating the risk to the environment (Knäbel et al., 2014, Knäbel et al., 2016). Additionally, FOCUS Pelmo was developed primarily for the use of pesticides on agricultural land and has only limited applicability on urban soils. Due to the current need to assess the impact of substances found in urban runoff, it is necessary to develop a substance transport model that includes the characteristics of urban scenarios. The applicability of this model must comply with the standards and scenarios previously discussed and determined by authorities in the matter.

2 Research objectives and hypotheses

The available data show that the release of substances from façade coatings is influenced by many factors. The complex interaction between these factors has not been clarified yet. On the one hand, there are great differences between the leaching mechanisms of inorganic and organic substances. On the other hand, however, the release also varies greatly within a substance group and from recipe to recipe.

Based on the retrieved data, the following subjects are needed to be addressed within this dissertation:

- the identification of essential leaching mechanisms,
- the development of a model that can describe the leaching mechanism of substances in a plaster and mortar façade during a random rain event,
- the mathematical description of the substance transport mechanisms on the façade until they reach the unsaturated zone or groundwater, and finally,
- the development of an assessment of the environmental properties of the leached substances should be carried out.

As result of this dissertation an integrated leaching and evaluation model for the environmental impacts caused by the substances released from the irrigated façades covered with plasters and mortars should be developed. This model should have as a starting point the physical properties and chemical composition of the selected studied plasters and mortars.

2.1 Development of a model able to predict the impinged water that sorbs, bounces off, runs off or remains as a film on a façade coated with plaster or mortar during a random rain event

Many studies in recent decades have focused on the prediction of impinging WDR on building façades. These models have focused on predicting the amount of WDR that affects a façade by using semi-empirical formulas (ISO, 2009) and numerical simulations with Computational Fluid Dynamics (CFD). A summary of these methods can be found in Blocken et al. (2012). To approach WDR to a façade, there exist two different methods according to Abuku et al. (2009): (1) The average moisture flux of a façade is supplied by the total mass of all raindrops impinging on the material surface during a defined time interval established by the meteorological input data and (2) the WDR is the sum of individual raindrops impinging on the façade in a spatially and temporally discrete modus. In the CFD model, the airflow patterns were studied using computational fluid dynamics.

The surface runoff that occurs following water saturation of the façade material is of special interest because leaching is controlled by the availability of water on the surface as well as the transport processes within the materials (Schoknecht et al., 2016).

The first research objective was to model the runoff of a façade coated with mineral plasters and mortars by combining a variety of process, e.g., WDR impingement in the vertical plane, material absorption, and surface runoff. The modeling should be based on previously developed models, methods and assumptions. The calculation of impinged raindrops in the façade, as well as the amount of absorbed water and the surface runoff should be assessed.

Research hypothesis 1: *A model to predict the runoff of a façade covered by plaster or mortar during and after a random rain event can be developed from pre-existing mathematical methods.*

In order to compare the results between the model and the runoff volumes obtained during the field tests, real weather parameters derived from the investigations from Fraunhofer IBP (see section 1.4) as well as the physical properties of the materials will be used as input parameters.

2.2 Modeling the leaching processes and material transport on façades

Some models are able to predict the amount of substances released from façades under real outdoor conditions (e.g., Jungnickel et al., 2004, Walser et al., 2008, Wittmer et al, 2011b, Coutu et al., 2012, Burkhardt et al., 2018). These models focus on the leaching of biocides and not on metals or anions. The models use predefined emission functions to determine the amount of substance leached through input parameters (e.g., type of material, substance characteristics, geometry of the façade, and weather factors). These functions can be also derived by the user and are obtained from the results obtained in experimental studies, making them suitable for certain materials in some cases. However, the simulation process for leachate substances in this model neither predicts nor describes the physical (transport) or chemical (equilibrium or kinetic reactions) mechanisms that occur inside and outside the material compartments during the outdoor exposure. It is therefore important that the model starts from the chemical composition of the façade materials in order to predict the leaching of the substances. With this, it is not necessary to carry out new experimental studies or couple the unknown emission function of a new material with the emission functions offered by the database of these programs to model the leaching of substances during outdoor exposure conditions.

The objective of this research is the development and evaluation of a model for leaching processes and material transport on façades. Using an already developed PHREEQC coupled chemical-transport model by Schiopu et al. (2008) and storm water runoff parameters, it should be possible to determine façades runoff concentrations of the leached substances focusing on metals and anions.

Research hypothesis 2: *Based on the studies of Tiruta-Barna and Schiopu, PHREEQC is also applicable for the modeling the leaching of metals and anions from façades covered by mineral* *plasters or mortars using as input parameters the results obtained by the model that predicts the runoff of a façade covered by plaster or mortar during and after a random rain event.*

The model should be calibrated using an iterative process of comparing the leaching field tests resulting in an acceptable fit. The simulated eluates should have concentrations that correspond to those obtained in the leaching outdoor tests in order to test the hypothesis.

2.3 Evaluation and assessment of the environmental impact of common plasters and mortars by using a leachate forecast for groundwater risk assessment

To develop a new and improve existing methods as well as to harmonize methods for groundwater risk assessment the German Federal Ministry of Education and Research funded the joint research project “Groundwater Risk Assessment (GRA)” (Susset et al., 2011). The GRA focused on the assessment of contaminant leaching from various materials and reactive transport in the unsaturated soil towards the groundwater table (Oberacker et al., 2002). The goal of the evaluated results of the joint research project was to identify the key factors governing the release, transport and turnover of contaminants from various mineral recycling materials (e.g., mineral waste, industrial waste, concretes and soils) used in technical constructions. Another objective of the study was to derive the maximum concentration of contaminants acceptable in the leachate of certain mineral materials obtained by defined laboratory tests which are applied in various earthworks (e.g., roads, dams, landscaping, etc.). As a result, the GRA determined the “media related application values (MEs)”. These values are derived under specific technical boundary conditions and political conventions which aim for the prevention of adverse effects to the media soil and water. The MEs are dependent on the substances of interest and the hydraulics in construction soils and sub-soils. The goal of the MEs is to protect the environmental media soil and groundwater, considering technical boundary conditions and policy conventions.

The objective of this part of the research is to use the GRA and the simulated façade leached inorganic substances to evaluate the environmental characteristics of plasters and mortars. The results of the environmental evaluation should help to assess groundwater risk for special building products as well as serve as guideline for manufacturers or authorities to determine the suitable areas of application of these materials.

Research hypothesis 3: *An evaluation of the environmental properties of mineral plasters and mortars can be developed by adapting the GRA procedure (“Sickerwasserprognose”) and using the results of the façade leaching model as source term.*

2.4 Quantification of biocides leaching from two model houses containing two different plaster compositions with biocides which are oriented in all cardinal directions (north, east, south and west)

To gain information on the leaching of biocides from ETICS coatings a variety of studies have been carried out at the laboratory scale (e.g., Bollmann et al., 2016; Burkhardt et al., 2007; Schoknecht et al., 2009; Wangler et al., 2012; Styszko et al., 2016). Standard test methods at the laboratory scale are one approach to obtain data on the leachability of biocides form façade coatings (e.g., DIN EN 16105, CEN/TS 16637 -2)).

Examinations under field conditions focused on biocides from organic façade coatings (plasters and paints) are also reported. There are several studies which focus on investigations with vertical test panels or on side-oriented façades under real weather conditions (Burkhardt et al., 2011; Breuer et al., 2012, Wangler et al., 2012; Bester et al., 2014; Bollmann et al., 2016; Burkhardt et al., 2012; Hensen et al., 2018; Scherer, 2013; Schwerd, 2011, Schwerd et al., 2015). However, so far, no study has investigated the leaching of ingredients under real climatic conditions on façades oriented to different directions at the same time, which was the objective of the present study and base for further modeling of environmental behavior.

Research hypothesis 4: *Because wind driven rain is the main influencing factor on the release of biocides from building façades, the biocide load is highest at the weather side compared to the other sides.*

The hypothesis can only be verified with long-term experiments under real weather conditions on a real scale. For this, the results of the 18-month field tests from Fraunhofer IBP (see section 1.4) using model houses with two different plaster compositions and different biocides which were oriented in all cardinal directions (north, east, south and west) were evaluated. Leaching and weather conditions were monitored on all sides during the field test.

2.5 Environmental modeling and evaluation of leached biocides and their transformation products from façade coated with plasters until they reach a determined point of compliance

Whereas the leaching of biocidal substances from ETICS has been widely investigated, neither their pathway into the groundwater during infiltration nor the environmental fate of their transformation products (TPs) is well understood. Although there have been many publications on monitoring parent compounds (PC), the majority have not addressed the regulating of their TPs. These TPs are of special interest because they can be mobile, toxic, biologically active, and resistant to biodegradation (Lambropoulou et al., 2014; Picó et al., 2015). Currently, no significant data exist on the accumulation, distribution, and transportation of biocides from ETICS into soils. Additionally, biocides leached from the building materials are transferred in an irregular and uncontrolled way throughout the year, in the area proximate to the building (Reiß et al., 2021), often diluted by rainwater or other runoffs. The parameters which play a major role in the behavior in the soil passage are sorption and desorption of biocides in soil as well as biodegradation (Reiß et al., 2021). The factors relevant to the calculation of the behavior of biocides and their TPs in soil compartments include the soil organic carbon sorption coefficient (K_{oc}) and the half-life of TPs (DT_{50}) in soil.

The main objective of this study was to model the substance transport of four major biocide compounds and their TPs within an unsaturated soil compartment during infiltration until they reached a defined point of compliance in order to evaluate the relevance for groundwater contamination.

Research hypothesis 5: *A model that can describe the environmental properties of biocides and their transformation products leached from façades covered with pasty plasters and mortars can be developed by adapting the general conditions of the groundwater risk assessment and Van Genuchten´s substance transport modelling processes.*

To test the hypothesis various runoff scenarios based on real runoff data and soil scenarios had to be analyzed in order to compare the differences in the fate of the leached substances in the environment.

2.6 Dissertation Structure

The publication of five research articles with major contribution is the basis of this dissertation. Four of the research articles are already peer-reviewed and published, one of them is submitted to a journal. The basis for deriving this dissertation was the third basic work requirement (BWR 3) of the Construction Products Regulation (CPR) as stated in Chapter 1. Based on this, the main focus of three of the research articles is the development of a three-level model capable to predict the leaching of inorganic substances from façades coated with mineral plasters and mortars and assess their environmental fate. In addition, two other research articles refer to biocide leaching from ETICS and the modeling of their environmental fate.

The structure of the dissertation with the corresponding chapters, utilized methods, hypotheses and publications is shown in Figure 1.

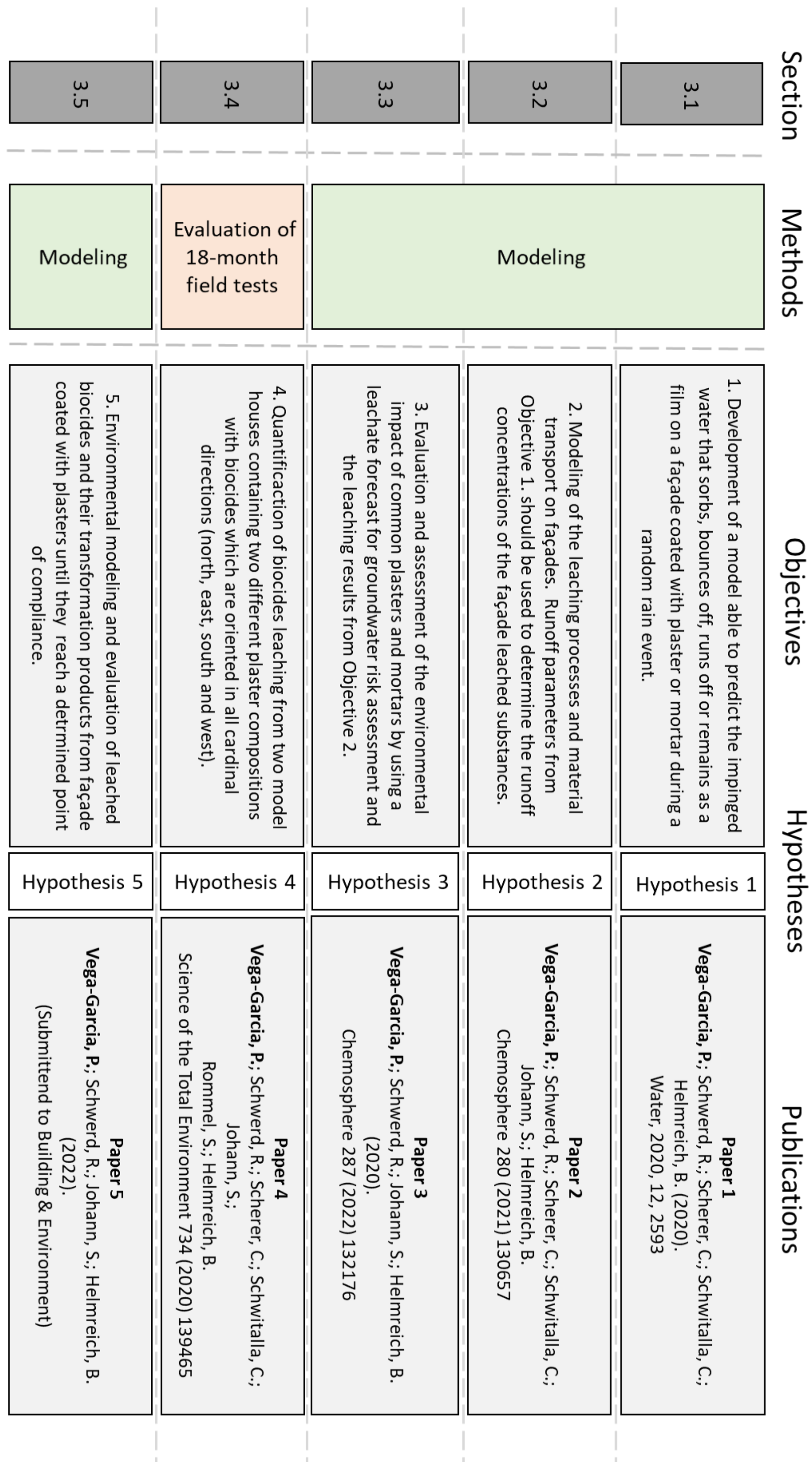

Figure 1: Structure of the cumulative dissertation.

3. Dissertation Results

3.1 Façade runoff model (Level 1)

A façade runoff model was developed to determine the volume of water that has contact with the façade during a random rain event. The model calculates the water volume that sorbs during the rain event, runs off it, remains on it as a film as well as the rain duration and the antecedent dry period. The developed façade runoff model bases on the integration of the dependence of the volume of the water running off a façade on the driving rain. The quantification of the runoff water volume depends on the driving rain distribution according to Blocken et al. (2006), water volume absorption (Hall et al., 2002) as well as climate data and material properties. These dependencies are also used in other modelling tools (e.g. COMLEAM) (Burkhardt et al., 2018) and the quantitative model of leaching of biocides from the Danish Ministry of the Environment (Bester et al., 2014).

3.1.1 Modeling assumptions and boundary conditions

To simulate the amount of stormwater that impinges the VTP, absorbs within the material, and then runs off, a grid was used as the model surface. VTPs of 0.5 m × 1.0 m in size were therefore divided into elements with areas of 10 mm x 10 mm. Once the WDR exceeds the absorption rate of the material, water starts to accumulate in form of a film on the studied surface. Water volumes caused by the drops first adhere to the surface and therefore lead to more incorporation of drops, rivulets and, finally, a flow film formation. When the water film reaches a certain thickness, the gravity forces exceed the tension forces produced between the impinged water and the material surface. This process allows the water film to flow down, producing runoff. In order to simulate the runoff in the VTP, each of the elements of the grid consisted of three main layers. The first layer is the (1) cumulative water film thickness (CWFT). This layer defines the point when the cumulated water starts to flow downward. If the water film on an element is larger than the CWFT, the water volume that exceeds this film thickness starts to flow downward, leaving behind a (2) trace film thickness. The trace film thickness leaves behind a trace volume which is equal to the trace water volume multiplied by the size of the grid element. This trace volume then accumulates in the particular element in which the trace volume passes over. The cumulative water film increases depending on the impinging rain amount. The increase in the CWFT is limited by (3) the maximum water thickness. This film thickness limits the amount of water that can accumulate in one grid element. If the cumulative element water reaches the maximum water thickness, the excess water volume flows down.

In the end, the runoff volume is defined as the runoff volume that has flown all the way down to the bottom of the grid and leaves the plane. This process is calculated for every single grid element within each calculation loop. After this, a new time step defined by the time between each impinging raindrop is created and the next calculation begins.

Actual weather parameters measured by on site weather stations and material properties serve as input parameters for the developed model. Measured weather parameters, precipitation, wind direction, wind speed and rain duration were considered to calculate the amount of water that will impinge the façade during a defined rain event. When it comes to the material properties, the water absorption coefficient and the layer thickness are of important interest. Exact numerical values of the different materials are not necessary. It is sufficient to classify materials in predetermined "categories", e.g. like those defined in DIN EN 998-1.

3.1.2 Obtained results

The model is able to calculate the total amount of water that has impinged the vertical surface or façade, the total amount of water that has been absorbed by the material during the rain event, the behavior of the water transport (runoff flow) in the selected surface depending on the material parameters and finally, the total runoff. The results for the calculation of the total runoff were compared to data obtained by field tests. In general, a very good accordance could be shown. Remaining differences can be explained by several reasons, e.g. the model does not include evaporation processes. These obtained results are subsequently used as input parameters in the "model for leaching processes and material transport on façades" (Level 2).

3.1.3 Conclusion

Hypothesis 1 can be accepted. The results indicate that it is possible to replicate the obtained outdoor collected runoffs with the developed model. When comparing the simulation results with the field test accumulated runoffs, the model exhibited a difference of no more than 3.5 % for each of the 17 analyzed mineral plasters and mortars. The simulation results are satisfying and demonstrate the feasibility of the modelling approach for the runoff assessment of façades covered with a variety of plasters and mortars.

3.1.4 Scientific publication

The results were published in following peer-reviewed journal (Publication see Appendix A. 1):

Vega-Garcia, P., Schwerd, R., Scherer, C., Schwitalla, C., Helmreich, B. (2020): Development of a model for stormwater runoff prediction on vertical test panels coated with plasters and mortars. *Water* 12, 2593; doi.org/10.3390/w12092593.

3.2 Model for leaching processes and material transport on façades (Level 2)

The model of Level 2 simulates the substance concentrations in eluates obtained through leaching processes. The focus lies on the discharge of metals and anions from mineral plasters and mortars. In order to achieve this goal, a two-step approach is necessary. In the first step, the leaching mechanism will be defined, in the second step the mass transfer in the façade coating will be simulated. The works of Tiruta- Barna et al. (2008) and Schiopu et al. (2008) are used as the basis for the definition of the leaching mechanisms in mineral mortars and plasters. For this purpose, the system is divided into two compartments. The first compartment is the "porous matrix" (material), the second compartment is the "leaching compartment" (surface of the material in contact with the eluate). The PHREEQC program (Parkhurst, 1995) is used to model all chemical processes and to simplify the calculation of the kinetic reactions and speciation of the elements in the individual compartments.

3.2.1 Modeling assumptions and boundary conditions

To model leaching outdoor tests (LOT) including alternating precipitation and drying periods, the model was divided into two scenarios. The first scenario is the “efficient rain event” scenario. This scenario corresponds to the time when the rainwater runs off over the VTP during a raining event and can be collected. The second scenario is the “duration between rain events” scenario. This scenario takes into account the physico-chemical processes within the material compartments during the drying periods of the VTP. The results of the Façade runoff modell (Level 1) are used as input parameters (see Figure 2).

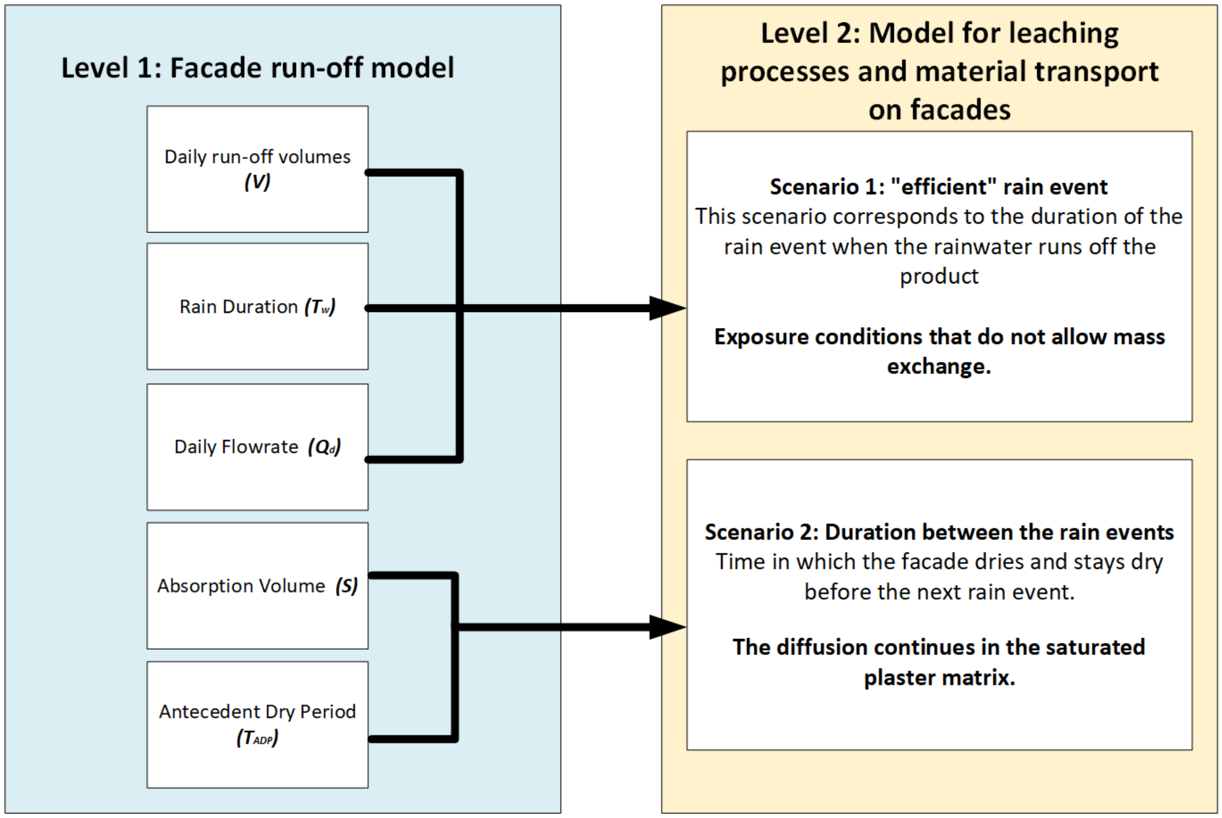

Figure 2: Leaching process (chemistry and transport) and coupling with Level 1 (Façade runoff model).

3.2.2 Obtained results

By using the recipes of different materials, a set of chemical composition for each material was established. The obtained leaching results from the model were plotted against the experimental results obtained by the outdoor tests.

It was observed that the relevant leached substances from plasters and mortars under real weather conditions are sulfate, calcium, chrome, zinc, vanadium, and strontium. Furthermore, it was also noticed that under real weather conditions, different substances found in the VTPs runoff can originate from the rainwater or other external media to the materials (e.g., zinc). Likewise, during the simulations and the calibration process it was observed that the physical characteristics of the material (e.g., thickness, absorption capacity) strongly affects the leaching of substances in façades or panels covered with plaster and mortar. The lower the thickness and absorption capacity of the material applied, the greater the runoff and discharge of leached substances. This last behavior plays an important role in the accuracy of the model because fewer simulated points are available for the validation of materials generating less runoff.

3.2.3 Conclusion

The developed leaching model confirms the hypothesis that it is possible to investigate and reproduce the leaching behavior of VTPs characterized by a specific plaster or mortar for a defined location and period and obtain a good approximation of the amount of substances leached. To model the amount of substances leached, a model developed with PHREEQC was adapted for the prediction and evaluation of substance leaching behavior from VTPs with the incorporation of simulated runoff conditions from the Level 1 façade runoff model.

3.2.4 Scientific publication

The results were published in following peer-reviewed journal (Publication see Appendix A. 2):

Vega-Garcia, P., Schwerd, R., Schwitalla, C., Johann, S., Scherer, C., Helmreich, B. (2021): Leaching prediction for vertical test panels coated with plaster and mortars exposed under real conditions by a PHREEQC leaching model. *Chemosphere* 280, 130657, doi.org/10.1016/j.chemosphere.2021.130657.

3.3 Groundwater risk assessment for inorganic substances (Level 3)

By using the groundwater risk assessment (GRA) (Susset et al. 2011) an environmental evaluation of façade leached substances was developed. This evaluation shows whether the substances leached from mineral plasters and mortars imply a hazardous potential risk for soil and groundwater or not.

The GRA is a process-based concept for identifying suitable application scenarios for mineral materials in various technical constructions and permanent applications. The evaluation process itself is carried out in form of a simplified risk assessment by comparing substance concentrations (source term) to "media related application values (MEs)", which are derived depending on the concentration decline of salts and retardation and/or attenuation and accumulation of metals in soils and on the hydraulic properties of technical constructions (using the transport term) (Susset et al., 2011 and Susset et al., 2018). The MEs are specific allowed maximum concentrations of a substance in the seepage water at the bottom of a technical construction (permanent/non-permanent) with mineral material or permanent earthworks.

3.3.1 Groundwater risk assessment procedure and boundary conditions

By using the groundwater risk assessment procedure "Sickerwasserprognose" (Susset et al., 2011) an environmental evaluation of the source term, in this case the façade leached contaminants is possible for the example of infiltration to groundwater. During the development of the leachate forecast, an extensive preparatory work has already been carried out. The future estimation of the environmental impact of inorganic substances released from the impinged façades will be based on the methods obtained by these works. To determine the validity of a certain mineral plaster or mortar in accordance with the GRA, several steps are necessary.

1. In a first step, relevant substances for mineral plasters and mortars have to be identified based on the eluate concentrations obtained by Level 2 model taking into account the insignificance threshold values (GFS-values).
2. The relevant substances and their simulated concentration values for the mineral plasters and mortars are subjected to a statistical evaluation.
3. For façades coated with mineral plasters and mortars, a technical construction application must be selected from the GRA to derive the respective MEs.
4. The results of the statistical evaluation for each of the simulated plasters and mortars eluates are compared with the values defined for the different scenarios MEs of the selected technical construction application.

3.3.2 Obtained results

As a result of the comparison between the simulated leached concentrations from the mineral plasters and mortars and the GFS-values, V, Cr, and Pb were considered to be relevant substances for further considerations. These substances presented concentrations above the GFS-values and might imply a hazardous potential to the chemical status of seepage water at the point of compliance. All 18 tested mineral plasters and mortars consistently showed these substances as relevant. Finally after comparing the statistical concentrations with the correspondent MEs it was concluded that Cr is the only substance with 90th percentile values above MEs that would not allow the use of 3 of the examined mineral plasters and mortars for application within the (for most common façades unrealistic) “unfavorable case scenario” of the selected technical construction application.

3.3.3 Conclusion

The GRA served as a guideline to evaluate the environmental characteristics of different mineral plasters and mortars. Substance concentrations obtained by the Level 2 model for leaching processes and material transport on façades were used as source term for the assessment. With this, the hypothesis that an evaluation of the environmental properties of mineral plasters and mortar can be developed by adapting a GRA procedure and using the results the façade leaching model is confirmed.

3.3.4 Scientific publication

The results were published in following peer-reviewed journal (Publication see Appendix A. 3)

Vega-Garcia, P., Schwerd, R., Johann, S., Helmreich, B. (2022): Groundwater risk assessment of leached inorganic substances from façades coated with plasters and mortars. *Chemosphere* 287 (3), 132176. doi.org/10.1016/j.chemosphere.2021.132176.

3.4 Influence of façade orientation on the leaching of biocides

The first two partial models Level 1 and Level 2 allow to calculate the release of relevant metals and anions from mineral mortars and plasters. As the model of Level 2 is yet limited to mineral plasters and mortars, data from field tests from preliminary studies for biocide emission from pasty plasters had to be discussed in order to obtain reliable starting concentrations for the modeling of the environmental behavior of biocides.

3.4.1 Data acquisition (leaching outdoor tests and statistical analysis)

The results of the 18-month field tests from Fraunhofer IBP (see section 1.4) using model houses with two different plaster compositions and different biocides which were oriented in all cardinal directions (north, east, south and west) were evaluated. A correlation analysis between the weather data and the observed biocide emissions was performed in order to investigate the relations between the different weather parameters and the amount of leached biocides. For this correlation analysis the following data was included: façade runoff volume (RV), wind-driven rain (WDR), temperature during precipitation (T), wind speed during precipitation (WS), wind direction during precipitation (WD), rain intensity (RI), rain duration (RD), total precipitation volume (P), antecedent dry period (ADP) prior to the main rain event, median UV irradiation (UV) during ADP, median solar radiation (SR) during ADP, pH-value, electrical conductivity (EC), total organic component (TOC) of individual runoff samples and the TB, DR, OIT and CD runoff loads.

3.4.2 Leaching outdoor tests and statistical analysis results

The investigation has pointed out that the monitoring of all cardinal direction sides is essential for the assessment whether on-site treatment facilities have to be installed at all sides of a building or only at the weather side.

Given the results of the LOTs it could be demonstrated that the concentrations on all sides were higher than e.g. the insignificance threshold values (GFS-values) (LAWA, 2016) for groundwater and the predicted no-effect concentration (PNEC) values. For on-site treatment systems, however, it must also be kept in mind that very different hydraulic loads can be expected. When the wind came from the west / southwest direction, the amount of collected runoff volume during the sampling period increased depending on the façade orientation and was up to 34 times higher at the weather side (here west side) compared to the opposite side (here east side). The monitoring of the concentrations demonstrates that not only the weathered side (west and southwest direction in our case) has to be taken into account for the installation of on-site treatment facilities, due to the fact that higher concentrations were presented in the façades with less runoff, because less dilution is carried out. This observation also affects the dimensioning of the treatment facilities for each side of the building.

The results of the correlation analyses have confirmed that the main parameter that influences the leaching of biocides is the WDR. Weather parameters during and before the rain event such as rain intensity, wind speed, wind direction, total precipitation, temperature and UV irradiation have no significant detected influence when they are correlated as isolated parameters, because they fail to reflect the complex interactions that affect the emissions.

3.4.3 Conclusion

The hypothesis that the biocide load is highest at the weather side (west) compared to the other sides (north, south and east) has been proven. The results of the correlation analyses confirmed that the main parameter that influences the leaching of biocides is the WDR. Additionally it could be demonstrated that the concentrations on all sides were higher than e.g. the GFS-values for groundwater and the PNEC values.

3.4.4 Scientific publication

The results were published in following peer-reviewed journal (Publication see Appendix A. 4):

Vega-Garcia, P., Schwerd, R., Scherer, C., Schwitalla, C., Johann, S., Rommel, S.H., Helmreich, B. (2020): Influence of façade orientation on the leaching of biocides from building façades covered with mortars and plasters, *Science of The Total Environment* 734, 139465. doi.org/10.1016/j.scitotenv.2020.139465.

3.5 Groundwater risk assessment for organic substances (biocides) (Level 3)

Most of the leached biocides are not included within the ground water risk assessment. So far, only the active ingredient DR is part of the GRA, whereas other biocides like OIT, CD and TB which also can be leached out of building products have not been covered by it yet. The transport of these biocides and their transformation products in the unsaturated zone has to be modeled in order to evaluate their environmental properties. The main objective of this part of the dissertation was to model the substance transport of four major biocide compounds and their TPs within an unsaturated soil compartment until they reach a defined point of compliance.

3.5.1 Modeling assumptions and methods

Runoff data from model houses located at Fraunhofer Institute for Building Physics IBP was used as source term (Vega-Garcia et al., 2020a). Transformation products of four commonly-found organic parent compounds (PCs), namely CD, DR, OIT and TB should be analyzed and modelled based on their biodegradation performance in soil.

The automation of the substance transport calculation of PCs and their TPs in the unsaturated soil compartment was developed using MATLAB. The model was mainly based on estimated parameters from existing database and experimental results from past literature. General condition assumptions were taken into account with reference to the GRA (Susset et al., 2011 and Susset et al., 2018). Finally, results of the simulation were analyzed.

The point of compliance (OdB), which is also assumed as the groundwater table, is considered to be at 1 m below the soil surface. For all 4 biocides in the scope of this project, the GFS-value is 0.1 µg/L (LAWA, 2016). With hydrophobic organic contaminants, a constant source term is assumed.

Transformation processes of biocides were analyzed in two types of soil, namely sandy soil with moderate retardation and natural attenuation and loamy, silty and clayey soils with high retardation and natural attenuation. These two soil categories were defined by Beyer et al. (2007, 2008) and Grathwohl et al. (2006) based on a statistical evaluation of the main soil units in Germany. Additionally, a third scenario including a 30 cm top layer with an organic carbon content (C_{org}) of 2% was calculated in order to show the impact of treatment measures for runoff water from façades.

3.5.2 Obtained results

For DR the highest calculated concentration was found at OdB, followed by CD and OIT at house 1. At house 2, the calculations led to predictable concentrations for TB only. When comparing two different soil types, the calculated concentration peaks were lower and shifted to the right hand side with a broader base width for the loamy/silty/clayey soil. This means that it took longer for the substances to be transported in this soil type compared to the sandy soil.

For the top soil scenario the calculated maximum concentrations of biocides found at OdB were decreased by a factor almost 10 when compared to those obtained in the other scenarios. This implies that a layer with a higher organic carbon content considerably decreases the maximum concentration found at the OdB. The reason for this is greater sorption and degradation of the biocides within the first 30 cm of transport.

All TPs show very low concentrations compared to their PCs input concentrations. All PCs and TPs transportations demonstrate a similar pattern: (1) a substance takes time to reach the OdB, (2) the concentration at OdB slowly builds up and increases, (3) concentration reaches the maximum after a period of time, (4) the concentration slowly decreases as the load is not high enough to maintain at the maximum, (5) the concentration approaches zero indicating the substance leaving the system. All the TPs presented a behavior similar to their PCs, where the higher maximum concentrations at the OdB were found in the scenario in which the roof runoff was not included. They were transported faster within the sandy soil. This behavior is due to the fact that the increase or decrease of the TPs is directly related to the magnitude of concentration of PCs that are in the system at a certain time.

3.5.3 Conclusion

The hypothesis that by means of simulations using the Van Genuchten´s substance transport equation (Van Genuchten et al., 1982) and general condition assumptions of a Ground Water Risk Assessment (GRA) it is possible to assess the environmental fate of biocides and their transformation products in an unsaturated soil compartment until they reach a defined point of compliance can only be partially confirmed. The model needs experimental input to improve the data situation for sorption parameters. The fact that only sorption to organic matter is assumed when using the soil types according to the GRA can lead to wrongly overestimated values at the OdB. In this context it is assumed that the façade runoff seeps into the unsaturated soil zone directly and without contact with topsoil which has a higher organic content.

The model described above can be a very helpful tool for estimating the substance- and site-depending relevance of biocide discharge from facades into the ground water and for the choice of suitable treatment measures in form of the introduction of additional soil layers with higher organic content.

3.5.4 Scientific publication

The results were submitted as a manuscript to the journal *Building and Environment* and is currently "under review" (Manuscript see Appendix A. 5):

4. Conclusions, impact and novel research topics

A three-level model was developed capable of evaluating the environmental properties of common outdoor plasters and mortars. This model was based on an extensive database from long-term outdoor experiments by Fraunhofer IBP. Each level of the model is dependent on the previous one: the results given by the previous level serve as input parameter for the following level. The setup and the required input parameters for each “Level” is represented in Figure 3.

