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Characterisation of leaching of biocidal active substances of main group 2 'preservatives' from different materials under weathering conditions

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16. Zusammenfassung

Anwendungen von Bioziden in Materialien für Außenanwendungen sind mögliche Quellen für Biozide in Umweltkompartimenten infolge von witterungsbedingten Auswaschprozessen.
Im Bericht werden Leachingprozesse und -parameter als auch Methoden zu deren Untersuchung unter Labor- und Freilandversuchsbedingungen beschrieben. Vorteile und Grenzen der verschiedenen Herangehensweisen zur Untersuchung von Leachingprozessen werden diskutiert.
Standardisierte Auswaschtests sowie in der Fachliteratur publizierte Auswaschexperimente werden zusammenfassend dargestellt.
Es wird beschrieben, wie Leachingdaten gemäß Technischem Leitfaden zur Biozidprodukten-Richtline 98/8/EG für eine Risikobewertung genutzt werden.
Ein alternativer Ansatz zur mathematischen Modellierung von Leachingtest-Daten wurde erprobt und wird im Bericht erläutert. Potentiell lassen sich mit dem vorgeschlagenen Ansatz bestimmte gegenwärtig auftretende Schwierigkeiten bei der Risikobewertung umgehen.

17. Schlagwörter
Biozid, EU Biozidproduktenrichtlinie 98/8/EG, Materialschutzmittel, Topf-Konservierungsmittel, Beschichtungsschutzmittel, Schutzmittel für Fasern, Leder, Gummi und polymerisierte Materialien, Schutzmittel für Mauerwerk, Bewitterung, Auswaschung, Testverfahren, Laborversuche, Freilandversuche, Mathematische Modellierung, Risikobewertung

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16. Abstract
Applications of biocides in outdoor materials are potential sources of biocides in environmental compartments due to leaching processes under weathering conditions.
Leaching processes and parameters as well as methods to investigate leaching processes under laboratory and semi-field conditions are described in the report. Benefits and limitations of different test approaches are discussed.
Standardised leaching tests as well as leaching experiments reported in scientific literature are listed.
The application of leaching data for risk assessments according to the Technical Guidance Documents for the Biocidal Products Directive (98/8/EC) is described.
An alternative approach for mathematical modelling of leaching data was tested and is Explained in the report. Certain difficulties that currently appear during risk assessments may be circumvented by the proposed approach.

17. Keywords
Biocide, EU Biocidal Products Directive 98/8/EC, Material preservatives,
In-can preservatives, Film preservatives, Fibre, leather, rubber and polymerised materials preservatives, Masonry preservatives, Weathering, Leaching, Test procedures, Mathematical Modelling, Risk Assessment

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Content

Abbreviations

BBIT	n-Butyl-1,2-benzisothiazolin
BPD	Biocidal Products Directive 98/8/EC
BIT	1,2-Benzisothiazolinone
CMIT	5-Chloromethylisothiazolin-3-one
DCOIT	4,5-Dichloro-2-n-octyl-4-isothiazolin-3-one
DOC	Dissolved organic carbon
DT_{50}	Time for 50 % loss, half life
EOTA	European Organisation for Technical Approval
ETAG	European technical approval guideline
ETICS	External thermal insulation composite systems
HPLC	High performance liquid chromatography
IC	Industrial Category
IPBC	3-Iodo-2-propinylbutylcarbamate
K_{ow}	*n*-Octanol-water-partition coefficient
MIT	2-Methylisothiazolin-3-on
OBPA	10,10’-Oxybisphenoxarsine
OIT	2-n-Octyl-4-isothazolin-3-one
pPVC	Plasticised polyvinyl chloride
PT	Product type
QAC	Quaternary ammonium compounds
TCPP	2,4,4’-Trichloro-2’-hydroxydiphenyl ether
TGD	Technical Guidance Document
WPC	Wood-plastic-composites

1. Introduction

Fungi, algae and bacteria have the potential to colonise materials and impair their stability, functionality, durability, and aesthetic quality. This happens especially to materials that are used under outdoor conditions, like paints, coatings, masonry, concrete, polymerised materials and technical textiles. Certain materials can also be colonised by lichens and mosses, destroyed by plant roots or attacked by insects.

Materials can be colonised whenever the moisture, temperature and nutritional supply are suitable. Light is a growth controlling factor for phototrophic organisms, like algae and cyanobacteria. However, colonisation is not only related to the exposure conditions, but also to material properties that contribute to the anchorage and development of different types of organisms. The surface roughness, moisture content, chemical composition, structure and texture of the material are important properties that affect the growth of microorganisms.

Different strategies are applied to prevent the growth of organisms on material surfaces. One approach is to control (micro)organisms by biocidal products [PAULUS (2005)]. The biocidal substances often act via release into a water film on the material's surface. However, this can also cause leaching of substances into environmental compartments if materials are exposed to outdoor weathering.

The Biocidal Products Directive 98/8/EC (BPD) of the European Parliament was adopted in 1998 with the aim of regulating the market placement of biocidal products when considering potential effects on the environment among other things. A review program was started in the member states to assess all active substances in biocidal products that are already on the market with the aim to decide on their further authorisation for the European market. The same authorisation procedure applies to new substances. The assessment of environmental risks consists of an exposure and effects assessment, subsequently compared for the characterisation of risk.

Critical input parameters required for estimating emissions are leaching rates which are also part of the required data set for the authorisation of active substances and biocidal products. These leaching rates are to be used as input data into agreed exposure scenarios. However, there is no harmonised set of leaching tests or appropriate methods available to calculate leaching rates for most of the applications of biocidal products in materials during their service life. This lack of agreed procedures causes uncertainty for applicants as well as regulators and makes a harmonised risk assessment at the stage of product authorisation difficult.

The purpose of this study is to give an overview of available leaching test methods and to assess these methods for their applicability to biocidal products belonging to the main group 2 'preservatives' according to the BPD. This report briefly describes various applications of biocidal products in materials that are the subject of the project. Only materials that are exposed to outdoor conditions are considered in this study. This includes products belonging to product types 7 (PT 7, film preservatives), PT 9 (fibre, leather, rubber and polymerised materials preservatives) and PT 10 (masonry preservatives). In certain cases, in-can preservatives (PT 6) may be present in materials and exposed to weathering. Biocidal products that are either used in materials that are not exposed to outdoor weathering or applied in processes [PT 11 (Preservatives for liquid-cooling and processing systems), PT 12 (Slimicides) and PT 13 (Metalworking-fluid preservatives)] are not considered. Wood preservatives (PT 8) were not included in this study since leaching tests for this product type have already been adopted by CEN and OECD. However, the applicability of these leaching test methods for other materials has to be considered.

A mathematical approach for the interpretation of (laboratory) leaching test data was developed in cooperation with mathematicians with the intention of circumventing difficulties in the current approach (see related Technical Guidance Documents /TGDs) when using leaching test data in the available emission scenarios.

2. Biocides in outdoor materials

2.1. Active substances

Approximately 15,000 biocidal products are registered in Germany according to the „Biozid-Meldeverordnung“, about 2,400 belonging to product types 6, 7, 9 and 10. More than 70 % of the registered products are based on a single active substance, 20 % include two, and the remaining products contain three up to five active substances. The most commonly used active substances among them are a mixture of the isothiazolinones CMIT and MIT (CAS 55965-84-9; 1714 products), and OIT (CAS 26530-20-1; 1030 products) [BAuA as at 2009-11-25].

About 320 active substances, notified in about 1300 applications of active substances in different product types, have to be assessed during the EU review process. Inclusion directives have been adopted for 35 combinations of active substances and product types (i.e. wood preservatives, rodenticides, insecticides, slimicides) so far by April 2010 [BPD Annex I, 2010-04-19]. The review programme has been running since February 2007 for active substances of product type 6, and since May 2008 for product types 7, 9 and 10, respectively.

Table 1 summarises the number of biocidal products registered in different product types belonging to main group 2 and the number of active substances that have to be assessed during the EU review process.

Table 1: Number of biocidal products and active substances per product type

Product type	Number of products registered in Germany (November 2009)*	Number of active substances (2010-05-19) **
In-can preservatives (PT 6)	919	54
Film preservatives (PT 7)	571	31
Fibre, leather, rubber and polymerised materials preservatives (PT 9)	572	41
Masonry preservatives (PT 10)	338	34

[*BAuA, Biozidmeldeverordnung (2005); **Commission Regulation (EC) 1451/2007 Annex II]

Organic substances used as microbicides usually have to penetrate cell walls. This limits the size of the molecules and requires certain water solubility and lipophilicity. Therefore the molecular masses of active substances commonly range between 100 and 500, water solubilities between 2 and 300 mg/l and octanol-water partition coefficients between log 1 and log 4. Low volatility is required for many applications. [PAULUS (2005), TOMLIN (2009), see also Annex II].

Certain properties of active substances make them eligible for special applications. For instance, substances with relatively low stability, i.e. the isothiazolinones BIT and the mixture CMIT/MIT are predominantly used to temporarily prevent the growth of microorganisms during production and storage (PT 6). Applications, where different types of organisms have to be controlled, may require combinations of active substances with different modes of action. Film preservatives (PT 7), for instance, often contain combinations of algicides and fungicides to prevent colonisation with algae as well as fungi. The usage of many active substances covers several product types of main group 2 (e.g. isothiazolinones, quarternary ammonium compounds, triazines, triazoles, Bronopol, Carbendazim, IPBC, Silver chloride, Thiabendazole, Zn-pyrithione), and to some extent product types of other main groups of the BPD (e.g. disinfectants) or plant protection products. On the other hand, materials may contain active substances belonging to different product types, e.g. paints may contain remnants of an in-can preservative and formulations with different active substances for film preservation. This situation implies that it is difficult to identify emission sources on the basis of environmental data. Risk assessments that are based on single active substances in defined product types can only look at a fraction of the service life situation.

Some properties and applications of selected active substances used in material preservatives are given in Annex II. Comprehensive review articles on biocides and their possible uses for the preservation of materials can be found in [PAULUS (2005)] for instance.

Knowledge of the actual amounts of active substances used in certain product types should be helpful in identifying the applications of biocidal products that may cause noteworthy emissions. However, sources of information are limited. In Germany, the Federal Statistical Office provides data on output volumes of a number of products. However, these figures do not include information on the actual use of biocides.

The use of active substances for different purposes including material preservation was investigated by LASSEN ET AL. (2001) for Denmark and by BÜRGI ET AL. (2007) for Switzerland. BAUMANN ET AL. (2000) and GARTISER ET AL. (2005) describe the uses of biocidal products. These studies were considered to identify important active substances as well as those uses which may cause emissions due to weathering during service life.

Based on estimations for Denmark [LASSEN ET AL. (2001)] and data from Switzerland BÜRGI ET AL. (2007) the authors state that active substances for ‘disinfectants and general biocidal products’ (main group 1) account for about 70 to 75 % of the amount of active substances used in biocidal products. About 50 % of the amount of active substances was estimated to be used in ‘private area and public health area disinfectants and other biocidal products’ (PT 2). ‘Preservatives’ (main group 2) contain about 20 to 25 % of the amount of active substances on the biocidal products market. ‘Wood preservatives’ (PT 8) dominate within this group (10 to 15 % of the total amount of active substances on the market), whereas active substances for PT 6, 7, 9 and 10 account for about 0.3 up to 2 % each. The fraction of active substances for ‘in-can preservatives’ (PT 6) was estimated to be 5 % in Denmark. However, only part of it is used for the protection of materials.

Comprehensive information on the biocides market is offered with costs in a yearly ‘Global Biocides Report’ by ‚Biocide Information’ - an information provider of global biocides industry on the web [BSI (2009)].

2.2. Protection of outdoor materials

2.2.1. Building materials

Different building materials may be protected by biocidal products. BARBEROUSSE ET AL. (2006 and 2007) demonstrated that materials that are easily colonised by microorganisms due to its physical characteristics require protection by a preservative. Release into the environment via leaching during service life is assumed to be most relevant for materials with large surface areas that are exposed to weathering, i.e. coated or uncoated walls and roofs. Examples are described in the following.

Coatings

The output of coatings in Germany was 3.15 million tonnes in 2008. The different types of coatings produced are listed in Table 2. However, there is no information on the percentage of products containing biocides.

Formulations for coatings may be contaminated by microorganisms during production mainly via the water supply and raw materials. Therefore preservatives are added to protect water based formulations during production and storage (PT 6). Usually, less stable substances are preferred to provide temporary protection. Therefore, many water based coatings contain CMIT/MIT, BIT or Bronopol at least as part of the preservation system. Cu^{2+} ions can be added to stabilise CMIT and in this way decrease the necessary amount of CMIT [PAULUS (2005)].

Active substances providing higher stability are required for the protection of coatings on exterior building materials against microorganisms (PT 7). Combinations of active substances with different modes of action are commonly used to control different organisms. Mobility and stability of the active substances within the matrices (i.e. polymeric binder matrices) have to be balanced to achieve long lasting biocidal effects by slow release. Carbendazim, IPBC, OIT, DCOIT, Zinc-pyrithione, Diuron, Irgarol 1051 (Cybutryn), Terbutryn, Folpet and Dichlofluanid were identified as important active substances for paints and renders. [see also PAULUS (2005), BAGDA ET AL. (2000)]

Table 2: Production volume of coatings in Germany 2008

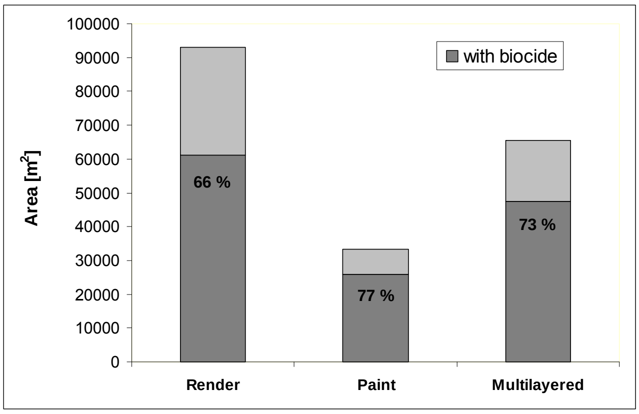
Type of product	Weight of whole production [t] *	Number of companies*
Paints for exterior applications	160,025	50
Paints and varnishes based on alkyd resin	24,862	23
Paints and varnishes based on polyester	75,048	29
Synthetic resin renders	171,830	23
Silicate bonded renders	44,342	11
Silicone resin bonded renders	22,496	6
Factory-dry mortar: plaster, not fire resistant	2,306,595	38
Factory-dry mortar: fining coat, not fire resistant	263,165	16

* Source: Federal Statistical Office, Wiesbaden 2009-09-17

A survey of plasterer companies was carried out in the summer of 2009 to find out the extent of biocide use in small building companies. Table 3 presents the most important results of this survey. Most of the 20 companies who responded to the survey use systems with biocides for plastering or painting and hold that the use of biocides has increased or was constant during the last few years. Only three companies provided information on the biocides included in the products they use. Also three of the respondents work with mineral based systems without biocides.

Table 3: Results of survey

Responding companies	20
Number of colleagues (∑)	166
Area of applied render [m²]	93100
Area of applied paint [m²]	33450
Multilayered applications [m²]	65400
Estimation of the use of biocides:	
Increasing [%]	53
Constant [%]	42



Cleaning products that are intended to remove microorganisms from colonised surfaces are not considered here since application and possible introduction into the environment are single events and not related to leaching processes. Nevertheless, for emission estimation in the risk assessment the release of biocides due to cleaning of the treated surface (rinse due to spray drift and run-off) has to be considered [Emission Scenario Document for PT 10, EUBEES/INERIS (2002)].

Roofs

Colonisation of roofs can be avoided by using metals (e.g. copper) or materials with glazed surfaces. Another approach is photocatalyic destruction of organic substances, i.e. by titanium dioxide. Roof paints – that may contain biocides (see coatings, PT 7) - are mainly offered for the restoration of roofs that are intact but appear weathered. Isothiazolinones, Diuron, Terbutryn and Carbendazim are active substances that are commonly used in roof paints in Germany [MENGE ET AL. (2005)]. Bituminous sealing membranes may be protected against root penetration by the addition of herbicides [i.e. Mecoprop, BUCHELI (1998A)].

Masonry and Concrete

Biocidal products are used to avoid the growth of algae, lichens, mosses and/or weeds on mortar or concrete or to remove them from surfaces. Mortar and concrete may contain biocides that were added for temporary protection of (water-based) raw materials during production. For instance, formaldehyde and formaldehyde-producing compounds, phenollic compounds and isothiazolinone preparations are used for this purpose. Masonry cleaners that may contain active substances, e.g. Benzalkoniumchloride and sodium hypochlorite, represent a number of PT 10 products.

Water-repellents are used to prevent liquid water penetration into masonry or cementitious building materials by capillary action. This modification of the surface is intended to reduce colonisation through limiting access to moisture. However, it has been observed that water-repellents do not prevent the growth of microorganisms, but simply delay it. The effect of water-repellents can be supported by the additional application of biocides [URZI AND DE LEO (2007), MOREAU ET AL. (2008) DE MUYNCK ET AL. (2009)].

Masonry may also be treated with fungicides to protect adjacent wood from certain basidiomycetes.

Bronopol, Carbendazim, Chloracetamid, Diuron, Glutaraldehyd, IPBC, Isothiazolinones, Oxazolidin, quarternary ammonium compounds (e.g. Benzalkoniumchloride), Terbutryn and Zn-pyrithione were often identified in PT 10 products [LASSEN (2001), BAUMANN (2000), BÜRGI (2007)]. Chloracetamid has not been supported by a BPD dossier.

2.2.2. Synthetic materials

Synthetic materials may be exposed to outdoor weathering, e.g. if these materials are used for pipework in contact with soil, swimming pools, ponds, ditch liners, roofing membranes, wall coverings, tents, tarpaulins, patio furniture.

The production of synthetic materials in Germany in 2008 was about 20 million tonnes (polyolefins, polystyrenes, PVC, poly(ethylene terephthalate) and others, inclusive resins, coatings, varnishes, glues and fibres). This also includes raw materials for coatings and textiles. The biggest consumers of synthetic materials are the packaging industry (32 %) and the building industry (25 %) [PLASTICSEUROPE DEUTSCHLAND (2009)].

Synthetic materials are often thought to be unsusceptible to microbial degradation but plasticizer and other small additives diffuse to the surface and serve as a C-basis for microorganisms. Degradation processes cause discoloration, odour or loss of physical properties. Therefore biocides may be added to synthetic materials to avoid colonisation with microorganisms.

Global consumption of formulated biocides for plastics was 15,400 tonnes in 2005, with about one-third consumed in Europe. About two-thirds of formulated biocides, mainly OBPA, OIT, and DCOIT are used in PVC. About 20 % of the consumed biocides are used in polyolefins, and about 10 % in polyurethane foam respectively. Zn-pyrithione, IPBC, BBIT, TCPP and silver ions are further important active substances used in plastics. [MARKARIAN (2006), DYLINGOWSKI AND HAMEL (2005)]

Despite protecting materials themselves, polymers may also contain biocides to generate hygienic surfaces, i.e. to avoid infection via contact with microorganisms on material surfaces. The range of active substances (quaternary ammonium compounds, phenols, iodine, metal salts of silver and tin) used for this purpose differs from the substances applied for material preservation [MAKAL ET AL. (2006)].

The active substances are only loosely entrapped and may be exposed to excess leaching especially during the initial phase of use if biocides are added directly to the polymers during production. Therefore there are strategies to control release rates and optimise release processes. One approach is encapsulation of the active substances, e.g. within siliceous frameworks such as silica and zeolite [COULTHWAITE ET AL. (2005)]. Another approach is polymer surface modification, i.e. non-covalent or covalent bonding of active substances to the polymer surface. This approach has been developed mainly for hygienic surfaces, but will also be adapted for textiles and packaging. [GODDARD AND HOTCHKISS (2007), MAKAL ET AL. (2006)]

The fast growing wood-plastic-composites (WPC) market is an important growth area for biocides. The production volume of WPCs in Europe was estimated with 100,000 tonnes in 2007. In Germany, the production of WPCs increased from 5,000 tonnes in 2005 to approximately 20,000 tonnes in 2007 [NOVA-KONGRESSBERICHT (2007)]. Wood-plastic-composites are expected to be increasingly used for terraces and garden furniture as a substitute for tropical wood. DCOIT based formulations were designed to protect WPCs from fungal attack. At the beginning of 2009 a new biocidal product especially tailored for WPCs and based on IPBC and Thiabendazole was presented [PLASTICS TECHNOLOGY (2009)].

2.2.3. Technical textiles

Examples of technical textiles under outdoor exposure conditions are textile roofs, sails, awnings, tarpaulins for vehicles or agriculture. In addition, tensile fabric structures have been increasingly accepted as a component of modern architecture since they offer attractiveness, freedom of design and cost effectiveness. Membranes permit large area designs such as stadia roofing, which are aesthetical, light and durable.

Technical textiles may be considered as special applications for synthetic materials (polymer fibres) in many cases. There are applications of organic fibres under outdoor conditions, i.e. cotton in tents, awnings and tarpaulins. However, modern fibre composites including organic fibres have so far mainly been used for indoor applications [TECHNICAL TEXTILES (2009)].

About 13,100 tonnes of tarpaulins and awnings and 18,000 tonnes of tents were produced in Germany in 2008 [FEDERAL STATISTICAL OFFICE (2009)].

Certain liquids required for sizing, finishing during the production of textiles and inks may contain preservatives (PT 6). In addition, textiles may be protected by the addition of biocidal products during storage and transport (import). This also includes insecticides.

Biocides that are used in synthetic polymers are described under 2.2.2. Carbendazim, Ethyl ziram, o-Phenylphenol (2-Biphenylol), TCMTB (thiocyanic acid (2-benzothiazolylthio)methyl ester and Zn-pyrithione, have been identified as being used in textiles for outdoor use [LASSEN (2001), BÜRGI (2007)]. Combinations of active substances may be applied to achieve long-term efficacy against a number of organisms. Biocide formulations may also include water-repellents to support material protection.

Technical textiles often consist of different layers and in addition, the fibres may be coated. In processed panels only certain layers may contain biocides, or the coatings may contain biocides rather than the fibres themselves.

Geotextiles in contact with groundwater have to fulfil the limits of drinking water regulation. Therefore no biocides are used in such products in Germany (information from an expert).

3. Leaching of biocides from outdoor materials

3.1. Materials as sources of biocide emissions to the environment

Various materials treated with biocides that are used outdoors potentially release biocides. Leaching from the material into a water film is essential for biocidal activity for certain applications, and leaching processes have to be optimised to guarantee long-term efficacy of the biocidal products. Some service life situations are described in Emission Scenario Documents (see Annex III). However, there are only a limited number of reports on biocides in environmental compartments that originate from materials. KAHLE AND NÖH (2009) analysed the origin of biocides in surface waters and attributed the pollution also to material preservatives besides disinfectants, preservatives for liquid-cooling and antifouling products.

BUCHELI ET AL. (1998A) identified roof sealing membranes as a source of the herbicide Mecoprop found in roof runoff waters. The emissions of copper - which is not only used as a component of biocidal products but also as a building material that resists colonisation by microorganisms and mosses - from roofs, roof gutters and façades into surface water were estimated to be about 60 tonnes per annum in Germany [HILLENBRAND ET AL. (2005)]. BURKHARDT ET AL. (2007) determined Terbutryn, Diuron, Carbendazim, Irgarol 1051 and Mecoprop at the discharge of an urban catchment area into a brook. They were able to trace the entire pathway from a building envelope to the receiving surface water for Irgarol 1051.

Leachability of active substances from different materials was demonstrated in laboratory and/or fields studies, e.g. for outdoor paints [LINDNER (1997)], plastics [ZITKO (1999)], roof paints [MENGE ET AL. (2005)], paints, mortar, polymer sheets and carpets [SCHOKNECHT ET AL. (2002)]. Detailed laboratory and semi-field studies have been performed with façade coatings [BURKHARDT ET AL. (2009 and 2009A)], SCHOKNECHT ET AL. (2009], BORHO - pers. commun.]. Publicly available reports on leaching of biocides from technical textiles were not found.