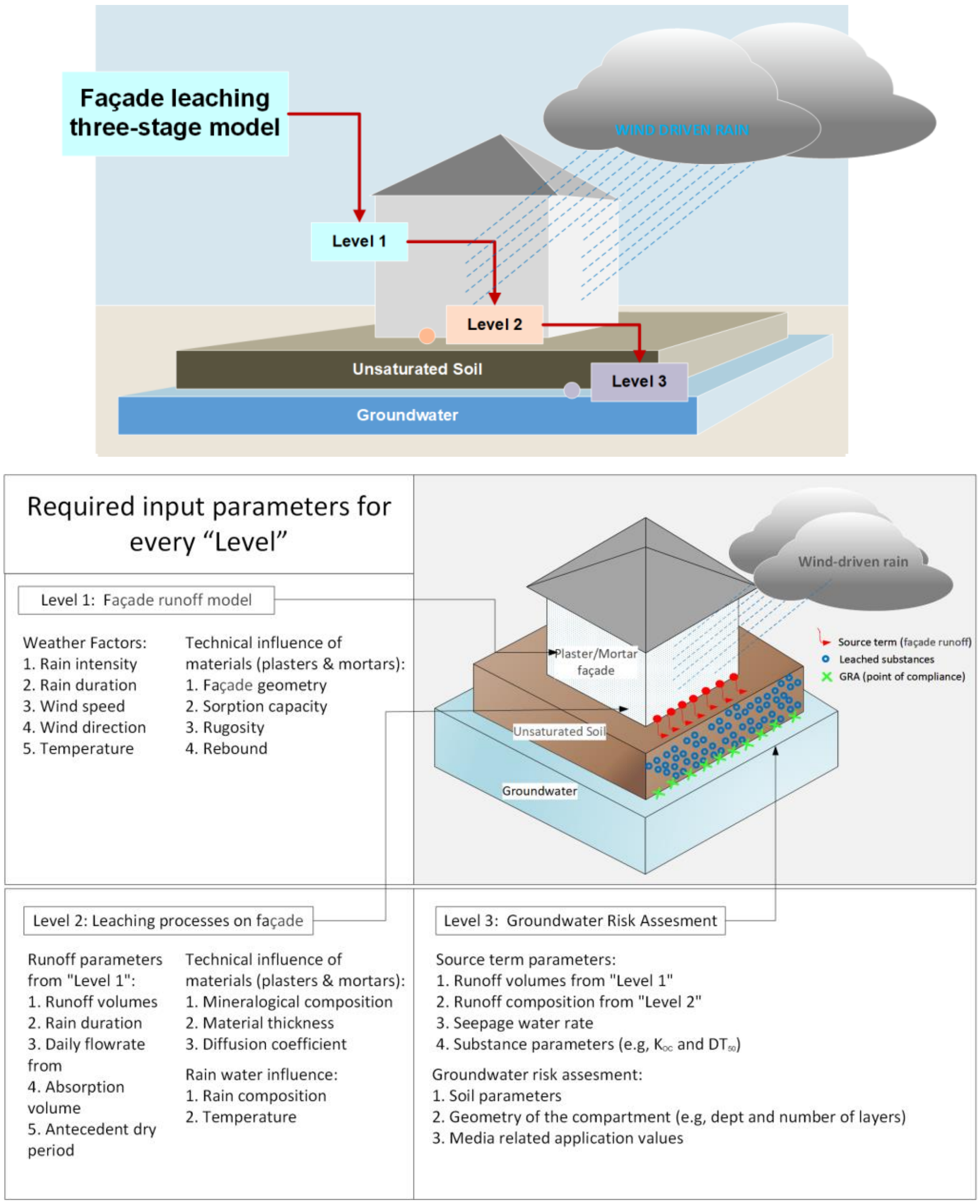

Figure 3: Three-level model setup and required input parameters.

The first sub-model, namely “Façade runoff model” is Level 1 of the three-stage model. In the model described, existing modeling methods were adapted for the prediction and evaluation of rainwater runoff from VTP. The advantage of having a complete and detailed experimental dataset made it possible to validate the accuracy of the model by comparing the simulated results with those collected in the field. The presented Level 1 model makes it possible to investigate and reproduce the runoff response of VTP characterized by a specific plaster or mortar for a defined location and period and obtain a good approximation of the amount of runoff for different materials. Firstly, the rain loads can be calculated and visualized with the aid of the simulation program; secondly, the total absorption of the material can be estimated at any time in accordance with the used absorption model, and, finally, the runoff volume and water flow rate on the VTP can be determined. The moisture content of the VTP is largely dependent on the supplied WDR and the material characteristics. It was observed that higher runoff volumes and flow rates are more likely to appear on materials with a lower capillary absorption capacity.

Given the results obtained by the simulations, the advantages and limitations of the model can be described. For the most part, the limitations of the model go hand in hand with the permanent variation in the weather data in reality vs. the assumptions made in the model (e.g., VTP surface temperature at 20 °C). It is possible that these types of assumptions limited or influenced the calculation of runoff volumes and gave underestimated or overestimated results for certain simulated rain events. Simulated values in certain rain events can be overestimated because drying or evaporation were not included in the model. For very weak rain events, these processes can have a very important impact and can be noticeable in the simulation of the first rain events, which were characterized by very weak precipitation. Another limitation of the model was that the method used to give roughness to the VTP is the same for all three types of materials. The materials used in the field experiments showed physical differences in their surfaces, depending on the grain size of the mixture. This physical characteristic of the material may play an important role in stream formation and could complicate the runoff patterns.

A method for correctly defining the difference between the roughness of varying materials should be evaluated in future investigations. The improvement of this model in the future should include processes that are currently simplified, such as the inclusion of drying periods influence on the material, evaporation on the material surface and material aging. With these integrated and non-simplified processes, a more accurate and robust model could be obtained that allows reducing the overestimations and underestimations that the model presents in extreme rain events.

In the Level 2 model, namely “Model for leaching processes and material transport on façades”, an existing leaching model developed with PHREEQC was adapted for the prediction and evaluation of substance leaching behavior from VTPs coated with plaster and mortar under real outdoor exposure conditions. With the incorporation of simulated runoff conditions from the Level 1 model, which predicts the runoff, it was possible to simulate the leaching behavior of the VTPs covered with plasters and mortars of a series of rain events over a period of 18 months. Despite the complexity of non-controlled outdoor conditions, the LOT simulation was able to reproduce the experimental results of the substances leaching from VTP coated with different plasters and mortars.

The leaching model makes it possible to investigate and reproduce the leaching behavior of VTPs characterized by a specific plaster or mortar for a defined location and period and obtain a good approximation of the amount of substances leached for different materials. It was observed that the relevant leached substances from plasters and mortars under real weather conditions are sulfate, calcium, chrome, vanadium, lead and strontium. With this model it was capable to observe that the physical characteristics of the material (e.g., thickness, absorption capacity) strongly affects the leaching of substances in façades or panels covered with plaster and mortar. The lower the thickness and absorption capacity of the material applied, the greater the runoff and discharge of leached substances. This last behavior plays an important role in the accuracy of the model because fewer simulated points are available for the validation of materials generating less runoff.

As well as for the Level 1 there are some processes that are not included in this model. In the future their inclusion to the Level 2 model could lead to an improvement in the results precision. Currently, this model does not include in its method the process of evaporation of water in the pores or at its surface, which could influence the chemical processes that take place in the porous matrix of the material and in the material surface. The evaporation process can also lead to differences in the substance transport in and over the coating. The model also does not include the wear of the material (aging) over time, which could influence both the chemical processes within the porous matrix of the material and the transport of substances on the surface of the façade. This process leaves an extensive field of research where the determination of the aging of the material would be included and how this could influence the aforementioned processes, in addition to the search for a way to include these processes within the model.

The Level 3 is the last sub-model of the three-stage model for evaluating the environmental characteristics of mineral plasters and mortars. For this sub-model the "Ground Water Risk Assessment (Sickerwasserprognose)" served as a guideline. This sub-model considered the evaluation of the runoff concentrations obtained by the Level 2 model. The media related application values (MEs) of technical construction application No. 13 from the GRA were selected to validate the applicability of the source term concentrations. The assumptions made within this application represent a conservative approach when estimating the impact of a building product on the environment. Following the steps of the GRA the relevant substances were determined as a first step. Comparing the results of the simulated VTPs cumulative loads with the theoretical GFS cumulative loads, it was obtained that the relevant substances found in the materials runoffs were vanadium, chromium and lead. The VTPs runoff concentrations for these substances were then subjected to a statistical analysis which results then served as values to compare against the MEs of the technical application No. 13 from the GRA.

After comparing the statistical evaluation values against the MEs it was determined that chromium was the only substance considered to limit the application validity of some of the mineral materials for the unfavorable case scenario of the technical application No. 13.

It should be noted that the three-stage model focusses on mineral mortars and plasters as well as inorganic ingredients not on organic ingredients. Since there is great interest in the impact of leached organic substances from façades with organic coatings, research within the scope of this dissertation was included. This part of the research project focused on the effect of leached biocides from façades coated with external thermal insulation composite systems (ETICS). From leaching outdoor tests results obtained by tests with model houses, simulations were developed to observe the behavior of leached biocides and their transformation products in an unsaturated soil compartment using the GRA specifications as a guideline. The first step of this part of the investigation was to analyze the influence of wind driven rain and different weather factors in the leaching of the biocides from façade coatings. Due to the magnitude of the leached substances, the hypothesis that it is necessary to install on-site treatment plants is reaffirmed. The data collected was also used as a source term for the simulation of its environmental fate.

The investigation under real climatic conditions on two model houses with different compositions has pointed out that the monitoring of all cardinal direction sides was helpful for the assessment whether on-site treatment facilities have to be installed at all sides of a building or only at the weather side. The hypothesis that, although wind driven rain is the main influencing factor on the release of biocides from building façades, it is necessary to install treatment facilities on all sides of a building if on-site treatment is required, has been proven. This could be demonstrated because the concentrations on all sides were significantly higher than e.g. the GFS-values for groundwater and the PNEC values. Above all, the concentrations were higher on the sides that received less rain volume. For on-site treatment systems, however, it must also be kept in mind that very different hydraulic loads can be expected. As the wind came from the west / southwest direction, the amount of collected runoff volume during the sampling period increased depending on the façade orientation and was up to 34 times higher at the weather side (here west side) compared to the opposite side (here east side). This affects the dimensioning of the treatment facilities.

The biocide load is decisive for the design of the sorption materials of the on-site treatment facilities. Sorption materials only have a certain sorption capacity. If a much higher biocide load arrives (e.g. on the weather side), the lifetime of the sorption material in the treatment facility is shorter. The material must therefore be replaced more often.

The results of the correlation analyses have confirmed that the main parameter that influences the leaching of biocides is the WDR. Weather parameters during and before the rain event such as rain intensity, wind speed, wind direction, total precipitation, temperature and UV irradiation have no significant influence when they are correlated as isolated parameters, because they fail to reflect the complex interactions that affect the emissions. More research results are necessary in the degradation processes of the biocidal products used in ETICS, as well as investigation on aging processes of the material and the influence of climatic factors like UV irradiations, as they can affect the composition of organic substances during the life time of the product. Once this will be done, it would be possible to develop a Level 2 model that allows predicting the leaching of the biocides used in ETICS during random rain events.

As for inorganic substances, the transport of biocides in the unsaturated zone was determined by using the GRA (Level 3). Collected data depicted in section 3.4 was used as source term for modeling the fate of this substances in the environment (unsaturated soil compartment). Using the obtained concentrations from field tests, substance characteristics from literature and some boundary conditions assumptions defined in the GRA, it was possible to model the environmental fate of façade leached biocides and their transformation products in three determined unsaturated soil compartments.

The results between the seepage water scenarios with roof runoff and without roof runoff showed that the difference in the calculated maximum concentrations found at OdB as well as the time it took to reach these concentrations are attributed to the magnitude of the substance loads, which are dependent on the source term concentrations and the seepage water rate. Higher concentrations were found at OdB for the scenario B (source term with higher concentrations). Meanwhile, for this scenario, it took longer to reach a maximum concentration of PCs at OdB due to a lower seepage water rate (lower seepage water volumes). This behavior was presented for DR, TB and OIT in both houses and both soils. However, OIT showed a contrary behavior, influenced by its higher degradation rate which makes it not very persistent in the studied compartment, as most of OIT degrades before it can reach the point of compliance.

In accordance to the simulation results, the inclusion of the roof runoff helps to reduce the final maximum concentrations at the OdB, this due to the direct influence of the seepage water volume on the percolation rate and higher substance dilution, thus, lower concentrations found on the source terms. For this reason, for future simulations, a precise analysis must be made of whether the architecture of the building roofs influence or not the volume of runoff filtered in the building edges, since this will have a considerable influence on the magnitude of the concentrations found at the studied OdB.

The loamy/silty/clayey soil scenario showed lower maximum concentrations at the OdB and it took longer to reach maximum concentrations when comparing to the sandy soil scenario. The reason for this has to do with a lower retardation factor of the loamy/silty/clayey soil. Substances in the loamy/silty/clayey soil take longer to be transported, because of which they are subjected to greater degradation and results in lower concentrations at the point of compliance when comparing with the sandy soil scenarios.

Finally, a third scenario was included in the modeling of the transport of the biocides in the unsaturated environmental compartment. This scenario contained a topsoil layer of 30 cm within the 1 m soil compartment where the organic carbon content (C_{org}) was of 2%. When comparing the results of this scenario with the ones obtained in the scenario with seepage water volume not including the roof runoff, it was found that the calculated concentrations found at the OdB decrease by a factor of almost 10. This implies that a layer with a higher organic carbon content considerably decreases the maximum concentration found at the OdB. The reason for this is greater sorption and degradation of the biocides within the first 30 cm of transport.

Overall it can be stated that the concentrations of PCs found at the OdB by modeling, with exception of OIT, are higher than the suggested GFS-values (LAWA, 2016) when the environmental soil compartment does not contain a topsoil layer with high organic content. When adding a topsoil layer with higher organic content, all biocides with exception of diuron were below the suggested GFS-values. Yet, enhancement in the organic content may only help to reduce leaching into soil layers with great uncertainties. It was proved that usage of biocides (except for biocides with a short half-life, e.g. OIT) on building façade may pose a risk to clean groundwater. Manufacturers of façade coatings should take great consideration in the use of biocides with low half-life in their recipes, this in order to mitigate their persistence in the environment.

The three-stage model already allows the simulation of potential environmental effects for mineral formulations. To do this, various material properties of any product and the weather data from any location must be given into Level 1 (see Figure 3). The results then run through Level 2 by the help of the product recipe. Finally, after Level 3, the user can obtain a "Conformity Statement" in which it is stated if the construction product is applicable for a determined construction scenario.

A large number of products including worst-case formulations have already been examined in previous research projects. Based on the results of these studies and the results given by the model described above it can be expected that limit concentrations at the point of compliance will not be exceeded for any of the plasters or mortars. It should be considered if under these circumstances product regulations are necessary at all. If so, there must be a general decision whether to use the results of leaching tests or simulated results given by the three-stage model. Possible scenarios are a national, possibly product-related or an EU-wide more general approach. In any case, the regulating authorities must be involved in the process. For pasty systems and biocides such a procedure is not yet possible since there is currently no final consensus as to which scenarios, input parameters, etc. are to be used for the leachate forecast (Level 3).

Table 2 shows a summary of the status of each level of the model for the two groups of products and substances to be evaluated. As mentioned before, the three-stage model is mainly completed in the three levels for mineral products. For pasty products the Level 1 model can be adapted for use due to the fact that the processes for determining the runoff volume from façades are identical to those used for mineral products. For this, the existing input parameters have to be adapted. The Level 2 model, due to the complexity of its processes (Blocken et al., 2012; Schoknecht et al., 2009; Styszko et al., 2016; Uhlig et al., 2019) should be subject to an extensive research to develop a Level 2 model that is suitable to the three-stage model concept. Finally, the Level 3 model for pasty plasters is still under development due to the lack of a clear definition of the scenarios in which the transport of biocides and their transformation products must be evaluated. Additionally, substance parameters, mainly for transformation products, are partly missing. However, a first approach to the evaluation of the fate of these substances in the unsaturated environmental compartments was included within the scope of this dissertation.

Table 2: Status of model development - overview

Model "Level"	Mineral plasters and mortars	Pasty plasters
Level 1: Façade runoff model	Completed. (see section 3.1)	Level 1 model for mineral plasters and mortars (see section 3.1) can be used if the corresponding input parameters are applied.
Level 2: Model for leaching processes and material transport on façades	Completed. (see section 3.2)	Not applicable. Alternative must be found. Extensive research should be carried out to determine the chemical and physical processes that promote the leaching of organic substances from façades. Once these processes have been determined, a suitable model must be developed and validated with the use of field results.
Level 3: Groundwater risk assessment	Relevant parameters: inorganic substances. All necessary material characteristics are available. Completed. (see section 3.3)	Relevant parameters: organic substance (biocides and their transformation products). GRA is applicable. An evaluation scenario has to be defined. Substance parameters have to be cleared especially for some transformation products. (see section 3.4 and 3.5)

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6. Appendix

A. 1 Development of a Model for Stormwater Runoff Prediction on Vertical Test Panels Coated with Plasters and Mortars

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Article

Development of a Model for Stormwater Runoff Prediction on Vertical Test Panels Coated with Plaster and Mortar

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Abstract: Leaching outdoor tests (LOT) are commonly used to assess the leaching of substances from construction materials. In this context, the amount of stormwater in contact with the surface material is of special interest for analyzing the runoff loads of substances from building façades. A numerical model was developed in MATLAB on the basis of previous analytical models to calculate the collected stormwater runoff volumes from the vertical test panels (VTP) during LOT. In the model, wind-driven rain (WDR) is considered to be the main mechanism for determining the amount of water impinging on the VTP, so it is a crucial factor in the modeling for the façade runoff. The new model makes it possible to simulate the runoff volumes from VTP that are covered with a wide variety of plaster and mortar. Using the new model, it was possible to relate the VTP runoff volumes obtained during an 18-month sampling period for LOTs performed at the Fraunhofer Institute for Building Physics in Valley, Germany. When comparing the simulation results with the field test accumulated runoffs, the model exhibited a difference of no more than 3.5% for each of the analyzed materials. The simulation results are satisfying, and the paper demonstrates the feasibility of the modelling approach for the runoff assessment of VTP covered with a variety of plaster and mortar.

Keywords: stormwater runoff; wind-driven rain; façade runoff; numerical simulation; plasters

1. Introduction

In the European Community, the evaluation of the environmental properties of building materials has been a high priority for some years. The Construction Products Regulation (CPR) addresses seven basic requirements for buildings [1]. The third requirement covers the area of hygiene, health and environmental protection. According to the latter, construction projects must be designed in such a way that, throughout their entire life cycle, they will not have an exceedingly high environmental impact. Plaster and mortar are mostly used as part of façade external thermal insulation composite systems (ETICS). During the exposure of these products to precipitation and ambient air, the stormwater runoff from the façades dissolves some ingredients from the plaster and mortar. The leached substances can be released into the environment in this way. Since not every substance has an environmentally hazardous potential, the release of substances from construction products in contact with stormwater does not necessarily imply a negative impact on the environment.

Vertical test panels (VTP) (see Figure 1) have been widely used to investigate the leaching of ingredients of building materials, e.g., façade coatings, ETICS, mortars or plasters [2–8]. These panels are commonly used to gain information on the leaching of substances from building products in real weather conditions. However, the evaluation of the leaching behavior of plaster and mortar in the case of a façade in contact with stormwater by using models is not yet possible, as there is no transfer model for reaching conclusions, from the results of leaching tests, on the actual impact of a building product on soil and groundwater.

Figure 1. Vertical test panels used during leaching outdoor tests in Valley, Germany.

During rain events, building ETICS façades become moist due to wind-driven rain (WDR), a horizontal velocity component of the wind that is driven against the windward façade of buildings. WDR is the most important contributor to the moisture load on building façades [2,4,9–13]. Burkhardt [4] first postulated that weather conditions (precipitation, rain intensity, wind speed, wind direction, temperature), façade geometry (height, weight), site characteristics (latitude, altitude) and façade exposure (orientation) are the main influencing factors of the leaching process.

Many studies in recent decades have focused on the prediction of impinging WDR on building façades. These models have focused on predicting the amount of WDR that affects a façade by using semi-empirical formulas [14] and numerical simulations with Computational Fluid Dynamics (CFD). A summary of these methods can be found in Blocken et al. [10]. To approach WDR in a façade, there exist two different methods according to Abuku [15]: (1) The average moisture flux of a façade is supplied by the total mass of all raindrops impinging on the material surface during a defined time interval established by the meteorological input data and (2) the WDR is the sum of individual raindrops impinging on the façade in a spatially and temporally discrete modus. In the CFD model, the airflow patterns were studied using computational fluid dynamics. By using this method, the catch ratios can be calculated by simulating the raindrop trajectories based on the airflow patterns. The raindrop catch ratios are then used to construct distributions for different zones, as a function of the rain intensity and the wind speed. Heat-Air-Moisture (HAM) models have been assessed to take into account the absorption as well as the moisture response of the façade caused by impinging WDR, including drop bouncing and runoff along the surface [16–20]. Liquid film flow models have been largely studied in the past for other disciplines [21–24], but very few investigations have been done coupling them with vertical surfaces and the hygrothermal behaviors of façades [11]. Blocken et al. [9,10] numerically studied the coupling between façade liquid film flows in combination with simplified absorption models like that of Hall and Hoff [25,26]. Simulations typically overestimate the measured moisture content in facades. This may be caused partly by two errors: (1) errors in the difference in absorption and evaporation between an averaged WDR flux and a flux composed of randomly impinging drops, and (2) errors concerning the behavior of the raindrops, as splashing and bouncing may be processes that decrease the availability of water for absorption and laminar flow [20].

The surface runoff that occurs following water saturation of the façade material is of special interest because leaching is controlled by the availability of water in the surface as well as the transport processes within the materials [27]. To model the runoff of the VTP, it is necessary to combine a variety of processes, e.g., WDR impingement in the vertical plane, material absorption, and surface runoff. In this study, the runoff caused by WDR on VTP coated with three different types of plaster and mortar will be simulated. Based on previously developed models, methods and assumptions, the calculation of impinged raindrops in the VTP, as well as the amount of absorbed water and the surface runoff will be assessed. In order to compare the results between the model and the runoff volumes obtained during the field tests, real weather parameters as well as the physical properties of the materials will be used as input parameters.

Over a period of 10 years, the Fraunhofer Institute for Building Physics IBP has carried out systematic and extensive investigations on a large number of formulations of plaster and mortar. A series of field scale tests using vertical test panels comprising various plaster and mortar coatings has been carried out in order to analyze the leaching behavior during real weather conditions as well as in constant physical conditions. The data were used as a basis in the development process of a three-stage model to assess the environmental properties of common plaster and mortar:

- Level 1: Façade runoff model
- Level 2: Model for leaching processes and material transport on façades
- Level 3: Evaluation of the environmental impact by using the leachate forecast for groundwater risk assessment

This study will focus on the "Level 1: Façade runoff model", in which a runoff numerical simulation model for VTP in MATLAB was developed. The model calculates the water volume that sorbs during the rain event, bounces off the façade, and runs off it or remains on it as a film. The method in this simulation is based on stated assumptions found in previous research papers and existing WDR, absorption, and surface water flow models.

2. Materials and Methods

2.1. Model Parameters

2.1.1. Assumptions and Boundary Conditions

To simulate the amount of stormwater that impinges the VTP, absorbs within the material, and then runs off, a grid was used as the model surface. VTP 0.5 m × 1.0 m in size were therefore divided into elements with sizes of 10 mm × 10 mm. Once the WDR exceeded the absorption rate of the material, water started to accumulate in the form of a film on the studied surface. Water volumes caused by the drops first adhered to the surface and therefore led to more incorporation of drops, rivulets and, finally, a flow film formation. When the water film reached a certain thickness, the gravity forces exceeded the tension forces produced between the impinged water and the material surface. This process allowed the water film to flow down, producing runoff. In order to simulate the runoff in the VTP, each of the elements of the grid consisted of three main layers. The first layer was the (1) cumulative water film thickness (CWFT) (Section "*Cumulative Water Film Thickness (CWFT)*"). This layer defined the point when the cumulated water started to flow downward. If the water film on an element was larger than the CWFT, the water volume that exceeds this film thickness started to flow downward, leaving behind a (2) trace film thickness (Section "*Trace Film Thickness*"). The trace film thickness left behind a trace volume which was equal to the trace water volume multiplied by the size of the grid element. This trace volume then accumulated in the particular element in which the trace volume passed over. The cumulative water film increased depending on the impinging rain amount. The increase in the CWFT was limited by (3) the maximum water thickness (Section "*Maximum Water Thickness*"). This film thickness limited the amount of water that could accumulate in one grid element. If the cumulative element water reached the maximum water thickness, the excess water volume flowed down.

Water rivulets form after water volumes start to run off. Rivulets flow down straight or meander, depending on the flow speed of the rivulet, which is dependent of the flow rate (Section "*Flow Speed, Flow Rate and Flow Types*"). To simulate individual rivulets in the VTP, the size of the rivulet was proportional to the width of the grid element. The flow path on a grid element was determined by the flow rate and a randomly distributed roughness distribution (Section "*Roughness*") that was given to the VTP grid. The approximation of the different flow rates used for selecting whether the rivulet flowed straight or meandered was based on the research of Le Grand-Piteira [28].

The raindrop size distribution was defined by the horizontal rainfall intensity presented by the weather data. This distribution created random raindrops with random diameters in accordance with the mean size presented in the studied area. The random drop impinged a random grid element in every calculation loop defined by a specific time step. Every time a raindrop impinged the VTP, a part thereof splashed off. The remaining volume was partly absorbed, and the rest created a film in the correspondent grid element. If a specific thickness condition was reached, the water flowed down or remained in the grid element as a film waiting for more water to cumulate. The water volume that flowed down was then transported to the grid element beneath. The flow selected the grid element with the lower roughness given by the random roughness distribution. After the volume flowed downward, a part of it left behind a trace volume. If the grid element to which the runoff volume flowed already complied with the condition of the CWFT, the runoff volume continued its way downward, leaving a trace volume in each of the grid elements. The runoff volume stopped in a grid element which had not yet reached the condition of the CWFT and was absorbed or stayed there, depending on the condition of the grid element, until more water cumulated and had the possibility to flow down. In the end, the runoff volume was defined as the runoff volume that flowed all the way down to the bottom of the grid and left the plane. The program ran through every single grid element within each calculation loop and verified the presented conditions. After the program verified the conditions of each of the single grid elements, a new time step defined by the time between each impinging raindrop was created.

2.1.2. Raindrop Size Distribution

The raindrop size distribution used in this study was based on the work described by Best [29]. The model creates a raindrop diameter distribution with a minimum drop diameter (*d0min*) in mm of 0.2 and a maximum drop diameter (*d0max*) in mm of 5.0. A total of 50 raindrop diameter classes (*NF*) were generated in accordance with the minimum and maximum drop diameter. The class length (*CL*) was defined by the next equation:

$$CL = \frac{d0max - d0min}{NF} \tag{1}$$

Every class has an average raindrop diameter (d_{avg}) in mm:

$$d_{avg,i} = \frac{(d0_{min,i} + CL)}{2} \tag{2}$$

The class raindrop volumes ($d_{vol,i}$) in mm are created with respect to the average diameters:

$$d_{vol,i} = \frac{4}{3} \cdot \pi \cdot \left(\frac{d_{avg,i}}{2}\right)^3 \tag{3}$$

After obtaining the class raindrop volumes, the Best [29] raindrop distribution is formed. This distribution gives the fraction of the water volume (F_d) in mm^3 present in air with diameters equal to $d_{vol,i}$ of a rain event with a specific intensity (R_n) in mm:

$$F_{d,i} = 1 - \exp\left(-\left(\frac{d_{avg,i}}{1.3 \cdot {R_n}^{0.232}}\right)^{2.25}\right) \tag{4}$$

A raindrop diameter distribution can be constructed by generating a specific quantity of average raindrop diameters for every class. The specific quantity of diameters ($NUM\_F_{d,i}$) and the fraction of liquid water per unit volume of air (*fra_air*) in mm are calculated with the next equations:

$$NUM\_F_{d,i} = \frac{F_{d,i} \cdot 10 \cdot fra\_air}{d_{vol,i}} \quad (5)$$

$$fra\_air = 67R_n^{0.846} \quad (6)$$

To determine the amount of drops that have to be generated in order to represent a specific event of vertical rain with an intensity equal to R_n, it was necessary to calculate the total water volume of the drops (V_{distr_total}) in mm^3 being generated in that specific rain event with the volume $d_{vol,i}$:

$$V_{distr\_total} = NUM\_F_{d,i} \cdot d_{vol,i} \quad (7)$$

Following the determination of the total water volume of the drops present in a specific rain event, it was necessary to determine how this volume would be distributed on the surface of the grid during the rain event duration (h):

$$V_{in\_total} = \frac{R_n}{3600} \cdot h \cdot row \cdot col \cdot DHS \cdot DLS \quad (8)$$

where *DHS* and *DLS* are the width and height (mm) of the VTP elements, respectively, and *row* and *col* are the number of rows and columns in which the surface was divided.

Lastly, the number of drops that impinge on the surface during a specific rain event ($Raindrop_{num\_prosurface}$) with intensity R_n can be calculated with the next equation:

$$Raindrop_{num\_prosurface} = \left(\frac{V_{in\_total}}{V_{distr\_total}}\right) \cdot NUM\_F_{d,i} \quad (9)$$

The incidence time between each raindrop in seconds d_t was calculated (10). The time between each raindrop determined the time between each calculation loop in the simulation. For each calculation loop, a random raindrop from the raindrop diameter classes was selected. The random raindrop impinged a random grid element.

$$d_t = \frac{T}{Raindrop\_num\_prosurface} \quad (10)$$

2.1.3. Wind-Driven Rain Distribution (CFD Model by Blocken)

The assessment of the WDR intensity in the VTP was based on the catch ratio distribution developed by Blocken [30]. The CFD distribution depends on the wind speed (*w_speed*), the wind direction (*w_direction*) and the vertical rainfall intensity (*rain_int*).

Several assumptions were made with respect to this model. The first assumption was that the catch ratio of the WDR distribution is independent of the horizontal rainfall intensity. The second assumption was the linear relationship between the magnitude of the catch ratios of the WDR distribution and the wind speed. Therefore, if the wind speed equaled twice the reference wind speed used to calculate the catch ratio in the WDR distribution, the catch ratio was also doubled. The third and last assumption was related to the wind direction. Depending on the wind direction given by the weather file, a WDR distribution was given to the VTP grid. Assuming that all VTP were oriented westward, the relations between the wind direction and the used WDR distribution were as follows:

- [270°–292.5°] distribution derived from 0° wind direction;
- [292.5°–315°] distribution derived from 22.5° wind direction;
- [315°–337.5°] distribution derived from 45° wind direction;

- [337.5°–360°] distribution derived from 67.5° wind direction.

To implement these WDR distributions, each distribution was divided by the amount of grid elements used in the VTP grid. Five hundred grid elements with a specific catch ratio were then determined. This method was used to generate a discrete distribution for each of the four wind directions. To calculate the amount of water impinging (*wall_vol*) the grid elements of the VTP during a rain event in mm, the following equation was implemented:

$$wall\_vol(i,j) \ = \left(wall_{vol(i,j)} + \ d_{vol,i}\right) \cdot WDR\_BC(i,j) \cdot \left(1 - \left(\frac{SP}{100}\right)\right) \tag{11}$$

where $d_{vol,i}$ is the raindrop volume that impinged on the grid element, $WDR\_BC(i,j)$ is the catch ratio defined by the wind speed and the wind direction, and SP is the splash percentage, which is defined as a constant 30% of the total amount of water impinging on the VTP.

2.1.4. Absorption

The absorption model used for this simulation is that of Hall and Hoff [25]. This model has been used in past runoff models and is tailored to the needs of our simulation [9–12]. The model is composed of two phases. The first describes the absorption of WDR by the VTP surface materials. This absorption requires a constant flux as a boundary condition. This first phase lasts until the saturation of the material, defined by the capillary water absorption coefficient of the material (A), and the impinged water volume ($wall_{vol(i,j)}$) is achieved. The saturation time (t_{sat}), in seconds, is expressed by the following equation:

$$t_{sat} \ = \frac{A^2}{2 \cdot \left(wall_{vol(i,j)}\right)^2} \tag{12}$$

If the saturation of the material is not yet reached, the total amount of water that will be absorbed by the VTP (vol_{abs}) will be equal to the total impinged water volume ($wall_{vol(i,j)}$) that can be absorbed per grid element by a specific time (tn). After saturation is reached, the total amount of water that can be absorbed per grid element (vol_{abs}) by a specific time (tn) will be equal to:

$$t_n \le t_{sat} : \ vol_{abs} \ = \left(wall_{vol(i,j)}\right) \tag{13}$$

$$t_n > t_{sat} : \ vol_{abs} \ = \min\left(wall_{vol(i,j)}\right), \ \frac{A}{2 \cdot \ \sqrt{tn}}(DHS \cdot DLS) \tag{14}$$

The initial condition assumed by this model is that the material is dry. This assumption can present a limitation, as mentioned by Blocken [9]. Another limitation of this simplified model is that it does not take material thickness into account. Therefore, the model assumes that, before and after the material is saturated, the moisture from the surface can freely penetrate the material. Since the VTP runoff model focuses on the physical and numerical aspects of stormwater runoff rather than on moisture transfer walls, and our case concerns panels covered with a plaster layer with a maximum thickness of 20 mm (lime cement plaster) rather than walls, the simplified sharp front model by Hall and Hoff [25] fits our purpose.

2.1.5. Runoff

The model includes an assumption that the rainfall intensity is uniformly distributed over the VTP surface. Within each time step, a raindrop impinges on a random grid element in accordance with the raindrop distribution created. A portion of the impinged water splashes, another portion is absorbed and disappears from the surface, and the remaining water flows down the grid element if its water volume is larger than the CWFT and then runs off if the grid element is situated at the bottom of the VTP grid.

Cumulative Water Film Thickness (CWFT)

The CWFT was defined according to Dussan's [21] force balance equation for droplets in critical static conditions. This derived equation is written in terms of the surface tension force that operates in relation to the contact line of the droplet with the surface and the gravity forces. The CWFT (cw_film_thick), in mm, is described by the following equations:

$$cw\_film\_thick = \left(\frac{cw\_film\_vol}{DHS \cdot DLS \cdot row \cdot col}\right) \tag{15}$$

$$cw\_film\_vol = \left(\frac{\left(\frac{96}{\pi}\right)^{0.5} \cdot \frac{(\cos(\theta_r)-\cos(\theta_a))^{1.5}(1+\cos(\theta_a))^{0.75}\left(1-1.5(\cos(\theta_a))+0.5\left(\cos^3(\theta_a)\right)\right)}{(2+\cos(\theta_a))^{1.5}(1-\cos(\theta_a))^{2.25}}}{\left(\frac{\rho_w \cdot \left(\frac{g}{1000}\right)}{s_w}\right)^{0.66} \cdot (1000)^3}\right) \tag{16}$$

where cw_film_vol is the volume of water corresponding to the CWFT (mm), θ_r and θ_a are the receding and the advancing contact angles (°) of the material, respectively, ρ_w is the water density $(\mathrm{kg/m^3})$, g is the gravitational acceleration $\left(\mathrm{m/s^2}\right)$ and s_w is the surface water tension $(\mathrm{N/m})$.

When the amount of water on a grid element reaches CWFT, the water volume will start to flow down to the grid element below or will run off the VTP if it is situated at the last row of the grid.

Trace Film Thickness

The trace film thickness is the water volume that remains on a grid element after the water flow passes down to the grid element below. Since information is scarce on this topic, a default value of $trace_{thick} = 0.002\ (\mathrm{mm})$ was used for each of the different materials.

Maximum Water Thickness

The maximum water thickness (max_film_thick) was defined by the minimum film thickness (δ_{min}) equation for stable films derived by El-Genk [31]. According to El-Genk, this thickness is determined by the minimal total energy equation. The equilibrium surface contact angle can be calculated if the receding (θ_r) and the advancing (θ_a) contact angles are given. To calculate the equilibrium contact angle (θ_0) (°), Tadmor [32] suggested the following equations:

$$\theta_0 = \arccos\left(\frac{r_a \cos\theta_a + r_r \cos\theta_r}{r_a \cdot r_r}\right) \tag{17}$$

With the advancing r_a and receding surface r_r tensions:

$$r_a = \sqrt[3]{\frac{\sin^3\theta_a}{2 - 3\cos\theta_a + \cos^3\theta_a}} \tag{18}$$

$$r_r = \sqrt[3]{\frac{\sin^3\theta_r}{2 - 3\cos\theta_r + \cos^3\theta_r}} \tag{19}$$

El-Genk gives an empirical relation for the dimensionless minimum film thickness:

$$\Delta_{min} = (1 - \cos\theta_0)^{0.22} \tag{20}$$

Finally, the maximum film thickness is given by the next equation:

$$max\_film\_thick = \frac{\Delta_{min}}{\left(\frac{\rho_w^3 g^2}{15\mu_l^2\sigma}\right)^{0.2}} \tag{21}$$

where ρ_w is the water density $(\mathrm{kg/m^3})$, μ is the dynamic viscosity of the water $\left(\mathrm{N{\cdot}s/m^2}\right)$, and σ is the surface tension of water $(\mathrm{N/m})$ at 20 °C.

Flow Speed, Flow Rate and Flow Types

To determine the flow speed of the water that flows during one time step, the parabolic velocity profile of the Nusselt solution [33] was used by simplifying the representation of thin film flow. The use of the Nusselt solution is determined for steady water films, but Blocken [9] proved that the Nusselt solution is plausible for the runoff of water films in vertical planes. The average flow speed of a vertical surface (u) $\left(\mathrm{mm/s^2}\right)$ is given by the following equation:

$$u = \frac{g \cdot tt^2}{3 \cdot v} \tag{22}$$

where g is the gravitational acceleration $\left(\mathrm{mm/s^2}\right)$, v is the kinematic viscosity of the water ($\mathrm{mm/s^2}$), and tt is the film thickness (mm).

The flow rate between grid elements was defined by the runoff volume. If the cumulative water thickness is complied with, a water volume equal to the runoff volume flowed down to the adjacent grid element beneath. When water volume flowed downward, a part of the water volume remained on the departure grid element (*vol_trace*). In this regard, the runoff volume was equal to the volume that surpassed the cumulative water thickness minus the trace volume. The runoff volume ($transfer\_vol$) divided by the grid element surface represents the transfer film thickness ($transfer\_thick$). The assumption was made for the flow rate that the cross-section of the rivulet spreads uniformly over the grid element. From the transfer film thickness and the use of the Nusselt solution, a flow speed (u) can be calculated. The flow rate (Q) in $\mathrm{mm^3/s}$ is then given by the following equation:

$$Q = u \cdot transfer\_thick \cdot DHS \tag{23}$$

Depending on the flow rate, different flow types may occur. According to Le Grand-Piteira [28], the different flow types and their transition flow rates were "drops" with $Q \leq 200$ $\mathrm{mm^3/s}$, "small straight" with $200 < Q \leq 470$ $\mathrm{mm^3/s}$, "meandering" with $470 < Q \leq 1330$ $\mathrm{mm^3/s}$ and "large straight" with $Q > 1330$ $\mathrm{mm^3/s}$, respectively.

Roughness

Roughness determines the direction of the flow, depending on its flow type. The water volume that flows down as a runoff volume will follow the path with the least resistance. The least resistance grid element below was consequently the one with the lowest roughness. Only the three grid elements beneath the grid element transferring water volume were taken into consideration in determining the flow direction. A change in direction only occurred if the flow rate corresponded to the meandering flow type ($470 < Q \leq 1330$). If the flow rate corresponded to the other flow types, the runoff volume went directly to the grid element below without changing direction.

To define a specific random roughness for every single grid element, a new grid was elaborated (*RT*). Random roughness coefficients were given to each of the grid elements. This new grid had the first and last column as boundaries. Each of these columns received the highest roughness coefficients in order to serve as an external limitation so that the runoff volume did not go beyond the area size established for the VTP.

Runoff Volume

The runoff volume ($runoff\_vol$) was the amount of water that flowed from one grid element to another grid element below. This water volume was the difference between the water volume of the grid element ($wall\_vol(i, j)$) and the water volume that stayed behind after runoff occurred (*trace_vol*). The runoff volume was given by the following equation:

$$runoff\_vol = wall\_vol(i, j) - cw\_film\_vol - (trace_{thick} \cdot (DHS \cdot DLS) \cdot 0.1) \quad (24)$$

The runoff volume for each of the grid elements was defined during each time step (d_t). So, if the water volume of the grid element (*i,j*) was larger than the contact water film volume, a quantity of water equal to the runoff volume flowed away from this grid element and arrived at the element below, which was defined by the flow type and the random roughness determined. If the runoff volume was located in the bottom row of the grid, the water then left the plane and was considered to be runoff ($runoff$).

2.2. Outdoor Tests for Model Validation

The VTP used during the outdoor tests were located in outdoor facilities at the Fraunhofer Institute for Building Physics (IBP) (47°52'30" N, 11°43'41" E) in Valley, Bavaria (Germany). Experimental VTP (each 0.5 m wide, 1 m high) consisting of stainless steel panels were covered by various plasters or mortars (see Figure 1). A detailed description of the sampling site and data analysis are provided in [6,13].

Stormwater runoffs from the VTP were channeled through stainless steel gutters into canisters. Forty-nine rain events were collected and analyzed over a monitoring period of 18 months. After each single rain event, the total volume of the runoff corresponding to each VTP was measured by weighing. A weather station (Davis Vantage Pro) was installed on site during the monitoring period. The weather station used was capable of recording wind speeds up to 322 km/h, temperatures between −40 °C and 65 °C, and precipitation height in 0.2 mm increments. Precipitation heights (vertical rain), temperature, wind speed and wind direction were recorded every 5 min. The recorded weather data of the study site were used as input data in the VTP runoff model.

In Valley, there are approximately 180 rainy days per year. The monthly precipitation during the test period, from October 2013 to March 2015, ranged from 8.7 mm (L/m^2) in December 2013 to 224 mm in August of 2014. Detailed information about the daily precipitation during the sampling period and the runoff sampling dates are provided in [13]. During the 526-day observation period, precipitation events with more than 0.1 mm of rain occurred for 255 days. The strongest rain event occurred on August 2, 2014, reaching 60.4 mm. The lowest temperature recorded during the study period was −16.1 °C (29 December 2014). The highest temperature of 32.1 °C was measured on 19 June 2014. The wind at the sampling site came mainly from the westerly and southwesterly directions [13]. The highest daily mean wind speed observation was 66 km/h on 31 March 2015. During this day, the gusts reached a maximum speed of 98 km/h [13].

The weather file was composed of an Excel file. Each of the columns of the file represented a measurement in 5-min intervals of rainfall intensity (*rain_int*) in mm/h, wind speed (*w_speed*) in m/s, wind direction (*w_direction*) in degrees, and temperature (*temp*) in °C. For each of the parameters, a column matrix was introduced into MATLAB, where each row represented the magnitude of the 5-min measurement.

To convert these micro-meteorological boundary conditions into impinging rain along the VTP, the WDR catch ratio distributions by Blocken [30] were used, as stated in Section 2.1.3.

2.3. Model Input Parameters

A combination of parameters was used in order to illustrate the comparison between the different input parameters of the model. The VTP had a surface of 1.0 m by 0.5 m. It was assumed that a rainfall intensity of 2.5 mm/h would impinge the VTP. The total duration of the rain event was set to 1, 2, 3 and 5 h. The wind direction was constantly perpendicular to the VTP (0°). A constant splash percentage of 30% was maintained during the simulation, and the absorption coefficient was set to

0.01 $mm^3/mm^2s^{0.5}$. The ambient temperature was fixed to 10 °C. The absorption coefficient values used in the simulation were taken out of the German standard norm DIN EN 998-1 [34].

2.4. Boundary Conditions for Runoff Simulation

A 315-day simulation run was conducted on the basis of weather data measured during the VTP runoff outdoor tests. The data were available on a 5-min basis, which is a permissible time step for WDR measurements in accordance with Blocken [35]. The daily sum of the 5-min intervals where the rain event occurred was equal to the effective daily rain duration. At the start of every simulation cycle, the VTP was in balance with the outdoor environment. The effects of previous moisture loads and drying periods were neglected due to this initial condition. The moisture fluxes on the VTP were only dependent on the impinged WDR. Due to the neglected previous processes and high relative humidity (near 100%) during rain events, evaporation processes were not considered.

The simulated runoffs were added up in order to obtain daily cumulative results. These results were then compared with the actual obtained cumulative runoffs from the outdoor tests in order to prove the veracity and accuracy of the model.

3. Results

The runoff was calculated using the established absorption model and the WDR distribution assessment model of Blocken [30]. The flow speed and the film thickness were analyzed and compared to the solutions of Beijer and Nusselt. Finally, the results were compared with existing runoff volumes obtained over an 18-month VTP outdoor testing period.

3.1. Wind-Driven Rain Distribution

In the CFD Model by Blocken [30], the WDR load in the VTP was determined by the multiplication of catch ratios with the rainfall intensity. In Figure 2, the WDR distribution for 0°, which was used for the previously specified rain event, can be seen. The figure shows that the magnitude of impinged water volume varies according to the exposure time of the VTP to the rain event. The upper edges of the VTP received the highest amount of WDR, while the lower part received the least amount of WDR.

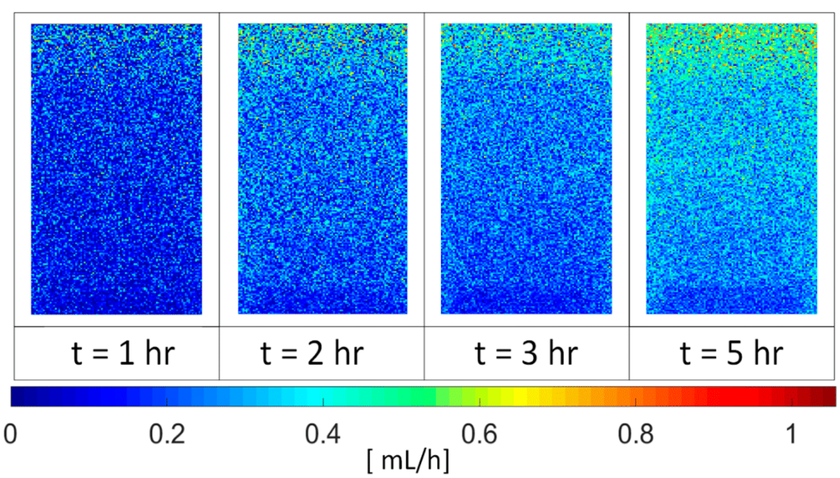

Figure 2. Impinged water volumes on vertical test panels (VTP) for time t = 1 h, 2 h, 3 h and 5 h using the wind-driven rain Computational Fluid Dynamics (CFD) model by Blocken [30].

For the VTP that was exposed for t = 5 h, some elements in the upper edges received up to 0.8 mL and 1.2 mL of water in comparison with the VTP exposed to t = 1 h, which only received up to 0.4 mL during the rain event. The cumulative WDR received by the VTP for the surface exposed to t = 1 h was 1.3 L, for t =2 h 2.5 L, for t = 3 h 3.8 L, and for t = 5 h 6.4 L.

3.2. Amount of Absorbed Water

The Hall and Hoff [25] model was implemented to include the absorption parameters in the model. To investigate the amount of absorbed water, the same standard parameters as those described in Section 2.3 were used in conjunction with the CFD model by Blocken. The total height of the VTP was assumed to have the same capillary water absorption coefficient.

For the VTP exposed to t = 2 h, a total absorption of 1.05 L was found. After t = 4284 s, the material was fully water saturated, and the water started to accumulate on the surface. The total amount of WDR available on the plane during the rest of the rain event was 0.87 L. This water volume was later available for runoff. The observed absorption and accumulated water volume in the material can be seen in Figure 3. The sorption capacity of the material led to a quick saturation of the surface and the building of runoff. If the water volume in the material was not taken into account, an underestimation of almost 45% of the moisture content after 1 h took place on the VTP. These results are similar to those presented by Van den Brande [12].

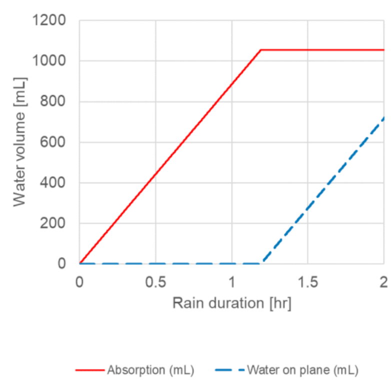

Figure 3. Accumulated water volume on the material and accumulated absorption during a defined standard rain event when implementing the Hall and Hoff [25] model.

3.3. Water Film Thickness

In Table 1 the CWFT, the absorption coefficient and the results for a rain event with a duration of 2 h are depicted for three façade materials. The rain event standard parameters presented in Section 2.3 were used for this simulation.

Table 1. Cumulative water film thickness (CWFT) simulation results for the three different plasters after 7200 s (2 h). Absorption coefficient values according to DIN EN 998-1 [34] and contact angles according to [36].

Material	CWFT [mm]	Equilibrium Contact Angle [°]	Capillary Absorption Coefficient [$mm^3/(mm^2*min^{0.5})$]	Absorption Volume [mL]	Surface Cumulative Volume [mL]	Runoff Volume [mL]
Facing masonry mortar	0.0204	83.8	0.16	210	1563	1539
Lime cement render	0.0212	82.9	0.39	1305	469	431
Scrap render	0.0215	83.1	0.31	836	939	871

These absorption coefficient values are commonly used in the plaster and mortar industry as standard values. In accordance with the contact angles given by Steffgen [36], mineral-bound plasters have angles of <90°. The CWFT is mainly influenced by the contact angles of the material, but this influence can be neglected because the plasters tested were mainly composed of mineral-bound materials and compositions very similar to those in Table 1. As seen in Table 1, the main parameter having an influence on the runoff volume was the absorption coefficient of the material. This parameter limits the amount of water that cumulates on the façade surface after a certain time duration of a rain event. The water film thickness varied with time (Figure 4). Film formation only started after the material's absorption boundary condition was complied with. For the lime cement render, this film thickness was formed after 1 h of receiving WDR impingement. Meanwhile, regarding the other two materials, this film was formed within the first hour of the rain event. The reason for this was that the lime cement render has a higher absorption coefficient ($A = 0.05$ mm^3/mm^{2}s$^{0.5}$) than the other two materials, thus absorbing more water. As a result, it needed more time to start forming a surface water film. The maximum film thicknesses during the rain event were 0.22 mm, 0.19 mm, and 0.23 mm for the facing masonry mortar, lime cement render, and scrap render, respectively. After applying the absorption boundary condition, the film thickness continued to grow, and the water travelled down the VTP. This behavior could also be observed in the flow rate figures when comparing the first hour of the facing masonry mortar with the plasters. Runoff started within the first hour for the facing masonry mortar, meaning that the wall absorbed enough water before complying with the absorption boundary condition and, subsequently, forming a water film thickness thick enough to start the transportation of the water down the surface of the VTP. This behavior was not evident for the other two materials, meaning that no runoff was present within the first hour. When runoff occurred, the flow rate at the center and bottom of the VTP was constant, meaning that most of the water impinging on the upper side of the VTP tended to flow downward, thus causing higher flow rates in the center and bottom part of the VTP. This effect was observed for all three materials. Higher flow rates were achieved in the facing masonry mortar (0.78 L/m), which tended to accumulate higher amounts of water volume on its surface due to a lower capillary absorption coefficient. With respect to the lime cement render and the scrap render, no flow rate resulted within the first hour of the rain event, meaning that there was not enough water on the surface of the VTP to start the runoff. This behavior was directly related to the formation of the water film thickness and the absorption capacity of the material.

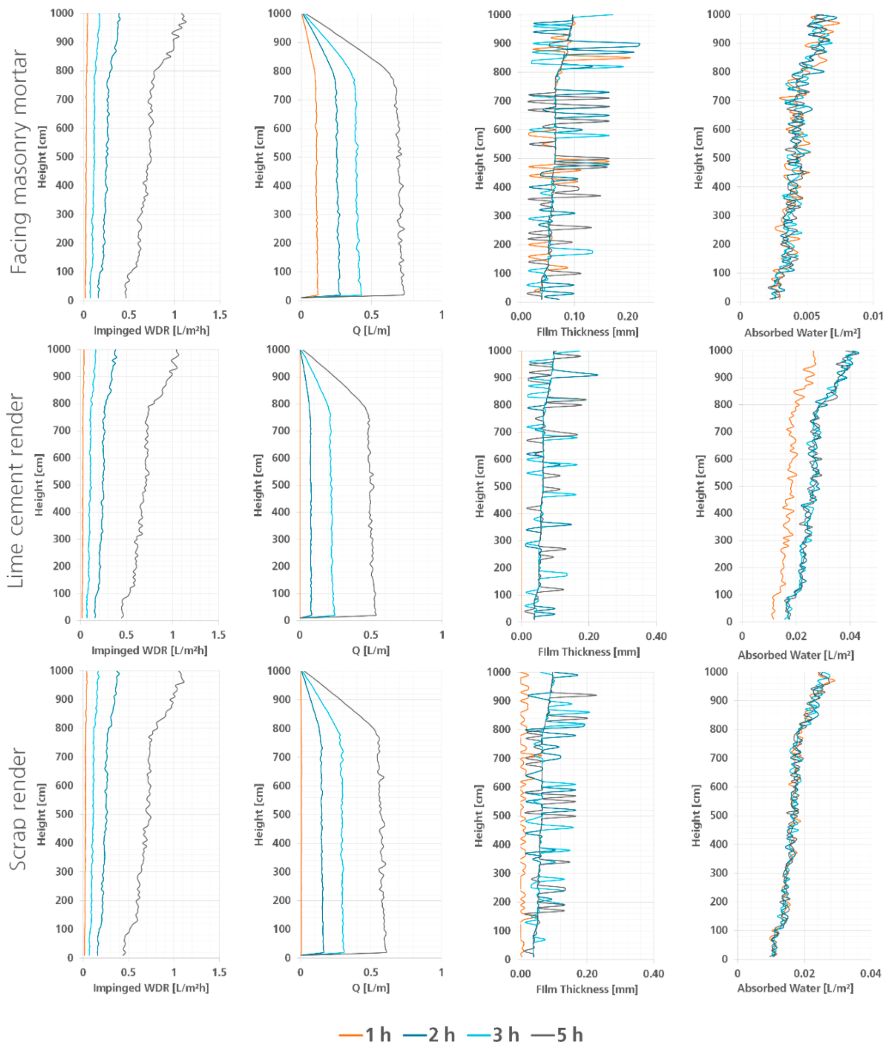

Figure 4. Impinged wind-driven rain during 1 h, 2 h, 3 h and 5 h intervals. Corresponding numerical results for the 1 m high VTP at different time steps and different materials, for flow rate, film thickness and total absorbed water.

3.4. Runoff Volume (Simulation and Model Validation with Outdoor Tests)

To demonstrate the possibilities of the VTP runoff model and to evaluate the results provided, actual rain events were simulated on VTP covered by three different types of plaster and mortar. The characteristics of the materials are shown in Table 1. The runoff results were then compared with those obtained during the outdoor tests.

A period of 315 days was simulated using the VTP runoff model. For the facing masonry mortar, the cumulative runoff volume obtained in the field tests after 315 days was 65.3 L, whereas the VTP runoff model obtained 63.1 L as a cumulative runoff result for this same material. The outdoor test cumulative runoff volumes for the lime cement render and the scrap render were 28.6 L and 45.4 L, respectively. The results obtained by the model for the previously mentioned materials were 29.5 L and 46.0 L. The difference between the results obtained in the field tests and the results provided by the model at the end of the simulation was less than 3.5%. The results of the simulation vs. the outdoor test cumulative runoff volumes for the three materials are depicted in Figure 5.

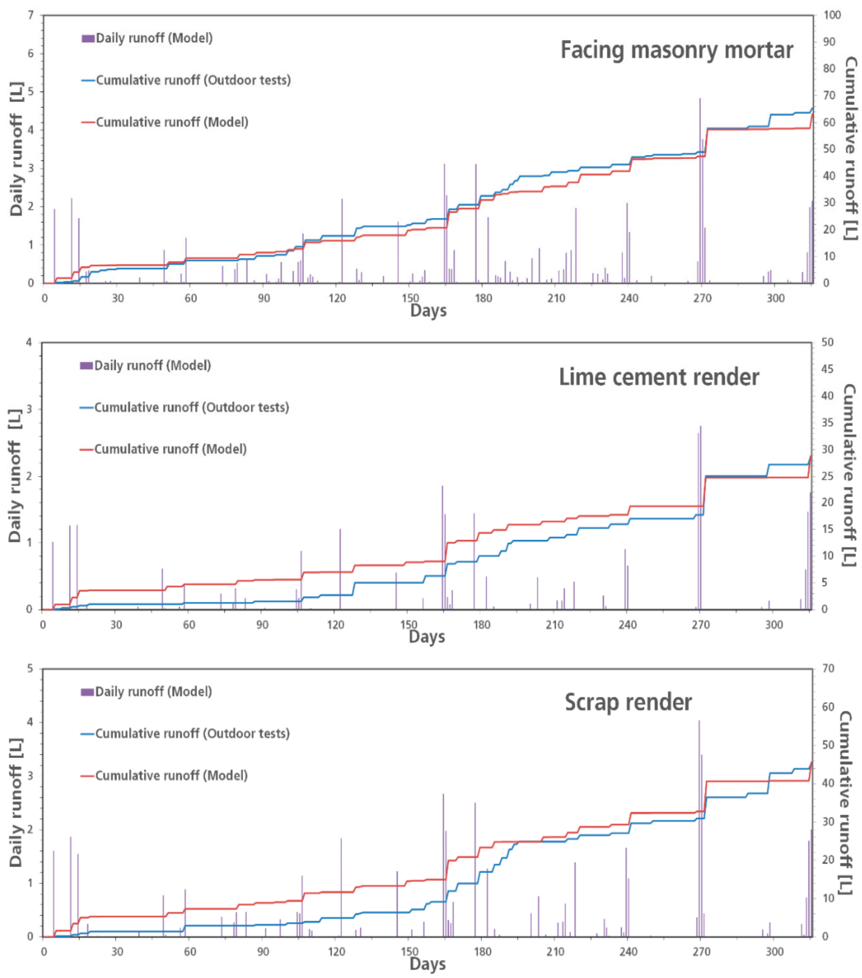

Figure 5. VTP daily-simulated runoff and cumulative simulated/actual runoff for facing masonry mortar (**up**), lime cement render (**middle**) and scrap renders (**down**).

The day with the highest collected runoff for the three VTP was 24 October 2014 (Day 268). The weather measurements indicated that, the day before the runoff was collected from the canisters, 38 mm of rain fell during a time span of 16 h with average wind speeds of 5.5 km/h, coming mainly from the southwest. During this day, total volumes of 8.8 L, 7.3 L and 5.5 L were collected for the facing masonry mortar, the lime cement render and the scrap render, respectively. The model also simulated the highest runoff on this day for the three VTP. The simulated runoff during this day for the facing masonry mortar was 10.1 L. For the lime cement render and the scrap render, simulated runoffs of 8.4 L and 7.9 L were obtained, respectively. The difference between the collected runoff and the modelled runoff can be attributed to several factors. Due to the intensity of the rain event and the time it lasted, these factors may have varied more. One of the possible reasons for the variation in the runoff might be that the amount of water that splashed off the VTP was more than that stipulated in the model (30%). It is likely that the existence of a greater number of drops impinging the VTP meant that they splashed due to the speed at which they were directed to the VTP surface. Another possible reason for this over-estimation is that the model does not include evaporation processes. Although the relative humidity during rain events like this type approaches 100%, it is possible that some quantity of water evaporated during and after the rain event.

The model simulated a total of 126 days when the VTP presented runoff on the facing masonry mortar, 53 days of which the runoff was below 100 mL, with 40 days between 100 mL and 500 mL, and 33 days over 500 mL. For the lime cement render, runoff was presented in 67 days, 33 of which presented a runoff below 100 mL, 18 days between 100 mL and 500 mL, and just 16 days over 500 mL. Finally, the scrap render presented 93 days with runoff, of which 40 days presented a runoff below 100 mL, 31 days between 100 mL and 500 mL, and 22 days over 500 mL. The lime cement render presented less runoff events than the facing masonry mortar and the scrap render. This behavior was mainly dependent on the capillary absorption capacity of the material. Despite the fact that the least rainy days were recorded during the first days of testing (the first 100 days), the model yielded runoff results on some days that were not obtained in the outdoor test samples. This behavior is shown in Figure 5, in which the first cumulative daily runoffs given by the model for the lime cement render and the scrap render were not observable in the outdoor test results. One reason for this might be that the VTP absorbed more water than predicted by the model. Another reason might be that, during these rain events, the relative humidity of the field was not very high due to the low rain intensity and higher evaporation on the surface of the VTP. This last process was not represented in the facing masonry mortar results. Often, these effects were not visible during the rain events with greater intensity because the amount of water absorbed was very low in comparison with all of the impinged WDR. It is also possible that, during the effects of heavy rain, the relative humidity of the area was very high, and the evaporation process may have been neglected.

3.5. Advantages and Limitation of the Model

Given the results obtained by the simulations, the advantages and limitations of the model can be described. For the most part, the limitations of the model go hand in hand with the constant variation in the weather data in reality vs. the assumptions made in the model (e.g., VTP surface temperature at 20 °C). It is possible that these types of assumptions limited or influenced the calculation of runoff volumes and gave underestimated or overestimated results for certain simulated rain events. One example of this can be seen in Figure 5, in which, during the first 100 days, the model showed runoff in some of the events although no runoff volumes were collected in the field. As also observed by Blocken [9], many of the limitations in the VTP model are caused by the adopted simplifications, e.g., the use of the Nusselt solution to determine the flow film while not taking into account wave behavior, especially in strong rain events. Simulated values in certain rain events can be overestimated because drying or evaporation were not included in the model. For very weak rain events, these processes can have a very important impact and can be noticeable in the simulation of the first rain events, which were characterized by very weak precipitation. Another limitation of the model was that the method used to give roughness to the VTP is the same for all three types of materials. The materials used in the field experiments showed physical differences in their surfaces, depending on the grain size of the mixture. One example of this is the lime cement render, which is a material with grains larger than plaster (max. 2 mm grain), making its surface less smooth. This physical characteristic of the material may play an important role in stream formation and could complicate the runoff patterns.

A method for correctly defining the difference between the roughness of varying materials should be evaluated in future investigations.

Despite the limitations caused by model uncertainties, the results obtained by the model and the results obtained in field tests (see Figure 5) exhibited a difference of no more than 3.5% of the accumulated runoff volumes for each of the analyzed materials. Using the runoff model, it is possible to investigate and to reproduce the runoff response of a VTP characterized by a specific plaster or mortar for a defined location and period of time, and obtain a good approximation of the amount of runoff that each material will have. The WDR load that is received by the VTP can be calculated on the basis of inputted weather parameters given by a weather dataset of the studied region. Depending on the weather conditions, an estimation of the runoff volumes can be determined. Additionally, the model can be adjusted to different materials. Given the use of some specific parameters like the capillary absorption coefficient and the contact angles, it is possible to differentiate the runoff behavior on the surfaces of various material types. In this way, the model makes it possible to predict the amount of runoff water volume from VTP results without needing to obtain samples of larger facades. These runoff results could help predict the runoff and leaching behavior of larger façades without having to reproduce them in the field in order to validate them.

4. Conclusions

Our runoff model is "Level 1" of a three-stage model. In the model described, existing modeling methods were adapted for the prediction and evaluation of rainwater runoff from VTP. Due to the incorporation of real weather data, it was possible to simulate a series of rain events over a period of 315 days. The advantage of having a complete and detailed experimental dataset made it possible to validate the accuracy of the model by comparing the simulated results with those collected in the field. Despite the limitations of the model, caused by uncertainties, the difference between the simulated and the field data was no more than 3.5% of the accumulated runoff volumes for the analyzed materials.

The presented runoff model makes it possible to investigate and reproduce the runoff response of VTP characterized by a specific plaster or mortar for a defined location and period and obtain a good approximation of the amount of runoff for different materials. First, the rain loads can be calculated and visualized with the aid of the simulation program; secondly, the total absorption of the material can be estimated at any time in accordance with the used absorption model, and, finally, the runoff volume and water flow rate on the VTP can be determined. The moisture content of the VTP is largely dependent on the supplied WDR and the material characteristics. We observed that higher runoff volumes and flow rates are more likely to appear on materials with a lower capillary absorption capacity.

Flow rates and runoff volumes are of significant importance and can be used for the prediction of leaching substances ("Level 2"). The development and evaluation of the models of "Level 2" and "Level 3" will be the subject of further publications.

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A. 2 Leaching prediction for vertical test panels coated with plaster and mortars exposed under real conditions by a PHREEQC leaching model

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Leaching prediction for vertical test panels coated with plaster and mortars exposed under real conditions by a PHREEQC leaching model

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A R T I C L E I N F O

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A B S T R A C T

A requirement of the Construction Products Regulation (CPR) in the European Union states that construction works must be designed in such a way that throughout their entire life cycle, they have no exceedingly high environmental impact. The objective of the current work was to simulate the leaching of selected metals and sulfate in vertical test panels (VTPs) covered by plaster and mortar. The investigation is based on 18-month leaching outdoor tests (LOT) under real weather conditions. A leaching model was developed using the geochemical model PHREEQC with the Lawrence Livermore National Laboratory (LLNL) thermodynamic data base and coupled with MATLAB in order to optimize the run-off and weather parameters. The model was calibrated by comparing the data from laboratory Dynamic Surface Leaching Tests (DSLT) with simulation results up to an acceptable fit. The parameters obtained were then used in the LOT simulations and validated. The model allows predictions on the substance discharge from various plasters and mortars under real weather conditions. Physical characteristics of the material (e.g., thickness and absorption capacity) play an important role in the leaching of substances in façades covered with plaster and mortar. The lower the thickness and absorption capacity of the material applied, the greater the run-off and discharge of leached substances.

1. Introduction

Evaluating the environmental properties of building materials is of high priority for the European Community. The Construction Products Regulation (CPR) addresses seven basic requirements for buildings. The third requirement covers the area of hygiene, health and environmental protection (European Parliament, 2011). According to this requirement, each construction work must be designed in such a way that it does not harm the user or the environment during its entire life cycle. Plasters and mortars are commonly used as part of the external thermal insulation composite systems (ETICS) and solid masonry of a façade. During their lifetime, these materials are exposed to precipitation and ambient air. The storm water run-off caused by the outdoor exposure conditions leads to the dissolution of metals and anions [Brameshuber et al., 2009; IBP 2011; Nebel et al., 2010; and Scherer, 2013]. Not all dissolved substances from construction products have an environmentally hazardous potential. Thus, not all products in contact with storm water necessarily imply a negative effect on the environment (European Parliament, 2008). In order to protect the environment and human health, the potentially harmful dissolved substances should be as low as possible. In Germany, the concentrations of substances released are compared to "Insignificance Threshold Values (German: *Geringfügigkeitsschwelle*, GFS) stated by the Working Group of the Federal States on Water (German: Bund/Länder- Arbeitsgemeinschaft Wasser, LAWA) [LAWA, 2016].

To investigate the leaching of building material components, façade coatings and ETICS in vertical test panels (VTP) have been widely used [Bester et al., 2014; Bollmann et al., 2014; Burkhardt et al., 2012; Hensen et al., 2018; Schwerd, 2011, 2017 and Schwerd et al., 2015]. The VTP are used mainly to gain information on the leaching of substances from building products under real weather conditions. These outdoor tests provide real scenario conditions. Common laboratory methods such as the Dynamic Surface Leaching Test (DSLT) (CEN/TS, 16637-2) or methods with intermittent water contact including drying intervals (EN, 16105) are also available. They can lead to reproducible results but do not reflect the leaching behavior of a building product under realistic

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conditions, which is controlled by various factors such as façade geometry, temperature, site characteristics (latitude, altitude), façade exposure (orientation), wind-driven rain (WDR), and length of antecedent dry period (ADP) [Burkhardt et al., 2012; Blocken et al., 2013; Bester et al., 2014; Schoknecht et al., 2016a, 2016b; Vega-Garcia et al., 2020a and Weiler et al., 2020]. Unfortunately, the results from common experimental laboratory leaching tests cannot easily be extrapolated to field conditions [Schiopu et al. (2007)]. Vega-Garcia et al., [2020b] developed and evaluated a model for storm water run-off volume prediction on VTPs coated with plaster and mortar exposed under real conditions. However, the model presented focused on run-off volume and not on run-off composition.

Some models are able to predict the amount of substances released from façades under real outdoor conditions (e.g., Jungnickel et al., 2004; Walser et al., 2008; Schiopu et al., 2008; Wittmer et al., 2011; Coutu et al., 2012; Burkhardt et al., 2018). These models, for example the model presented by Burkhardt et al. (2018) using the software COMLEAM as a base, focus on the leaching of biocides and not on metals or anions. The models use predefined emission functions to determine the amount of substance leached through input parameters (e.g., type of material, substance characteristics, geometry of the façade, and weather factors). These functions can be also derived by the user and are obtained from the results obtained in experimental studies, making them suitable for certain materials in some cases. However, the simulation process for leachate substances in this model neither predicts nor describes the physical (transport) or chemical (equilibrium or kinetic reactions) mechanisms that occur inside and outside the material compartments during the outdoor exposure. If the simulated materials are not available in the database of the model, are new, or are under development, the user is limited to the predefined emission functions these programs offer or must obtain their own functions from experimental studies. It is therefore important that the model starts from the chemical composition of the façade materials in order to predict the leaching of the substances. With this, it is not necessary to carry out new experimental studies or couple the unknown emission function of a new material with the emission functions offered by the database of these programs to model the leaching of substances during outdoor exposure conditions.

Numerical tools coupled with huge thermodynamic data bases, (e.g., PHREEQC, PHAST and HYTEC) [Parkhurst et al., 2010, 2013 and Van der Lee et al., 2003], are capable of modelling the chemical phenomena and transport processes that occur within the material compartments. The geochemical model PHREEQC presents an advantage for modelling the leaching of substances from mineral materials like plaster and mortar subjected to outdoor exposure conditions. PHREEQC is able to couple the chemical leaching mechanism with transport phenomena, thereby allowing the simulation of percolation and diffusion processes while maintaining the numerical performances [Parkhurst et al., 2013]. Another advantage of PHREEQC is that it is compatible with several data bases (e.g., WATEQ4F, LLNL, and MINTEQA2), is open source, and can be coupled with application programming interfaces such as Python, C++, and MATLAB [Parkhurst et al., 2013].

During the last decade, the Fraunhofer Institute for Building Physics IBP, Valley, Germany, has carried out systematic and extensive investigations on many formulations of plasters and mortars. A series of field scale tests using VTP with various plaster and mortar coatings have been carried out in order to analyze the leaching behavior during real weather conditions as well as under constant physical conditions. The data were used to develop a three-stage model to assess the environmental properties of common plaster and mortar: Level 1: Façade run-off model, Level 2: Model for leaching processes and material transport on façades, and Level 3: Evaluation of the environmental impact by using the leachate forecast for groundwater risk assessment [Vega-Garcia et al., 2020b]. The three-stage model focuses on the mineral mortars and plasters, and its purpose is to help the manufacturers or authorities to evaluate their environmental characteristics and, on this basis, determine suitable areas of application.

By using the Level 1- model, the runoff volumes that occur on façades covered with plasters and mortars after random rain events and time periods can be determined. The objective of this paper will focus on the "Level 2" model and thus the development and evaluation of a model for leaching processes and material transport on façades covered with mineral plasters and mortars. Using a PHREEQC coupled chemical-transport model developed by Schiopu et al. (2008) and storm water runoff parameters given in the results from "Level 1: Façade runoff model" [Vega-Garcia et al., 2020b], it should be possible to determine VTPs runoff concentrations of the leached substances focusing on metals and anions. The simulated eluates should have concentrations that correspond to those obtained in the leaching outdoor tests (LOT). The results can serve as input parameters for the Level 3-model mentioned above in future. The three-stage model system is schematized in Fig. 1.

2. Materials and methods

2.1. Leaching outdoor tests

The VTPs used during the outdoor tests were located in outdoor facilities at the Fraunhofer Institute for Building Physics IBP (47°52′30″N, 11°43′41″E) in Valley (Bavaria), Germany. Experimental VTPs (each 0.5 m wide, 1 m high) consisting of stainless steel panels were covered by various plasters or mortars (e.g., facing masonry mortar, lime cement render, and reinforced render). Forty-seven rain events with collection of the sample after every separate rain event in the period from October 2013 to March 2015 (18 months) were collected and analyzed. Detailed information about the daily precipitation during the sampling period, the run-off sampling dates, and the cumulative run-off of the VTP is depicted in Fig. 2. A detailed description of the sampling site, hydrological balance, and run-off data analysis are presented elsewhere (Vega-Garcia et al., 2020a,b).

The composition of pure rainwater without contact to VTPs during the LOT can be seen in supplementary data Table S.1.