Indirect conclusions on the leaching of active substances from materials can be made from their occurrence in water samples. Investigation of surface water and the outfall of waste water treatment plants indicate emissions of active substances into water that can not be related to agricultural applications either because of its occurrence in areas without agriculture, at points in time when agricultural application is unlikely, or as enantiomer mixtures that can be related to certain applications. [BUCHELI (1998A), GERECKE ET AL. (2002), SKARK ET AL. (2004), QUEDNOW (2007), STEINMANN AND NIEDERHAUSER (2008), SINNIGER ET AL. (2009)]. KIEFER AND STURM (2008) summarise monitoring data collected from 2000 to 2006 in Germany for active substances that were frequently found in surface waters. Diuron, Isoproturon, Terbutryn, Fenpropimorph and Mecoprop, that are used in material preservatives, and also for other applications, were either frequently detected and/or detected in high concentrations and were therefore classified as important for the protection of surface waters. Terbutryn, which is not permitted to be used as a pesticide for agricultural applications in Germany any longer, was frequently found in surface waters [KIEFER AND STURM (2008), QUEDNOW AND PÜTTMANN (2007)]. BALSIGER (2004) summarised monitoring data from 1999-2003 from surface waters in Switzerland. Mecoprop was included in 33 %, Isoproturon in 12 %, and Diuron in 1 % of the samples at concentrations above 0.1 µg/l. These data, of course, depend on the substances that were included in the investigation. Screening programmes in Sweden were directed at the elucidation of the main sources and levels of biocides in the environment [REMBERGER ET AL. (2006), TÖRNEMANN AND JOHANSSON (2009)]. The sampling strategies were related to the use of a series of active substances. REMBERGER ET AL. (2006) detected the quaternary ammonium compound N-didecyldimethylammoniumchloride in a series of environmental samples (sediment and sludge) at concentrations that were assessed to be below risk levels. Propiconazole was detected only at the site of a wood impregnation plant, so the authors concluded that this substance may only be of local concern in Sweden. Bronopol was not detected in any of the samples, although its annual consumption in Sweden amounts to about

100 tonnes, and the substance is widely used in cosmetics, hygiene products, in chemical products such as glue and paint, as a slimicide and bactericide in industrial processes. TÖRNEMANN AND JOHANSSON (2009) did not find any of the screened substances [Tolylfluanid, Chlorothalonil, Diuron, Cypermethrin, Kathon (i.e. CMIT/MIT), Propiconazole] at levels that cause any immediate environmental and/or health concern in environmental samples from Sweden. Some of the main sources apply to material preservation: paint industries and storage sites for treated wood (Propiconazole, Tolylfluanid, Diuron), soils below outdoor building surfaces that had been recently painted (Tolylfluanid), intermittent storage sites for timber (Cypermethrin), storm water from detached houses (Cypermethrin). There was no relationship between the amounts of biocides used and the occurrence in the environment. For instance, CMIT and MIT were not detected in any of the samples, although Kathon is used in a large number of products. Diuron is used in smaller amounts, but has been found in lakes located in areas where Diuron has not been used, i.e. background lakes (explained by air transport) and at different point sources.
It remains unclear to what extent preservatives for materials contribute to the pollution since almost all substances are simultaneously used for different purposes [see also KAHLE AND NÖH (2009)]. This applies not only to product types of the BPD and pesticides in agriculture, but there may also be applications in the chemical or pharmaceutical industries. Environmental data may also be influenced by the deposition of air-borne pollutants. For several pesticides that are present in the air it was shown that they settle on surfaces and are washed off during rainfall [BUCHELI ET AL. (1998), ZOBRIST ET AL. (2000), TRAJKOVSKA (2009)].

The actual occurrence of active substances in the environment depends on distribution processes. WALSER ET AL. (2008) developed a rainfall-discharge model for Terbutryn and Irgarol 1051 originating from façade runoffs in urban areas under different scenarios with the intention of predicting its concentration in surface waters.

Publicly available information about amounts of active substances used is limited. Available production data do not allow identification of all the examples of biocidal products in materials with relevant emissions. Biocide containing materials with large surfaces exposed to the weather (e.g. roofs or coated façades) suggest that leachability of biocides should be investigated.

3.2. Leaching processes and parameters

3.2.1. Leaching processes in materials

Leaching processes are based on complex interactions of substances with the material matrix and water.

Basic knowledge of leaching processes has been developed mainly by investigation of inorganic constituents (e.g. heavy metals) in different matrices (e.g. construction products, contaminated soil and waste). Different transport mechanisms are responsible for the transfer of constituents from the matrices into water:

> **Advection**, i.e. the transport of constituents with (rain) water percolating through porous materials or running across the product
>
> **Diffusion**, i.e. transport of constituents due to the movement of molecules in the absence of flow
>
> **Surface wash-off**, i.e. the initial wash-off of soluble materials on the outside of monolithic products (similar to advection)

Diffusion is a time-dependent process driven by the concentration gradient of the constituents between the matrix and the contacting water phase. Diffusion can be the limiting step before constituents are transported due to further advection. After initial wash-off, diffusion is normally the major transport mechanism for compact materials having low permeability and porosity.

So far, knowledge about leaching processes is less detailed for organic compounds, which are commonly used in material preservatives [VAN DER SLOOT AND DIJKSTRA (2004)]. Only a limited number of reports are available on leaching of organic biocides from materials, paints, surface coatings [LINDNER (1997), TOGERÖ (2004), BURKHARDT ET AL. (2007, 2009, 2009A), MENGE ET AL. (2005), VOLKMAR AND SCHWARZE (2008) SCHOKNECHT ET AL. (2003, 2004, 2005, 2009).

Factors controlling release were summarised by VAN DER SLOOT AND DIJKSTRA (2004). Comprehensive information about leaching is also available at the ‚leaching.net'-website.

Important parameters are described in the following with special emphasis on organic substances in materials.

3.2.2. Properties of the active substances

Leachability of an active substance depends on its **chemical properties** as well as its **interaction with a specific matrix**. These parameters determine the diffusion coefficients for the active substances in defined materials. Diffusion - as the major transport process for leaching of substances from materials - also depends on the **concentration** and **distribution** of the active substances within the material since it is driven by concentration gradients.

Water solubility and **lipophilic versus hydrophilic properties** affect the release of active substances from materials into water. It has been demonstrated that leaching of organic substances is related to its water solubility and the coefficient of **n-octanol-water-partition (K_{OW})** (see Figures 1 and 2 for examples). However, the influence of water solubility and K_{OW} is modulated by additional factors, even under defined laboratory test conditions. [BURKHARDT ET AL. (2008, 2009, 2009A), SCHOKNECHT ET AL. (2009)]. The log K_{OW} values are also key parameters in the assessment of its environmental fate since many distribution processes are driven by log K_{OW}, i.e. sorption to soil and sediment.

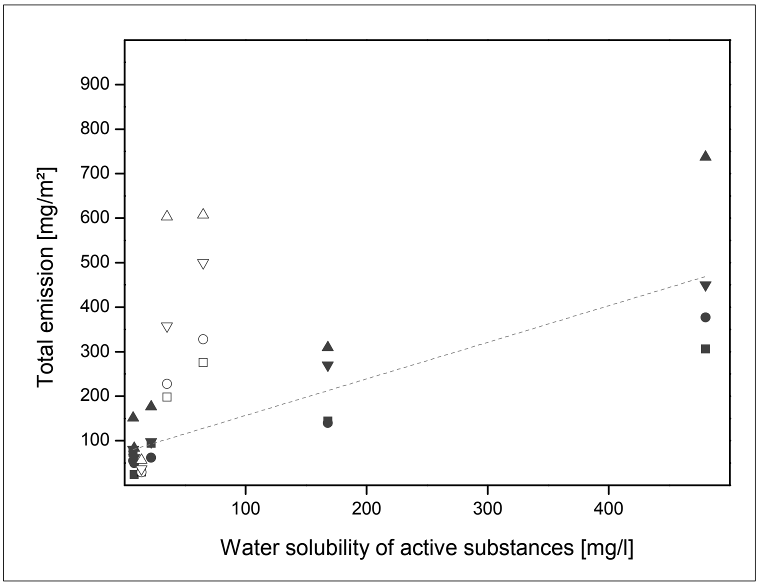


Figure 1: Influence of the water solubility of different active substances (Irgarol 1051, Carbendazim, DCOIT, Terbutryn, Diuron, Isoproturon, IPBC, OIT - listed according to increasing water solubility) on total emissions in laboratory leaching tests. The substances were leached from textured façade coatings applied on polystyrene test specimens by a test procedure including intermittent wetting and drying cycles (see Chapter 4.2.2 and Annex IV.2). The original amount was 2250 mg/m² for each active substance. Symbols represent different coatings. The results for DCOIT, Diuron and Isoproturon (water solubility: 14, 35 and 65 mg/l, respectively, indicated by open symbols) deviate from the general tendency illustrated by the straight line. [SCHOKNECHT ET AL. (2009)]

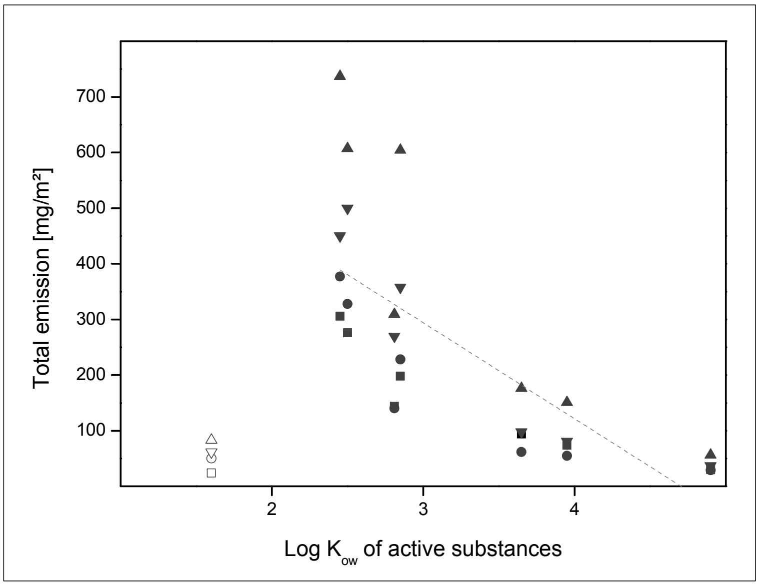


Figure 2: Influence of the octanol-water partition coefficient (log K_{ow}) of different active substances (Carbendazim, IPBC, OIT, Isoproturon, Diuron, Terbutryn, Irgarol 1051, DCOIT - listed according to increasing log K_{ow}) on total emissions in laboratory leaching tests. The substances were leached from textured façade coatings applied on polystyrene test specimens by a test procedure including intermittent wetting and drying cycles (see Chapter 4.2.2 and Annex IV.2). The original amount was 2250 mg/m² for each active substance. Symbols represent different coatings. The results for Carbendazim (log K_{ow}: 1.6, open symbols) deviate from the general tendency illustrated by the straight line. [SCHOKNECHT ET AL. (2009)]

Structure similarities (functional groups) of the active substances determine interactions with the materials, like **adsorption** onto material components and the **rate of chemical reactions** with material components. The triazines Terbutryn (N-(1,1-dimethylethyl)-N'-ethyl-6-(methylthio)-1,3,5-triazine-2,4-diamine; water solubility: 22 mg/l) and Irgarol 1051 (Cyclopropyl-N'-(1,1-dimethylethyl)-6-(methylthio)-1,3,5-triazine-2,4-diamine, water solubility: 7 mg/l) differ in water solubility, but were leached to similar extents from façade coatings in laboratory leaching experiments [Schoknecht et al. (2009)] as well as in a weather chamber [Burkhardt et al. (2009)].

Additives or admixtures to the biocidal products - i.e. their polarity, solubility in water, hydrophobic properties - affect the interaction of the biocides with the material, the composition of the leachates, and in this way also, the solubility of the active substances.

The amounts of leached organic substance and its actual concentration in environmental compartments are determined by its **stability** in the materials as well as under environmental conditions. Therefore, the concentrations of active substances in environmental compartments can be low even if a substance is readily leached. For instance, CMIT is known to be unstable under alkaline conditions, i.e. its half-time in paints and buffer solutions amounts to about one day at pH 9,5 at 40 °C compared to several months at pH 8.5 and 30 °C. Its hydrolysis is negligible at pH-values below 8 and normal temperatures [Lindner (2005)]. IPBC is known to be susceptible to degradation by UV-radiation, alkaline conditions or catalytically active metals. (see Annex II for chemical properties of selected active substances)

In principle, organic substances can be substrates for **biodegradation.**

3.2.3. Material properties

Chemical composition, **structure** and **geometry** of the materials influence the leaching of active substances.

Components of the materials (e.g. dissolvable organic carbon), pH, acid-base buffering capacity, have an impact on the **interaction with active substances** as well as the **composition of the leaching wate**r.