The examinations were run for 18 different mineral mortars and plasters. Three of them are described in this publication. The dry composition of the three plasters and mortars were as follows:

- Facing masonry mortar (FMM): 79.8% quartz sand, 15.0% CEM I 42.5 R, 5.0% fly ash, 0.05% Na-oleate, 0.14% cellulose ether, and 0.05% air entraining agent.
- Lime cement render (LCR): 62.5% quartz sand, 14.0% CEM I 42.5 R, 14.5% calcium carbonate, 6.0% calcium hydroxide, 1.5% perlite, 0.6% organic light aggregate (EPS), 0.3% Zn-stearate, 0.1% cellulose ether, 0.001% thickener, and 0.04% air entraining agent.
- Reinforced render (SR): 40.0% quartz sand, 35.0% CEM I 32.5 R, 20.5% calcium carbonate, 4.0% ethylene-vinyl acetate, 0.1% Zn-stearate, 0.1% Na-oleate, 0.2% cellulose ether, 0.06% thickener, and 0.04% air entraining agent.

Before application on the VTP the FMM, LCR, and SR were mixed with water requirements according to the manufacturer's specifications (12%, 34%, and 26%, respectively). The density of the FMM, LCR and SR after application was of 1741 g/l, 1284 g/l, and 1645 g/l, respectively. The air void contents of FMM, LCR, and SR were 15%, 14.5%, and 14%, respectively. The applied layer thickness for the FMM, LCR, and SR was 10 mm, 20 mm, and 5 mm, respectively.

During the sampling period, the effluents from each VTP were channeled through glass gutters into polyethylene (PE) canisters. After each single rain event, the total volume of the run-off was measured, and an aliquot was taken out of the sampling device and filled into 0.5 l glass bottles. The aliquots were prepared the same day for the analyses. Blank rainwater samples were obtained using this same process.

General parameters such as run-off volume and pH-value were determined as part of this analysis. The pH value was analyzed

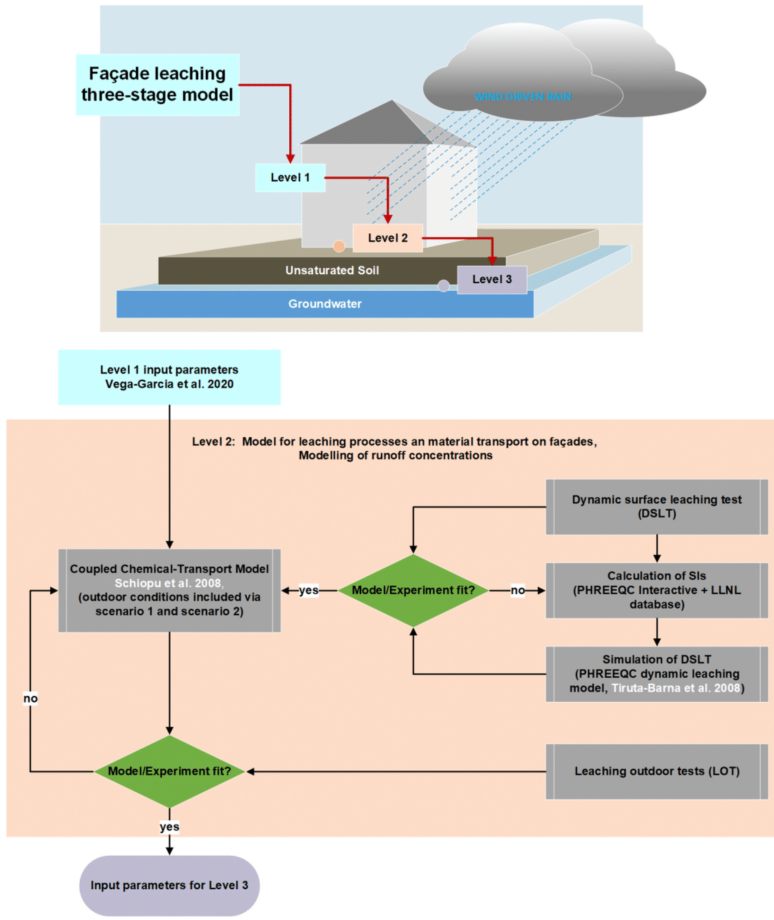

Fig. 1. Scheme of façade run-off model.

according to (EN, 10523) using a three-channel multi-parameter meter with electrodes with a measuring range from 0 to 14 pH and an accuracy of ±0.004 (WTW-Multi 3430; Electrodes WTW-Sentix940). Eluate ion concentrations were obtained by ion chromatography (IC), and heavy metals and trace elements by mass spectrometry with inductively coupled plasma (ICP-MS) tests. Detailed information on quantification limits are given in supplementary data Table S2.

2.2. Dynamic surface leaching tests (DSLT)

The dynamic surface leaching tests (DSLTs) was carried out based on CEN/TS 16637-2. The test specimens were produced at the same time as the test specimens for the leaching outdoor tests.

The mineral mortars were subjected to the process in the form of prisms after a conditioning time of 56 days at a V/O ratio of 74 l/m^2 (according to test specification: V/O = 80 ± 10 l/m^2). The dimensions of the tested mineral mortars prisms were 4 cm × 4 cm x 16 cm with a total leachable area of 0.027 m^2. The prisms were submerged into glass containers filled with a total eluent volume of 2 l of ultrapure water. The temperature was held constant at 23 °C. The eluent was renewed in eight time intervals (6 h, 1 d, 2.25 d, 4 d, 9 d, 16 d, 36 d, and 64 d) resulting in a total water contact time of the surface of 1536 h. The cumulative contact water volume for each prism after completion of the test was of 590 l/m^2. The leachates were analyzed immediately after every renewal.

2.3. Material chemical composition

To identify and quantify the phases controlling the substance release during the outdoor tests, results from DSLTs (CEN/TS 16637-2) and PHREEQC Interactive (version 3.5.0–14000) [Parkhurst et al., 2013] using the LLNL data base were used. As a first step, the DSLT results and the PHREEQC tool SOLUTION_SPREAD were used to calculate the saturation indices (SI) of the different eluates. From the SI, it is possible to recognize the phases that control the substance release. In PHREEQC, the SI is calculated with the formula:

$$SI = \log\left(\frac{\Pi a_i^{v_i}}{K}\right) \qquad (1)$$

where a_i is the activity of the target element, v_i is the stoichiometric coefficient, and K is the solubility product equilibrium constant. According to Alpers et al. (1994), a negative SI indicates an unsaturated solution, a positive SI indicates a supersaturated solution, and a SI equal

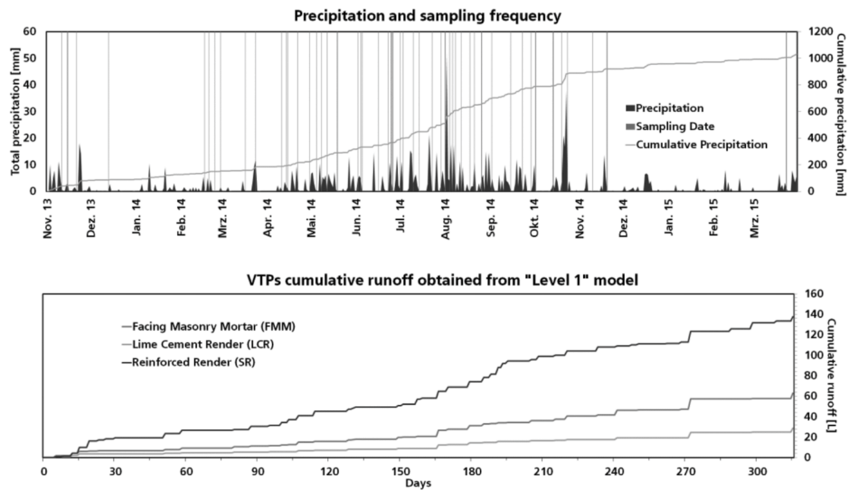

Fig. 2. Precipitation, sampling frequency, and cumulative run-off of VTP.

to zero indicates equilibrium conditions. The SI close to zero are considered to be the controlling phases because they are close to an equilibrium state with the leachate

Based on the SI information and the recipes of the materials used for the outdoor tests, a mineralogical composition was defined.

As a second step, a simulation of the DSLTs was made using the PHREEQC dynamic leaching model (TLM) developed by Tiruta-Barna (2008) to verify the plausibility of the selected mineralogical composition and to quantify the maximum amount of different minerals that can dissolve (data block EQUILIBRIUM_PHASES). This model can simulate a porous block (diffusion compartment) in contact with periodical renewal of leachate. The principles of this model are listed here.

For each chemical element of concentration C, the mass balance equation taking into account 1-D diffusion in pore-water is:

$$\frac{\partial C}{\partial t} = D_e \frac{\partial^2 C}{\partial x^2} - \sum \frac{\partial q}{\partial t} \tag{2}$$

with

$$D_e = f(\tau) D \tag{3}$$

where D is the molecular diffusion coefficient in water, $f(\tau)$ is a tortuosity function, and D_e is the effective diffusion coefficient. The second term in equation two (2) represents the source/sink term resulting from all dissolution/precipitation reactions, thereby implying the considered chemical element; q is the concentration of a solid phase involved in a kinetic reaction.

- The boundary condition used at the bottom face ($x = 0$):

$$\left.\frac{\partial C^{pores}}{\partial x}\right|_{x=0} = 0 \tag{4}$$

- at the leachate/material interface ($x = h$):

$$\omega D_e \left.\frac{\partial C^{interface}}{\partial x}\right|_{x=h} = k_{SL}\left(C^{leachate} - C^{interface}\right) \tag{5}$$

with

$$h = \frac{V_{block}}{A_{block}} \tag{6}$$

where $C^{leachate} - C^{interface}$ is the concentration (mg/l) in the diffusion compartment at the leachate interface, ω is the open porosity, k_{SL} (m/s) is the mass transfer coefficient between the leachate and the pore-water at the surface of the block, V_{block} is the material volume (imposed by the block mass balance), and A_{block} is the contact surface area which is exposed to the leachate.

The flux from the material, the transport resulting from convection, dissolution/precipitation reactions of solid phases, and surface corrosion determine the leachate compartment element accumulation. The time-dependent balance equation for each element ($C^{leachate}$) in the leachate is as follows:

$$\frac{dC^{leachate}}{dt} = -a_{SL} k_{SL}\left(C^{interface} - C^{leachate}\right) + \frac{Q}{V_{leachate}}\left(C^{leachate} - C^{leachant}\right) - \sum v_k \frac{\partial q'_k}{\partial t} + a_{GL} F_{abs} \tag{7}$$

where $C^{interface}$ is the concentration (mg/l) of an element in soluble form, $C^{leachate}$ is the concentration of the leachate in contact with the material, $C^{leachant}$ is the concentration of the element in the leachate, $V_{leachate}$ is the volume (l) of the leachate in liquid phase, Q is the flow rate (ml/s),v_k is the stoichiometric coefficient in the reaction, q' are the concentrations of solid phases presented in the leachate and on the corroded surfaces layer, F_{ab} is the gas absorption flux (mol/(m^2•s)), a_{GL} (m^2/m^3) is the specific gas/liquid exchange surface, and a_{SL} (m^2/m^3) is the specific solid/liquid exchange surface.

For modelling 1-D diffusion adapted to the applied DSLTs tests conditions, the PHREEQC program contains the following data blocks and boundary conditions:

1) The model is divided into several compartments representing the material, the material surface in contact with the leachate, and the leachate. In turn, these compartments are divided into grids that are numbered in cells. The material compartment is represented by the grid with cells from 1 to 100; the surface in contact with the leachate is cell 1, and this will always be linked to cell 102 (stagnant cell). The function of cell 102 is to accumulate the leached substances after the

transport processes. A mixing process between cells 1 and 102 will always be necessary in order to take into account the diffusion term (block MIX).
2) The width of each cell (data block TRANSPORT, lengths) corresponds to the width of the submerged monolith divided by the number of cells (e.g.,lengths $= 100\cdot(4\cdot10^{-5})(\mathrm{m})$.
3) The properties of the materials and eluates were defined in the data blocks EQUILIBRIUM_PHASES (cells 1–100 and 102) and SOLUTION (cells 1–100 and 102). The composition of the phases were obtained from the aforementioned SI analysis. An iterative process of comparing the simulated results with the results obtained in laboratory tests (element concentration values in leachate of same order of magnitude) was used to fit the maximum amount of dissolved phases (data block EQUILIBRIUM_PHASES).
4) TRANSPORT block with diffusion_only option and one stagnant cell (numbered 102). The D_e (diffusion_coefficient) used for the high soluble elements (e.g., Na, K, and Cl) was determined by fitting the transport model using the experimental results of the DSLTs. The diffusion coefficient obtained was $D_e = 4\cdot10^{-12}$ ($m^2\cdot s^{-1}$).
5) In order to take into account the diffusion term while transfer and convection in the leachate inter-phase mass occur, MIX block for grid cell 1 and the stagnant cell 102 was used. The value of MIX parameters is the leachate volume fraction of the respective cell, (e.g., $\mathrm{Mix1} = V_{block}/(V_{leachate}*\mathrm{cells})$and $\mathrm{Mix102} = 1 - \mathrm{Mix1}$).
6) The PHREEQC model for the DSLTs was fitted to 8 successive simulations that correspond to the eight time intervals in which the leachate of the sample was renewed. TRANSPORT time intervals (time_step) were fixed according to the periods of time the monoliths were submerged: 6 h, 1 d, 2.25 d, 4 d, 9 d, 16 d, 36 d, and 64 d.
7) For the 8 simulations, the leachate was stagnant ($Q = 0$) because there was no flow rate but rather a sequential leachate renewal at different time intervals.

The quantification of the maximum amount of dissolved minerals (EQUILIBRIUM_PHASES) was based on an iterative process comparing the experimental results obtained in the DSLTs and the simulated results given by the dynamic leaching test model. These mineralogical compositions were simulated for each of the three materials and served as an input parameter for the simulation of the outdoor exposure conditions tests.

2.4. Outdoor exposure conditions tests model approach

The model used to simulate the LOT is the same chemical-transport model used above (procedure detailed elsewhere [Schiopu et al., 2008]). The model fitting for this scenario contains hydrological balance and run-off parameters simulated in the "Level 1" model (e.g., flow rate, runoff volume, and rain duration) (procedure details in [Vega-Garcia et al., 2020b]). The material characteristics were estimated fitting the simulated results with the experimental results of the DSLTs. As a difference to the model used to simulate the DSLTs, this model will include a stagnant/non-stagnant flow condition and an atmospheric CO_2 uptake process.

Carbon dioxide (CO_2) dissolved into the leachate was included in the chemical model. The mineral materials leachate serves as an alkaline medium were the CO_2 from the air reacts with the hydroxyl ion ($OH-$). This process is important because the CO_2 affects the leachate pH and then the chemical properties of the mineral material, which becomes increasingly carbonated. The gas absorption flux F_{ab} is dependent on the specific absorption model. The model used in this approach is the one used by Tiruta-Barna and Schiopu (2008) and it is defined by:

$$F_{ab} = k_{SL}\cdot\left(\frac{P_{CO_2}}{K_H} - C^{leachate}_{CO_2(aq)}\right) \tag{8}$$

where, k_{SL} (m/s) is the mass transfer coefficient between the gas and the leachate, $P_{CO_2}$is the partial pressure of CO_2 in air (bar), K_H is the Henry constant ($bar\cdot m^3\cdot mol^{-1}$), and $C^{leachate}_{CO_2(aq)}$ is the CO_2 concentration in the leachate (mol/m^3).

To model outdoor leaching tests in which precipitation and drying periods occur, the model is divided into two scenarios. The first scenario is (1) the "efficient rain event" scenario. This scenario corresponds to the time when the rainwater runs off over the VTP during a raining event and can be collected. The second scenario is (2) the "duration between rain events" scenario. This scenario will take into account the physico-chemical processes within the material compartments during the drying periods of the VTP.

Based on the outdoor exposure conditions and the scenarios depicted above, a set of boundary conditions were implemented in the PHREEQC data blocks in order to replicate the leaching existing processes during LOTs. These boundary conditions are described as follows:

1) The PHREEQC model for the LOT was fitted to 47 "efficient rain event" scenarios and 47 "duration between rain events" scenarios. TRANSPORT time intervals (time_step) were fixed according to the rain duration for the first scenario and the antecedent dry periods (ADP) for the second scenario. The duration of each scenario was retrieved from the results of the "Level 1" model. The frost scenarios with temperatures <0 °C were not considered within the scenarios nor within the substance leaching calculation.
2) The temperatures of pore water and run-off (SOLUTION 0 and SOLUTION 102) were simplified to 14 °C, which is the average temperature of the non-frost months in Valley, Germany area.
3) The width of each cell (data block TRANSPORT, lengths) corresponds to the surface thickness of the tested materials (cells 1–100, lengths) divided by the number of cells. The thickness for FMM, LCR, and SR are: lengths $= 100\cdot0.0001(\mathrm{m})$, lengths $= 100\cdot0.0003(\mathrm{m})$, and lengths $= 100\cdot0.00005(\mathrm{m})$, respectively.
4) MIX block as well as in the DSLT modelling is used to model the material/leachate interface transfer (see boundary condition 5 in section 2.3).
5) The various mass transfer flows were calculated using the RATES and KINETICS data blocks. To simulate these processes in the first scenario, runoff volumes and the flow rates ($Q \neq 0$) obtained in the "Level 1" model were used. For the second scenario, ADP and the absorbed water volume obtained in the "Level 1" model were used. The method used by PHREEQC in this data block to assimilate the first order kinetics with the hydrodynamics law of the leachate is the Runge-Kutta algorithm.
6) The rain water composition used in data block SOLUTION (cell 102) is the one obtained from blank samples tested in the LOT (supplementary data Table S1).
7) The carbonation rate by CO_2 was calculated in the RATES and KINETICS data blocks. The k_{SL} used in the model was estimated by fitting the model with pH-values obtained in the LOT. The values used for k_{SL} was of $3.3\cdot10^{-4}$(m/s).

The pH-values and the concentrations of all elements in the leachate were obtained after modelling the three different plasters and mortars. Simulated results given by the simulations should have concentrations and pH-values that correspond to those obtained in the LOT.

2.5. Model accuracy and validation

To estimate the precision of the results, the root mean square deviation (RMSD) was used. This measure is frequently used to estimate the difference between the predicted values of the model and the values observed in the field tests (Armstrong and Collopy, 1992). The RMSD represents the square root of the mean square errors of the values given by the model and the values obtained in the results of the field tests:

$$RMSD = \sqrt{\frac{\sum_{i=1}^{n}(x_{1,i} - x_{2,i})^2}{n}} \quad (9)$$

where $x_{1,i}$ is the actual test result, $x_{2,i}$ is the model result, and n is the number of measured points.

The value of this measurement is always positive, and a value of 0 would indicate a perfect fit of the simulation results with the results obtained in the field tests. In general, a lower RMSD is better than a higher one. However, comparisons between different types of data are not valid because the measure depends on the scale of the numbers used. For practical purposes it was decided to normalize (NRMSD) for this measure in order to facilitate the comparison between the results of substance leaching with different scales. The result of the normalized measurement is given in percentages and can be described as follows:

$$NRMSD = \frac{RMSD}{y_{max} - y_{min}} \cdot 100 \quad (10)$$

where y_{max} is the maximum measured value and y_{min} is the minimum measured value.

3. Results and discussion

3.1. SI analysis and DSLTs

The composition of the three materials are described in Table 1 (given with their respective SI at the pH of an eluate in contact with the material: FMM, pH = 11.5; LCR, pH = 11.7, and SR, pH = 11.7).

The simulations of the DSLT results were used to define the plausibility of the phase composition obtained from the SI analysis. The DSLTs were simulated using the coupled chemical-transport model developed by Tiruta-Barna (2008) and applied to the experimental conditions of the laboratory tests (depicted elsewhere in (Section 2.2) [CEN/TS 16637-2]). The experimental and simulation results of the DSLTs for the three different materials are shown in Fig. 3.

The highest amount of substances discharged occurs during the first 16 days of the test. Afterwards, the discharge of substances tends to be lower and starts to remain constant. This behavior is reflected both in the experimental results and in the simulations. The simulated results represent only the leachate composition at the end of each leaching sequence. The results are thus dependent on the duration of each water renewal interval described.

The pH-value increases during the first days of testing and then stabilizes. This behavior is reflected in the experimental and simulated curves. This is because it depends on the leaching of substances (e.g., calcium (Ca), sodium (Na), and potassium (K)), which are highly soluble elements. These substances (and others) are leached mainly during the first days of testing and affect the pH-value [Tiruta-Barna et al., 2005]. During DSLTs, the water is renewed (with neutral pH (CEN/TS 16637-2)) at every specific time interval. The composition of the eluate in contact with the material is dependent on the amount of substances released (Schiopu et al., 2008). Physicochemical processes (e.g., dissolution/precipitation of various phases, variation of concentration gradient) induced by the sequential renewal of the leachate has a considerable artificial influence on the substance release. The mean pH-values for the FMM, LCR, and SR in the experimental results were pH = 11.5, pH = 11.7, and pH = 11.7, respectively. The mean pH-values for the FMM, LCR and SR obtained in the simulations were pH = 11.5, pH = 11.2, and pH = 11.1, respectively.

From the three different plasters and mortars evaluated, the following substances were identified to be relevant in the experimental and simulated eluates because of their high discharge: sulfate (SO42−), calcium (Ca), barium (Ba), vanadium (V), and strontium (Sr). The SO42− was controlled by ettringite at high pH (FMM = 11.5, LCR = 11.7, and SR = 11.7) as well as by the Ca release. The Ca, Ba, V, and Sr release was controlled by different mineralogical phases in very high pH media: barite, celestite, portlandite, calcite, anhydrite, and vanadium oxide. In the DSLTs, zinc (Zn) and copper (Cu) were not considered as relevant due to their low loads. This behavior may be due to the high alkalinity of the pore water.

Table 1
Material chemical composition and SI analysis.

Material chemical composition and saturation indices derived from DSLTs eluates			
Mortar	Mineral phase	Formula	SI
Facing masonry mortar (FMM), pH = 11.5	Calcite	$CaCO_3$	−2.0
	Quartz Sand	SiO_2	−3.4
	Anhydrite	$CaSO_4$	−3.4
	Barite	$BaSO_4$	−1.4
	Celestite	$SrSO_4$	−4.7
	Tobermorite-11A	$Ca_5Si_6O_{16}(OH)_2{\cdot}4H_2O$	−3.0
	Portlandite	$Ca(OH)_2$	−2.7
	Ettringite	$Ca_6Al_6(SO_4)_3(OH)_{12}{\cdot}26H_2O$	−10.2
	Cr-Ettringite	$Ca_6Al_6(CrO_4)_3(OH)_{12}{\cdot}26H_2O$	−12.5
	Zincite	ZnO	−2.1
	Tenorite	CuO	0.9
	Gypsum	$(CaSO_4{\cdot}2H_2O)$	−3.2
	Vanadium Dioxide	V_2O_4	−38.3
Lime cement render (LCR), pH = 11.7	Calcite	$CaCO_3$	−0.9
	Quartz Sand	SiO_2	−3.9
	Anhydrite	$CaSO_4$	−3.6
	Barite	$BaSO_4$	−1.3
	Celestite	$SrSO_4$	−5.2
	Tobermorite-11A	$Ca_5Si_6O_{16}(OH)_2{\cdot}4H_2O$	−3.1
	Portlandite	$Ca(OH)_2$	−2.0
	Ettringite	$Ca_6Al_6(SO_4)_3(OH)_{12}{\cdot}26H_2O$	−10.4
	Cr-Ettringite	$Ca_6Al_6(CrO_4)_3(OH)_{12}{\cdot}26H_2O$	−12.6
	Zincite	ZnO	−2.3
	Tenorite	CuO	0.3
	Gypsum	$(CaSO_4{\cdot}2H_2O)$	−3.5
	Vanadium Dioxide	V_2O_4	−38.9
Scratch render (SR), pH = 11.7	Calcite	$CaCO_3$	−1.1
	Quartz Sand	SiO_2	−4.8
	Anhydrite	$CaSO_4$	−3.7
	Barite	$BaSO_4$	−1.4
	Celestite	$SrSO_4$	−4.6
	Tobermorite-11A	$Ca_5Si_6O_{16}(OH)_2{\cdot}4H_2O$	−2.6
	Portlandite	$Ca(OH)_2$	−2.4
	Ettringite	$Ca_6Al_6(SO_4)_3(OH)_{12}{\cdot}26H_2O$	−10.2
	Cr-Ettringite	$Ca_6Al_6(CrO_4)_3(OH)_{12}{\cdot}26H_2O$	−11.9
	Zincite	ZnO	−2.3
	Tenorite	CuO	0.3
	Gypsum	$(CaSO_4{\cdot}2H_2O)$	−3.5
	Vanadium Dioxide	V_2O_4	−39.6

Soluble salts as Na, K and Cl are also included in the three material assemblages.

The accuracy of the DSLT-tests simulations for the three materials ranged between NRMSD = 2.6% and NRMSD = 5.7%. For each of the materials, the variation in accuracies between each leached substance is in the same order of magnitude. This behavior may be a result of the controlled conditions under which the laboratory tests were conducted with few conditions that can vary and affect the leaching behavior of the materials. The controlled conditions help the model to simulate the leaching process more accurately by giving the correct input parameters depending on the conditions in which the DSLTs are being carried out. From the results obtained from NRMSD (see Fig. 3), it can be concluded that the comparison of the simulation results with the results obtained

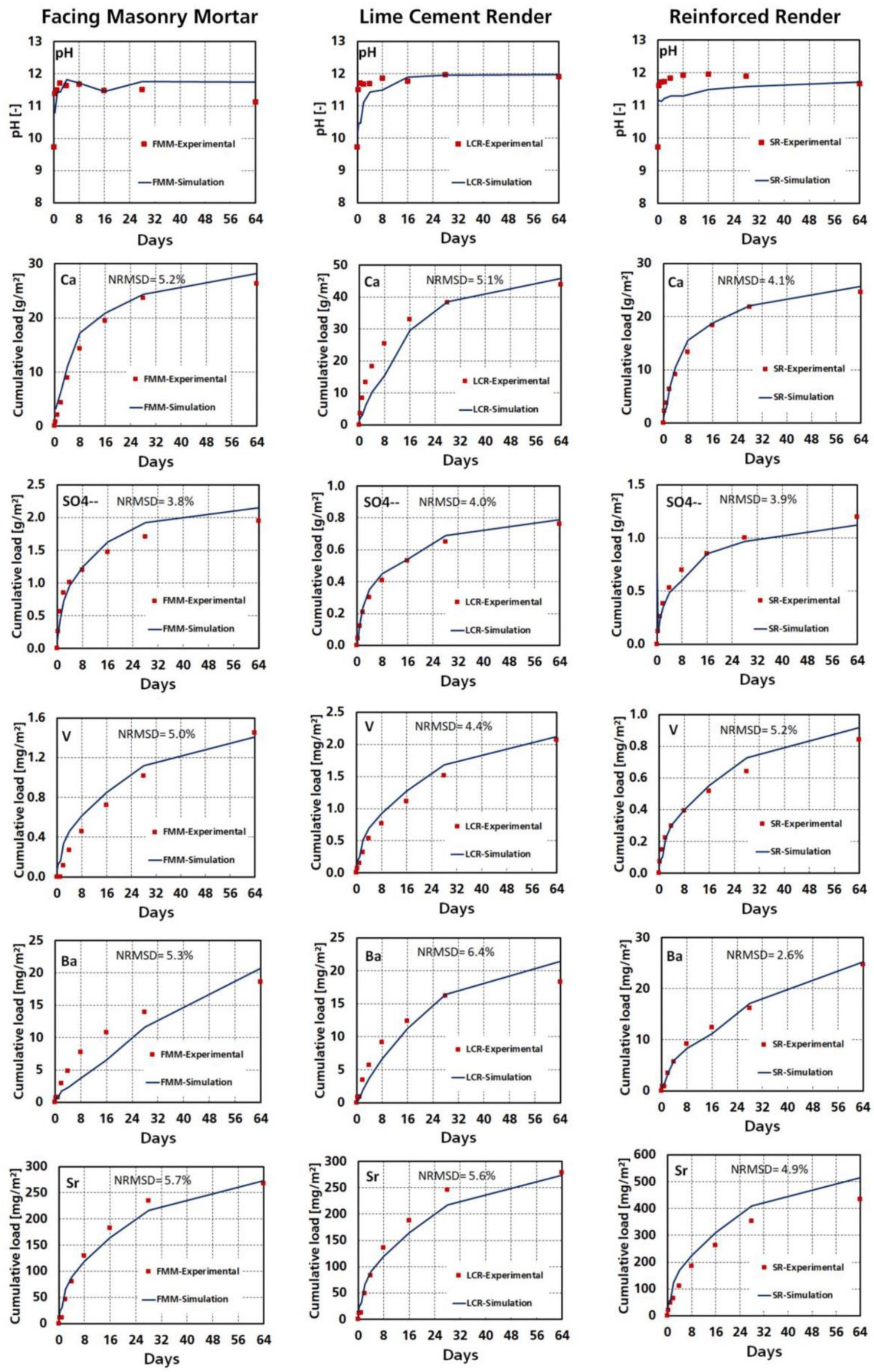

Fig. 3. Experimental and simulation results (DSLTs) for facing masonry mortar (FMM), lime cement render (LCR), and reinforced render (SR).

experimentally are in a good agreement with a deviation in precision not greater than NRMSD = 5.7%.

From these results, we were able to establish the set of phases to be used in the coupled chemical-transport model for LOT.

3.2. Leaching outdoor tests

For the LOT, there were 47 “efficient rain event” scenarios (first scenario) and 47 “duration between rain events” scenarios (second scenario). These scenarios correspond to and were distributed over the LOT period of 18 months. The shortest “first scenario” was 0.4 h long, and the longest was 31.2 h. The shortest “second scenario” was 24 h long

Table 2
LOT model input parameters.

LOT runoff parameters necessary for “Level 2” model simulations									
first scenario								second scenario	
Rain event	Time, h	FMM-runoff volume, mL	FMM-flowrate, mL/s	LCR-runoff volume, mL	LCR-flowrate, mL/s	SR-runoff volume, mL	SR-flowrate, mL/s	Dry Period	Time, h
1	1.2	250	$4.9{\cdot}10^{-1}$	140	$1.8{\cdot}10^{-1}$	680	$9.5{\cdot}10^{-1}$	1	96
2	1.9	200	$6.5{\cdot}10^{-3}$	220	$1.0{\cdot}10^{-3}$	810	$6.0{\cdot}10^{-3}$	2	24
3	4.0	430	$1.9{\cdot}10^{-1}$	210	$6.8{\cdot}10^{-2}$	2760	$3.3{\cdot}10^{-1}$	3	24
4	6.6	1520	$4.3{\cdot}10^{-2}$	210	$1.1{\cdot}10^{-2}$	5560	$4.9{\cdot}10^{-2}$	4	24
5	6.6	1900	$1.1{\cdot}10^{-1}$	270	$3.7{\cdot}10^{-2}$	6300	$1.8{\cdot}10^{-1}$	5	48
6	0.4	520	$2.8{\cdot}10^{-1}$	0	$3.0{\cdot}10^{-3}$	1240	$2.3{\cdot}10^{-3}$	6	72
7	3.0	400	$1.4{\cdot}10^{-2}$	0	$2.6{\cdot}10^{-3}$	920	$1.5{\cdot}10^{-2}$	7	48
8	2.3	280	$1.2{\cdot}10^{-2}$	0	$1.0{\cdot}10^{-2}$	1080	$5.1{\cdot}10^{-2}$	8	24
9	3.6	1680	$4.3{\cdot}10^{-2}$	0	$1.2{\cdot}10^{-2}$	4220	$5.3{\cdot}10^{-2}$	9	432
10	12.2	1260	$2.5{\cdot}10^{-2}$	260	$6.2{\cdot}10^{-3}$	3260	$3.2{\cdot}10^{-2}$	10	120
11	3.5	540	$9.6{\cdot}10^{-2}$	0	$2.8{\cdot}10^{-2}$	520	$1.4{\cdot}10^{-1}$	11	768
12	9.5	1180	$4.1{\cdot}10^{-2}$	260	$1.4{\cdot}10^{-2}$	3040	$7.9{\cdot}10^{-2}$	12	96
13	2.6	420	$1.6{\cdot}10^{-2}$	0	$3.2{\cdot}10^{-3}$	1280	$2.5{\cdot}10^{-2}$	13	144
14	6.2	1560	$5.3{\cdot}10^{-2}$	0	$1.8{\cdot}10^{-2}$	2840	$1.0{\cdot}10^{-1}$	14	24
15	4.9	1520	$1.0{\cdot}10^{-1}$	0	$3.6{\cdot}10^{-2}$	2680	$1.9{\cdot}10^{-1}$	15	24
16	6.5	2460	$6.2{\cdot}10^{-2}$	740	$1.9{\cdot}10^{-2}$	3940	$9.9{\cdot}10^{-2}$	16	24
17	12.8	1580	$1.7{\cdot}10^{-2}$	400	$4.2{\cdot}10^{-3}$	4000	$2.4{\cdot}10^{-2}$	17	24
18	14.1	2860	$2.3{\cdot}10^{-2}$	2320	$2.5{\cdot}10^{-2}$	2000	$3.4{\cdot}10^{-2}$	18	192
19	1.2	200	$1.0{\cdot}10^{-2}$	0	$3.0{\cdot}10^{-2}$	1080	$2.4{\cdot}10^{-1}$	19	24
20	3.0	540	$2.9{\cdot}10^{-2}$	0	$7.5{\cdot}10^{-3}$	1100	$3.8{\cdot}10^{-2}$	20	24
21	5.6	580	$1.4{\cdot}10^{-2}$	0	$2.3{\cdot}10^{-3}$	1180	$2.6{\cdot}10^{-2}$	21	312
22	9.8	1460	$4.2{\cdot}10^{-2}$	1260	$1.4{\cdot}10^{-2}$	5100	$7.4{\cdot}10^{-2}$	22	72
23	3.9	240	$1.6{\cdot}10^{-2}$	0	$3.6{\cdot}10^{-3}$	940	$3.1{\cdot}10^{-2}$	23	48
24	17.2	3560	$6.8{\cdot}10^{-2}$	2280	$1.9{\cdot}10^{-2}$	6680	$9.2{\cdot}10^{-2}$	24	24
25	3.9	1680	$5.4{\cdot}10^{-2}$	380	$1.4{\cdot}10^{-2}$	4320	$9.3{\cdot}10^{-2}$	25	96
26	12.5	3300	$4.0{\cdot}10^{-2}$	1080	$1.0{\cdot}10^{-2}$	5230	$6.5{\cdot}10^{-2}$	26	24
27	7.2	1320	$4.2{\cdot}10^{-2}$	0	$1.0{\cdot}10^{-2}$	4000	$6.7{\cdot}10^{-2}$	27	168
28	5.1	1060	$2.1{\cdot}10^{-2}$	920	$4.8{\cdot}10^{-3}$	3320	$3.5{\cdot}10^{-2}$	28	72
29	6.7	1960	$1.2{\cdot}10^{-1}$	1440	$1.1{\cdot}10^{-1}$	6540	$6.4{\cdot}10^{-2}$	29	24
30	3.0	1360	$8.7{\cdot}10^{-3}$	480	$1.4{\cdot}10^{-3}$	3680	$1.6{\cdot}10^{-2}$	30	24
31	0.8	1700	$6.7{\cdot}10^{-1}$	0	$2.7{\cdot}10^{-1}$	2480	$1.6{\cdot}10$	31	24
32	15.3	280	$1.7{\cdot}10^{-2}$	0	$5.8{\cdot}10^{-3}$	1660	$3.1{\cdot}10^{-2}$	32	24
33	4.2	1240	$6.8{\cdot}10^{-2}$	580	$2.2{\cdot}10^{-2}$	2940	$1.4{\cdot}10^{-1}$	33	24
34	7.3	520	$2.6{\cdot}10^{-2}$	520	$6.8{\cdot}10^{-3}$	1260	$3.7{\cdot}10^{-2}$	34	48
35	9.8	1260	$2.5{\cdot}10^{-2}$	1260	$5.7{\cdot}10^{-3}$	3860	$5.0{\cdot}10^{-2}$	35	24
36	8.5	1060	$1.8{\cdot}10^{3}$	700	$6.5{\cdot}10^{2}$	3880	$3.4{\cdot}10^{3}$	36	24
37	9.9	2720	$1.5{\cdot}10^{-1}$	1060	$5.6{\cdot}10^{-2}$	1040	$3.0{\cdot}10^{-1}$	37	24
38	2.8	420	$3.2{\cdot}10^{-2}$	0	$7.4{\cdot}10^{-3}$	1040	$5.1{\cdot}10^{-2}$	38	24
39	6.8	440	$1.4{\cdot}10^{-2}$	0	$3.1{\cdot}10^{-3}$	1220	$2.4{\cdot}10^{-2}$	39	24
40	1.5	340	$3.6{\cdot}10^{-2}$	0	$9.3{\cdot}10^{-3}$	340	$5.0{\cdot}10^{-2}$	40	96
41	4.7	720	$4.2{\cdot}10^{-2}$	720	$1.3{\cdot}10^{-2}$	1440	$8.2{\cdot}10^{-2}$	41	288
42	31.2	8780	$1.1{\cdot}10^{-1}$	7340	$7.1{\cdot}10^{-2}$	10,540	$1.7{\cdot}10^{-1}$	42	48
43	5.9	780	$5.9{\cdot}10^{-3}$	0	$1.0{\cdot}10^{-3}$	2400	$4.3{\cdot}10^{-3}$	43	24
44	5.9	780	$5.9{\cdot}10^{-3}$	0	$1.0{\cdot}10^{-3}$	2400	$4.4{\cdot}10^{-3}$	44	264
45	12.7	4420	$2.0{\cdot}10^{-2}$	2160	$1.9{\cdot}10^{-3}$	5840	$9.9{\cdot}10^{-3}$	45	240
46	9.6	700	$5.7{\cdot}10^{-3}$	0	$9.3{\cdot}10^{-4}$	1700	$7.0{\cdot}10^{-3}$	46	144
47	12.1	1700	$7.1{\cdot}10^{-2}$	1400	$2.1{\cdot}10^{-2}$	4320	$8.3{\cdot}10^{-2}$	47	96

and the longest was 748 h (Table 2.). The first scenario corresponds to 6.7% of the exposure time, and the second to 93.7% of the exposure time of the VTPs. The frost periods were not taken into account in the LOT model. The complete hydrological balance can be found elsewhere [Vega-Garcia et al., 2020a, 2020b]. The pH-value from rainwater without contact to VTPs ranged between 4.7 and 7.4.

The input parameters necessary for LOT simulation of FMM, LSR, and SR are summarized in Table 2. These input parameters were obtained by the “Level 1” model based on real weather parameters and material characteristics. Details of the run-off parameters simulation and its validation compared with the experimental results are presented elsewhere [Vega-Garcia et al., 2020b]. The highest simulated run-off volumes of the FMM, LSR, and SR test specimens that occurred during rain event 42 and were 8.7 l, 7.3 l, and 10.5 l, respectively. The highest flow rates for FMM, LSR, and SR were presented in rain event 36; these were 1800 ml/s, 650 ml/s, and 3400 ml/s, respectively.

The experimental and the simulation results of the LOT are shown in Fig. 4. The pH-values remain stagnant throughout the test period. The mean pH values obtained during the experimental LOT for FMM, LCR, and SR were 8.3, 7.6, and 7.8, respectively. For the LOT simulations, the mean pH-values for FMM, LCR, and SR were 8.3, 8.3, and 8.2 respectively.

For the three different plasters and mortars considered in this paper, the following substances were identified to be relevant in the experimental and simulation eluates because of their high load: SO42-, Ca, Cr, Zn, V, and Sr. The SO42− was controlled by gypsum at neutral pH and thus indirectly by the Ca release as mentioned by Schiopu et al. (2008). The release of Ca, Cr, V, and Sr in the outdoor tests was controlled by different mineralogical phases at close to neutral pH: celestite, portlandite, calcite, anhydrite, Cr-ettringite, and vanadium oxide. The case of Zn is of particular interest because it is possible that the loads of this element correspond to the rainwater composition as well as leaching capacity of the material. The high concentrations of Zn in rainwater can be seen in supplementary data Table S1.

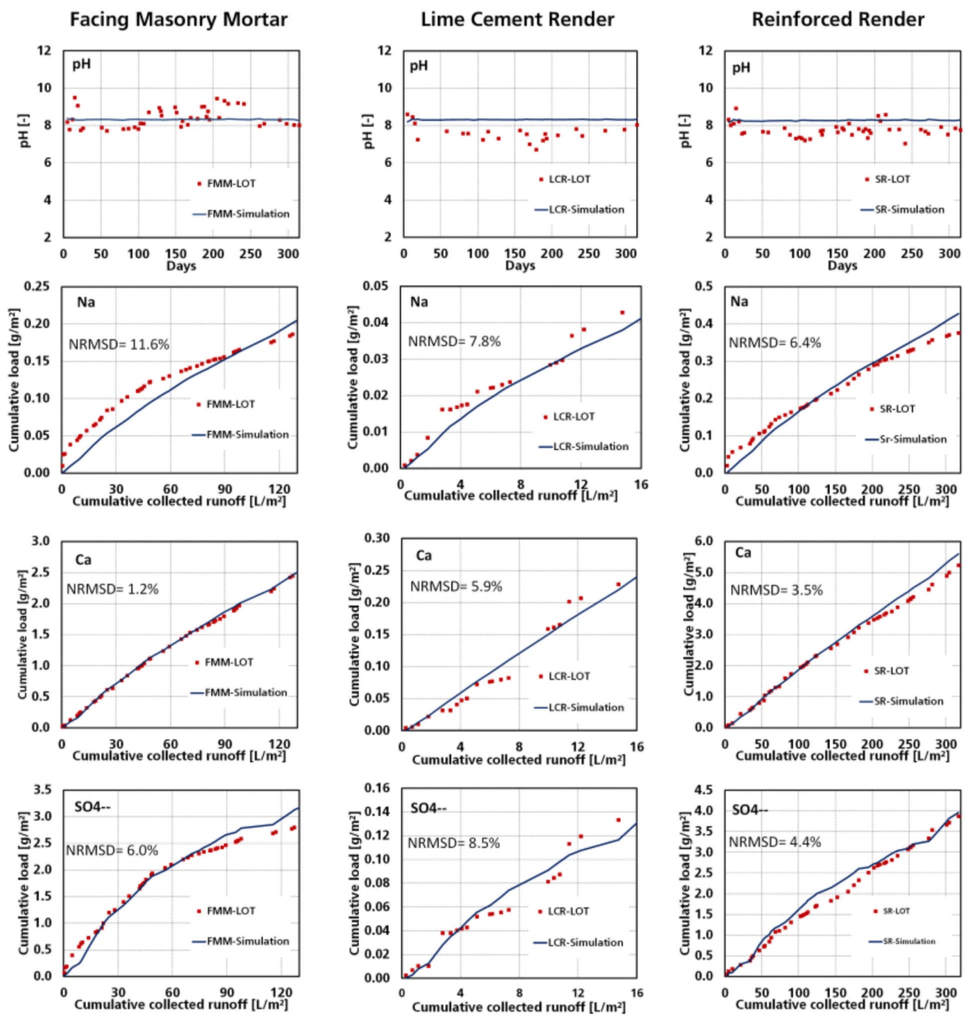

Fig. 4. Experimental and simulation results (LOT) for facing masonry mortar (FMM), lime cement render (LCR), and reinforced render (SR).

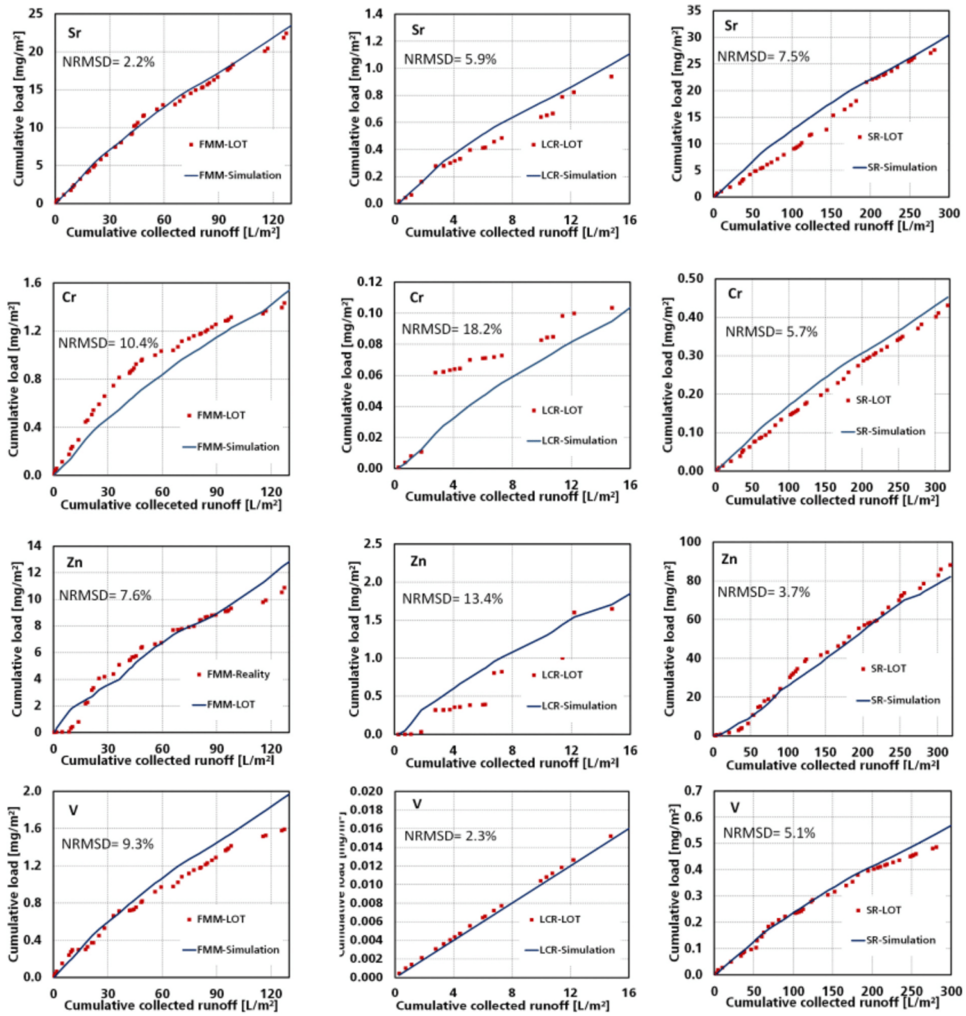

Fig. 4. (*continued*).

The magnitude of the leached substances varies within each material. This behavior may be due to the differences in the run-off volumes from each product obtained during the LOT (Table 2). This behavior is derived from the physical characteristics of the materials (e.g., thickness and absorption capacity) [Vega-Garcia et al., 2020b]. The SR with the lowest thickness had the highest substance loads as well as the highest run-off volumes. The LCR with the thickest layer had the lowest substance discharges and the lowest run-off volumes. The influence of the physical characteristics of the materials is also reflected in the number of samples taken because there were rain events during which run-off from FMM and SR – but not from LCR – was collected. This behavior can be observed when comparing the amount of LOT experimental measurement points from each of the tested materials (Fig. 4). As a consequence, this can lead to differences in the accuracy of the simulation because there are less collected run-off events to compare the leaching results of thicker materials or materials with greater absorption capacity. This behavior is visible in the NRMSD measurements, where the simulation was less accurate for the material with fewer measured loads (LCR) such as chromium (NRMSD = 18.2%) and zinc (NRMSD = 13.4%) compared with the material with more measured loads (SR) (Cr, NRMSD = 5.7%; Zn, NRMSD = 3.7%). During the LOTs, the material with less run-off may have had substance loads that did not correspond to the simulation. This is because in events with less rain, there is less run-off flow, which is necessary to completely wash off the leached substances. These were then washed-off in the consecutive rain event. This mechanism is not included within the model. In the case of LCR, this results in abrupt differences between data points of the experimental loads (e.g., Ca, SO42−, Cr, and Zn). In contrast, the model results showed a smoother substance load because it considers that all the leached substance in each rain event is transported within the established flow. This process can be seen for the three materials, where the material with the highest run-off and measured loads (SR) is the material in which the model gave the most accurate results (NRMSD = 3.5–7.5%). Meanwhile, the material with the lowest run-off and measured loads (LCR) is the material in which the model gave the most inaccurate results (NRMSD = 5.9–18.2%).

The influence of dry periods can also be an important factor in the leaching of substances. These periods affect the structure of the pores and accelerate the carbonization. The CO_2 can enter the pores better and dissolve in the pore water by a partial drying of water filled pores. Although the model does not include the change in the pore size due to carbonation, it considers the change of pH and the chemical structure of the material which becomes more and more carbonated (degradation of Ettringite and Tobermorite-11A and formation of calcium carbonate) [Schiopu et al., 2008 and Weiler et al., 2020]. It is possible that a large part of the leaching of the substances has occurred after the dry periods which can lead to a further increase of the anionic substances. For this reason, it can also be assumed that SR has had higher substance loads compared to other materials due to its higher cement content.

Despite the complexity of the non-controlled outdoor conditions, the LOT simulation is able to reproduce the experimental results of the substances leaching from VTP. Using the "Level 1" run-off results and fitting material parameters (e.g., effective diffusion coefficient, mass transfer coefficient), the coupled chemical-transport model is able to simulate the leaching of different mineral materials exposed to real weather conditions. The model thus enables a prediction of the amount of leaching substances from VTP without the necessity of sampling larger façades, which would imply higher LOT costs. These results could help to predict the leaching of substances from plasters and mortars without having to reproduce these events in the field in order to validate them. A comparison with results obtained for similar materials is not yet possible because of the lack of similar experimental data. Additional field tests with comparable materials should be done for a more accurate validation of this model.

4. Conclusions

In the model described, an existing leaching model developed with PHREEQC was adapted for the prediction and evaluation of substance leaching behavior from VTPs coated with plaster and mortar under real outdoor exposure conditions. With the incorporation of simulated run-off conditions from a previously published model, which predicts the run-off, it was possible to simulate the leaching behavior of the VTPs covered with plasters and mortars of a series of rain events over a period of 18 months. The comprehensive experimental dataset made it possible to validate the accuracy of the model by comparing the simulated results with those collected in the field.

Despite the complexity of non-controlled outdoor conditions, the LOT simulation was able to reproduce the experimental results of the substances leaching from VTP coated with different plasters and mortars.

The leaching model presented makes it possible to investigate and reproduce the leaching behavior of VTPs characterized by a specific plaster or mortar for a defined location and period and obtain a good approximation of the amount of substances leached for different materials. We observed that the relevant leached substances from plasters and mortars under real weather conditions are sulfate, calcium, chrome, zinc, vanadium, and strontium. We noticed that under real weather conditions, different substances found in the VTPs run-off can originate from the rainwater or other external media to the materials (e.g., zinc). Likewise, we observed that the physical characteristics of the material (e.g., thickness, absorption capacity) strongly affects the leaching of substances in façades or panels covered with plaster and mortar. The lower the thickness and absorption capacity of the material applied, the greater the run-off and discharge of leached substances. This last behavior plays an important role in the accuracy of the model because fewer simulated points are available for the validation of materials generating less run-off.

Knowledge about substance leaching loads of different materials during real weather conditions are highly important for evaluating their environmental impact. The evaluation of the hazardous potential of plasters and mortars is "Level 3" of the three-staged model and will be subject of further publications.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2021.130657.

Credit author statement

Pablo Vega-Garcia: Writing – original draft preparation, valdidation, formal analysis, conceptualization, data curation. Regina Schwerd: Conceptualization, supervision, writing - reviewing and editing, project administration. Sabine Johann: investigation, data recopilation. Christoph Schwitalla: investigation, data recopilation. Christian Scherer: funding acquisition, reviewing and editing; Brigitte Helmreich: methodology, supervision, writing - reviewing and editing.

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A. 3 Groundwater Risk Assessment of Leached Inorganic Substances from Façades Coated with Plasters and Mortars

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Groundwater risk assessment of leached inorganic substances from façades coated with plasters and mortars

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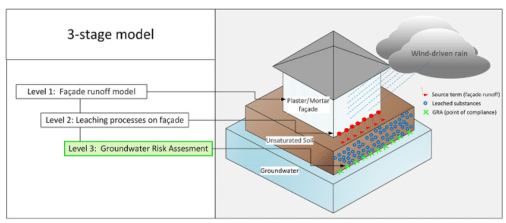
HIGHLIGHTS

- A ground water risk assessment for plasters and mortars façade runoff was developed.
- V, Cr and Pb were identified to be relevant substances due to their high load.
- Cr is limiting parameter for the application of a mortar in a construction scenario.

GRAPHICAL ABSTRACT



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ABSTRACT

A requirement of the Construction Products Regulation (CPR) in the European Union states that construction materials and works must be designed in a way that throughout their entire life cycle, they have no exceedingly high impact on the environment. The objective of the current work was to evaluate the environmental risk of stormwater runoff from plasters and mortars using the Groundwater Risk Assessment (GRA). The source term eluates are based on the results obtained by a model for leaching prediction of inorganic substances for vertical test panels (VTPs) coated with plasters and mortars. During the evaluation, it was determined that vanadium, chromium, lead and zinc are relevant substances leached by plasters and mortars during rain events due to the high magnitude of concentrations, which can lead to a significant alteration in the chemical status of groundwater. The evaluation showed that chromium is the only leached substance that invalidates the applicability of one of the materials for a particular scenario of a selected technical construction application.

1. Introduction

Evaluating the environmental properties of buildings is of high priority for the European Community. The Construction Products Regulation (CPR) addresses seven basic requirements for buildings. The third requirement covers the area of hygiene, health and environmental protection [European Parliament, 2011]. According to this requirement, each construction work must be designed in a way that it does not harm the user or the environment during its entire life cycle, for example, by leaching substances during rain events. Plasters and mortars are commonly used as part of the external thermal insulation composite systems (ETICS) and solid masonry of a façade. During their lifetime,

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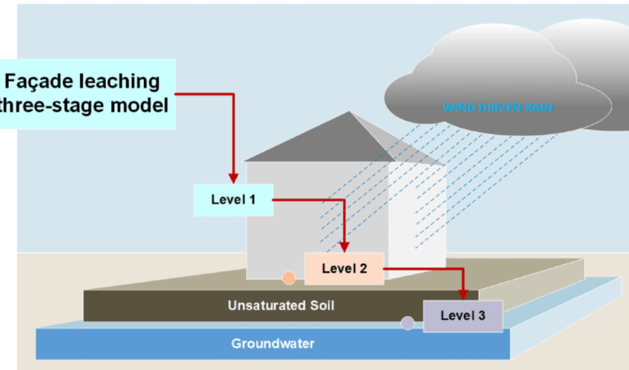

Fig. 1. Scheme of a three-stage model used for the evaluation of the environmental characteristics of plasters and mortars.

these materials are exposed to precipitation and ambient air. The stormwater runoff caused by the outdoor exposure conditions leads to the dissolution of metals and anions [Brameshuber et al., 2009; IBP 2011; Nebel et al., 2010; and Scherer, 2013]. Not all dissolved substances from construction materials have an environmentally hazardous potential. Thus, not all products in contact with stormwater necessarily imply a negative effect on the environment [European Parliament, 2008]. In order to protect the environment and human health, the potentially harmful dissolved substances should be as low as possible. In Germany, the concentrations of substances released should not exceed the "Insignificance Threshold Values" (German: *Geringfügigkeitsschwellenwerte*, GFS) stated by the Working Group of the Federal States on Water (German: Bund/Länder- Arbeitsgemeinschaft Wasser, LAWA) [LAWA, 2016] at the point of compliance (in German: *Ort der Beurteilung* (*OdB)*).

In 2005, the German Federal Ministry of Environment implemented a legislative procedure for a "Decree for the Requirements of the Use of Alternative Mineral Building Materials in Technical Constructions and for the Amendment of the Federal Soil Protection and Contaminated Sites Ordinance" (hereafter referred to as German Recycling Decree) in order to have a guideline for all German federal states that allows the application of leaching standards for different mineral materials. This guideline provides a special focus on the protection of soil and groundwater (e.g., contaminant release from mineral materials in technical constructions to soil and water), sustainable waste management and the protection of primary resources [German Federal Ministry of Environment, 2017].

To develop a new and to improve existing methods as well as to harmonize methods for groundwater risk assessment, the German Federal Ministry of Education and Research funded the joint research project "Groundwater Risk Assessment (GRA)" [Susset and Grathwohl, 2011]. The GRA focused on the assessment of contaminant leaching from various materials and reactive transport in the unsaturated soil toward the groundwater table [Oberacker and Eberle, 2002]. The goal of the evaluated results of the joint research project was to identify the key factors governing the release, transport and turnover of contaminants in various mineral recycling materials (e.g., mineral waste, industrial waste, concretes and soils) used in technical constructions. Another objective of the study was to derive the maximum concentration of contaminants acceptable in the leachate of certain mineral materials which are applied in various earthworks (e.g., roads, dams, landscaping, etc.). As a result, the GRA determined the "media related application values (MEs)". These values are derived under specific technical boundary conditions and political conventions which aim for the prevention of adverse effects to the media soil and water. The MEs are dependent on the substances of interest and the hydraulics in construction soils and sub-soils. These values may be the same or higher than threshold concentrations such as the GFS. The derivation of these values starting point is the maximum acceptable concentration in the seepage water at the groundwater table (*OdB)*. The goal of the MEs is to protect the environmental media soil and groundwater, taking into account technical boundary conditions and policy conventions.

For a generalized regulation concept of the GRA a limited number of scenarios have been introduced. Not all sub-soil scenarios are considered within the concept, just two of them, the sub-soil with most favorable terms and its counterpart with adverse conditions. These two soil scenarios were sandy soils with moderate retardation and natural attenuation and loamy, silty and clayey soils with high retardation and natural attenuation. These two soil categories were defined by Beyer et al. (2007, 2008) and Grathwohl et al. (2006) based on a statistical evaluation of the main soil units in Germany. The statistical evaluation included basic soil characterization parameters (e.g., thickness of soil units, clay contents, pH-values, total organic carbon contents and hydraulic properties). It was defined from the statistical evaluation that 90% of the soils in Germany meet the assumed sorption quality for the selected two soil scenarios.

In the case of the mineral materials as well as for the sub-soils, not all of them can be investigated for all possible applications. Therefore, a leachate based quality of a mineral material has been defined by a set of limit concentrations for the relevant substances measured in eluates at a liquid to solid ratio (LS) of 2 (ratio between the amount of liquid and the amount of solid expressed in L/kg dry matter). These limit concentrations were obtained from short-term column percolation tests (DIN 19528, 2009) which results were comparable with field lysimeter tests elaborated by Susset and Leuchs (2008). A high variability in the quality of the materials can be found caused by the high heterogeneity of the technical constructions, different "material classes" were defined within the GRA. These material classes are established by different sets of limit concentrations in eluates for the same mineral material [Grathwohl and Susset, 2009]. As a result of comparing the limit concentrations in eluates and MEs, the GRA is able to help make a decision toward which technical applications are viable for certain mineral materials and which are not.

To investigate the leaching of building material components, façade coatings and ETICS vertical test panels (VTP) have been widely used [Bester et al., 2014; Bollmann et al., 2014; Burkhardt et al., 2012; Hensen et al., 2018; Schwerd, 2011, 2017 and Schwerd et al., 2015]. Outdoor test with VTP are mainly used to gain information on the leaching of substances from building products under actual weather conditions. Common laboratory methods such as the Dynamic Surface Leaching Test (DSLT) [CEN/TS 16637–2] or methods with intermittent water contact, including drying intervals [EN 16105, 2011], are also

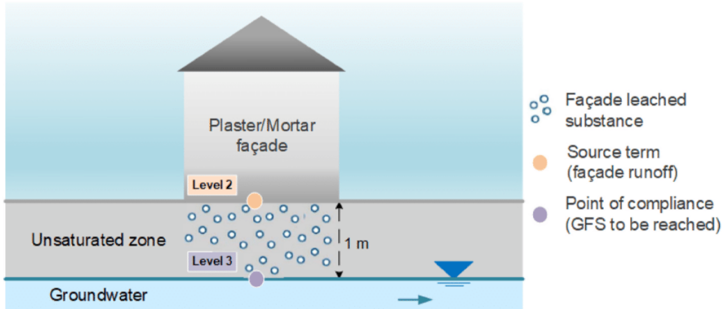

Fig. 2. Source term of the leaching substances (façade runoff), unsaturated transport zone and point of compliance where the GFS acts as a target concentration.

available. They can lead to reproducible results but do not reflect the leaching behavior of a building product under realistic conditions, which is controlled by various factors such as façade geometry, temperature, site characteristics (latitude, altitude), façade exposure (orientation), wind-driven rain (WDR), and length of antecedent dry period (ADP) [Burkhardt et al., 2018; Blocken et al., 2013; Bester et al., 2014; Schoknecht et al., 2016a, 2016b; Vega-Garcia et al., 2020a and Weiler et al., 2020]. Unfortunately, the results from common experimental laboratory leaching tests cannot easily be extrapolated to field conditions [Schiopu et al., 2007]. Vega-Garcia et al., [2020b, 2021] developed and evaluated a model for stormwater runoff volume and leaching prediction on VTPs coated with plaster and mortar exposed under actual conditions.

During the last decade, the Fraunhofer Institute for Building Physics IBP, Valley, Germany, has carried out systematic and extensive investigations on many formulations of plasters and mortars. A series of field scale tests using VTP with various plaster and mortar coatings have been carried out in order to analyze the leaching behavior during actual weather conditions as well as under constant physical conditions. The data were used to develop a three-stage model to assess the environmental properties of common plaster and mortar: Level 1: Façade runoff model, Level 2: Model for leaching processes and material transport on façades, and Level 3: Evaluation of the environmental impact by using the leachate forecast for the groundwater risk assessment [Vega-Garcia et al., 2020b, 2021].

The objective of this paper focus on “Level 3” of the three-staged model (Fig. 1). Using GRA and the simulated VTPs leached inorganic substances from “Level 2” model [Vega-Garcia et al., 2021], it should be possible to evaluate the environmental characteristics of plasters and mortars. The results of the environmental evaluation should help to assess groundwater risk for special building products as well as serve as guideline for manufacturers or authorities to determine the suitable areas of application of these materials.

2. Materials and methods

2.1. Leaching outdoor tests

The VTPs used during the outdoor tests were located in outdoor facilities at the Fraunhofer Institute for Building Physics IBP (47°52′30″N, 11°43′41″E) in Valley (Bavaria), Germany. Experimental VTPs (each 0.5 m wide, 1 m high) consisting of stainless steel panels were covered by 18 different mineral mortars and plasters. Three of them are described in this publication: facing masonry mortar (FMM), lime cement render (LCR) and reinforced render (SR). Forty-seven rain events with collection of the sample after every separate rain event in the period from October 2013 to March 2015 (18 months) were collected and analyzed. A detailed description of the sampling site, hydrological balance, rainwater composition, tested materials and runoff data analysis procedure is presented elsewhere [Vega-Garcia et al. (2020a, 2020b and 2021)].

2.2. Level 1: façade runoff model

Stormwater runoff parameters on VTPs covered with different plasters and mortars under actual weather conditions were simulated with the “Level 1” model. This model is able to calculate the water volume that sorbs during a rain event, bounces off the façade, and runs off it or remains on it as a film. The method in this simulation is based on stated assumptions found in previous research papers and existing wind driven rain (WDR), absorption, and surface water flow models [Vega-Garcia et al., 2020b].

2.3. Level 2: model for leaching processes and material transport on façades

The leaching process and material transport on VTPs covered with different plasters and mortars under actual weather conditions were simulated with the “Level 2” model [Vega-Garcia et al., 2021]. The runoff concentrations of VTPs covered with FMM, LCR and SR were calculated using input parameters from the “Level 1” model and then compared to the runoff concentrations obtained for the VTPs in the leaching outdoor tests for validation. The simulated runoff concentrations will serve as source term concentrations for the “Level 3” Groundwater Risk Assessment (GRA).

The “Level 2” model was developed using the geochemical model PHREEQC with the Lawrence Livermore National Laboratory (LLNL) thermodynamic data base and coupled with MATLAB in order to optimize the run-off and weather parameters. This model is based on the chemical-transport model developed by Schiopu et al. (2008) and adapted for the prediction and evaluation of substance leaching behavior from VTPs coated with plaster and mortar under real outdoor exposure conditions. To validate the accuracy of this model a comparison was done between the leaching outdoor tests (VTPs) collected dataset and the simulated results.

The simulated runoffs compositions of VTPs coated with FMM, LCR and SR can be seen in supplementary data Table S.1, Table S.2 and Table S.3, respectively.

2.4. German insignificance threshold values and determination of relevant substances

In order to derive the relevant substances from the concentrations obtained by the “Level 2” model, the GFS values were used.

The GFS are concentration-based values derived from eco- and human toxicological tests. They are defined as the concentrations that do not cause any significant alteration of the chemical status of the groundwater or a "no-effect level" [LAWA, 2016]. According to the "precautionary principle," the GFS are not quality targets or targets concentrations for groundwater. The point of compliance (OdB) within the insignificance threshold values should be localized in the seepage water above the groundwater table (1 m below the bottom line of the technical construction or unsaturated transport zone)—in the transition zone between unsaturated and saturated zone—to ensure that the groundwater is not negatively affected [German Federal Ministry of Environment, 2018 and Susset and Grathwohl, 2011] (Fig. 2).

Due to political conventions, the GFS have to be met at the point of compliance over a time period (appraisal time) of 200 years for technical constructions and over a time period of 500 years for permanent applications.

Due to the fact that the GFS act as target concentrations in the seepage water at a point of compliance, they can be used as a first reference to determine the relevant substances to be evaluated in our case. If the concentrations simulated by the "Level 2" model are lower than the GFS, these substances should not be relevant for the evaluation of the environmental characteristics of the plasters and mortars. Only substances with concentrations higher than the GFS will be determined as relevant substances and will be subjected to further steps of the GRA.

The GFS values can be seen in supplementary data Table S.5.

2.5. Groundwater risk assessment

The GRA is a process-based concept for using mineral materials in various technical constructions and permanent applications. This evaluation process is capable of being used as a simplified risk assessment by using the MEs, which are derived depending on the concentration decline of salts and retardation and/or attenuation and accumulation of metals in soils and on the hydraulic properties of technical constructions [German Federal Ministry of Environment, 2018 and Susset and Grathwohl, 2011]. Due to the simplicity of comparing the simulated runoff concentrations from façades coated with mortars and plasters and the detailed MEs table values, the GRA was chosen to serve as an environmental risk assessment to demonstrate the potential use of a mineral material in different applications.

Table 1
Media related application values (MEs) for the selected application No. 13 of GRA and the relevant substances obtained from in Vega-Garcia et al., (2021). Application No 13: Base and sub-base layers without binding agents, land improvement areas, soil consolidation zones, substructures up to 1 m thick from the subgrade and excavation pits and pipe trenches under the surface layer.

MEs	Unfavorable case scenario, highest expected groundwater level close (0.1–1 m) to the bottom line of the technical construction	Favorable case, highest expected groundwater level >1 m below the bottom line of the technical construction	
		Sand	Loam/ silt/clay
V (µg/L)	30	53.9	452
Cr (µg/L)	15	151	284
Cd (µg/L)	3	3	7
Pb (µg/L)	34.5	91.3	252
Cu (µg/L)	30	105	173
Zn (µg/L)	150	155	839

The MEs are specific maximum concentrations of a substance in the seepage water at the bottom of a technical construction (permanent/ non-permanent) with mineral material or permanent earthworks. They account for natural processes such as attenuation (degradation and sorption) and dilution [German Federal Ministry of Environment, 2018 and Susset and Grathwohl, 2011].

The MEs for salts and metals were calculated within the GRA with relevant concentrations, depending on the evaluated mineral material and its technical application. The principles for the calculation of these values are listed here:

1) For determining salts MEs, retardation and attenuation processes were not taken into account due to the fact that the retardation of these substances in the seepage water within the unsaturated zone ($\geq$1 m transport distance) is much lower than the appraisal period of 200 years and therefore not relevant from a regulatory point of view. A short-term concentration decline of salts below the GFS occurs within 4 years in the seepage water at the point of compliance. For this reason, the MEs for salts are independent from the transport scenario and the groundwater level below the technical construction and are dependent on the source term (material release behavior), climate factors (e.g., precipitation, evapotranspiration, etc.), hydraulics (seepage water flow rates and dilution), materials and technical specifications of the construction (e.g., thickness of the material layer, construction-specific bulk densities, etc.).
2) MEs were calculated for each relevant metal and each of the applications of mineral materials. The values account different hydraulic conditions (dilution factors and seepage water flow rates in different technical constructions), retardation and attenuation processes in the unsaturated zone and accumulation within the soil solids. The MEs for metals have to comply with the GFSs at the end of the 1 m deep transport zone over the appraisal time periods of 200 and 500 years (see section 2.4).
3) Retardation and attenuation processes can be considered if the highest groundwater level to be expected stays more than or equal to 1 m below the bottom of the technical construction or permanent application construction with mineral materials. If the groundwater level is between 0.1 and 1 m of the bottom of the technical construction or permanent application construction (unfavorable case scenario), the MEs for retarded/attenuated substances are lower as no retention process can be taken into account [Bannick et al., 2009]. In these cases, if there is no dilution effect within the transport zone, the MEs are equal to the GFSs.

Detailed tables with the MEs for each relevant substance accounting for specific mineral recycling materials in different technical construction applications and different soil scenarios are presented elsewhere [German Federal Ministry of Environment, 2018 and Susset and Leuchs, 2008]. Seventeen different technical construction applications were modeled to develop these tables, each of them defined in accordance to published technical construction rules and standards.

2.6. Boundary conditions for the evaluation of the environmental characteristics of plasters and mortars using the groundwater risk assessment

To determine the validity of a certain mineral plaster or mortar in accordance with the GRA, several steps are necessary. These steps will be considered as boundary conditions and are listed here:

1) In a first step, relevant substances for mineral plasters and mortars have to be identified based on the eluate concentrations obtained by "Level 2" model by taking into account the GFS. For this step, as mentioned in section 2.4, the eluate concentrations obtained by the

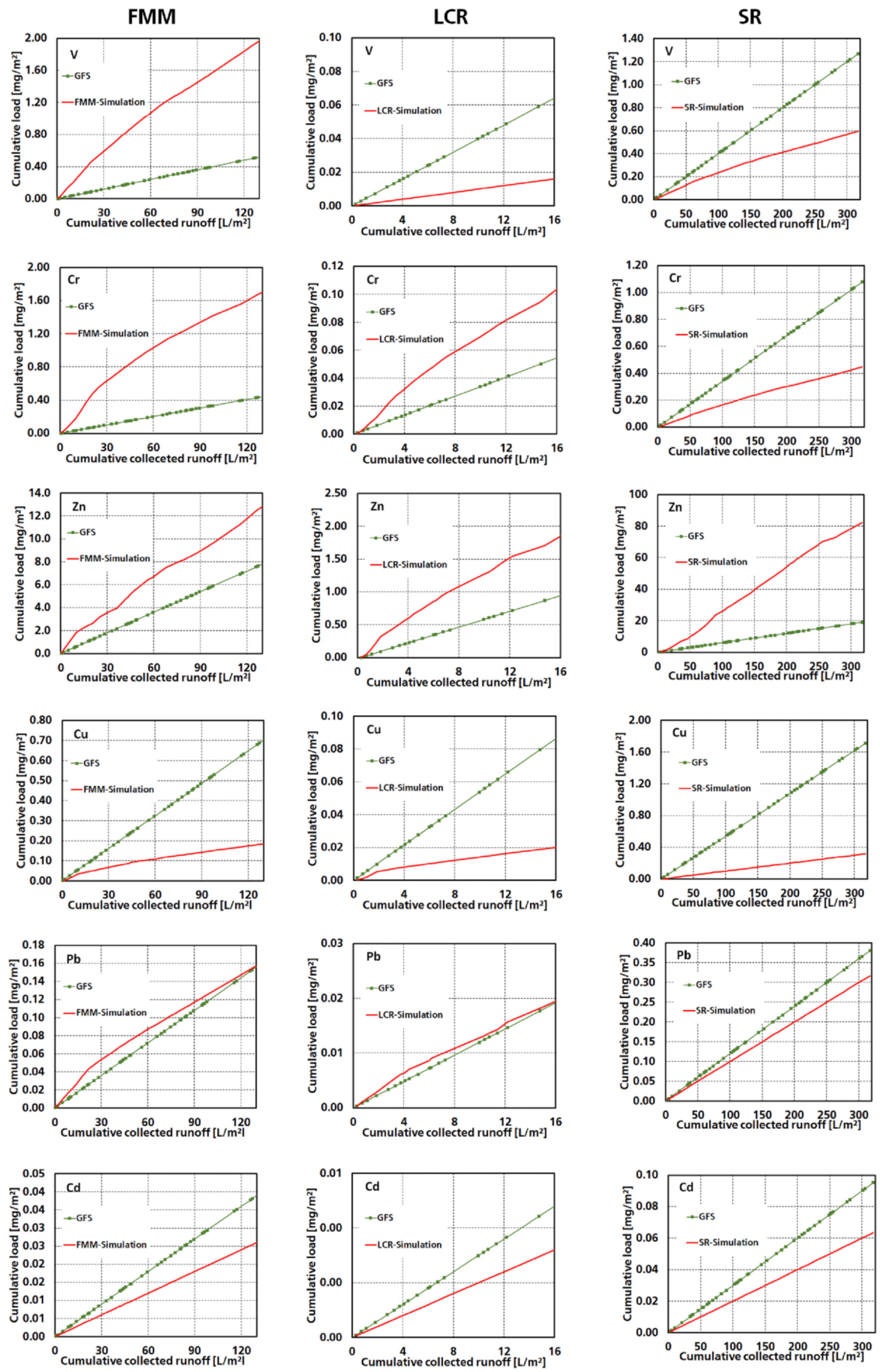

Fig. 3. Comparison results between simulated vertical test panels (VTPs) loads for facing masonry mortar (FMM), lime cement render (LCR), and reinforced render (SR) and the theoretical GFS loads at the point of compliance.