Binders exert a storage effect for active substances in coatings. Lindner (2005) describes that binders can immobilise OIT in coatings and increase its pH-stability to provide reasonable service life for this active substance with relatively high water solubility and limited pH-stability. Emissions of active substances from façade coatings of similar chemical composition slightly differed between the single products, but were observed to be in characteristic ranges for each substance in laboratory immersion tests as well as in weather chambers [Burkhardt et al. (2009a), Schoknecht et al. (2009), see Figure 3 for an example].

Materials composition and structure also determine the **moisture balance** within the material and on its surface while exposed to humidity (steam, condensation, thaw, rain, surface water), especially if wet periods alternate with dry conditions. **Porosity, internal pore structure** and **surface structure** influence the **availability** and **distribution of water** within the materials. Water migrates into pores of monolithic materials, but - depending on composition - materials can also take up water by swelling. Relatively low release rates have to be expected in fine channelled materials. Hydrophobic surfaces may cause water films to form on the surface, and this way increase the contact time with water. Parameters like water absorption coefficient and water vapour permeability are applied to characterise building materials. Transport processes within the material do not only occur during wet periods, but also while materials are drying. Therefore the surface temperature and thermal conductivity of the materials - depending on composition - influence leaching processes.

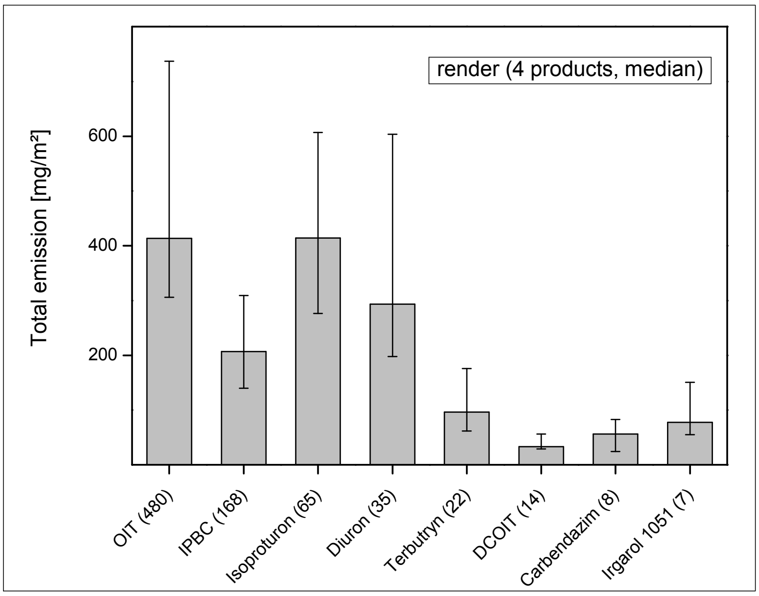


Figure 3: Emission of active substances from façade coatings with similar chemical composition [textured coatings ('renders') based on styrene acrylates]. The coatings were applied on polystyrene test specimens and leached by a laboratory method including intermittent wetting and drying cycles (see Chapter 4.2.2 and Annex IV.2). Total amounts of the active substances were 2250 mg/m². The numbers in brackets represent water solubility in mg/l. Error bars represent minimum and maximum emissions. [SCHOKNECHT ET AL. (2009)]

Water permeability of materials is usually low compared to granular matrices so that most of the water flows around the material. Therefore leaching of materials is more readily controlled by diffusion than by advection (see Chapter 3.2.1).

Size and shape of products influence leaching processes via the exposed surface area per mass unit and the distance that the active substances have to be transported within the materials by diffusion.

Leaching - as a time-dependent process - is also modulated by changes of the materials with time during service life. Environmental factors causing degradation as well as the degradation processes themselves are described by WYPYCH (2008). For instance, UV radiation may change chemical properties of the materials, whereas erosion, caused by water and frost, may increase the material's surface area. **Weathering resistance** has been intensively studied for different materials that are exposed to outdoor conditions, like coatings for buildings [BAGDA (1985)], roof materials [BERDAHL (2008)], automotive coatings [HARDCASTLE AND MEEKS (2008)], textiles and plastics for automobiles [LAMPE ET AL. (1997)], BERDAHL ET AL (2008) summarise the influence of environmental factors like sunlight, high temperatures, moisture, deposition of particles and growth of organisms on roofing materials during service life.

3.2.4. Exposure conditions

Leaching processes are controlled by natural weather conditions. Materials used outdoors are exposed to:

- **Rain, snow, hail,** varying in frequency, intensity, duration, quantity
- **Humidity** as a consequence of condensation on surfaces or fog
- **Wind,** varying in velocity and direction
- **Air temperature** and its daily and seasonal variation
- **Sunlight,** i.e. variable radiation intensity and duration
- **Dust**, atmospheric **gases** and **airborne pollutants**

Local microclimates can be observed on material surfaces.

Materials used in direct contact with water or soil are exposed to different ranges of pH, dissolved organic carbon content and complexing agents, salinity as well as diverse redox systems. Water quality is less variable if materials are exposed to precipitation. Alternating wet and dry conditions determine the transport of active substances in the material and their release into water. Processes like solution, cross linking of material components, or degradation are accelerated with temperature.

The interaction of all parameters results in variable conditions for treated materials, changing with time and location.

The **exposure orientation** of inclined and vertical surfaces is a key parameter for actual exposure to weathering. The interaction of wind and precipitation determines the amount of water that impacts these surfaces. The surface runoff is not proportional to the amount of rain, but modulated by the direction of exposure. The amount of surface runoff was 2 to 3 times higher for test specimens that were oriented towards the main wind direction compared to test specimens that were oriented southwards, in an experiment described by GROTH (leaching test workshop 2010, see Annex V).

Data for surface runoff depending on the size of vertically exposed test specimens and facades were summarised by BORHO at the leaching test workshop 2010 (see Annex V). The ratio of runoff related to total amount of rain decreased with the size of the exposed surfaces (see Figure 4). BORHO observed that test specimens fixed in the upper row of the rack (see RMI experiment in Figure 4) tend to have higher amounts of runoff. GROTH as well as BORHO reported at the leaching test workshop 2010 (see Annex V) that the surface structure had only a minor effect on the amount of runoff from test specimens (see Figure 5).

Actual exposure conditions are investigated on a model house at the Fraunhofer IME (Schmallenberg) in a recently started research project initiated and supported by an expert group of six manufacturers of biocidal active substances. The study is intended to further explain the complexity of risk assessments and identify options for refining risk assessments (GROTH, leaching test workshop 2010, see Annex V).

WALSER ET AL. (2008) modelled the total runoff from different surfaces in an urban area taking into account the inclination of surfaces, losses due to moistening of dry surfaces and in troughs of rough surfaces and the retention of water, e.g. in the soil of green roofs. The precipitation-runoff-model predicted 97 % of the actual measured data. Several models have been developed to describe wind-driven rain deposition on building facades and were compared by BLOCKEN ET AL. (2010).

However, rain events without runoff are also relevant for leaching because humidity within the material supports the transport of active substances to its surface when drying [BURKHARDT ET AL. (2009), SCHOKNECHT (2009)]. VOLKMAR AND SCHWARZE (2008) demonstrated that the active substance IPBC was transported from treated wood into a coating by water vapour in an experimental set-up.

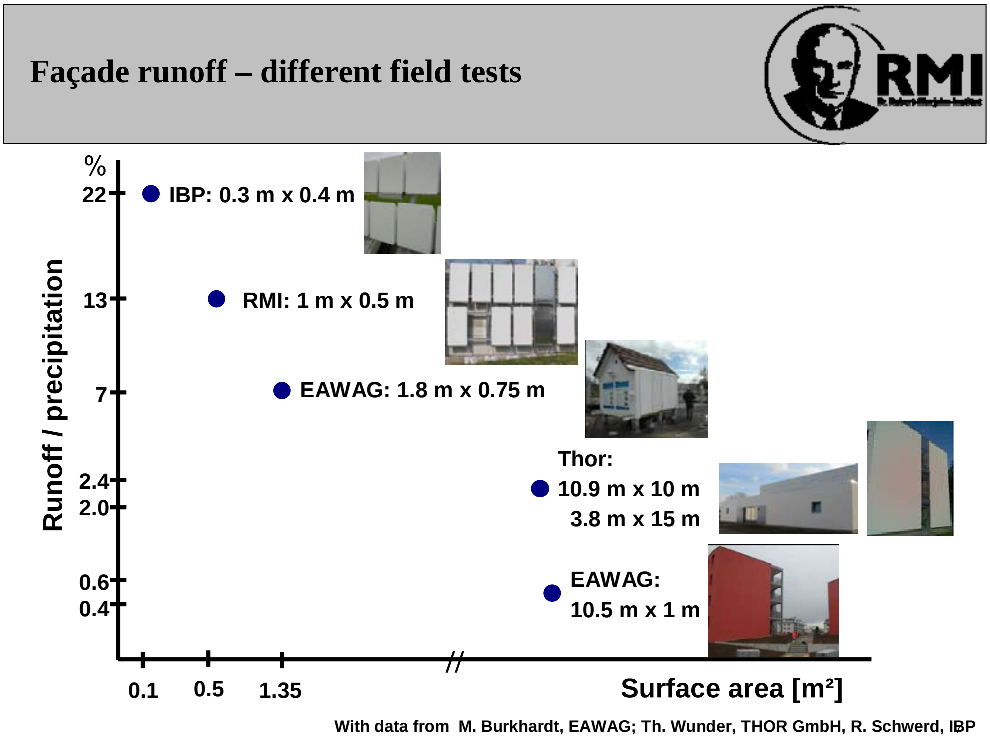


Figure 4: Runoff related to the total amount of precipitation reported by different authors for different test specimens, façades and locations, i.e. this observation can be influenced by the actual weathering conditions (kindly provided for this report by BORHO and BAGDA; presented at the leaching test workshop 2010, see Annex V).

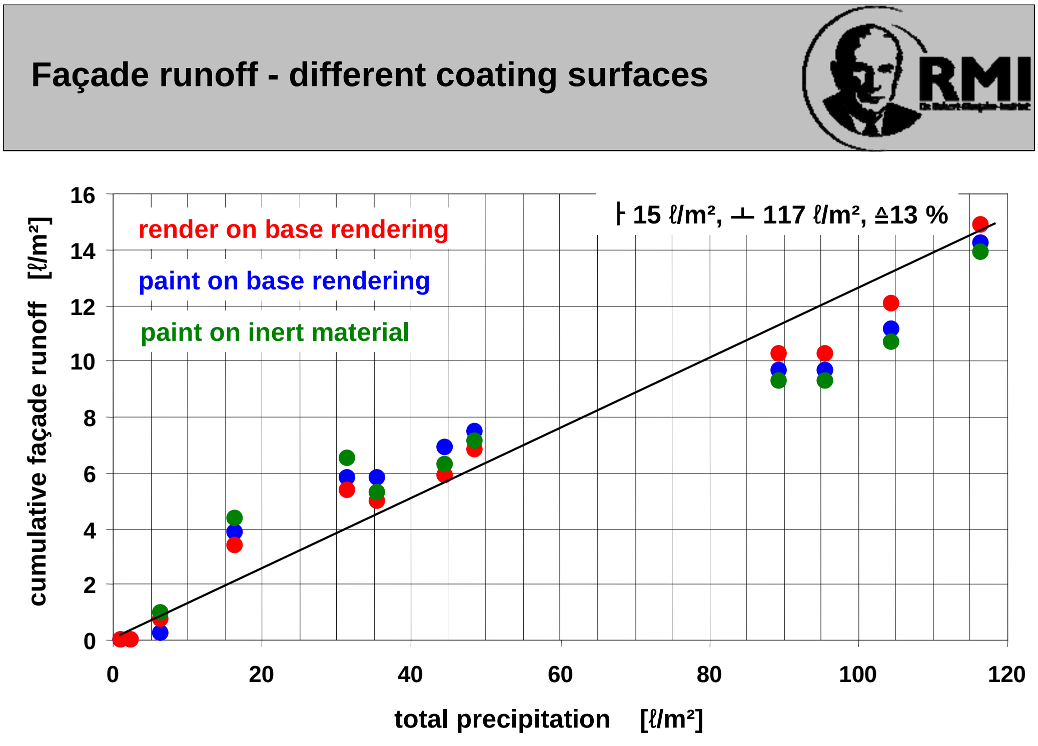


Figure 5: Amount of runoff from test specimens with different coatings in semi-field tests. Explanation: 117 l/m² precipitation caused about 15 l/m² runoff from vertically exposed surfaces (kindly provided for this report by BORHO and BAGDA; presented at the leaching test workshop 2010, see Annex V).