"Level 2" model (see Table S.1, Table S.2 and Table S.3) will be compared to the GFS (Table S.5). Leached substances with concentrations that are below the GFS target concentrations can then be discarded as they imply a no-significant alteration to the chemical status of the seepage water at a point of compliance. As single rain events have little meaning due to the many factors influencing the resulting runoff concentrations, cumulative substance loads obtained from VTPs during the observed time period and the corresponding theoretical GFS cumulative loads at the point of compliance were taken into account during the comparison. The runoff volumes, which are relevant for the aim of the study, are taken into the consideration as well.

Once the relevant substances have been obtained (substances that, due to their high load are greater than the theoretical GFS loads), they will be subject to the next step of the evaluation.

2) The relevant substances and their simulated concentration values for the mineral plasters and mortars are subjected to a statistical evaluation. The statistical evaluation will be done using the available Microsoft Excel tools. This statistical evaluation leads to the minimum, maximum, average, median, 70th percentile, 80th percentile and 90th percentile values of the concentrations obtained in the "Level 2" simulation. The statistical evaluation of the eluate concentrations is performed for each of the materials.
3) For façades coated with mineral plasters and mortars, a technical construction application must be selected from the GRA to derive the respective MEs. In such a case, technical construction application No. 13 is selected (Table 1). Technical construction application No. 13 of the GRA includes the following applications: base and sub-base layers without binding agents, land improvement surfaces, soil consolidation zones, substructures up to 1 m thick from the subgrade and excavation pits and pipe trenches under the surface layer. Base and sub-base layers without binding agents are comparable to an open gravel parking lot with no vegetation. The properties of the layer covering the groundwater according to Application No. 13 are hydrologically the most sensitive due to its high seepage water rate (859 mm/a) which allows a limit value derivation on a conservative side for façade runoffs [German Federal Ministry of Environment, 2018].
4) As a last step, the results of the statistical evaluation for each of the simulated plasters and mortars eluates are compared with the values defined for the different scenarios MEs of the selected technical construction application.

In accordance with the German Federal Ministry of Environment (2018) and Susset and Grathwohl (2011) the use of mineral plasters and mortars for a specific application in technical constructions is valid if the 90th percentile of the concentration values of all relevant substances comply with all MEs derived for the according application.

3. Results and discussion

3.1. Determination of relevant substances

The results of the comparison between the simulated VTPs cumulative loads and the theoretical GFS cumulative loads at the point of compliance to determine the relevant substances can be seen in Fig. 3. The graphs show the development of the cumulative loads depending on the duration of the weathering experiment and therefore the cumulated runoff volumes during this time period.

The cumulative load of vanadium (V) for the FMM (FMM = 1.98 mg/m^2) was above the theoretical GFS cumulative load (GFS-FMM = 0.52 mg/m^2). This is not the case for the LCR and the SR which have cumulative loads (LCR = 0.001 mg/m^2 and SR = 0.60 mg/m^2) below the V theoretical GFS cumulative loads (GFS-LCR = 0.07 mg/m^2 and GFS-SR = 1.27 mg/m^2).

For chromium (Cr) the cumulative loads for the FMM and the LCR were of 1.71 mg/m^2 and 0.11 mg/m^2, respectively. These loads were above the Cr theoretical GFS cumulative loads of GFS-FMM = 0.44 mg/m^2 and GFS-LCR = 0.06 mg/m^2. The Cr cumulative load for SR was below its respective theoretical GFS cumulative load (SR = 0.45 mg/m^2 and GFS-SR = 1.08 mg/m^2).

In the case of zinc (Zn), the three materials shown in Fig. 3 presented cumulative loads above the theoretical GFS cumulative loads. The Zn cumulative loads for FMM, LCR and SR were of 12.9 mg/m^2 1.95 mg/m^2 and 82.1 mg/m^2, respectively. In the meantime, the Zn theoretical GFS cumulative loads for FMM, LCR and SR were of 7.84 mg/m^2 1.00 mg/m^2 and 19.0 mg/m^2, respectively. However, the high concentrations of Zn in the eluates originate from the rainwater without contact with mortar and plaster as mentioned in Vega-Garcia et al., (2021). Therefore, despite having high concentrations, this substance will not be subject to the following evaluation steps.

Lead (Pb) was also one of the substances that presented high cumulative loads when compared to the theoretical GFS cumulative loads. This case was presented for FMM (FMM = 0.17 mg/m^2 and GFS-FMM = 0.16 mg/m^2) and LCR (LCR = 0.02 mg/m^2 and GFS-LCR = 0.02 mg/m^2) but not for the SR (SR = 0.32 mg/m^2 and GFS-SR = 0.38 mg/m^2).

For copper (Cu) and cadmium (Cd), none of the three materials cumulative loads were above their correspondent theoretical GFS cumulative loads.

As a result of the comparison between the simulated cumulative loads and the theoretical GFS cumulative loads, V, Cr, and Pb are considered to be relevant substances. All 18 tested mineral plasters and mortars consistently showed these substances as relevant. These substances presented loads above the theoretical GFS cumulative loads and might imply a hazardous potential to the chemical status of seepage water at the point of compliance. Only these substances will be subjected to the next steps of the GRA.

Table 2
Statistical evaluation for facing masonry mortar (FMM), lime cement render (LCR) and reinforced render (SR) simulated relevant substances concentration values.

FMM	pH	μg/L		
		V	Cr	Pb
Minimum	8.2	1.9	5.8	1.0
Maximum	8.4	23.8	29.4	2.2
Average	8.3	15.2	13.9	1.3
Median	8.3	13.9	11.6	1.0
70th Percentile	8.3	16.6	14.6	1.2
80th Percentile	8.3	18.8	17.7	1.7
90th Percentile	8.3	21.6	23.0	2.0
LCR	pH	**μg/L**		
		V	**Cr**	**Pb**
Minimum	8.2	1.0	1.5	1.0
Maximum	8.3	1.0	17.4	2.8
Average	8.3	1.0	7.3	1.3
Median	8.3	1.0	6.7	1.2
70th Percentile	8.3	1.0	7.8	1.6
80th Percentile	8.3	1.0	8.6	1.7
90th Percentile	8.3	1.0	9.5	1.8
SR	pH	**μg/L**		
		V	**Cr**	**Pb**
Minimum	6.7	1.0	1.0	1.0
Maximum	8.3	2.9	2.2	1.0
Average	8.3	1.9	1.4	1.0
Median	8.3	1.7	1.3	1.0
70th Percentile	8.3	2.0	1.5	1.0
80th Percentile	8.3	2.3	1.6	1.0
90th Percentile	8.3	2.7	1.8	1.0

Table 3
Groundwater risk assessment by comparison between statistical evaluation values (lower right number in cell) and media related application values (MEs) (upper left number in cell) for facing masonry mortar (FMM), lime cement render (LCR) and reinforced render (SR). Red cells: statistical values above their respective MEs. Green cells: 90th percentile values are below the MEs and suggest that the substance concentration is permissible for the selected technical application.

Groundwater risk assessment for mineral plasters and mortars		FMM			LCR			SR		
		V	Cr	Pb	V	Cr	Pb	V	Cr	Pb
Unfavourable case, highest expected groundwater level close (0.1-1m) to the bottom line of the technical construction	Minimum	30 / 1.9	15 / 5.8	34.5 / 10	30 / 1	15 / 1.5	34.5 / 1	30 / 1	15 / 1	34.5 / 1
	Maximum	30 / 23.8	15 / 29.4	34.5 / 2.2	30 / 1	15 / 17.4	34.5 / 2.8	30 / 2.9	15 / 2.2	34.5 / 1
	Average	30 / 15.2	15 / 13.9	34.5 / 1.3	30 / 1	15 / 7.3	34.5 / 1.3	30 / 1.9	15 / 1.4	34.5 / 1
	Median	30 / 13.9	15 / 11.6	34.5 / 1.0	30 / 1	15 / 6.7	34.5 / 1.2	30 / 1.7	15 / 1.3	34.5 / 1
	70th Percentile	30 / 16.6	15 / 14.6	34.5 / 1.2	30 / 1	15 / 7.8	34.5 / 1.6	30 / 2	15 / 1.5	34.5 / 1
	80th Percentile	30 / 18.8	15 / 17.7	34.5 / 1.7	30 / 1	15 / 8.6	34.5 / 1.7	30 / 2.3	15 / 1.6	34.5 / 1
	90th Percentile	**30 / 21.6**	**15 / 23**	**34.5 / 2**	**30 / 1**	**15 / 9.5**	**34.5 / 2**	**30 / 2.7**	**15 / 1.8**	**34.5 / 1**
Sand	Minimum	53.9 / 1.9	151 / 5.8	91.3 / 10	53.9 / 1	151 / 1.5	91.3 / 1	53.9 / 1	151 / 1	91.3 / 1
	Maximum	53.9 / 23.8	151 / 29.4	91.3 / 2.2	53.9 / 1	151 / 17.4	91.3 / 2.8	53.9 / 2.9	151 / 2.2	91.3 / 1
	Average	53.9 / 15.2	151 / 13.9	91.3 / 1.3	53.9 / 1	151 / 7.3	91.3 / 1.3	53.9 / 1.9	151 / 1.4	91.3 / 1
	Median	53.9 / 13.9	151 / 11.6	91.3 / 1.0	53.9 / 1	151 / 6.7	91.3 / 1.2	53.9 / 1.7	151 / 1.3	91.3 / 1
	70th Percentile	53.9 / 16.6	151 / 14.6	91.3 / 1.2	53.9 / 1	151 / 7.8	91.3 / 1.6	53.9 / 2	151 / 1.5	91.3 / 1
	80th Percentile	53.9 / 18.8	151 / 17.7	91.3 / 1.7	53.9 / 1	151 / 8.6	91.3 / 1.7	53.9 / 2.3	151 / 1.6	91.3 / 1
	90th Percentile	**53.9 / 21.6**	**151 / 23**	**91.3 / 2**	**53.9 / 1**	**151 / 9.5**	**91.3 / 2**	**53.9 / 2.7**	**151 / 1.8**	**91.3 / 1**
Loam/silt/clay	Minimum	452 / 1.9	284 / 5.8	252 / 10	452 / 1	284 / 1.5	252 / 1	452 / 1	284 / 1	252 / 1
	Maximum	452 / 23.8	284 / 29.4	252 / 2.2	452 / 1	284 / 17.4	252 / 2.8	452 / 2.9	284 / 2.2	252 / 1
	Average	452 / 15.2	284 / 13.9	252 / 1.3	452 / 1	284 / 7.3	252 / 1.3	452 / 1.9	284 / 1.4	252 / 1
	Median	452 / 13.9	284 / 11.6	252 / 1.0	452 / 1	284 / 6.7	252 / 1.2	452 / 1.7	284 / 1.3	252 / 1
	70th Percentile	452 / 16.6	284 / 14.6	252 / 1.2	452 / 1	284 / 7.8	252 / 1.6	452 / 2	284 / 1.5	252 / 1
	80th Percentile	452 / 18.8	284 / 17.7	252 / 1.7	452 / 1	284 / 8.6	252 / 1.7	452 / 2.3	284 / 1.6	252 / 1
	90th Percentile	**452 / 21.6**	**284 / 23**	**252 / 2**	**452 / 1**	**284 / 9.5**	**252 / 2**	**452 / 2.7**	**284 / 1.8**	**252 / 1**

Application no 13: Base and sub-base layers without binding agents, land improvement areas, soil consolidation zones, substructures up to 1 m thick from the subgrade and excavation pits and pipe trenches under the surface layer

3.2. Statistical evaluation for the concentrations of the relevant substances

As a second step, the identified relevant substances from section 3.1 were subjected to a statistical evaluation. The simulated concentrations for V, Cr and Pb for the three tested materials FMM, LCR and SR (see Table S.1, Table S.2 and Table S.3) were evaluated. The results of the statistical evaluation are presented in Table 2.

The results in Table 2 give an example of the concentration distribution for FMM, LCR and SR eluates (μg/L). The substance with the highest concentrations for the three plasters and mortars was Cr (FMM = 29.4 μg/L, LCR = 17.1 μg/L and SR = 2.2 μg/L). At the same time, the substance with the lowest concentrations was Pb (FMM = 2.2 μg/L, LCR = 2.8 μg/L and SR = 1.0 μg/L). It is important to mention that not all evaluated substances are above the GFS values for some materials (e.g., LCR = V and SR = V, Pb and Cr). However, they are included in the evaluation for practical comparison purposes. When comparing the statistical evaluation for FMM with LCR and SR, it can be seen that this material presented higher concentrations for each of the determined relevant substances and therefore might be the material with the highest hazardous potential.

3.3. Comparison between statistical evaluation values and media related application values (MEs)

As a last step, the MEs (Table 1) and the values from statistical evaluation (Table 2) were compared to determine the applicability of the mineral plasters and mortars regarding to the selected technical application (see section 2.6) of the GRA. The results can be seen in Table 3.

For the unfavorable case scenario where the groundwater level is between 0.1 and 1 m under the bottom of the technical construction or permanent application, the 90th percentile values of Cr concentrations for FMM are above the MEs. The 90th percentiles for V, Cr and Pb for the sand scenario were all below the MEs. For the loamy, silty and clayey soil scenario none of the statistical evaluation values for any of the materials were above the MEs.

As mentioned in section 2.6, in accordance with the German Federal Ministry of Environment (2018) and Susset and Grathwohl (2011), the use of a mineral construction product for a specific application in a technical construction is valid if the 90th percentile of the statistical concentration values of all relevant substances comply with all MEs derived for the according application. In accordance with the presented results, the FMM cannot be used for the unfavorable case scenario (groundwater level is between 0.1 and 1 m of the bottom of the technical construction or permanent application) in the selected technical application (application No. 13). The reason for this is that for the FMM, Cr 90th percentile values are above the MEs. For the sand soil scenario the three materials applicability are valid for the technical application scenario because the 90th percentiles of V, Cr and Pb are below the MEs. For the loamy, silty and clayey soil scenario the 90th percentiles of all substances for the three materials are below their respective MEs. Hence, the applicability of the FMM, LCR and SR is valid for this technical application scenario.

From the results presented, it can be concluded that Cr would be the only substance with 90th percentile values above MEs that would not allow the use of FMM for the unfavorable case scenario. Meanwhile, the other substances would favor the validity of the three materials in the remaining scenarios (sand soil and loamy, silty and clayey soils) within the selected technical application.

4. Conclusions

The GRA served as a guideline to evaluate the environmental characteristics of different mineral plasters and mortars. This evaluation is considered within the three-stage model as "Level 3." Three examples are presented in this contribution based on simulated VTPs runoff concentrations obtained by a previous study ("Level 2" model). The media related application values (MEs) of technical construction application No. 13 from the GRA were selected to validate the applicability of the source term concentrations. This technical construction application contemplates the characteristics of surface and sub-surface layers commonly found in urban areas where most of the façades coated with plasters and mortars are found.

Following the steps of the GRA the relevant substances were determined as a first step. Comparing the results of the simulated VTPs cumulative loads with the theoretical GFS cumulative loads, it was obtained that the relevant substances found in the materials runoffs were vanadium, chromium and lead. The VTPs runoff concentrations for these substances were then subjected to a statistical analysis which results then served as values to compare against the MEs of the technical application No. 13 from the GRA.

After comparing the statistical evaluation values against the MEs it was determined that chromium was the only substance considered to limit the application validity of the FMM for the unfavorable case scenario of the technical application No. 13.

In conclusion, the validation for the applicability of the LCR and SR in the unfavorable case scenario for technical construction application No. 13 of the GRA is positive, as it is also the validation for the applicability of the FMM, LCR and SR for the sand soil scenario and the loamy, silty and clayey soils scenario.

It should be noted that the three-stage model was limited to mineral mortars and plasters as well as inorganic ingredients. Due to the fact that environmental impact of material leached substances are of high importance nowadays a GRA within a three-stage model for organic plasters containing biocides will be subject of further publications.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2021.132176.

Credit author statement

Pablo Vega-Garcia: Writing – original draft preparation, valdidation, Formal analysis, Conceptualization, Data curation; Regina Schwerd: Conceptualization, Supervision, writing - reviewing and editing, Project administration; Sabine Johann: investigation, data recopilation; Christoph Schwitalla: investigation, data recopilation; Christian Scherer: funding acquisition, reviewing and editing; Brigitte Helmreich: methodology, Supervision, writing - reviewing and editing.

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A. 4 Influence of façade orientation on the leaching of biocides from building façades covered with mortars and plasters

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Influence of façade orientation on the leaching of biocides from building façades covered with mortars and plasters

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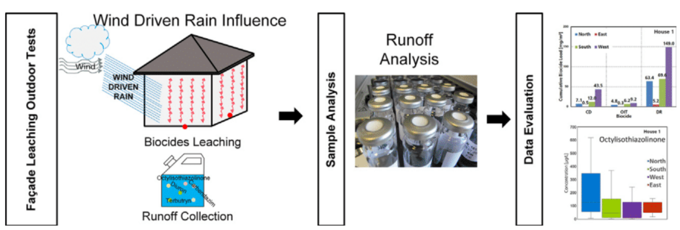
HIGHLIGHTS

- Façade leaching was investigated under real conditions at all cardinal directions.
- The weather side has a higher runoff load of biocides.
- The results could influence the development of on-site treatment plants.

GRAPHICAL ABSTRACT



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ABSTRACT

Biocides used in building façades to prevent potential growth of algae, fungi and bacteria are of major concern regarding the quality of stormwater runoff. The aim of the study was to analyze the influence of the façade orientation on the biocide release under real weather conditions to gain information for the development of on-site treatment systems. Field tests with model houses containing two different plaster compositions were carried out over a period of 18 months. The results of the analyzed rain events demonstrate that façade orientation plays an important role in the leaching loads of biocides. Biocide loads in the runoff decreased corresponding to the wind direction. High cumulated active substance discharges of diuron (149 mg/m^2), carbendazim (43.5 mg/m^2), terbutryn (9.3 mg/m^2) and octylisothiazolinone (OIT) (31.9 mg/m^2) were found in the runoff of the façades facing the predominant weather orientation. Meanwhile, the highest concentrations of diuron (2.8 mg/L) and OIT (0.7 mg/L) were observed in the runoff from façades with smaller runoff volumes. The obtained results demonstrate that treatment facilities have to be installed at all building sides. The hydraulic and the substance load is highest at the weather side, which has a strong influence on the dimension and the lifetime of the treatment system.

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1. Introduction

Plasters and mortars are mostly used as part of façade external thermal insulation composite systems (ETICS) as coatings and are mostly containing biocides as active substances to prevent the potential algal, bacterial and fungal growth and to enhance the durability of the

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materials. Biocides from building materials are meanwhile of major concern regarding the quality of receiving waters (surface water and groundwater) [e.g., Bester et al., 2014; Bollmann et al., 2014; Hensen et al., 2018; Wittmer et al., 2011a; Wangler et al., 2012; Wicke et al., 2015; Paijens et al., 2019]. Their general leaching and wash off effect and also the transport of biocides with stormwater runoff is summarized in Paijens et al. (2019). Leached biocides are also subject to several processes, such as dilution, degradation and sorption that reduce their concentrations before they reach receiving waters [e.g., Burkhardt et al., 2011; Coutu et al., 2012; Bollmann et al., 2017; Hensen et al., 2018].

Leaching of biocides from ETICS does not only depend on the availability of water, but is also controlled by transport processes within the materials and the stability of the observed substances [Schoknecht et al., 2016a, 2016b]. The leaching mechanism occurs as follows: 1) water which is adsorbed at the surface of the façade is transported to deeper layers, 2) biocides are dissolved from particles or microcapsules, 3) the biocide is transported via diffusion (driven by concentration gradient, dependent on temperature, etc.), 4) some biocides are degraded via photolysis or hydrolysis, leading to a reduction of some biocide concentrations, and 5) the biocide is transferred to the water on the surface of the coating where evaporation and water up-take occurs [Blocken et al., 2013; Schoknecht et al., 2009; Styszko and Kupiec, 2016; Uhlig et al., 2019]. Wangler et al. (2012) further found out that a temperature increase results in an increased emission rate.

During rain events, ETICS become moist due to wind driven rain (WDR), a horizontal velocity component of the wind that is driven against the windward façade of buildings [Blocken et al., 2013]. WDR is the most important contributor to the moisture load on building façades [Burkhardt et al., 2012; Blocken et al., 2013; Bester et al., 2014]. While Burkhardt et al. (2012) first postulated that weather conditions (precipitation, rain intensity, wind speed, wind direction, temperature), façade geometry (height, weight), site characteristics (latitude, altitude) and façade exposure (orientation) are the main influencing factors of the leaching process, Bester et al. (2014) and Schoknecht et al. (2016a, 2016b) argued that the amount of WDR in contact with the surfaces is the only weather parameter that influences the leaching of biocides. Others, such as precipitation, rain intensity, length of the dry period, solar irradiation during the dry period etc., had no detectable influence on the emissions of biocides from façades. The more WDR, the higher the leaching [Bester et al., 2014; Bollmann et al., 2014].

The maximum concentrations of biocides in the stormwater runoff of façade coatings tend to be higher in the early lifetime of the coatings, reaching fairly constant concentration levels later on, generally in the range of hundreds of μg/L to mg/L [Burkhardt et al., 2009; Burkhardt et al., 2012; Bollmann et al., 2014]. Uhlig et al. (2019) argued that the leaching is not fairly constant, instead there exist phases of higher leaching events far beyond the initial exponential decay. These events reveal changes in the slope after several years of field exposure.

To gain information on the leaching of biocides from ETICS coatings a variety of studies have been carried out at the laboratory scale [e.g., Bollmann et al., 2016; Burkhardt et al., 2007; Schoknecht et al., 2009; Wangler et al., 2012; Styszko et al., 2014] or under field conditions [e.g. Burkhardt et al., 2011; Burkhardt et al., 2012; Wangler et al., 2012], focused on biocides from organic façade coatings (plasters and paints). Models to examine the biocide leaching process have been developed [e.g., Wittmer et al., 2011b; Coutu et al., 2012]. Standard test methods at the laboratory scale are one approach to obtain data on the leachability of biocides form façade coatings [e.g., EN 16105, 2011; CEN/TS 16637-1:2014-11, 2014; CEN/TS 16637-2:2014-11, 2014]. The procedures use a fixed volume-to-surface ratio and are based on long-term immersion in eluent or consist of wetting cycles and drying phases where the eluent is regularly renewed. While in laboratory experiments the production of a test specimen and its experimental procedure are defined, in outdoor tests, specimens are subjected to real weather influences like WDR that affect the surface of an exposed coating. Temperature and UV irradiation can influence organic substances through transformation and degradation processes [Bollmann et al., 2016, 2017; Schoknecht et al., 2009].

Concentrations found in laboratory leaching tests are not directly comparable to real-life situations with actual weather conditions [Bandow et al., 2018]. When assessing treatment options with respect to effective biocide elimination, it is not sufficient to focus only on first flushes because biocide discharges occur throughout the entire lifetime of the ETICS [Bollmann et al., 2014]. A database of a long-term study is the precondition for the modelling of biocide releases. With regard to treatment options, both concentration and load measurements are important for different weathering situations (different orientations of the façades). The question arises whether treatment systems have to be built on all sides of the building or whether it is sufficient to install a system only on the weather side. This can only be evaluated under realistic weather conditions and with long-term tests.

The first investigations on the leaching of ingredients from ETICS under real climatic conditions began at the Fraunhofer Institute for Building Physics IBP in 2004. The focus was initially not on the environmental compatibility of the façade coatings but on the durability of the protective effect of the biocides used depending on the plaster matrix [Schwerd, 2011Schwerd et al., 2015]. There are only some studies which focus on investigation with vertical test panels or on side-oriented façades under real weather conditions [Bester et al., 2014; Bollmann et al., 2016; Burkhardt et al., 2012; Hensen et al., 2018; Scherer, 2013; Schwerd, 2011;Schwerd et al., 2015]. However, so far no study has investigated the leaching of ingredients under real climatic conditions on façades oriented to different directions at the same time, which is the objective of the present study.

The hypothesis of the study is that, because wind driven rain is the main influencing factor on the release of biocides from building façades, the biocide load is highest at the weather side compared to the other sides. This could influence further investigations on the development of on-site treatment plants. The hypothesis can only be verified with long-term experiments under real weather conditions on a real scale.

In order to obtain a meaningful database, field tests were carried out using model houses containing two different plaster compositions with biocides which were oriented in all cardinal directions (north, east, south and west). Leaching and weather conditions were monitored on all sites during a time period of 18 month.

2. Materials and methods

2.1. Sampling site

The sampling site was located in the yards of Fraunhofer Institute for Building Physics IBP (47°52′30"N, 11°43′41″E) in Valley (Bavaria), Germany. Two square experimental houses (each 3 m wide, 2.4 m high façades) consisting of prefabricated wooden house elements with a tent roof were constructed. On the wooden house elements, insulation panels consisting of polystyrene were attached. The panels were covered by reinforced fabric and a basecoat mortar which did not contain any biocides. The roofs were covered with bituminous membranes. Stormwater runoff from the roof was collected using rain channels and drained directly to the ground surface without any contact with the façades. A third house was built in order to house the power supply, the wind driven rain gauges and the on-site weather station. The three houses were oriented towards the main cardinal points (see Fig. 1).

Before the test period, two different plasters with a defined composition and mixed with 7.6 g/m^2 (house 1) and 8.9 g/m^2 (house 2) of biocide formulation were applied to the reinforcement layers of the model houses. The compositions were as follows:

- House 1: 12% Dispersion polymer, 3% white pigment, 4% marble grain, 27% marble flour, 40% dolomite grain, 3% flame retardant, 2% coalescent and 9% water.
- House 2: 14% Dispersion Polymer, 3% white pigment, 40% marble

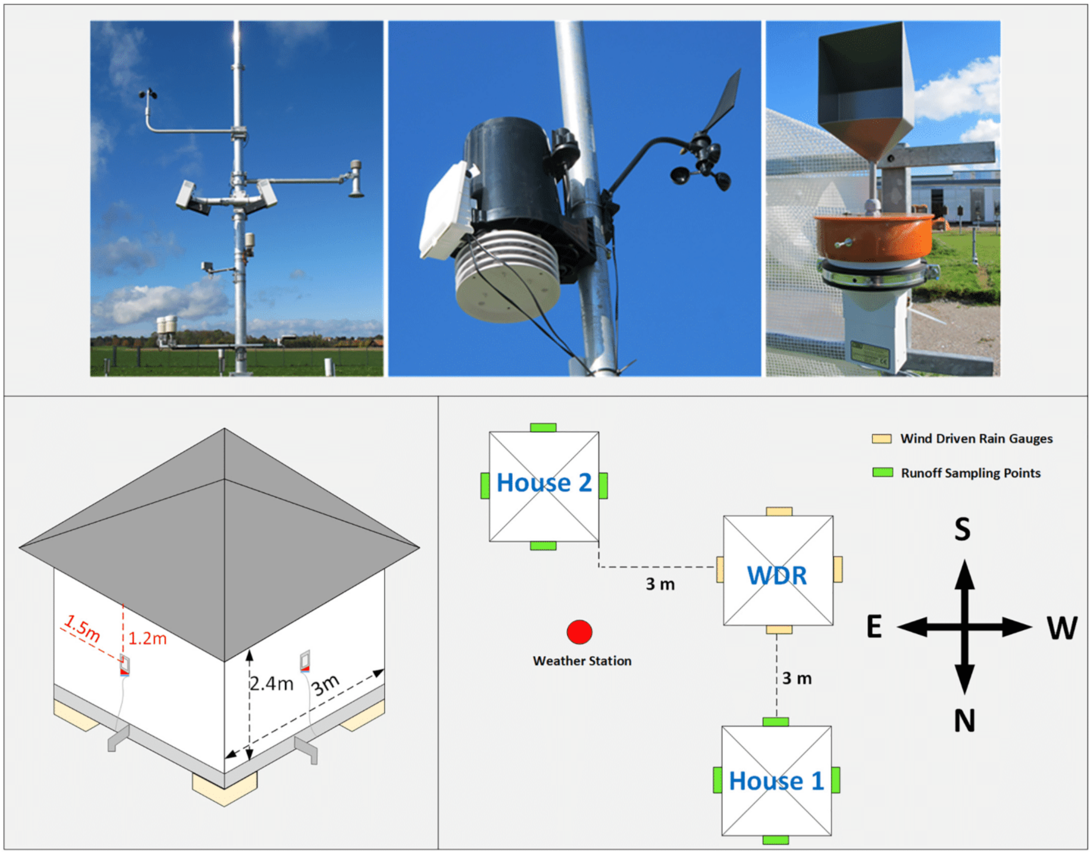


Fig. 1. Weather station and wind driven rain gauges installed on site (up). Sketch of the model houses and map of experimental site (down).

grain, 31% marble flour, 3% flame retardant, 2% coalescent and 7% water.

As a result, depending on the concentration of active ingredient in the biocide formulation which were added to the model houses, concentrations of 140 to 1000 mg/kg of active ingredient (biocide) per kilogram of original plaster were applied. House 1 included 3 mm of dispersion plaster (4.8 kg/m^2) with the "naked" biocides octylisothiazolinone (OIT), diuron (DR) and carbendazim (CD) with initial contents of 140 mg/kg, 1000 mg/kg and 450 mg/kg, respectively. Meanwhile, house 2 also included 3 mm of dispersion plaster (10.5 kg/m^2) with the encapsulated biocides: OIT, terbutryn (TB) and zinc-pyrithion (ZnPT) with initial contents of 225 mg/kg, 400 mg/kg and 225 mg/kg, respectively. The active ingredient ZnPT was not analyzed in the framework of this project.

The recipes were compiled especially for the research project and aimed at reflecting market products to get real conditions for the experiments to achieve representative data. The setup was achieved in cooperation with several important German companies of the construction industry. The ETICS recipes selected for this study were considered as realistic scenario formulations which are not available on the market and contain a maximum proportion of potentially ecologically questionable components. The experimental setup was based on 10 years of experience at the Fraunhofer IBP with a large number of formulations of plasters and mortars [Scherer, 2013; Schwerd, 2011; Schwerd et al., 2015]. More than a hundred test specimens with over 20 (mineral and pasty) mortars and plasters were set up, as well as the three especially constructed test houses in order to capture the influence of WDR as realistic as possible.

The physical-chemical properties of the analyzed encapsulated biocides are given in Table 1.

2.2. Measurement of weather conditions

A weather station (Davis-Vantage Pro) was installed directly beside the model houses (see Fig. 1). The weather station used is capable of recording wind speeds up to 322 km/h, temperatures between −40 °C and 65 °C, and precipitation height in 0.2 mm increments. Precipitation heights (vertical rain), temperature, UV irradation, wind speed and wind direction were recorded every 5 min.

In order to record the amount of WDR on the vertically exposed house façades, several WDR gauges were installed. The customized rain gauges were manufactured by Fraunhofer IBP with the following characteristics: collecting surface of 200 cm^2, 0.2 mm resolution and measuring accuracy of ±3% in the range of up to 5 mm/min (see

Table 1
CAS numbers, groups, molecular masses, physical-chemical properties (Octanol-water-partitioning coefficient (Log KOW) and Water solubility (WS) [Bester et al., 2014], half-life time (DT50) [Paijens et al., 2019], median lethal dose (DL50) [PubChem Database], predicted-no-effect concentrations (PNEC) [Burkhardt et al., 2009] and German insignificance threshold values for groundwater (GFS) [LAWA, 2016].

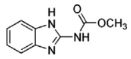
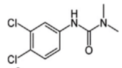
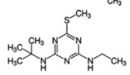
Compound (Abbreviation)	Group	Chemical structures	Molecular mass (g/mol)	Log K_{OW} at pH 7	WS (mg/L)	PNEC (μg/L)	GFS LAWA (μg/L)	DT50 in fresh waters (days)	DL50 (mg/kg)	CAS-No.
Carbendazim (CD)	Carbamates		191.2	1.55	3112	0.034	0.1	42–350	>6400	10,605–21-7
Diuron (DR)	Phenylureas		233.1	2.67	102	0.020	0.05	113–2190	3750	330–54-1
Octylisothiazolinone (OIT)	Isothiazolinones		213.3	2.61	309	0.013	0.1	30	550	26,530–20-1
Terbutryn (TB)	Triazines		241.4	3.77	42	0.034	0.1	354	>2000	886–50-0

Fig. 1). Four gauges were placed in the center of each side of the third house, aligned in the direction of the cardinal points.

2.3. Sampling process and analysis

During the sampling period, the effluents from each façade of the model houses were channeled through stainless steel gutters into buried canisters. A total of 49 rain events (with collection of the sample after every separate rain event) were analyzed over the 18 months monitoring period.

After each single rain event, the total volume of the runoff was measured and an aliquot was taken out of the sampling device and filled into 0.5 L brown glass bottles. The rest of the collected water was discarded. Subsequently, the aliquots were prepared the same day for the analyses.

General parameters such as runoff volume and pH-value were determined as part of this analysis. The pH value was analyzed according to EN ISO 10523 (2012) using a three-channel multiparameter meter with electrodes with a measuring range from 0 to 14 pH and accuracy of ±0.004 (WTW-Multi 3430; Electrodes WTW-Sentix940). Biocide concentrations were quantified according to method DIN 38407-36, 2014 with Ultra-High Performance Liquid Chromatography (UHPLC) coupled with Tandem Mass Spectrometry (LC-MS/MS) (ACQUITY UPLC I-Class, Xevo TQ-S (Waters), gradient water (0,01% HCOOH) / methanol (0,01% HCOOH); column: C18 EC 100 mm × 2,1 mm, 1,7 μm (Waters); injection volume 1 μL) using electrospray ionization in positive mode (ESI (+)). Detection limits for the analyzed biocides were: DR: 0.012 μg/L, CD: 0.005 μg/L, OIT: 0.016 μg/L, and TB: 0.003 μg/L.

2.4. Statistical analysis

A correlation analysis between the weather data and the observed biocide emissions was performed in order to investigate the relations between the different weather parameters and the amount of leached biocides. For this correlation analysis the following data was included: façade runoff volume (RV), wind-driven rain (WDR), temperature during precipitation (T), wind speed during precipitation (WS), wind direction during precipitation (WD), rain intensity (RI), rain duration (RD), total precipitation volume (P), antecedent dry period (ADP) prior to the main rain event, median UV irradiation (UV) during ADP, median solar radiation (SR) during ADP, pH-value, electrical conductivity (EC), total organic component (TOC) of individual runoff samples and the TB, DR, OIT and CD runoff loads. The Spearman's rank correlation coefficients were calculated due to the high robustness against outliers.

Spearman correlations and heat maps were performed using Spyder (Open source package that distributes the Python programming language) version 3.3.6. Heat maps were used to plot the results of the correlation analysis. The colors of the heat map denote the rank values. The darkest blue color refers to the strongest positive correlation (perfect positive association of ranks, +1.0), the darkest red color refers to a negative correlation (perfect negative association of ranks, −1.0) and the white color refers to a non-relationship between the considered weather parameters (non- linear relationship, 0.0). Throughout this paper, the strength of the Spearman's correlation coefficients was defined as follows:

0.00–0.19, very weak; 0.20–0.39, weak; 0.40–0.59, moderate; 0.60–0.79, strong and 0.80–1.00, very strong [Kendall, 1970].

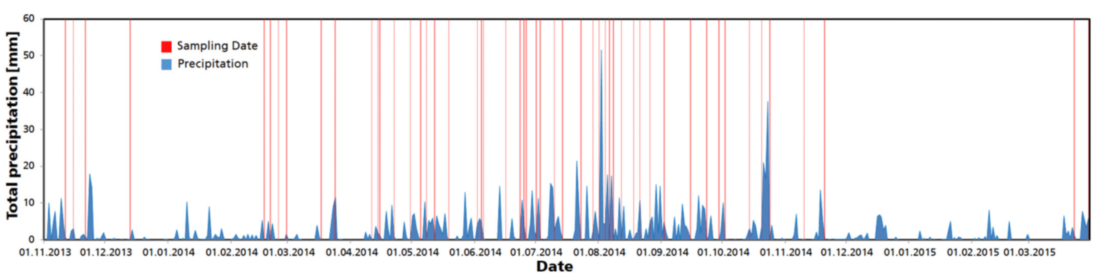


Fig. 2. Precipitation daily values and runoff sampling dates.

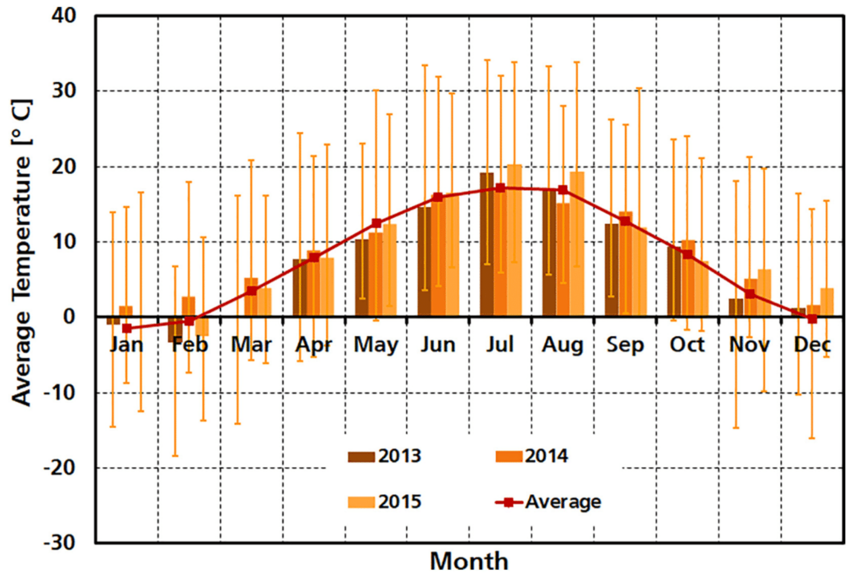


Fig. 3. Course of the monthly mean temperature, minimum and maximum.

To report the statistical significance of the correlation analysis, the p-value between the variables were used to determine the probability that a correlation occurred by chance. A high statistical significance of $p \leq .05$ indicates that the data used in the correlation analysis is a perfectly random sample, a large statistical significance of $p \geq .05$ indicates that the data is a weak sample and finally a statistical significance of $p > .5$ indicates that the data can be considered marginal [Biau et al., 2010]. The selected significance level of the analysis was $p = .05$.

3. Results and discussion

3.1. Weather conditions and collected runoff volumes

In Valley, there are approximately 180 rain days per year. The monthly precipitation during the weathering period of October 2013 to March 2015 ranged from 8.7 mm (L/m^2) in December 2013 to 224 mm in August of 2015. Detailed information about the daily precipitation during the sampling period and the runoff sampling dates is depicted in Fig. 2. During the 526-day observation period, precipitations with >0.1 mm occurred during 255 days. The strongest rain event occurred on August 2, 2014, reaching 60.4 mm.

The lowest temperature recorded during the study period was −16.1 °C (December 29, 2014). The highest temperature of 32.1 °C was measured on June 19, 2014. In Fig. 3, the maximum, minimum and mean temperatures during the study period are shown.

The wind at the sampling side comes mainly from the west and southwest directions (Fig. 4). The highest daily mean wind speed observation was 8 Bft (66 km/h) on March 31, 2015. During this day, the gusts reached a maximum speed of 10 Bft (98 km/h).

The amount of collected runoff volume during the sampling period increased depending on the façade orientation. The ratio of obtained

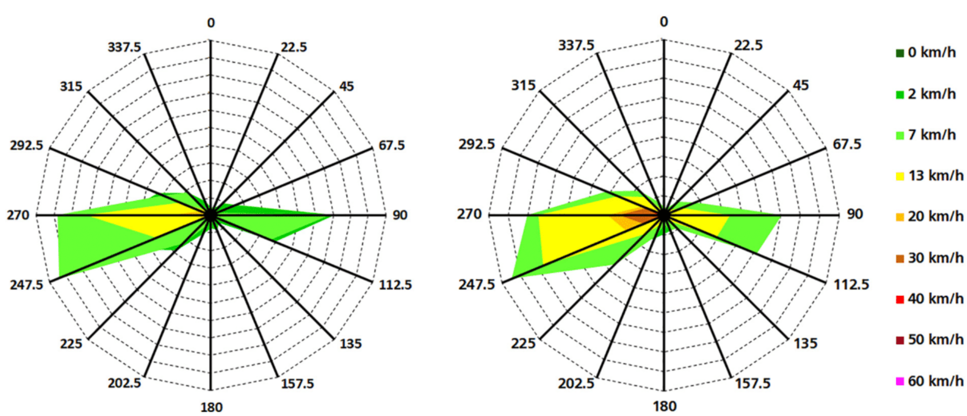


Fig. 4. Prevailing wind direction, average wind speed (left) and maximum wind speed (right).

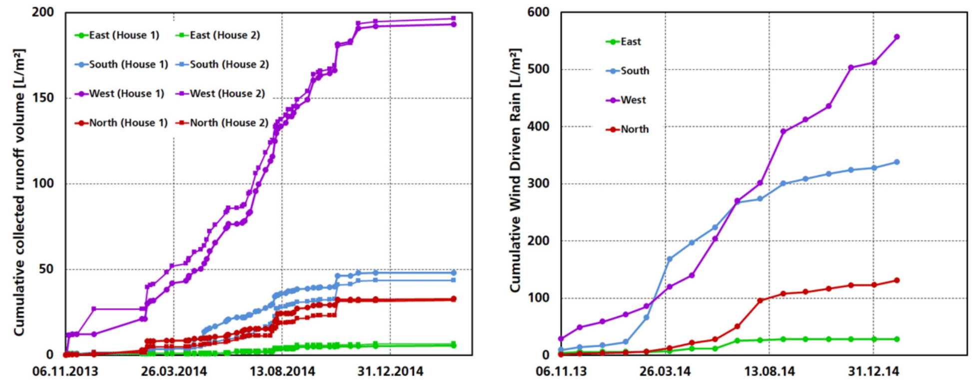


Fig. 5. Right: Cumulated collected runoff volume of house 1 and house 2 during the monitoring period depending on the orientation. Left: Wind Driven Rain measurement of house 1 and house 2 during the monitoring period depending on the orientation.

runoff volumes was: East:North:South:West = 1:6:8:34, which ultimately reflects in the wind direction (see Fig. 4). The lowest cumulative collected runoff volume in both houses over the monitoring period was 5 L/m^2. This runoff volume corresponds to an east-facing façade. On the other hand, the highest cumulative collected runoff volume was approx. 200 L/m^2 and was obtained at a west-facing façade (Fig. 5). The amount of runoff is directly related to the amount of water that impinged the façade. This relationship can be seen in Fig. 5 where the highest WDR measurement during the test months as well as for the collected runoff volume was observed on the west façade (556 L/m^2). This same behavior was observed on the east façade, which had the lowest WDR measurement (28 L/m^2) as well as the lowest collected runoff volume. The ratio of measured WDR was: East:North:South:West = 1:6:12:20, which as well as the collected runoff, reflects the wind direction.

With regard to the dimensioning of on-site treatment facilities, it must be taken into account that on the weather side the runoff volume to be treated is many times higher compared to the other sides, which can make drainage a hydraulic challenge. On the other hand, the

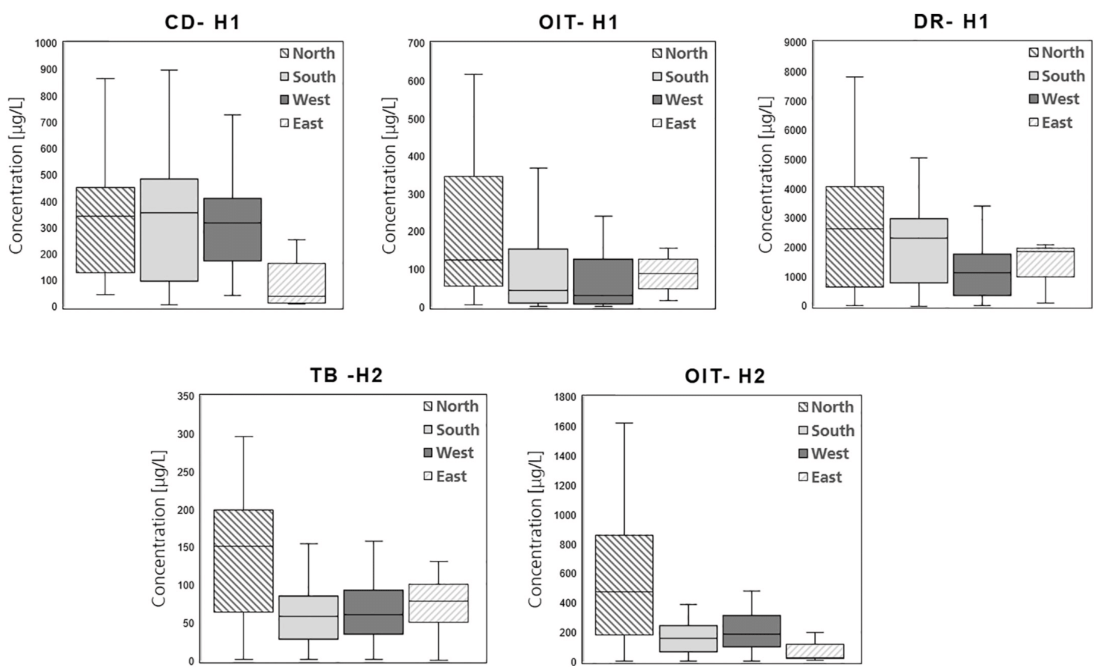


Fig. 6. Biocides concentrations in the runoff of house 1 (up) and house 2 (down) for each of the façade orientations. Note: To construct the box plot the numerical data from the concentrations is divided into quartiles, a box is drawn between the first and third quartile, with an additional line drawn along the second quartile to mark the median, the minimum and maximums out the first and third quartiles are represented with lines.

treatment facilities on the other building sides can be made smaller for hydraulic reasons. It is therefore very important to always know the climatic conditions on side.

3.2. Biocide concentrations and loads

The biocide concentrations in the runoff from the two model houses are shown in Fig. 6, relating to the cardinal directions.

In general, the runoffs had high median active substance concentrations of 2.6 mg/L (DR, house 1, north façade), 0.3 mg/L (CD, house 1, north façade), 0.5 mg/L (OIT, house 2, north façade) and 0.1 mg/L (TB, house 2, north façade), respectively. When concentrations were found, the lowest biocide concentrations were of 1.2 mg/L (DR, house 1, west façade), 96 μg/L (CD, house 1, west façade), 87 μg/L (OIT, house 1, east façade) and 63 μg/L (TB, house 2, south façade). Detailed data on concentrations and loads given in supplementary data S1. It can be seen that the highest median biocide concentrations of all biocides were observed in the runoff from the north façade of both houses. All median concentrations were over the insignificance threshold values for evaluating locally restricted groundwater pollution in Germany (GFS-values, see Table 1) (LAWA, 2016). The Groundwater EU Directive 2006/118/EC (2006) of the European Union mentions 0.1 μg/L as quality standard for single substances. All median concentrations exceed the values for predicted-no-effect concentration (PNEC) (see Table 1), which is necessary for their intended uses and should be evaluated at the point of assessment after consideration of the distribution pathways. However, the runoff concentrations are also of concern to the environment when it is discharged to surface waters. For example, DR is on the EU list of priority substances in the field of water policy and has a maximum allowable concentration of 1.8 μg/L for surface waters [EU 2008/105/EC, 2008]. As for different target areas (e.g. groundwater, surface water) different criteria at defined "points of concern" are to be applied, transport processes and distribution scenarios have to be taken into account when evaluating the environmental impact of runoff waters. Anyway it is helpful to compare the criteria to the concentrations of façade runoff directly to get an idea of the overall necessity of further modelling.

As a result, the monitoring of the concentrations demonstrates that not only the weathered side (wind comes mainly from the west and southwest directions, see Fig. 4 and runoff volume was highest at the west side, see Fig. 5) has to be taken into account for the installation of on-site treatment facilities. Regarding concentrations, the runoff from all sides has to be treated in order to avoid groundwater contamination.

Table 2
Magnitude of the biocide loads in respect of the façade direction.

House	North (N) [mg/m²]	South (S) [mg/m²]	West (W) [mg/m²]	East (E) [mg/m²]	Load Magnitude Order
House 1					
CD	7.1	11.9	43.5	0.5	W > S > N > E
DR	63.4	69.6	149.0	5.2	W > S > N > E
OIT	4.8	6.7	9.2	0.3	W > S > N > E
House 2					
OIT	16.3	7.3	31.9	0.6	W > N > S > E
TB	3.4	1.9	9.3	0.4	W > N > S > E

The cumulative load of biocides in the runoff was calculated with the measured concentrations and runoff volumes. The cumulative runoff volume decreased in the following order West > South > North > East, corresponding to the main wind directions. Fig. 7 shows as result that biocide loads are also in the expected order: West > South > North > East. The magnitude of the loads according to the previous presented order can be seen in Table 2 for house 1. However, for house 2, the cumulative loads at the north side were lower than on the weather-favored west side, and sometimes higher than on the south side, which was more wind-oriented (see Table 2). The reason for this could be that the north side remains moist due to the lower solar irradiation, in comparison to the south side, which dries off quickly, especially in the summer, leading to less biocide degradation and therefore higher concentrations of the original substances in the ETICS [Bollmann et al., 2016 and 2017; Burkhardt et al., 2011; Coutu et al., 2012; Schoknecht et al., 2009]. This effect could lead to a higher concentration in the runoff of the north façade. In contrast to this, high solar irradiation on the south façade may lead to photolytically induced degradation. Additionally, higher temperatures may result in higher biocide losses due to evaporation of substances [Schwerd, 2011Schwerd et al., 2015].

It can be highlighted that the statement that the WDR leads to the highest leaching [Bester et al., 2014; Bollmann et al., 2014] cannot be proven due to concentration measurements. However, based on load calculations, the WDR is the most influencing factor on the leaching. The development of on-site treatment systems is not topic of this investigation, but for the development it should be taken into account that the load is decisive for the design of on-site treatment facilities.

The cumulative biocide load decreases in the order of DR > CD > OIT based on the initial biocide contents. This was the case for house 1, but not for house 2 where the initial TB content was almost two times higher compared to OIT. In house 2 the cumulative OIT load was much higher than the cumulative TB load after the 18-month period (e.g., 31.9 mg/m², OIT- West >9.3 mg/m²; TB- West). One reason for this could be the significantly lower water solubility but higher log

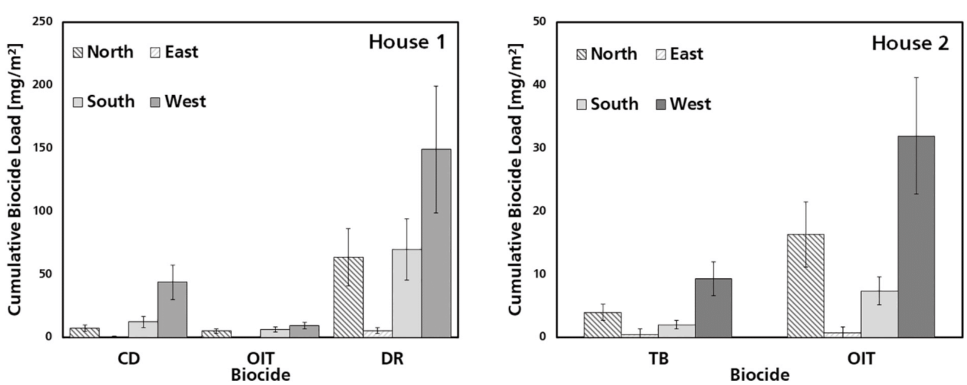


Fig. 7. Façade orientation dependent cumulative active substance load in the runoff from house 1 and house 2 after 18 months of weathering.

k_{OW} of TB compared to OIT (see Table 1). The mean pH values for both houses' runoffs were 7.2, where log k_{OW} can be applied. The pH values of the runoffs from both houses were in the range of 6.1 to 8.1, with a median value of 7.19.

In addition, it was possible to relate the determined loads with the calculated initial content of active substances in the façade. The highest load percentages in relation to the initial content were always found on the west façades. For house 1 there were 2.0%, 1.4% and 3.1% of the initial content of CD, OIT and DR, respectively, released from the west façade during the 18 months of the weathering experiment. For house 2, 0.2% and 1.4% of the TB and OIT initial content were resulting after the same time. This demonstrates that <5%, and thus only a small proportion of the active ingredients used, was released from the ETICS via runoff over the 18-month test period.

The results coincide with findings from other research projects, suggesting that temperature increase, UV radiation, degradation, transformation, diffusion into ambient air etc. also have an influence on the durability of active ingredients in façade ETICS [Bollmann et al. 2016 and 2017; Burkhardt et al., 2009; Burkhardt et al., 2012; Schwerd, 2011; Schoknecht et al., 2016a, 2016b; Styszko et al., 2015; Styszko and Kupiec, 2016; Uhlig et al., 2019]. However, the residual active ingredient content in the ETICS after the end of the field trial, as well as any transformation product formed in the eluate, were not determined in the present research project.

Finally, it has to be stated that experiments with panels which are only oriented to the WDR side could lead to an overestimation of the active ingredient runoff load of a building because only the strong weathered side of the building is considered during the runoff sampling. Therefore, a differentiated view of the building orientation is important.

3.3. Correlation analysis

The Spearman correlation analysis for west-side façades from both houses is shown in Fig. 8.

The findings demonstrate that the biocide emissions for the two houses were controlled by similar factors (RV and WDR). Although the observed parameter that controlled the emissions were the same for all façades, the magnitude of the ranges varied between r_s=0.61 (house 1-west) and r_s=0.95 (house 1-east). This difference in the correlation coefficients may be attributed to the statistical significance of the correlations, which is related to the number of samples obtained for each of the façades. The correlation coefficient between WDR and DR of house 1-west was 0.50, with a p-value of <0.0001. This r_s of 0.50 reflects a moderate positive correlation with a very high statistical significance level. In contrast, the correlation coefficient of WDR and DR of house 1-east was 0.99, but with an insignificant p-value of 0.0643. This revealed a perfect positive correlation between ranks, which is however insignificant. Even though the correlation coefficients for the façade facing west is not as positive as for the east side, the relationship was significant. This difference in the levels of statistical significance can be attributed to the lower sample number of the east side of house 1 in comparison to the west side of the same house. The same behavior can be observed for house 2, where the correlation coefficient of WDR and TB in west-oriented façade was 0.67 with a p-value of 0.0011 (≤ 0.05), while for east-oriented façade r_s was 0.96 with a p-value of 0.1690 (≥ 0.05). Heat map of Spearman's rank correlation coefficients between weather parameters and biocide loads in the runoff from house 1 and house 2 of all façades is given in supplementary information S2. The p-values for each of the facade sides and each of the parameters are included in the supplementary data S3. The Spearman correlation indicates the effect of parameters that directly cause the emissions, in particular WDR and RV, but failed to indicate the influence of isolated parameters like T, UV, SR and ADP. Thus, the correlation analysis was not able to reflect the complex interactions of these weather parameters affecting the emission processes of the biocides. For example, higher temperatures increase the diffusion in wet material, hence a higher amount of biocide will be available for transfer into the façade runoff [Styszko et al., 2015; Styszko and Kupiec, 2016; Uhlig et al., 2019]. The correlation coefficients of T and DR, OIT and CD loads for all sides of house 1 range between −0.15 and 0.36. This refers to a very weak negative or a very weak positive relationship between the biocide loads. Similar results were observed for T, OIT and TB loads for all sides of house 2, with r_s values between −0.33 and 0.28. These correlation results failed to demonstrate the influence of T on the emissions of the biocides. This is also the case for degradation processes that are especially enhanced by the combination of temperature and UV radiation. These processes cause lower amounts of biocides that are available for transfer into runoff [Bollmann et al., 2016, 2017; Schoknecht et al., 2009]. Furthermore, the correlation analysis failed to show the complex interaction between UV, T and the biocide loads in the runoff. There is a very weak negative to very weak positive correlation between UV and DR, OIT and CD loads of all sides of house 1. Correlation ranks for these parameters were between −0.48 and 0.33. Same behavior was noticed at all sides of house 2, with correlation coefficients of UV and OIT and TB loads between −0.37 and 0.24. Since the calculated ranks show a very weak relation or no relation at all, the correlation analysis was not able to represent the influence of UV in the emissions.

As proven by Bester et al. (2014) and Bollmann et al. (2014), the WDR is the main weather parameter that influences the leaching of

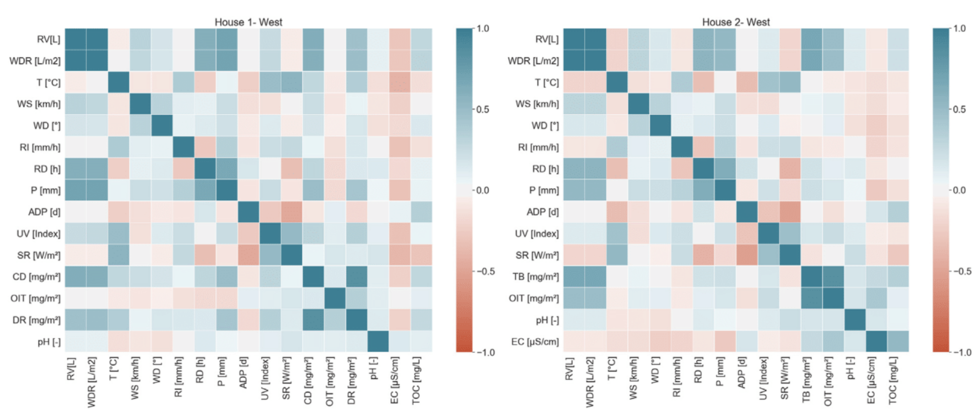


Fig. 8. Heat map of Spearman's rank correlation coefficients between weather parameters and biocide loads in the runoff from house 1 and house 2 west-side façades.

the biocides. The influence of this parameter was observed at all façades, indicated by a positive correlation between the emission loads and the WDR. This behavior is not shown with any of the other analyzed parameters. Because the WDR is affected by WD, WS, RD and P, it cannot be said that it is the only parameter that influences emissions. However, it is the parameter which directly influences emission and is therefore most pronounced. If the effects of the other individual weather parameters are evaluated, no effect was observable, which is correct for UV, SR, T and ADP as well.

4. Conclusions

The investigation under real climatic conditions on two model houses with different compositions has pointed out that the monitoring of all cardinal direction sides was helpful for the assessment whether on-site treatment facilities have to be installed at all sides of a building or only at the weather side.

The hypothesis that, because wind driven rain is the main influencing factor on the release of biocides from building façades, the biocide load is highest at the weather side compared to the other sides, has been proven.

Additionally, it could be demonstrated that the concentrations on all sides were higher than e.g. the GFS values for groundwater and the PNEC values. For on-site treatment systems, however, it must also be kept in mind that very different hydraulic loads can be expected. As the wind came from the west / southwest direction, the amount of collected runoff volume during the sampling period increased depending on the façade orientation and was up to 34 times higher at the weather side (here west side) compared to the opposite side (here east side). This affects the dimensioning of the treatment facilities.

The biocide load is decisive for the design of on-site treatment facilities. If a much higher biocide load arrives (e.g. on the weather side), the lifetime of the treatment facility may be shorter.

The results of the correlation analyses have confirmed that the main parameter that influences the leaching of biocides is the WDR. Weather parameters during and before the rain event such as rain intensity, wind speed, wind direction, total precipitation, temperature and UV irradiation have no significant detected influence when they are correlated as isolated parameters, because they fail to reflect the complex interactions that affect the emissions.

In conclusion, it can be stated that an on-site treatment of façade runoff would be very useful and could make a contribution to environmental protection. However, on-site treatment systems still have to be developed to safely remove both, biocides and their transformation products.

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CRediT authorship contribution statement

Pablo Vega-Garcia: Writing - original draft, Validation, Formal analysis, Conceptualization, Data curation.**Regina Schwerd:**Conceptualization, Supervision, Writing - review & editing, Project administration. **Christian Scherer:**Supervision, Methodology, Funding acquisition, Writing - review & editing.**Christoph Schwitalla:**Investigation, Project administration.**Sabine Johann:**Investigation, Data curation.**Steffen H. Rommel:**Formal analysis, Conceptualization, Validation, Writing - review & editing.**Brigitte Helmreich:**Supervision, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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A. 5 Modelling the environmental fate and behavior of biocides used in façades covered with mortars and plasters and their transformation products (submitted for peer-reviewed publication)

Modelling the environmental fate and behavior of biocides used in façades covered with mortars and plasters and their transformation products

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Abstract:

Façade renders containing biocides are often used on external thermal insulation composite systems (ETICS), to avoid the growth of algae, fungi, and bacteria. The aim of this study was to model the transport of four organic parent compounds (PCs), namely carbendazim (CD), diuron (DR), octylisothiazolinone (OIT), and terbutryn (TB), as well as 10 of their transformation products (TPs) within an unsaturated soil compartment (sandy or loamy/silty/clayey soil) until they reached a point of compliance (OdB). The model was developed using van Genuchten´s substance transport equation and general condition assumptions with reference to a Ground Water Risk Assessment (GRA). Factors such as soil type, percolation rate, soil organic carbon sorption coefficient (K_{OC}), and the half-life (DT_{50}) of TPs were found to affect not only the PC and TP peak concentrations, but also the time-to-peak at the point of compliance and the time needed for the substances to leave the unsaturated soil compartment. It was found that the model delivered concentrations of PCs at the OdB are, with exception of OIT, higher than the suggested value of 0.1 µg/L, independently if it is only sandy or loamy/silty/clayey soil according to the general conditions of the GRA. However, by including an appropriate topsoil layer with an organic content of 2% the concentrations of the PCs can be reduced significantly.

Keywords: biocide leaching; façade material; plasters; modelling; unsaturated soil transportation; transformation product

1. Introduction

Plasters and mortars containing biocides (e.g., carbendazim (CD), diuron (DR), octylisothiazolinone (OIT) and terbutryn (TB)) are often applied in façade external thermal insulation composite systems (ETICS), for inhibiting the growth of algae, fungi, and bacteria at the façade surface. Plasters and mortars are part of construction work and must, according to the Construction Products Regulation (CPR), be designed in such a way that they do not harm the user or the environment during their entire life cycle (EU, 2011). The use of biocides in Europe is currently regulated by the Biocidal Products Regulation (EU, 2012). It is common practice to add a mixture of various biocidal substances to plasters and mortars, and the applied biocidal formulations can contribute to almost 0.5% wt% (i.e., dry weight percent) in paints and renders for outer building surfaces (i.e., masonry and wood-based products) (Burkhardt, et al., 2012). In recent years, there has been growing concern about the contamination of receiving waters (surface water and groundwater) by biocidal products from façade runoff. For example, (Bester et al., 2014; Bollmann et al., 2014; Hensen et al., 2018; Wittmer et al., 2011; Wangler et al., 2012; Wicke et al., 2015; Paijens et al., 2019). Paijens et al. (2019) have criticized that biocides are still poorly regulated and monitored in the aquatic environment even though they are widely used in urban areas. Schoknecht et al. (2022) recently described the principles of a target concept capable of integrating knowledge of emission sources, leaching processes, transport pathways and effects on the receiving compartments in order to serve as a basis for an environmental risk assessment for construction products.

The leaching behavior of biocides from façades is highly correlated with rain intensity and cumulative rain duration as well as temperature, wind direction, and speed (Burkhardt et al., 2012; Blocken et al., 2013; Bester et al., 2014; Jungnickel et al., 2008; Vega-Garcia et al., 2020). Further factors impacting leached biocide concentrations include dilution, degradation, and sorption (Burkhardt et al., 2012; Coutu et al., 2012; Bollmann et al., 2017(a); Hensen et al., 2018; Vega-Garcia et al., 2020). Whereas the leaching of biocidal substances from plasters and mortars has been widely researched, neither their pathway into the groundwater during infiltration nor the environmental fate of their transformation products (TPs) is well understood. Although there have been many publications on monitoring parent compounds (PC), the majority have not addressed the regulating of their metabolites. These TPs are of special interest because they can be mobile, toxic, biologically active, and resistant to biodegradation (Lambropoulou et al., 2014; Picó et al., 2015).

Currently, no significant data exist on the accumulation, distribution, and transportation of biocides from plasters and mortars into soils. Additionally, biocides leached from the building materials are transferred in an irregular and uncontrolled way throughout the year, in the area proximate to the building (Reiß et al., 2021), often diluted by rainwater or other runoffs. The parameters which play a major role on behavior in the soil passage are sorption and desorption of biocides in soil as well as biodegradation (Reiß et al., 2021). The factors relevant to the calculation of the behavior of biocides and their TPs in soil compartments include the soil organic carbon sorption coefficient (K_{OC}) and the half-life of TPs (DT_{50}) in soil. The K_{OC} values can, for instance, be calculated based on the Molecular Connectivity Index (MCI) or the octanol water partition coefficient (K_{OW}). Both methods require correction factors when considering polar compounds. The MCI derives topological indexes from molecular and bonding structures (Bahnick and Doucette, 1988), so molecular size, bond terms, branching, and cyclization are considered (Kier and Hall, 1976). The alternative to using K_{OW} to predict K_{OC} has been stated by various studies, which have found that there is a strong linear relationship between K_{OC} and K_{OW} (Lyman et al., 1982; Di Toro, 1985). Recent publications such as Doucette (2003) have investigated estimation methods based on K_{OW} for compound groups such as carbamates, triazines, and phenylureas.

Additionally, DT_{50} is an important parameter in consideration of the compound's degradation rate. Bollmann et al. (2017(b)) proved that OIT with a half-life <10 days degraded rapidly and approached 0% of the initial concentration at day 120, whereas DR, with a much higher half-life of 135 days presented a more persistent behavior. In addition, Hensen et al. (2018) have demonstrated that, in the transport of biocides through stormwater infiltration system to groundwater, 14% of OIT and its TPs were detected (maximum concentration at 1.4 ng/L), whereas 100% of DR were often quantified (maximum concentration at 8.8 ng/L). This shows that DR, which has a particularly high half-life, might be continuously released from the soil into groundwater (Paijens et al., 2019). This indicates that substances persist longer in soil with a longer half-life.

The main objective of this study was to model the substance transport of four major biocide compounds and their TPs within an unsaturated soil compartment during infiltration until they reached a defined point of compliance in order to evaluate the relevance for groundwater contamination. Runoff data for the PCs, CD, DR, OIT, and TB from model houses located at the Fraunhofer Institute for Building Physics IBP were used as a source term (Vega-Garcia et al., 2020). Ten TPs of the applied PCs, namely 2-aminobenzimidazole (2-AB), N‘-[3,4-dichlorophenyl]-N,N-methylurea (DCMPU), 3,4-dichloroaniline (DCA), N‘-3,4-dichlorophenylurea (DCPU), octylamine, octylmalonamic acid, 2-hydroxy-terbutryn (TB-OH), desbutyl-2-hydroxy-terbutryn (TB-OH-DesB), desethyl-terbutryn (M1), terbutryn-sulfoxide (TB-SO) were analyzed and modelled based on their biodegradation performance in soil within an unsaturated soil compartment until they reached a point of compliance (OdB). The automation of the substance transport calculation of PCs and their TPs in the unsaturated soil compartment was developed using MATLAB. This model was mainly based on estimated substance parameters from existing database and experimental results from the previous literature. In addition, due to a lack of information and experimental data on some of the TPs characteristic properties, an investigation was made regarding the two main parameters by means of the EPI (Estimation Programs Interface) Suite^{TM} Package (EPA US., 2012), specifically K_{OC} and DT_{50}. For DT_{50}, the BIOWIN4 outputs were interpreted by various methods and compared to data from the International Union of Pure and Applied Chemistry (IUPAC) (International Union of Pure and Applied Chemistry, 2021). General condition assumptions were considered with reference to the joint research project “Ground

Water Risk Assessment (GRA)" (In German: *Sickerwasserprognose*, German Federal Ministry of Environment, 2018 and Susset and Grathwohl, 2011). Finally, the simulation results were then analyzed.

The hypothesis behind this work is that, through simulation, using the assumptions of the Ground Water Risk Assessment (GRA) from the German Federal Ministry of Environment and van Genuchten´s substance transport equation, it is possible to assess the environmental fate of biocides and their transformation products from building façades in an unsaturated soil compartment until they reach a defined point of compliance. Various runoff scenarios based on real runoff data and soil scenarios had to be analyzed in order to compare the differences in the fate of the leached substances in the environment.

2. Materials and Methods

Data from ten years of investigation on the leaching of ingredients from plasters and mortars under real climatic conditions from the Fraunhofer Institute for Building Physics IBP were used as a basis for the development process of a three-stage model used to assess the environmental properties of common plasters and mortars containing biocides (Schwerd, 2011; Schwerd et al., 2015; Vega-Garcia et al., 2020).

2.1 Site description and leaching data

The evaluated site was located at the Fraunhofer Institute for Building Physics IBP (47°52'30''N, 11°43'41''E) in Valley (Bavaria), Germany. Runoff samples were collected from two square experimental houses, both with 3 m wide, 2.4 m high façades. A detailed description of the sampling site, hydrological, and runoff data analysis has been presented elsewhere (Vega-Garcia et al., 2020).

During the investigation, two different plasters having a defined composition (see Vega-Garcia et al., 2020) mixed with 7.6 g/m^2 (House 1) and 8.9 g/m^2 (House 2) of biocide formulation were applied to the reinforcement layers of the model houses. House 1 included

3 mm of dispersion plaster (4.8 kg/m²) with the "naked" biocides OIT, DR, and CD containing initial contents of 140 mg/kg, 1000 mg/kg, and 450 mg/kg, respectively. Meanwhile, House 2 also included 3 mm of dispersion plaster (10.5 kg/m²) containing the following encapsulated biocides: OIT, TB, and zinc-pyrithion (ZnPT) at an initial content of 225 mg/kg, 400 mg/kg, and 225 mg/kg, respectively. The active ingredient, ZnPT, was not analyzed within the framework of the project. Details about the composition of the materials and a detailed description of the runoff analyses can be found in Vega-García et al., 2020. The cumulative loads of biocides obtained from each façade, the cumulative seepage water volume, and the mean leached biocide concentrations for House 1 and House 2 which represented input parameters for the simulation are presented in Table 1.

Table 1: Cumulative biocide loads from each façade, cumulative water discharge, and the mean leached biocides concentrations which served as a source term from House 1 and House 2 (Vega-García et al., 2020).

House	**Biocide**	**Cum. Biocidal Loads [mg/m²]**					**Cum. seepage water volume scenario A [L]**	**Cum. seepage water volume scenario B [L]**	**Biocide concentration scenario A [µg/L]**	**Biocide concentration scenario B and scenario C [µg/L]**
		West	*North*	*East*	*South*	**SUM**				
1	CD	45.3	7.65	0.59	13.0	**66.6**	**20,157**	**9,357**	23.7	51.5
	OIT	10.0	5.21	0.3	6.7	**22.2**			7.9	17.0
	DR	163	68.7	5.7	75.6	**313**			112	240
2	TB	10.1	4.25	0.38	2.13	**16.8**	**20,143**	**9,343**	5.6	12.4
	OIT	34.6	17.6	0.7	7.95	**60.8**			21.6	47.2

The cumulative seepage water volumes from two scenarios were used in order to compare the influence of the seepage water volume and the source term concentration in the simulation: Scenario A consisted of façade runoff, the runoff from the edges of the house (surface area of the house edges: 6 m², width of the edge strip: 0.5 m), and the roof runoff (roof surface: 9 m²). Scenario B included only façade runoff and the runoff from the edges of the house (without roof runoff). The resulting volumes from both scenarios (see also Table 1) served as a source term in the model.