Organic and inorganic substances can interact with **dissolved organic carbon**. This may increase its leachability on the one hand, but reduce the bioavailability for sensitive organisms in water and soil on the other hand. However, data for interactions of organic substances with dissolved organic carbon in leaching experiments are rare compared to the amount of data available for inorganic ingredients [Van der Sloot et al. (2004), Dubey et al. (2007)].

UV radiation not only causes **photodegradation** of the biocidal active substances and other sensitive organic materials like plastics, paints, wood and organic pigments [Wypych (2008)], but also, the increased temperature, as a consequence of solar absorption leads to acceleration of chemical reactions and can hasten the diffusion of low molecular components like biocides [Berdahl et al. (2008)].

It was also demonstrated that UV radiation on test specimens prior to laboratory leaching tests reduced the leached amounts of several biocides (see Figure 6) and induced the occurrence of the triazine degradation product M1 [2-(Methylthio)-4-(*tert*-butylamino)-6-amino-*s*-triazine] in the eluates [Schoknecht et al. (2009)]. The concentrations of the active substances in the coatings tended to be lower after UV radiation than in the unexposed specimens, which may indicate photolysis of these substances in the coatings under the experimental conditions [Schoknecht, unpublished preliminary results].

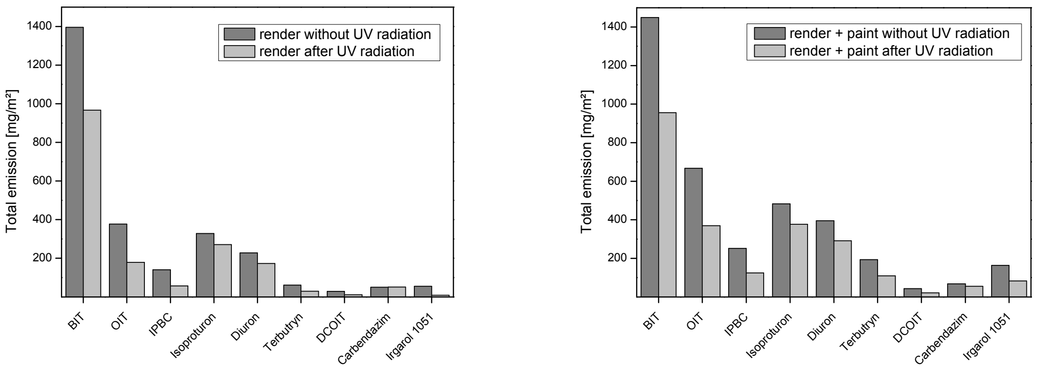


Figure 6: Influence of UV-radiation on leaching of active substances from façade coatings [textured coating (‘render’) based on styrene acrylates and the same render coated with a silicon resin based paint (render + paint)]. The coatings were applied on polystyrene test specimens and leached by a laboratory method including intermittent wetting and drying cycles (see Chapter 4.2.2 and Annex IV.2). Total amounts of the active substances were 2250 mg/m² for the render, and 3000 mg/m² for the systems of render and paint. A part of the specimens were exposed to UVA light in an accelerated weathering machine (QUV, Pausch Messtechnik) for 7 days with 6 cycles of 3 h irradiation and 1 h darkness per day resulting in an applied dosage of 22 J/m² (irradiance: 48.6 W/m², i.e. 0.89 W/m² at 340 nm) prior to the leaching experiments. [Schoknecht et al. (2009)]

4. Investigation of leaching processes

4.1. General Remarks

Release of active substances into water during the service life does not happen as a single event, but is a process with decreasing emission rates over time under constant exposure conditions. Leaching tests should differentiate between early and later stages of this process.

Generally, leaching processes can be investigated either in laboratory tests or in experiments under outdoor exposure conditions. Benefits and limitations of these approaches are discussed under 4.2 and 4.3.

Standardised leaching tests exist only for a limited number of materials. A few tests are currently under development. These tests and selected leaching studies including a short description are listed in Annex IV.

Apart from the urgent necessity for harmonised procedures for estimating emissions of biocidal active substances from materials into environmental compartments, the limited availability of harmonised test procedures provides the chance to develop a consistent methodology that applies to a variety of materials. Although the impact of individual parameters may differ for different applications, the driving forces and factors that modulate leaching processes are universally valid. Dominant factors can be identified and quantified in a limited number of tests for a wide range of products and a wide range of application scenarios as described by VAN DER SLOOT AND DIJKSTRA (2004). This concept has already been followed in leaching tests for waste and construction products as the ‘horizontal approach’ by CEN/TC 292 and CEN/TC 351.

Laboratory leaching tests for preserved materials that are directed to certain service life conditions have been developed for wood preservatives and antifouling products. The exposure conditions of the tests for wood preservatives were designed for different conditions of use, either occasional or permanent contact with water (or soil), whereas the test procedure for antifouling products mirrors the specific conditions of use of this product type.

The approach followed for wood preservatives should also apply to materials of other product types. A procedure according to the test designed for wood with occasional contact with water is currently being considered to become a European Standard (prEN 16105) for coatings. The NT Build 509 procedure that was developed for treated wood can be the basis for semi-field studies with different materials as reported by KLAMER (leaching test workshop 2010, see Annex V).

The common principle of all leaching tests is to describe the effect of water on leachable substances in a material as a process depending on time, duration of water contact and/or the amount of water applied to test specimens.

Some of the factors described under 3.2.1 and 3.2.2 are relevant for the results of any leaching test:

Chemical structure and **physico-chemical properties** of the active substance as well as the actual **formulation** of the **biocidal product**, the **composition**, **structure** and **water permeability** of the **material** directly determine leaching test results.

Other factors are defined in the test protocols:

The definition of **size and structure of tests specimens** influence the results of laboratory tests as well as field-studies. The distance from the inner parts of the material to its surface (i.e. thickness of the specimens) may be relevant for the leaching process if it is controlled by diffusion within the material. As a consequence, depletion effects may appear earlier in leaching tests than during service life if the thickness of the test specimens is less than that of real products. The surface area of test specimens may be relevant for the actual exposure to rain water (see Chapter 3.2.4 and Figure 4) in semi-field studies.

The **matrix** may influence the water transport processes, and active substances may migrate into the matrix, e.g. if coatings have to be applied on a substrate.

In general, tests simplify the complex situation that can be observed in service.

4.2. Laboratory tests

Investigating leaching processes in the laboratory can be performed under conditions of permanent immersion, intermediate wetting and drying (short-term immersion) or artificial weathering.

Laboratory tests are characterised by a limited number of fixed and controlled parameters. This ensures reproducibility and comparability of experiments. De-ionised **water** with a certain **pH** or water representing certain environmental conditions (e.g. artificial seawater or rainwater) are required for most of the tests. **Duration of water contact** and **time schedule of water exchanges -** as crucial factors determining leaching processes especially for organic substances **-** are usually fixed in laboratory studies. Commonly, leaching experiments are performed at a **temperature** of about 20 °C. This may be rather high compared to average service life conditions, however, temperatures may be much higher for surfaces exposed to solar radiation. **Relative humidity** has to be defined for the preparation of test specimens as well as for drying periods during the experiments. Another critical parameter that has to be defined to ensure repeatability of laboratory tests is the **amount of water per surface area of the test specimens**. Emissions increase with the availability of water. Parameters like **wind**, **exposure orientation**, **local or regional conditions** and **change** of the conditions are difficult or impossible to be considered in laboratory tests. **Stability** of the active substances, e.g. to hydrolysis, photolysis, biodegradation, may be considered by specific test conditions or additional ‘aging methods’ in combination with leaching tests (UV radiation, pH and temperature changes), but is usually neglected in laboratory tests.

In most cases, laboratory tests are optimised for feasibility (e.g. detectable concentrations of substances in the eluates), repeatability and cost-efficiency. The laboratory tests are not designed to indicate actual quantities that are leached into environmental compartments during service life, not only because the service life conditions are complex, but also because the actual quantities of active substances that have to be indicated are not known for the majority of applications (see Chapter 3.1).

Laboratory tests are suitable to compare products concerning the leachability of active substances. It was observed that different test procedures provide similar relations between products (see Figure 7). More complex test procedures allow a higher degree of differentiation between products. However, this should be more relevant for the development and optimisation of products than for risk assessments. Furthermore, laboratory tests are also suitable for characterising leaching processes and the influence of selected parameters by investigating the time course of emissions depending on the variation of single parameters. Laboratory data are used as input for simplified emission models (see Chapter 5.1).

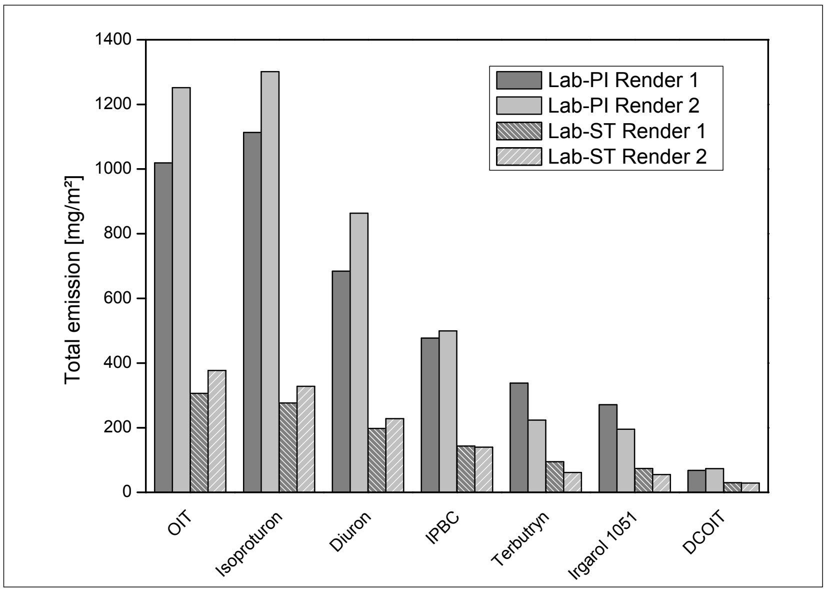


Figure 7: Total emissions of different active substances from test specimens coated with two different textured coatings (renders) in experiments with permanent immersion (Lab-PI, see Chapter 4.2.1 and Annex IV.1) and short-term immersion (Lab-ST, see Chapter 4.2.2 and Annex IV.2). The total amount of each active substance was 2250 mg/m². [SCHOKNECHT ET AL. (2009)]

4.2.1. Permanent immersion tests

Tests using permanent contact of materials with water are the classical way of investigating leaching phenomena under laboratory conditions. Basic knowledge of leaching processes has been derived from permanent immersion tests. Dynamic surface leaching tests, batch and percolation tests have been established for investigating leaching processes in matrices like waste and construction materials.

Other uses of leaching procedures are accelerated aging of test specimens prior to efficacy tests for biocidal products (DIN EN 84 for wood preservatives), or investigation of the stability of materials towards hot water and aggressive chemicals (DIN EN 14415 for geosynthetic barriers).

Dynamic surface leaching tests and single- and multi-stage batch tests are used to investigate leaching especially from monolithic materials, whereas column percolation tests are used to estimate leaching from granular materials. Certain tests are intended to characterise matrices, i.e. percolation tests describe leaching related to L/S ratios (Liquid/Solid). The maximum amount leached within 24 h related to the pH-value is determined by the ‘pH-stat-test’. As soon as a matrix has been described in detail, simple batch experiments can be performed to check the conformity of certain materials.

Most of the current knowledge concerning leaching processes refers to inorganic components. There are fewer reports about leaching tests based on organic substances, i.e. HJELMAR ET AL. (2000) and HANSEN ET AL (2004) report on their experience with Nordic tests (percolation and batch tests) that are aimed at investigating leaching of organic pollutants from contaminated soil and waste products. However, these methods apply to granular matrices.

Reproducible leaching experiments with organic substances require precisely defined ratios between water volume and exposed surface area as well as time schedules for water changes [SCHOKNECHT ET AL. (2004 and 2005)]. Analysis takes more effort for organic than for inorganic ingredients. Standardised analytical methods are available for inorganic ingredients of leachates (DIN EN 12506 and 13370). Inorganic components are stable and concentrations of water-soluble inorganic components in leachates are usually higher than the detection limits of commonly available analytical methods. Analytical methods for organic substances in leachates have not been standardised but have to be developed as in-house methods. Usually, organic substances have to be separated from the other components by chromatographic methods. Stability of the substances has to be considered, adsorption has to be avoided, and coelutants may cause matrix effects. It may be necessary to enrich organic substances in the leachates by additional steps (e.g. solid phase extraction) since the concentrations can be very low, especially for substances with low water solubility.

The appropriateness of permanent immersion tests for risk assessments is limited, since emission rates over time are unrealistically high, and transport processes within drying materials are not considered for materials that are only occasionally exposed to water or wet soil. In addition, materials (e.g. coatings) may be destroyed by permanent water contact.

An overview on permanent immersion tests for materials is given in Annex IV.1.

4.2.2. Short-term immersion tests

Tests including intermediate wetting and drying periods are directed to materials that are exposed to occasional contact with water, which applies to the majority of materials that are used outdoors, but also to certain materials that may contain preservatives and are used indoors (e.g. shower curtains).

Intermediate wetting and drying procedures were developed for wood treated with wood preservatives (CEN/TS 15119-1 and OECD Guidance Document No. 107). The procedures include dipping periods of, either one minute, one hour or two hours according to a defined time schedule, i.e. three immersion events of one minute, two immersion events of one hour or one immersion event of two hours per immersion day, with a total of nine immersion days within three weeks.

These tests are intended to mirror parameters that influence leaching processes under typical outdoor exposure conditions (short periods of water contact and transport of active substances in the materials during drying periods) and to protect materials from damage due to permanent water contact that is not expected to occur during service life. In addition, short-term immersion tests should represent actual emissions under these conditions better than do test procedures with permanent immersion.

Leaching processes during short-term immersion tests are mainly influenced by the schedule of dipping events including the duration of drying periods. The dipping schedules defined for wood were originally based on assumptions made on its water uptake. It was intended to allow only partial drying of the test specimens between dipping events of one immersion day, but drying the test specimens to their original moisture content between the immersion days. LEBOW ET AL. (2008) recorded moisture content profiles for small wooden test specimens that were exposed to either short-term immersions, or a simulated rainfall procedure, and compared the results with data on moisture content for wood exposed to natural weathering. Moisture content observed for wood under natural weathering ranged between 10 and 80 %. The maximum moisture content observed after one hour dipping events in the laboratory test was about 30 to 35 %. This was below the majority of maximum values reported for natural weathering. However, moisture content of the entire test specimen does not necessarily represent the amount of water available in the zone where leaching actually occurs.

The number of immersion days was defined so that sufficient data points for modelling of the test results could be obtained. Different modelling approaches may require a different number of data points. Therefore, in future the number of immersion days might be adapted to changing requirements when further information on the transfer of leaching test results into calculations for risk assessments is available (see Chapter 5).

Defined dipping schedules are essential to obtain repeatable test results, but do not represent complex actual exposure conditions. So far, there are only preliminary observations on the relationship between short-term immersion tests and service life conditions (see Chapter 4.4).

The implementation of drying periods causes increased emission rates during the subsequent immersion periods compared to water exchanges during permanent immersion tests (see Figure 8). It is assumed that this is induced due to an accumulation of active substances at the surface of the test specimens which is caused by transport of active substances with evaporating water during the drying periods. The active substances can be distributed again within the matrix during the wet periods.

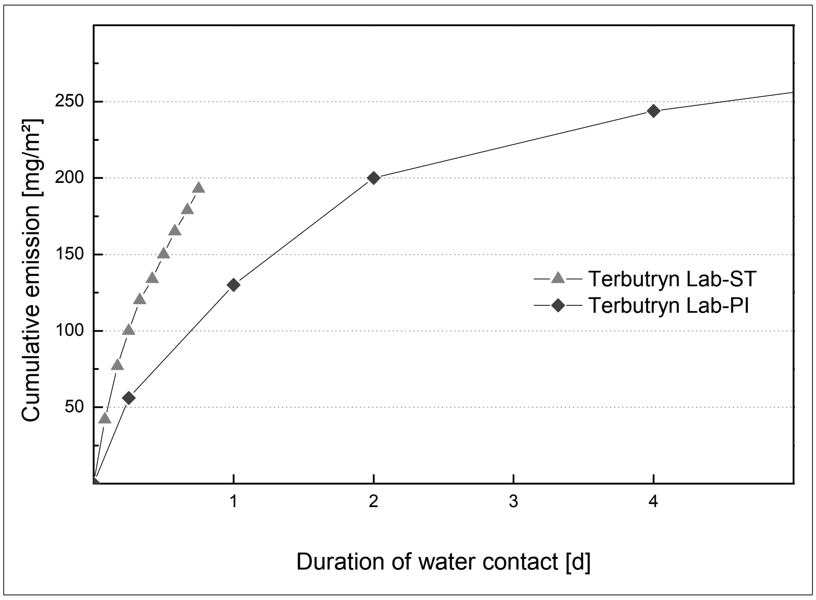


Figure 8: Cumulative emissions of Terbutryn with duration of water contact from test specimens coated with a system of textured coating and paint in experiments with permanent immersion (Lab-P, see Annex IV.1) and short-term immersion (Lab-ST, Annex IV.2). The total amount of Terbutryn was 3000 mg/m². [SCHOKNECHT ET AL. (2009)]

The time schedule including dipping events of one hour has been tested for façade coatings and was adopted for prEN 16105. A ring test with façade coatings was organised and evaluated by BORHO and SCHOKNECHT (paper in preparation) in 2009 to support the development of this standard. Eight laboratories from research institutes and industry exposed specimens coated with either a textured coating or paint according to the proposed schedule and analysed the leachates following in-house analytical methods. The results were repeatable within certain ranges for six active substances of different chemical structures (see Figure 9).

The proposed exposure conditions are also intended to be used for coating components other than biocides in accordance with the concept of a horizontal approach for leaching tests.

An overview of short-term immersion tests for various materials is presented in Annex IV.2.

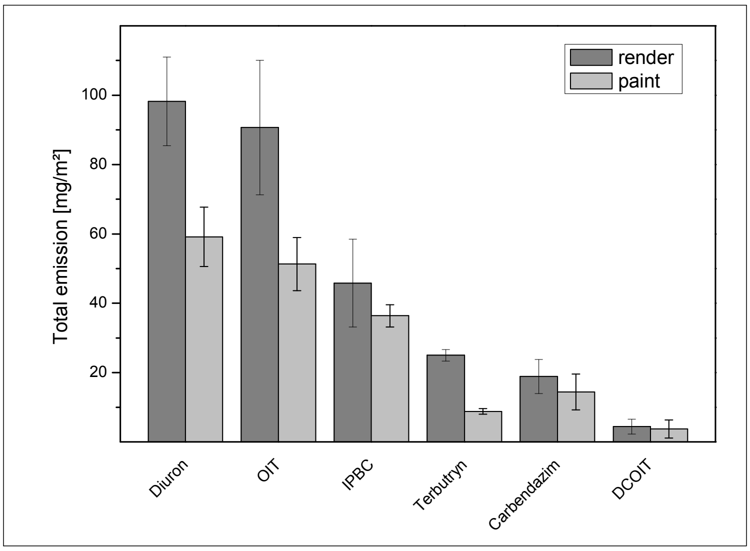


Figure 9: Total emissions of different active substances from a textured coating or a paint on EPS (expanded polystyrene) specimens in a ring test with eight participants according to prEN 16105. The results represent the sum of the analytical data for nine single leachates that were obtained during the leaching procedures. Relative standard deviations between the laboratories for the cumulative results were 7 - 31 % (DCOIT: 70 %) for the textured coating, and 9 - 36 % (DCOIT: 83 %) for the paint. Low emissions of DCOIT caused relatively high standard deviations for this substance.

4.2.3. Artificial weathering

Artificial weathering is commonly used to accelerate aging of test specimens with the aim of investigating damage mechanisms or to pre-stress specimens prior to other tests.

Usually artificial weathering tests simulate rain or water condensation, interrupted by dry periods in combination with UV-irradiation of certain wavelength, intensity and duration, and changing temperature regimes. Controlled weathering conditions assure repeatable results of these procedures. However, compliance with defined exposure conditions may also depend on the technical equipment. So far, it has been difficult to simulate rain quantities over time that correspond to natural rain events. Usually, the amount of water sprayed within a certain period of time is higher in weathering or spraying facilities than for natural rain events. Studies based on artificial weathering may benefit from controlled air quality, e.g. absence of contaminations in the air. Repeatability as well as the option to vary defined parameters allows investigation of the influence of parameters not only on aging and damaging, but also on leaching processes. However, in many cases, artificial weathering conditions do not represent service life conditions but are designed to be able to observe effects within a short period of time.

Standardised procedures are available for coatings, different types of polymeric materials, and wood (see Chapter 7, Standards).

BURKHARDT ET AL. [2008, 2009, 2009A, and leaching test workshop 2010 (see Annex V)] performed a series of tests with façade panels in a weathering chamber. The complex exposure conditions included spraying and drying periods, UV radiation, temperature and humidity profiles and where designed in accordance with the European technical approval guideline for ETICS with rendering (ETAG 004). The tests included 84 spray events of 80 l/h within 21 days. The highest concentrations of the active substances were observed at the beginning of the spray events with a decreasing tendency during the single spray events as well as during the course of the experiments. Intermediate drying periods caused increased emission rates during the following spray event. The concentrations of the active substances were not only analysed in the eluates, but also in the coatings at the end of the experiments. The losses observed in the coatings correspond with the total amounts of active substances detected in the eluates for several active substances, i.e. Terbutryn, Irgarol 1051, Diuron and Carbendazim, but were higher for IPBC, DCOIT, OIT and Zn-pyrithione. Degradation of these active substances by UV radiation, hydrolysis, or high temperatures is a likely reason for this observation.

Experiments including 10 spray events of 2.5 l/m² within 2 minutes produced the same ranking for nine active substances from a series of 6 test products as did experiments with either permanent or short-term immersions. However, the amount of water applied during the irrigation periods was not sufficient to describe the leaching processes themselves. [SCHOKNECHT ET AL. (2009)]

An overview on studies of leaching of biocidal active substances from materials under artificial weathering conditions is given in Annex IV.3.

4.3. Semi-field and field tests

Field investigations on the stability and functionality of materials under complex natural weather conditions are necessary because of the limited applicability of laboratory test results to service life conditions.

Test specimens are exposed to random natural weathering conditions, i.e. variable amount, quality and duration of precipitation as well as variable humidity, temperature and UV radiation. Weathering effects also depend on parameters like wind, exposure orientation, local or regional conditions. Air quality, e.g. contamination with anthropogenic pollutants, may also affect test results. Severe exposure, e.g. by selecting the location, exposure direction, and inclination of the test specimens, is often aimed at diagnosing possible changes reliably and at an early stage. The term ‘semi-field test’ is commonly used to indicate that these studies do not represent all parameters of service life.

Construction, size and shape of test specimens affect results of leaching studies (see Chapter 3.2.4 for the dependency between runoff and size of vertically exposed specimens). Water transport processes within the test specimens should resemble the situation in actual products as much as possible to get representative service life results. The concentration of active substances may be uncontrollably affected by randomly changing conditions during the studies.

WYPYCH (2008) summarises suggestions on how to cope with variability of weather conditions in field studies:

- expose replicates to avoid variability in samples and in their positions on the exposure racks
- start exposure in different seasons and different locations
- expose known reference materials to monitor the conditions
- do not assess a pass as a certain duration of exposure without failure, but perform tests until changes can be observed
- a statistically valid number of experiments should be conducted to account for the natural variability of testing
- monitor exposure conditions

Standardised weathering procedures are available for coatings, different types of polymeric materials, textiles, wood (see Chapter 7, Standards).

The Nordtest method ‘NT Build 509’ is aimed at investigating leaching of wood preservatives. Treated wood is assembled on test racks either horizontally or vertically. Runoff is collected depending on the amount of rain, e.g. the first sample may represent the period of 0 to 60 mm precipitation which corresponds to the average amount of rain within one month if the total amount of rain per year is assumed to be 720 mm. Runoff is sampled by defined stages within a minimum of one year. The duration of the test can be extended if necessary. This method should be adaptable to other materials [KLAMER, leaching workshop 2010 (see Annex V)].

Field or semi-field tests are suitable for observing leaching processes closely related to service life conditions. The leachability of active substances in different products can be compared, especially if the products are investigated simultaneously. However, results of independent weathering studies are difficult to compare.