2.2 Core assumptions in modelling

The main boundary condition assumptions in this research were set with reference to the Ground Water Risk Assessment (GRA) (German Federal Ministry of Environment, 2018 and Susset and Grathwohl, 2011). The retardation, accumulation, and attenuation of biocides are considered within 1 m of unsaturated soil until it reaches the groundwater. The OdB, which is also assumed as the groundwater table, is considered to be at least 1 m below the soil surface. Moreover, the insignificance threshold value (In German: *Geringfügigkeitsschwellenwerte* GFS) (Susset and Grathwohl, 2011 and LAWA, 2016), is defined as the concentration level for a substance, at which no significant change will be imposed on the groundwater (see Figure 1). The GFS should be met at the OdB over a time period of 200 years (Susset and Grathwohl, 2011). Regarding all 4 PCs in the scope of this project, the GFS is 0.1 µg/L (LAWA, 2016); there are no GFS defined for TPs. A constant source term is assumed with respect to hydrophobic organic contaminants. The leachate concentration should, after a period of time, remain constant, forming a concentration plateau.

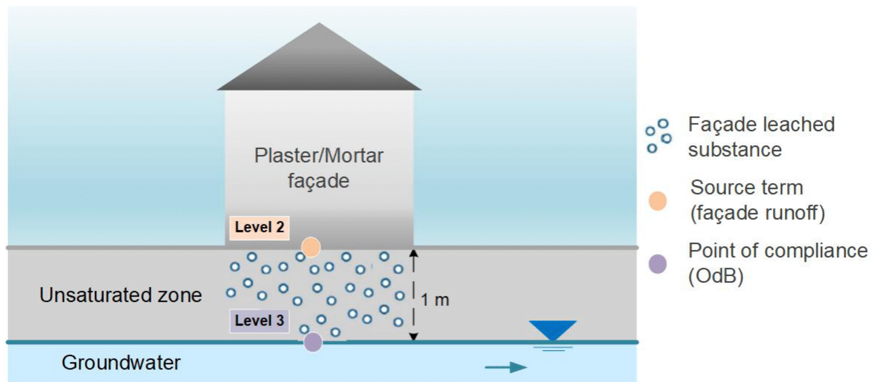

Figure 1. Source term of the leaching substances (façade runoff), unsaturated transport zone, and point of compliance (OdB), where the insignificance threshold value (GFS) act as a target concentration.

The source term for the scenario analyzed included the concentrations of the leached PCs and the seepage water volumes. The physical-chemical properties of the analyzed PCs are provided in Table S.1 of the Supplementary Information. These parameters served as input parameters for modelling the transport of the PCs within the unsaturated soil compartment.

The transformation processes of biocides were modelled for two types of soil, namely sandy soil with moderate retardation and natural attenuation, and a mixture of loamy, silty, and clayey soils with high retardation and natural attenuation. These two soil categories were defined by Beyer et al. (2007, 2008) and Grathwohl et al. (2006) based on a statistical evaluation of the main soil units in Germany. They contribute up to 85% of the soil distribution in Germany. It was also determined based on statistical evaluation that 90% of the soils in Germany meet the assumed sorption quality, pH-value, organic carbon content and hydraulic characteristics for the selected two soil scenarios. The sandy soil and loamy, silty, and clayey soil properties can be seen in Table 2.

In addition to the two seepage water volumes scenarios (scenarios A and B), a third scenario (scenario C) will be modeled for practical purposes of comparison of the influence of the organic carbon content in soil compartments. This scenario will integrate a top layer of 30 cm with an organic carbon content of C_{org} = 2% (layer in which the surface runoff is stored briefly and infiltrated through an overgrown soil zone in accordance to the German Association for Water, Wastewater and Waste (DWA) (DWA, 2020)), within the 1 m soil compartment. The remaining 70 cm of the 1 m soil compartment will have the carbon organic content corresponding to the two soil types (C_{org} = 0.1%). The seepage water volume and the source term concentration of scenario B will be used for the modeling of scenario C. Furthermore, only two PCs, diuron and terbutryn, will be analyzed within this scenario.

Table 2: Properties of sandy soil and loamy, silty, clayey soil (German Environment Agency, 2018) and the top layer (DWA, 2020)

Parameter	**Unit**	**Sandy soil**	**Loamy/silty/clayey soil**	**Top layer**
pH ($CaCl_2$)	-	4.8	6.6	4.8, 6.6
Clay content	%	2.5	12	2.5, 12
Effective porosity (n_e)	-	0.2	0.3	0.2, 0.3
Dry density (ρ_b)	kg/L	1.4	1.5	1.4, 1.5
Organic carbon content (C_{org})	%	0.1	0.1	2.0
Field Capacity	%	11	37	11, 37

The percolation rate (SWR) [mm/a] used for the transport modeling was defined by equation (1):

$$SWR = \frac{WV}{T * A} \qquad (1)$$

where WV [L] is the cumulative seepage water volume, T [a] is the duration of the emission, and A [m²] is the surface area of the house edges. In the simulation, the surface area of the house edges was considered to be 6 m² (width of the edge strip: 0.5 m).

The detailed analysis of Bollmann et al. (2017(b)) was used as a reference regarding transformations of OIT and TB. Both OIT and TB degradations were modelled as pseudo-first order kinetics at a constant degradation rate k (OIT, $k = -0.063$ and terbutryn, $k =$

-0.002). This assumption was made in accordance with previous studies and guidelines regarding the degradation of organic chemicals (OECD, 2006). At the same time, TP formations were modelled with reference to which function types fit best, which included linear, power, polynomial, and bell functions. The Curve Fitting Toolbox™ from MATLAB was used to obtain coefficients for the best-fitting equation (see Table 3). TPs having extremely low concentrations were neglected in this project (e.g., desethyl-2-hydroxy-terbutryn, terbumeton, and desbutyl-desthiomethyl-terbutryn derived from terbutryn, octylacetamide, and octylpropenamide derived from OIT). One suggestion was octylmalonamic acid derived mainly from OIT degradation (Bollmann et al., 2017(a)). Given that OIT contributes up to 3/5 of the total input concentration of PC, the results of octylamine were thus reduced to a fraction of 3/5 during calculation.

According to Bollmann et al. (2017(a)), TB-OH-DesB and TB-OH are TPs which increase linearly and constantly throughout the experimental period. M1 increases in a different behavior, i.e., nearly like a power function. Finally, the concentration of TB-SO increased rapidly in the first stage of the experiment, at a rate much faster than with other TPs.

Furthermore, in order to correlate the input concentrations of PCs with the formations of TPs, a vertical scaling of functions was conducted with respect to the coefficients of the best-fitted lines. In other words, the ratios between the initial concentrations of PCs and the constant coefficients in the TPs were calculated first. The output results from the transport model were then considered as the TP input concentrations. Given variations in input concentrations and time, the concentration of TPs at OdB can then be obtained.

The functions and the obtained best-fitted coefficients of OIT, TB, DR, and CD. The TPs can be seen in Table 3.

Table 3: Coefficient ratios of TP functions (PCs)

PC	TP		Fitting equation	Coefficient ratios

		Fitting type		a	b	c	d	e
OIT	Octylamine	Bell	$y = a * \exp(\frac{-(x-b)^2}{2c^2})$	0.13	15.32	10.13	-	-
	Octylmalonamic acid			0.28	14.32	9.4	-	-
TB	TB-OH	Linear	$y = ax$	136.07	-	-	-	-
	TB-OH-DesB			173.96	-	-	-	-
	M1	Power	$y = ax^b$	43.00	0.53	-	-	-
	TB-SO	Polynomial	$y = \frac{ax^2 + bx + +c}{x^2 + dx + e}$	59.18	0.08	0.24	31.60	389.7
				Fraction of formation (IUPAC)			Coefficient ratios	
CD	2-AB	Linear	$y = ax$	0.08			1492.54	
TR	DCPMU			0.33			373.12	
	DCPU			0.02			6250	
	DCA			0.25			502.51	

Few in-depth studies on TP formations were found regarding CD and DR. As a result, data from the IUPAC database were adopted for modeling (International Union of Pure and Applied Chemistry, 2021). According to the data of fraction of formation (FF), the change in TP concentrations was plotted against time for each TP. One limitation was that the data provided by IUPAC were only a constant, stating the percentage of TP that forms from the PC, regardless of time and formation rate. Four main assumptions were made in this method:

1) A time period of 120 days was considered, in accordance to the experimental period adopted in Bollmann et al. (2017(a)). This also enabled a better comparison among all of the four biocides chosen in this research.
2) An initial PC concentration in soil of 10 μg/g was assumed. This was with reference to Bollmann et al. (2017(a)), which, based on the emission rate of previous research, stated

that the final concentration in soil for diuron is assumed to be 10 μg/g (Burkhardt et al., 2012; Bollmann et al., 2016 and Bollmann et al., 2017(a)).

3) The half-life values of carbendazim and diuron were used to calculate the degradation constant k (resulting in: carbendazim, $k = -0.008$ and diuron, $k = -0.0003$) and giving a first-order degradation function against time.

4) A positive linear correlation between TP concentration and time was considered. This means that TPs continuously increase throughout the considered time period. The latter assumption was made based on the relatively long half-life of TPs from carbendazim and diuron, in contrast to TPs from OIT which form and degrade rapidly within the considered time period. Therefore, similar to TB-OH and TB-OH-DesB, the 3 TPs were plotted with a linear function. Given the hypotheses suggested above, a coefficient ratio between the PC and TP functions can be obtained.

2.4 K_{OC} and DT_{50} estimation

Due to the fact that the characteristics of metabolites from biocides have not been dealt with in depth in previous studies, the EPI (Estimation Programs Interface) Suite™ (EPA US, 2012) was adopted for more accurate assumptions. Two individual models, namely KOCWIN™ and BIOWIN™, were used to approximate the K_{OC} and DT_{50} of TPs in soil by using Simplified Molecular Input Line Entry System (SMILES) as an input. SMILES was required as an input and represented the chemical structure of the substance in a string code. The SMILES used for each of the TPs is depicted in Table 4.

Table 4: Corresponding SMILES code of TPs

TPs	SMILES code
2-AB	C1=CC=C2C(=C1)NC(=N2)N
DCPMU	CNC(=O)NC1=CC(=C(C=C1)Cl)Cl
DCA	C1=CC(=C(C=C1NC(=O)N)Cl)Cl
DCPU	C1=CC(=C(C=C1N)Cl)Cl
Octylamine	CCCCCCCCN
Octylmalonamic acid	CCCCCCCCNC(=O)CC(=O)O
TB-OH-DesB	CSc1nc(N)nc(NC(C)(C)C)n1
TB-OH	CCNc1nc(O)nc(NC(C)(C)C)n1
M1	CCNc1nc(O)nc(NC(C)(C)C)n1
TB-SO	CCNc1nc(NC(C)(C)C)nc(S(C)=O)n1

Previous studies determined the degradation rates of the PCs through experiments with plant protection agents (PPA) (IPCS, 2021 and Bollmann et al., 2017(a)). However, little information exists regarding the properties of TPs. Therefore, this project estimated the DT_{50} of TPs using the BIOWIN™ (BIOWIN4) package tool.

2.5 Unsaturated soil substance transport model

The MATLAB® programming language was used to model and plot the concentration of biocides at OdB. The latter programming language is suitable for numeric computing and data analysis applications. The aim of this research was to automate the evaluation of raw data of biocide leaching collected from the two model houses. The transportation of compounds within a soil compartment involves a variety of mechanisms such as convection, diffusion, dispersion, linear equilibrium adsorption, and zero-order or first-order production and decay (van Genuchten & Alves, 1982). Van Genuchten´s model presents a one-dimensional convective-dispersive solute transport equation and assumes zero-order production and first-order decay of PCs in steady-state flow. The governing equation of van Genuchten´s transport model is presented as follows:

$$\mathrm{R}\ \frac{dc}{dt} = \mathrm{D}\ \frac{d^2c}{dx^2} - v\ \frac{dc}{dx} - \mu c + \gamma \qquad (4)$$

where x (mm) is the substance transported distance, t (d) is the time it takes the substance to transport the correspondent distance, R is the retardation factor, c (μ/L) is the substance concentration, v (mm/d) is the pore water velocity, D (mm^2/d) is the dispersion coefficient, μ (1/d) is the rate constant for first-order decay, and γ (μ/L^3d) is the rate constant for zero-order production.

3. Results and discussion

3.1 TP Properties

A summary of the physical-chemical properties of the analyzed TPs obtained by the methods presented above are provided in Table S.2. Although the EPI Suite™ focuses on PPA and comes with a set of interpretations for PPA output, more recent research suggests different conversion methods for PPA output in soil experiments. One notable drawback of the EPI Suite™ translation rules is that it is a step-wise function which may lead to bias and inefficiency in predicting half-life values as compared to linear functions. In Fenner et al. (2009), the authors compared PPA interpretations by EPI Suite™ guidelines with the past literature (Arnot et al., 2005). They suggested that, for the 38 pesticides and pesticide TPs they analyzed, only the persistent pesticides lay closer to the estimation performed by the EPI Suite™ by a factor of ten. In contrast, the linear function claimed by Arnot et al. (2005) appears to offer a closer approximation of half-life, in which the coefficient of determination is R^2=0.78. These observations show that different methods may lead to different results, thus implying an influence on further modelling.

According to the guidelines from EPI Suite™, the MCI method has been used for a longer period of time. Table S.2, shows that the values obtained from the EFSA database for diuron are higher than the estimation performed by KOCWIN™. Since the values obtained were probably from field or laboratory experiments, factors such as temperature, pH, moisture level, and even the soil content itself can lead a variation in the K_{OC} value. It is also likely that the K_{OC} values are higher in real life than in computations, which can be explained by a possibly higher organic carbon content than expected. More experimental results on the K_{OC} values for TP will be required in order to better analyze the reliability of the theoretical K_{OC}. As for a comparison between the two methods used in KOCWIN^{TM}, the MCI method gives lower K_{OC} values for TPs from DR. In contrast, the K_{OW} method gives higher values for TPs from OIT. Additionally, for 2-AB and TB-SO, the differences in log K_{OC} are particularly high, whereby the log K_{OW} method gives a value of 72% higher than that from MCI for TB-SO. No trend in the output from these two methods has yet been observed. Although TB itself has the highest K_{OC} values among the 4 PCs, its TPs do not appear to have much higher K_{OC} values. In contrast, OIT has the lowest K_{OC} value as compared to other PCs. However, one of its TPs, octylamine, has the highest K_{OC} value when using the MCI estimation method. As a result, no apparent correlation between the K_{OC} values of PCs and TPs could be observed.

Due to a lack of experimental data, only the DT_{50} of TPs from DR were retrieved from the International Union of Pure and Applied Chemistry (IUPAC) database for comparison. Only DCPMU is classified as “very persistent”, with a long DT_{50} of 127 days, whereas DCPU is considered to be “non-persistent”, with a DT_{50} of 7.7 days. It is worth noting that these values were obtained under lab conditions at 20 °C, so they might vary under field conditions. The TPs from OIT have been shown to have the lowest DT_{50} (< 6 days), as compared to other TPs, which is consistent with its PC OIT, which also has the lowest DT_{50} (< 10 days) among all four biocides. It can be assumed that OIT and its TPs are less persistent, and probably a large percentage will degrade before reaching OdB. On the other hand, although DR has a longer DT_{50} (135 days) in relation to other PCs (OIT and Carbendazim), the DT_{50} of its TPs is not particularly high, especially when compared with the TPs from TB. Apart from TB-OH-DesB, all of the TPs from TB were estimated to have longer DT_{50} than TPs from diuron by the methods in both Arnot et al. (2005) and Fenner et al. (2009). The exception was DCPMU, where data from the IUPAC showed an extremely high DT_{50} of 127 days. Therefore, inadequate information exists regarding whether there is any correlation between DT_{50} of PC and its respective TPs. The majority of DT_{50} from EPI interpretation are underestimations. This method gives results that are significantly lower than when using other methods. Please note that the value for DCPMU is much higher from the IUPAC database, where results were collected based on the previous literature or past experiments. When DT_{50} is underestimated, the assumed degradation process speeds up. In other words, TPs might be assumed to be fully degraded before reaching the groundwater level. But, in reality, it still persists, has a long-lasting effect, and contaminates the groundwater. This suggests that the EPI Suite^{TM} might not offer a suitable calculation for the DT_{50} values.

Overall, the regression method suggested by Arnot et al. (2005) gives a higher value for DT_{50} than the method by Fenner et al. (2009). Regarding higher biocide output values, the differences between the methods are rather minimal (e.g., octylmalonamic). On the other hand, the half-life discrepancies can be up to more than double for a lower biocide output.

3.2 Modelling of Biocides and their TPs with assumptions

It was assumed that the façade runoff seeps directly into an unsaturated sandy or loamy/silty/clayey soil layer without contact with a topsoil layer. It should be noted that a high content of organic carbon should only be expected in the topsoil layer, not in the sandy or loamy/silty/clayey soil. For both investigated soils within the two seepage water volume scenarios the organic carbon content (C_{org}) is 0.1%. Figure 2 illustrates the concentrations of PCs at OdB in sandy soil and loamy/silty/clayey soil considering a time range of one year for both runoff scenarios, A and B. The CD, DR, and OIT results for House 1 are presented in Figure 2 along with the TB and OIT concentrations for House 2. Even though the OIT concentration was higher in House 2 than in House 1, these concentrations were very low after one year at OdB in both scenarios. Diuron had the highest concentration, followed by CD and OIT in House 1. At House 2, only TB was detectable at OdB after one year. When comparing the two different soil types, the peaks were lower in loamy/silty/clayey soil and shifted to the right with a broader base width.

Diuron reached a maximum concentration at the OdB of 39.8 µg/L from House 1 after 87 d in sandy soil for the cumulative seepage water volume in scenario A. On the other hand, it reached a higher concentration of 79.3 µg/L after 208 days in sandy soil in scenario B. This behavior was attributed to higher concentrations and lower seepage water rates for runoff scenario B, which excluded dilution by the roof runoff. As mentioned earlier, the loamy/silty/clayey soil showed lower maximum concentrations at the OdB (28.8 µg/L for scenario A, and 48.9 µg/L for scenario B), and it took longer to achieve this maximum concentration (127 d for scenario A, and 251d for scenario B) in comparison to the sandy soil. The reason for this relates to the retardation factor, which is directly influenced by the field capacity of the soil. According to the GRA, loamy/silty/clayey soil has a higher field capacity (FC=37) than sandy soil (FC=11), thus resulting in a lower retardation factor for the loamy/silty/clayey soil. As a result, the substance takes longer to be transported within loamy/silty/clayey soil, so it is subject to greater degradation. This results in lower concentrations at the point of compliance in comparison to sandy soil scenarios.

Carbendazim in House 1 reached a maximum concentration at OdB of 17.8 µg/L and 11.7 µg/L in sandy and loamy/silty/clayey soil, respectively, in scenario B. However, lower maximum concentrations at OdB were found in scenario A (sandy soil: 8.9 µg/L, and loamy/silty/clayey soil: 6.1 µg/L). Like DR, it took longer for the CD to reach a maximum concentration at OdB in scenario B (sandy soil: 182 d, and loamy/silty/clayey soil: 256 d) in comparison to scenario A (sandy soil: 91 d, and loamy/silty/clayey soil: 104 d). The differences in both the maximum concentrations found at OdB and the time it took to reach these concentrations are attributed to the magnitude of the substance loads, which are dependent on the source term concentrations and the seepage water rate for each of the scenarios. These results correspond to the findings regarding DR.

In House 1, OIT reached the peak concentration the fastest, but at a minimum level in both sandy and loamy/silty/clayey soils for both runoff scenarios A and B. The maximum concentration (1.7 µg/L) at OdB was found in scenario A. This behavior contrasts with that presented for DR and CD, which is due to the fact that these two substances have the maximum concentration at OdB in scenario B (lower seepage water rate and higher source term concentrations). This is attributed to the higher seepage water rate in scenario A and a higher degradation coefficient due to a very low DT_{50} time (9.3 d) for the substance, which made it less persistent in the studied compartment because most of substance degraded before it could reach OdB. This can also be observed in the concentrations of the loamy/silty/clayey soil scenarios, where the substance was retained for a longer time in the compartment. As a result, more degradation of OIT occurred during the transport, and very few substances were found at OdB. The same was observed in House 2 for the OIT, with the difference that the concentrations found at OdB were higher due to higher source term concentrations (see Table 1).

Finally, the TB in House 2 was the substance having the longest resistance time among all substances in both runoff scenarios. In scenario B, it took 315 d and 345 d to reach maximum concentrations at an OdB of 2.3 µg/L and 1.2 µg/L in sandy soil and loamy/silty/clayey soil, respectively. Like the DR and CD in House 1, the magnitude of concentrations of TB at OdB and the resistance time of the substances in the evaluated compartment were higher in scenario B. The high persistency of TB in comparison with the other analyzed substances was due to its higher DT_{50} (231 d).

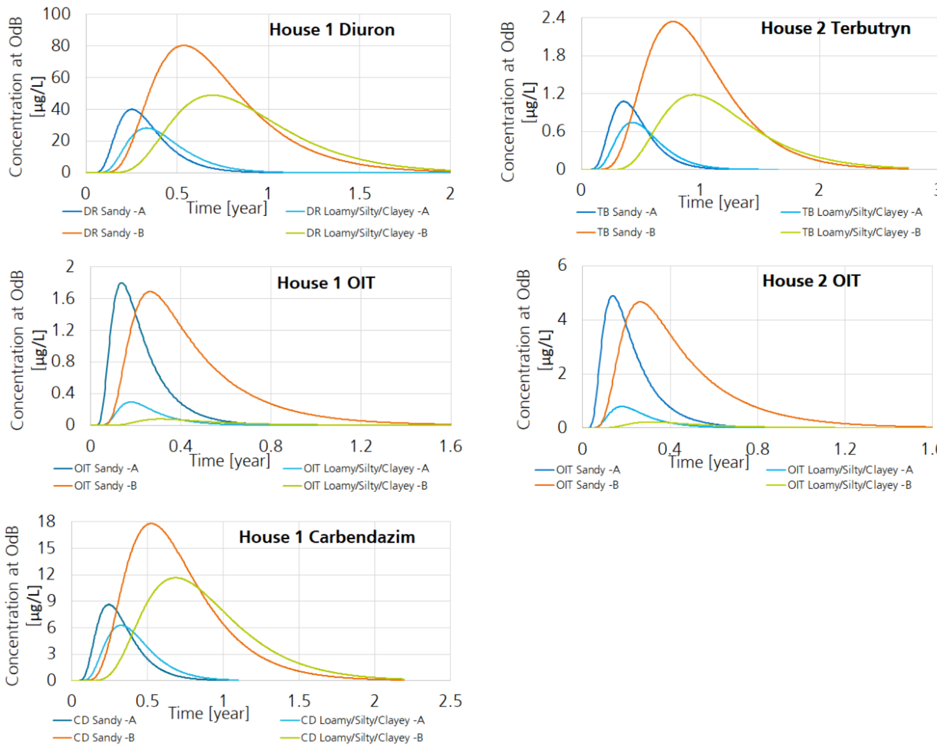

Figure 2. Modeled PC concentrations at OdB for House 1 and House 2 in sandy soil and loamy/silty/clayey soil for scenarios A and B.

In practice, however, infiltration often takes place via a topsoil layer. The DWA (2020) requires a topsoil layer of 30 cm for contaminated discharges with predominantly dissolved substances. Figure 3 illustrates the modeling results of scenario C, where the organic carbon content (C_{org}) is 2% for the first 30 cm (topsoil) of the 1 m soil compartment (infiltration through). Diuron reached a maximum concentration at the OdB of 5.95 µg/L from House 1 in sandy soil with the cumulative seepage water volume and source term concentration of scenario B. Meanwhile, for the loamy/silty/clayey soil it reached a maximum concentration of 4.37 µg/L. In the case of TB, the maximum concentration at the OdB in the sandy soil and loamy/silty/clayey soil with the cumulative seepage water volume and source term concentration of scenario B was of 0.19 µg/L and 0.16 µg/L, respectively. It can be seen that due to the higher organic content of the top layer in scenario C the maximum concentrations found at the OdB decrease of a factor of almost 10 when comparing the results with those obtained in scenario B (Figure 2). This implies that a layer with a higher organic carbon content considerably decreases the maximum concentration found at the OdB. The reason for this is greater sorption and degradation of the biocides within the first 30 cm of transport.

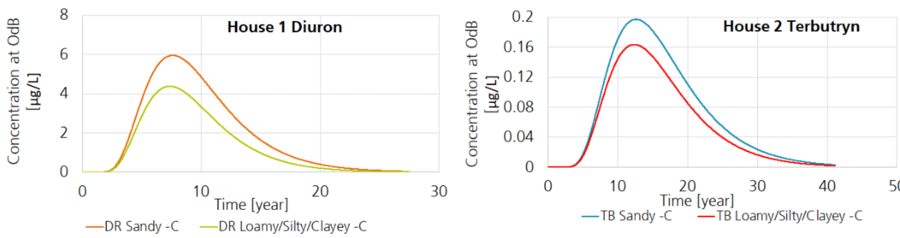

Figure 3. Modeled diuron and terbutryn concentrations at OdB for House 1 and House 2 in sandy soil and loamy/silty/clayey soil for scenarios C.

The concentrations of TPs at OdB for the two houses and the different runoff and soil scenarios can be seen in Figure 4. All of the TPs had low concentrations as compared to their PCs input concentrations. All of the PCs and TPs transportations demonstrated a similar pattern: (1) contamination takes time to reach OdB; concentration remains undetectable in the first stage of the transport, (2) concentration at OdB slowly builds up and increases, (3) concentration reaches the maximum after a period of time, (4) concentration slowly decreases as the loading is not high enough to maintain at the maximum, (5) concentration approaches zero, indicating contamination leaving the system. All of the TPs exhibited a similar behavior since their PCs were the higher maximum concentrations at the point of compliance and were found in the runoff scenario not including the roof runoff as well as being transported within a sandy soil. This behavior can be explained by the increase or decrease of the TPs being directly related to the magnitude of concentration of PCs in the system at a certain time (see section 2.2).

In House 1, TP 2-aminobenzimidazole (2-AB) reached the highest maximum concentration at the point of compliance of 8 ng/L after 1.2 years in the sandy soil scenario for the scenario having runoff with no roof runoff included. For the TPs of diuron, DCPMU reached the highest maximum concentration at the point of compliance of 0.7 µg/L, followed by DCPU and DCA with 0.5 µg/L and 0.1 µg/L, respectively. Like carbendazim, this behavior was exhibited after 1.2 years in the sandy soil scenario for the scenario having runoff without roof runoff included. As for the TPs of OIT, octylamine peaked at 8 ng/L, which was higher than that of octylmalonamic acid, at 3 ng/L in House 1. Like the PC scenarios and contrary to what was presented for the diuron and carbendazim PCs and TPs, the maximum concentrations of OIT's 2 TPs were found in the scenario having runoff including the roof runoff (Octylamine Sand w/Roof = 22 ng/L and octylmalonamic acid sand w/Roof = 10 ng/L). The time needed for the OIT TPs maximum concentration to reach the point of compliance was also shorter, reaching these maximum concentrations after only 24 days. It can also be observed from Figure3 that the persistence of the maximum concentrations of the OIT TPs at the point of compliance was also different from that of the diuron and carbendazim TPs. In the scenario of the OIT TPs, the maximum concentration remained constant at the point of compliance, creating a plateau for about a year. This was unlike the diuron and carbendazim TPs, which reached a maximum concentration and, after a short time, these decayed. This behavior is due to the fact that the OIT TPs did not persist long enough in the system to accumulate loads sufficient to influence the increase in concentration. As a result, the concentration remained constant until the substances were completely degraded or left the system.

However, in House 2, the maximum concentrations found at the point of compliance for octylamine and octylmalonamic acid were 22 ng/L and 10 ng/L, respectively. Both these TP concentrations and the OIT TP concentrations in House 1 were observed in the sandy soil scenario and the source term runoff including the roof runoff. Nevertheless, the TP concentrations of OIT in both scenarios were extremely low (close to undetectable), possibly due to their short half-lives. Among the four TPs of terbutryn in House 2, TB-SO achieved the highest concentration at the point of compliance of 0.5 ng/L, followed by M1 with 0.3 ng/L, TB-OH with 0.1 ng/L, and TB-OH-DesB at 0.7 ng/L. Both these maximum TP concentrations of from TB and the TPs from DR and CD in House 1 were found in the sandy soil scenario for the scenario with a source term not including the roof runoff. The maximum concentrations at OdB behaved similarly to the TPs from DR and CD, where the maximum concentrations were reached after 1.3 years, and then began to drop, until the substances were completely degraded or left the evaluated system.

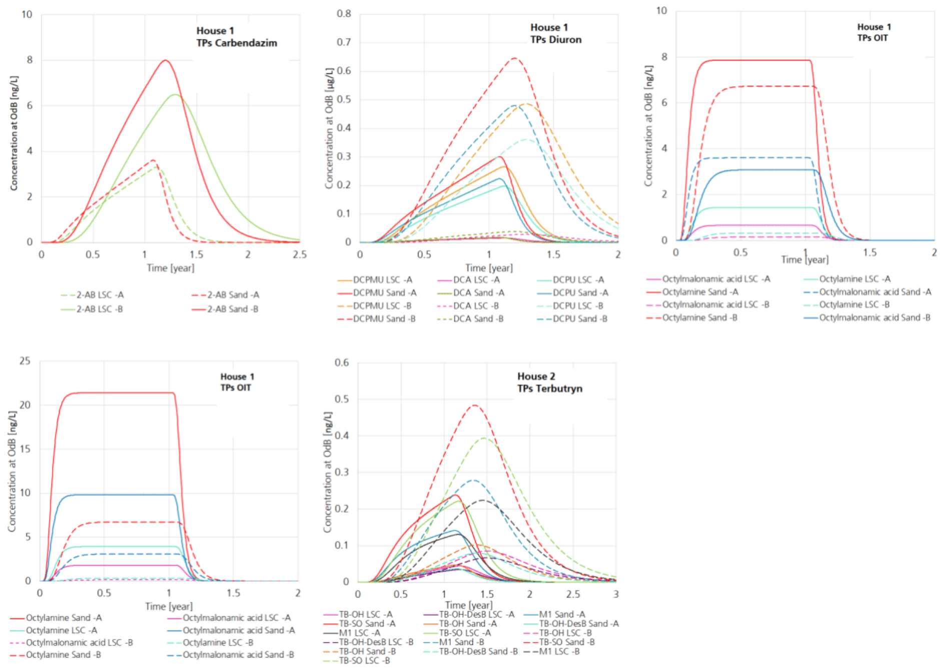

Figure 4. Modeled TPs concentrations at point of compliance for House 1 and House 2 in sandy soil scenario and loamy/silty/clayey soil for scenarios A and B.

Among the 10 TPs in the data collected from House 1, octylamine and octylmalonamic acid reached a maximum concentration in the shortest amount of time. This agreed with the behavior of their PCs, in which OIT reached the peak first among all 4 PCs. Meanwhile, DCPMU and DCPU achieved the highest maximum concentrations, peaking at 0.7 and 0.5 µg/L respectively. Similarly, DR also had the highest concentration in House 1. The TPs for OIT remained at a very low level but peaked within a short time period.

Regarding the TPs of OIT, octylamine reached the maximum concentration slightly earlier than octylmalonamic acid. Both TPs showed a similar pattern, which differed from that of the 1-year analysis: The concentration increased sharply after 23 d and stays constant for a long period time before leaving the system, thus forming a significant plateau in the middle, followed by a rapid drop when the TPs leave the system or degrade, and the concentration once again approaches 0. As for the TPs of TB, no flat plateau was observed. Instead, the TP concentrations continuously built up over a long period, starting at around 180 d and increasing at a relatively rapid rate.

TPs were more persistent in loamy/silty/clayey soil due to its high field capacity and clay content. It can be observed that TPs tend to arrive at OdB later, but at the same time remain at the detectable level in the system and leave after a longer period of time. There seems to be a shift of the peak when comparing two types of soils. For instance, 2-AB leaves the system after 2.5 years in loamy/silty/clayey soil, as compared to 2 years in sandy soil when applied to the example the scenario B. Similarly, for DCPMU, DCPU, as well as DCA, they remain in the loamy/silty/clayey soil system than in sandy soil. Meanwhile, the TP concentrations for OIT were very low, which was probably related to the short DT_{50} of OIT and its TPs. In particular, for the TPs of OIT in loamy/silty/clayey soil, the concentrations were not detectable. On the other hand, the TPs in loamy/silty/clayey soil reached a lower peak concentration than in sandy soil. For example, DCPMU, DCPU, and DCA achieved a peak concentration of 0.3 ng/L, 0.2 ng/L, and 0.03 ng/L in sandy soil, whereas these levels were only 0.25 ng/L, 0.18 ng/L, and 0.01 ng/L in loamy/silty/clayey soil under scenario A.

When validating the model, it becomes clear that the model has limits. The used sorption capacity relates only to the organic carbon content. No sorption coefficient for the biocides and their TPs on sandy or loamy/silty/clayey soil is included. Currently, the experimental data is not sufficient to make such assumptions. Therefore, fundamental investigations would have to be carried out to improve the model in order to determine the sorption capacities for the used soils. However, this was not feasible in the context of this study.

4. Conclusions

The hypothesis that by means of simulations using the van Genuchten´s substance transport equation and general condition assumptions with reference to a Ground Water Risk Assessment (GRA) it is possible to assess the environmental fate of biocides and their transformation products in an unsaturated soil compartment until they reach a defined point of compliance can only be partially confirmed. Including the half-life is very helpful, however, there is a lack of data on the sorption capacity of biocides and their TPs on the soils used in this study. The model needs experimental input to improve the data situation for sorption parameters.

The fact that only sorption to organic matter is assumed when using the soil types according to the GRA could lead to wrongly overestimated values at the OdB. In this context it is assumed that the façade runoff seeps into the unsaturated soil zone directly and without contact with topsoil which has a higher organic content.

Based on the calculations and the assumption that sorption only occurs on organic carbon, it can be stated that the concentrations of PCs found at the OdB are, with exception of OIT, higher than the suggested values by LAWA (2016), independently if it is sandy or loamy/silty/clayey soil and if it is diluted by roof runoff or not. By applying a topsoil layer with a higher organic content, concentrations of PCs at the OdB can be decreased significantly. This highlights the impact of treatment measures for when emitting runoff water from façades. It shows that treatment for biocides from stormwater runoff must be carried out before on-site infiltration over sand or loamy/silty/clayey soil for groundwater protection. Additionally, the manufacturers of façade coatings should pay attention to the use of biocides having low half-lives in their recipes in order to mitigate the persistence of biocides in the environment.

The model described above can be a very helpful tool for estimating the substance- and site-depending relevance of biocide discharge from facades into the ground water and for the choice of suitable treatment measures in form of the introduction of additional soil layers with higher organic content.

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Figures captions

Figure 1. Source term of the leaching substances (façade runoff), unsaturated transport zone, and point of compliance (OdB), where the insignificance threshold value (GFS) act as a target concentration.

Figure 2. Modeled PC concentrations at OdB for House 1 and House 2 in sandy soil and loamy/silty/clayey soil for scenarios A and B.

Figure 3. Modeled diuron and terbutryn concentrations at OdB for House 1 and House 2 in sandy soil and loamy/silty/clayey soil for scenarios C.

Figure 4. Modeled TPs concentrations at point of compliance for House 1 and House 2 in sandy soil scenario and loamy/silty/clayey soil for scenarios A and B.

Tables captions:

Table 1: Cumulative biocide loads from each façade, cumulative water discharge, and the mean leached biocides concentrations which served as a source term from House 1 and House 2 (Vega-García, et al., 2020).

Table 2: Properties of sandy soil and loamy, silty, clayey soil (German Environment Agency, 2018-A)

Table 3: Coefficient ratios of TPs functions (PCs)

Table 4: Corresponding SMILES code of TPs