Public data from semi-field leaching studies with preserved materials are rare. The results from several ongoing studies are intended to support the authorisation of biocidal products.

MORSING ET AL. (2004A) performed semi-field tests as a basis for developing the NT Build 509 procedure for preserved wood. The emission rates of the two triazoles Propiconazole and Tebuconazole decreased with the accumulated amount of rain. The amount of runoff differed considerably with the test specimen's exposure orientation. Between 2 to 10 % of the amount of rain was collected from the vertically installed, south oriented test specimens, compared to about 50 % from the horizontally installed test specimens. However, the concentrations of the leachates were comparable for both installations. The concentration in the runoff from vertically exposed test specimens was higher only at one sampling point. The authors assume that the vertically installed test specimens were exposed to a relatively high amount of 'horizontal' rain from the south during the corresponding test period. The accumulative amount of leached active substance per surface area of wood was higher from the horizontally installed compared to vertically installed test specimens if related to the accumulated amount of rain.

The emissions of copper and boron were relatively high during the first year compared to the later periods (years 2 to 6) of a semi-field test with a copper amine preservative [MORSING ET AL. (2010)]. Accumulated long term leaching was well predicted if the leaching data were fitted both to double logarithmic and linear functions of the accumulated quantity of rain if the data from the first year were excluded.

SCHERER AND SCHWERD [leaching workshop 2010 (see Annex V)] investigated façade coatings exposed to natural weathering. The leachability of different active substances (OIT, Terbutryn, Carbendazim, DCOIT, IPBC and Zn-pyrithione) was compared for different types of plasters (mineral, synthetic resin, silicate, silicone resin) and façade paints (silicate, dispersion, silicone resin). Leaching was primarily observed within the first 6 months of exposure. The leaching processes and total emissions differed for the active substances as well as the type of plaster or paint.

Façade panels, with a structure as required for ETICS, were installed on a model house in Zurich by BURKHARDT ET AL. [(2009A), leaching test workshop 2010, see Annex V]. The panels were 1.80 m high and exposed westwards without a roof overhang. The coatings were composed according to a frame formulation and different marketed products, but included an identical mixture of active substances. 62 runoff samples of up to 4.5 l/m² were obtained over one year. About half of the samples were analysed for the active substances. The total amounts of active substances in the analysed runoff samples corresponded to about 2.5 % of the original amount of Terbutryn and 7.2 % of the original amount of Diuron. The amounts of all active substances investigated range between 10 % for Isoproturon and 0.1 % for DCOIT. The concentrations of the active substances in the runoff samples were highest at the beginning of the experiment, e.g. about 5 mg/l for Terbutryn and 17 mg/l for Diuron. Later the concentrations ranged between about 0.5 and 3 mg/l for Terbutryn and about 1 and 8 mg/l for Diuron, depending on the actual exposure conditions.

An overview of semi-field tests on leaching of biocidal active substances from materials is given in Annex IV.4.

4.4. Comparison of field test and laboratory data

The difference between laboratory tests, field experiments and in-service situations is not just a different ‘degree’ of exposure, but a different ‘way’ of exposure. Table 4 demonstrates that most of the test parameters are defined in laboratory tests, whereas the test specimens are exposed to random conditions in field experiments. The influence of several factors modulating leaching processes is ignored in laboratory tests. Some parameters can be investigated by either variation of the test conditions, or inclusion of additional procedures. Structure, size and shape of test specimens are defined both for laboratory and field experiments. However, this may cause deviations from in service situations.

Table 4: Parameters in laboratory leaching tests (L) and field experiments (F)

Parameter	Defined	Outdoor conditions considered		Ignored
		Optional	Random	
Water (amount, quality, duration of contact)	L	(L)*	F	
Humidity	L	(L)	F	
Temperature	L	(L)	F	
Wind		(L)	F	L
UV radiation		(L)	F	L
Microorganisms		(L) (F)	F	L
Aging		(L) (F)	F	L
Test specimens (structure, size, shape)	L, F			
Exposure orientation	F			L
Local and regional conditions			F	L
Actual exposure during service life				L, F

* Brackets indicate that either inclusion or variation of the test parameters are possible, but not common practice.

As a consequence, there cannot be a scaling factor that balances results of different test approaches, whereas more or less constant ratios between different types of laboratory experiments can be expected. Similar ratios between the results of permanent and short-term immersion tests were observed in the experiments of SCHOKNECHT ET AL (2009) with façade coatings, i.e. these experiments mainly differed in the degree of exposure. The main factor determining leachability is the interaction of active substances and materials with water. Therefore, it should be possible to make rough estimates on ratios between the results of different test approaches. Certainly, it is important to consider each type of information that is available, e.g. knowledge on the sensitivity of the active substances towards actual exposure conditions.

Several authors tried to relate results from laboratory experiments to field experiments.

LINDNER (1997) investigated leaching of Diuron from painted test specimens from laboratory exposure to tap water and during outdoor exposure. The limited amount of sampling events did not allow the leaching processes to be described in detail. However, the recoveries of Diuron in the paint film after about 48 and 96 h of exposure to tap water (i.e. 1500 and 3000 l water/m²) were similar to the recoveries after about 330 and 660 days under outdoor conditions, respectively. Of course, the observed relation applies only for the actual conditions of both test procedures (see also Annex IV.1 and IV.4).

MORSING ET AL. (2004A) compared results from short-term immersion tests, including three dipping events of one minute per immersion day, and semi-field experiments with wood treated with a preservative containing Propiconazole and Tebuconazole. The data from the semi-field experiment were directly related to the schedule of seven immersion days within 60 days. Corresponding field data were higher than the data from the laboratory tests. The ratio of leaching between field exposure and laboratory testing differed with the active substance as well as the orientation of exposure of the test specimens in the semi-field test, and was not constant over the assessment period of about 60 days.

Laboratory tests, where water is applied in defined volumes at set times, result in exponentially decreasing emission rates with time, whereas data for single rain events result in ‘sawtooth’ profiles because of the inherent variability in natural weather both in timing and in the amounts of rainfall. This complicates comparisons of these test approaches. CANTRELL [(2009) and leaching test workshop 2010, see Annex V] in experiments with treated wood observed that data from laboratory tests and field experiments correlated when accumulated flux data were related to the total amount of rainfall. The emissions related to either rainfall or the amount of applied water were higher in the field experiment than in the laboratory test. However, there was no single correlation factor, but the ratio between laboratory tests according to CEN/TS 15119-1 and runoff from horizontally exposed test specimens differed with active substances and for the initial tests compared to the later stage of the experiments. Rough correlation factors for two active substances were between 7 and 10 for the first 60 mm of rainfall (corresponds to the first 30 days as applied in the OECD ESD for wood preservatives) and between 2.5 to 6 for the subsequent 660 mm of rainfall (corresponds to the time period of 30 to 365 days, assuming that the total amount of rain is 720 mm per year). However, CANTRELL recommends further investigations, especially for projections beyond one year.

A series of leaching tests according to different approaches were performed with identical façade coatings, i.e. textured coatings (renders) and systems of render and paint, all containing the same mixture of active substances at the same concentrations. Façade panels prepared with these coatings were exposed in a weather chamber (see Annex IV.3) and on a model house (see Annex IV.4) by BURKHARDT ET AL. [(2009, 2009A), leaching test workshop 2010, see Annex V]. Small test specimens were exposed to permanent and short-term immersion as well as irrigation (see Annex IV.1 to IV.3) by SCHOKNECHT ET AL. (2009). Similar ranking between the investigated products was observed for artificial weathering as well as the immersion tests. The percent losses were highest in the weathering chamber followed by permanent immersion for the whole duration of the experiments, and lowest due to short-term immersion. An exemplary selection of results from the different test procedures is given in Table 5. The concentrations of active substances in the runoff samples from the model house were relatively high compared to results from the laboratory tests, whereas the total losses obtained during one year were similar to losses within a few stages at the beginning of the laboratory experiments. Similar amounts of water caused similar emissions in the weather chamber and due to short-term immersion. Obviously, relatively long duration of water contact during permanent immersion (48 h) compared to short-term immersion (3 h) and artificial weathering (1 h) caused increased emissions related to similar amounts of water applied in the experiments. Additional influences on the panels at the model house, e.g. transport of active substances to the surface area during dry periods, should be responsible for higher emissions of Terbutryn with the amount of water applied per surface area as well as relatively high concentrations of Terbutryn and Diuron in the runoff samples compared to the results from the weather chamber and short-term immersion. The concentrations of the active substances in the runoff obtained in the irrigation experiments were also relatively high, probably since each spray event of only 2.5 l/m² represented the initial phases of rain events, and the active substances were transferred to the surface between the spray events. It has to be considered that ratios between the results only apply for the selected active substances and the actual test conditions.

Table 5: Results from different leaching experiments for Diuron and Terbutryn

	Diuron		Terbutryn		
	Concentrations in eluates / runoff		Concentrations in eluates / runoff		Losses related to similar amounts of water/surface area*
	Initial	Final stages	Initial	Final stages	
	mg/l	mg/l	mg/l	mg/l	% **
Model house (Annex IV.4)	17	1 - 8	5	0.5 - 3	4
Weather chamber (Annex IV.3)	4	0.06 - 0.1	1	0.06 - 0.1	2
Permanent immersion (Annex IV.1)	4.4 - 8.0	3.5 - 5.5	1.3 - 3.6	1.2 - 2.5	6
Short-term immersion (Annex IV.2)	1.3 - 4.4	0.2 - 0.7	0.3 - 1.1	0.1 - 0.35	2
Irrigation (Annex IV.3)	2.7 - 5.7	1.2 - 3.7	0.6 - 2.1	0.4 - 1.5	1 (25 l/m²)

* The runoff collected from the model house was about 70 l/m² during one year. The amounts of water applied per surface area were 80 l/m² during one spray event in the weather chamber, 75 l/m² in the immersion tests (corresponds to the first three immersion periods in the permanent immersion, and three immersion events in the short-term immersion experiments, respectively). A total amount of 25 l/m² was applied in the irrigation experiments.

** related to the original amount of active substance (the products, concentrations of active substances and thickness of the coatings were identical for all tests)

Generally, results of different tests should be compared on the basis of emissions per surface area. Comparisons based on percent losses are only possible for test specimens of identical size, structure and concentration of active substances.

Preliminary experience on comparisons between laboratory and field experiments can be summarised as follows:

1) The most reasonable basis to compare data from different tests is to relate accumulated emissions per surface area to the accumulated amount of applied water / rain. These leaching courses are modified by the duration of water contact and the exposure conditions between leaching events.
2) Ratios between results of different experiments depend on the leached substance, the actual test conditions and the stage of the experiments.

5. Application of test data to risk assessment

5.1. Risk assessment according to the Biocidal Products Directive

The general approach for environmental risk assessments for biocides is described in the 'Technical Guidance Document on Risk Assessment' (TGD, Part II).

The scheme in Figure 10 illustrates material parameters as well as environmental conditions that determine leaching test results and this way affect risk assessments. Environmental conditions are represented in the leaching test results in a different way and to different degrees, depending on the test approach. Water quality, temperature and the exposure schedule are defined in laboratory tests, whereas the results of field studies are influenced by variable environmental conditions.

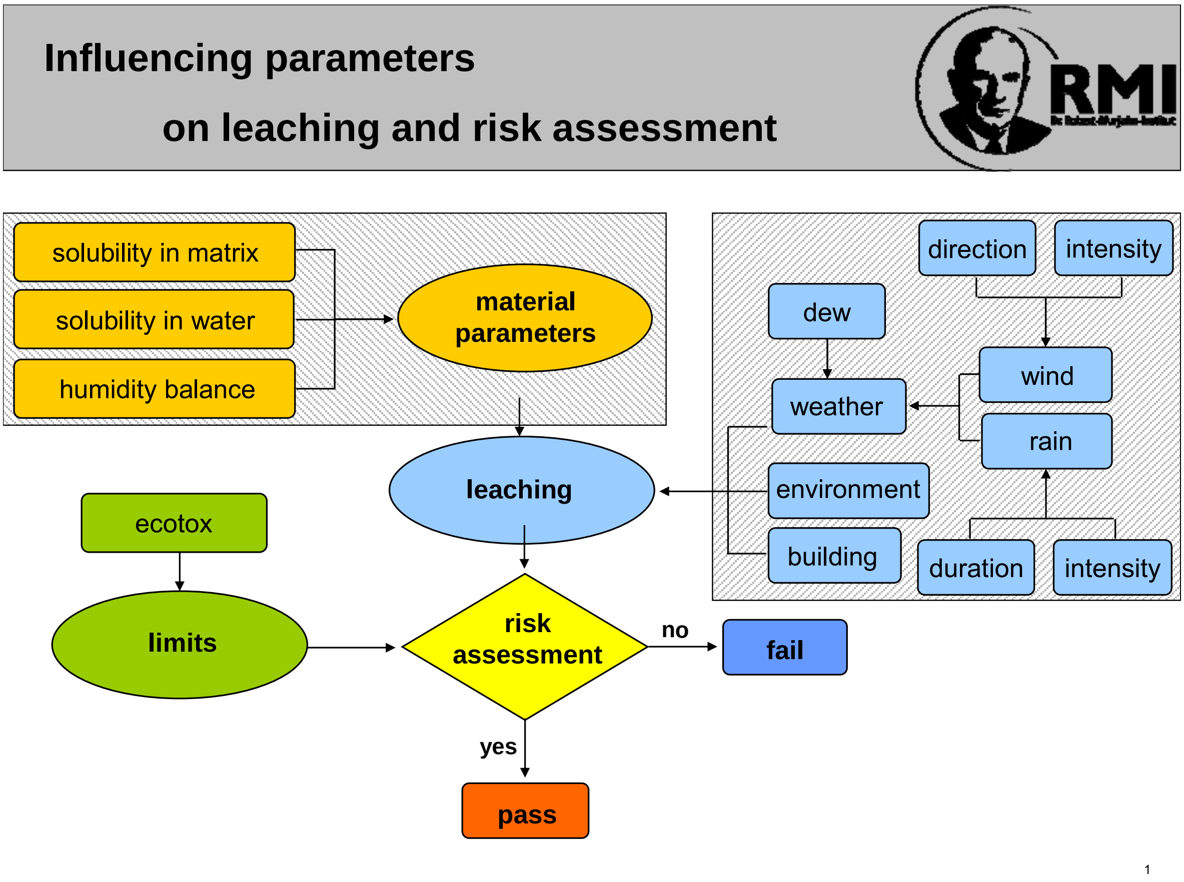


Figure 10: Parameters influencing leaching processes in service and risk assessments (kindly provided for this report by BORHO and BAGDA; presented at the leaching test workshop 2010, see Annex V)

Risk assessments take into account the release of active substances to environmental compartments. Emissions during service-life of long-life articles (e.g. preserved materials) are one of the input sources. It is assumed that emissions from long-life articles are highest at steady state, i.e. when the flow of an article into society equals the outflow. The annual release of active substances is described by Equation 1 (TGD, Part II, 2.3.3.5, Equation 10)

$$RELEASE = F * Q_{total} * T_{service} \tag{1}$$

RELEASE	Annual total release at steady state	$[tonnes * year^{-1}]$
F	Fraction of tonnage released per year	
Q_{total}	Annual input of a substance	$[tonnes]$
$T_{service}$	Service life of product	$[year]$

Equation 1 can be applied for single compartments as well as all relevant compartments. Calculations can be performed with either a default value for F (e.g. 10 %), or F-values that have been estimated for a certain product. Product specific F-values are described by Equation 2 (TGD, Part II, 2.3.3.5, Equation 16).

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$$F = \frac{EMISSION_{area} * 1000}{THICK * CONC} \tag{2}$$

$EMISSION_{area}$	Annual amount of substance emitted per area	$[g * m^{-2} * year^{-1}]$
THICK	Thickness of the emitting material	$[mm]$
CONC	Concentration of the active substance	$[kg * dm^{-3}]$

Alternatively to Equation 1, local emission rates can also be calculated according to a generic formula (Equation 3).

$$E_{local} = \frac{Q_{product} * C_{chemical} * F_{emission} * (1 - F_{abatement})}{T_{emission}} \tag{3}$$

E_{local}	Local emission rate	$[kg * day^{-1}]$
$Q_{product}$	Input of product	$[kg * day^{-1}]$
$C_{chemical}$	Concentration of active substance in the product	$[kg * kg^{-1}]$
$F_{emission}$	Fraction released	
$F_{abatement}$	Efficiency of risk/emission reduction measure	
$T_{emission}$	Number of emission days	$[day * 365 day^{-1}]$

The release rates are taken to estimate the local predicted environmental concentrations (PECs) by assuming standard environmental compartments into which the biocides are released. In general, input data for the estimation of local PECs are physico-chemical properties of the substances, characterisation of the environment, **emission data**, partition coefficients, degradation rates, and fate in sewage treatment plants.

Migné (2002) describes in the emission scenario document for product type 10, how local concentrations of active substances in the soil compartment around a house can be estimated (see Equation 4).

$$(4) \qquad C_{local,time} = \frac{Q_{leach,time} * AREA}{V_{soil} * RHO_{soil}}$$

$C_{local,time}$	Local concentration estimated for different assessment periods
$Q_{leach,time}$	Cumulative quantity of an active substance, leached over the assessment period
AREA	Leachable area in the relevant scenario
V_{soil}	Soil volume adjacent to surface treated
RHO_{soil}	Bulk density of wet soil

$Q_{leach,time}$ data should be derived from leaching tests. For product type 10, the ESD proposes performing leaching tests using a similar philosophy as for wood preservatives. Two different time windows are considered:

Time 1:	30 days for the initial assessment period
Time 2:	> 30 days for a longer assessment period

To perform an environmental risk assessment the PEC values for the compartment under consideration have to be compared with the ecotoxicological effects of the active substances, i.e. with the so-called predicted no effect concentrations derived from effects testing on selected test organisms in the respective compartment (PNEC values). A risk is identified if PECs exceed the corresponding PNECs. Information on the leaching behaviour of the active substance from treated materials is a key input parameter for environmental exposure assessment. In a first step, PECs might be calculated assuming a release of the total amount of active substances during the assessment period (so-called ‘worst-case assumption’). If these PEC values are below the PNEC values, in general no further data are required to describe actual emissions due to leaching processes. However, experiences during the EU review programme show that in most cases this approach results in a risk for the environment. Thus, if calculated PECs exceed PNECs, leaching test data are required for a refinement of the environmental exposure assessment. There are further options for a refined exposure assessment, e.g. taking into account degradation processes of the active substances in soils or water-sediment systems. Alternatively, monitoring data or emission data obtained under service life conditions can be used.

Due to the known differences between laboratory tests, field experiments and in-service situations and the different kind of exposure, assessment factors have been postulated at the stage of risk assessment for biocides. For instance, factors of 5 or 10 depending on the immersion schedule of laboratory leaching tests for wood preservatives have been applied in the review programme for existing active substances (EU leaching workshop, 2005).

The use of defined emission scenarios simplifies the estimation of PEC values. This implicates that data collected or calculated for model situations cannot be directly transferred to other conditions (see the data on actual exposure of facades depending on size and exposure orientation in Chapter 3.2.4 for an example). However, simplification is essential for risk assessments. It allows standardised procedures to be used for evaluating data and to compare data for different products.

The obstacle in this procedure is that a reasonable method of using data from laboratory leaching tests as input data for PEC calculations has not yet been developed. It has not been demonstrated how leaching test data can adequately fit into emission scenarios.

The Emission Scenarios represent ‘living documents’ that have only partly been proven in the risk assessment of biocides up to now and will have to be updated after getting more practical experience with them. One topic for further discussion should be whether the worst case scenario represented by the model house in the ESD for PT 10 (INERIS/EUBEES 2002) has to be adapted to observations on actual exposure. In addition, input is required for reasonable transfer of laboratory data into time-related calculations for risk assessments, and the duration of ‘Time 2’, i.e. the long-term assessment period, has not been defined yet.

5.2. Interpretation and modelling of leaching test results

Data obtained from laboratory leaching tests do not change randomly between the leaching periods (as service life data do), but can be described by a continuous trend (usually decreasing exponentially). The data trend can be described and extrapolated by mathematical functions. Different types of regression functions can be derived from leaching test data. FLEUREN (2006) compared regression models applied to wood preservatives based on either fluxes or cumulative leaching. Examples are given in Equations 5 (flux based model described in OECD ESD for wood preservatives) and 7 (biphasic model based on cumulative leaching). JUNGNICKEL ET AL. (2008) applied the biphasic model given in Equation 6 for results from leaching tests with roof paints.

$$\log_{10} FLUX(t) = a + b * \log_{10}(t) + c * \log_{10}(t)^2 \tag{5}$$

FLUX	Leaching rate	$[mg * m^{-2} * d^{-1}]$
t	Time	$[d]$
a, b, c	Parameters estimated by the model	

$$C(t)_{leached} = C_{leached,\max 1} * (1 - e^{-k_1 t}) + C_{leached,\max 2} * (1 - e^{-k_2 t}) \tag{6}$$

$C(t)_{leached}$	Cumulative amount leached over time t	$[mg * m^{-2}]$
t	Time	$[d]$
$C_{leached,max1}$	Maximum amount leached in the first phase, estimated by the model	$[mg * m^{-2}]$
$C_{leached,max2}$	Maximum amount leached in the second phase, estimated by the model	$[mg * m^{-2}]$
k_1	Emission constant during first phase	$[1 * time^{-1}]$
k_2	Emission constant during second phase	$[1 * time^{-1}]$

FLEUREN inferred from his calculations that, according to the different mathematical models, they can be applied to describe the test results, whereas the biphasic model provides the best fit. He recommends applying models that are based on cumulative data, since the results can easily be used to calculate cumulative leaching for any given time. However, FLEUREN also points out that even if different equations fit the analysed data well, it is not clear whether or not the data provide realistic leaching rates that can be used as input parameters for various emission scenarios, and recommends determination of further parameters like pH, solid organic carbon (binding sites in wood) and dissolved organic carbon to be able to use a more advanced diffusion model.

At least, the parameters determined in the regression functions depend on the exposure conditions. Extrapolations based on regression functions apply only to the actual test parameters.

A simplified procedure for the estimation of emissions during certain time periods was proposed for antifouling products (Draft DIN EN ISO 10890). The amount emitted per area and day is calculated on the basis of the total amount of biocide in the antifouling, service life time, and an assumption on the emission during service life (e.g. 90 %). Higher initial emission rates are considered using a correction factor.

Although regression functions of laboratory test data do not describe leaching processes under outdoor conditions, laboratory investigations allow the identification of driving forces and phases of leaching processes. Logarithmic plots of cumulative emissions versus time can be applied to identify diffusion controlled release, depletion of leachable species, delayed release, surface wash-off, wash-out of mobile species as well as a change in chemical conditions (NEN 7345). Figure 11 shows an example for leaching data from different tests with coatings.

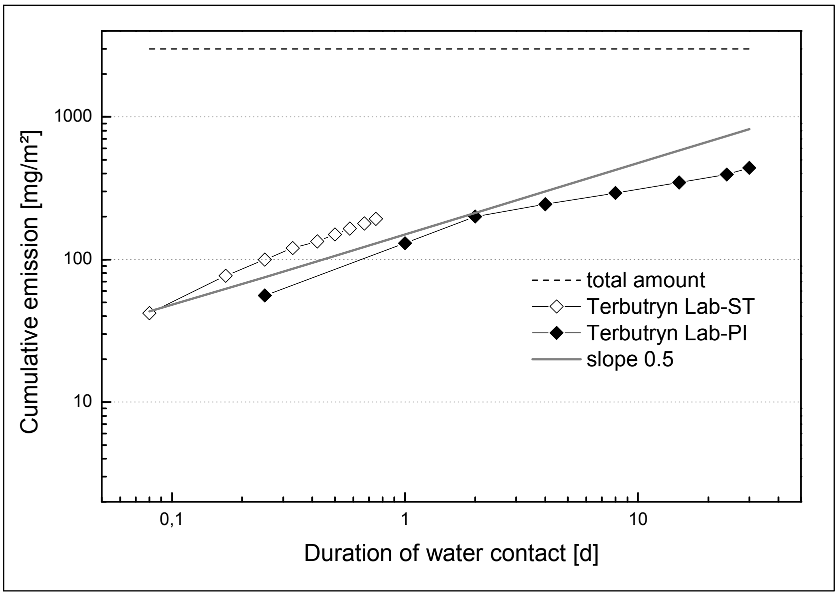

Figure 11: Logarithmic plots of cumulative emissions of Terbutryn with duration of water contact from test specimens coated with a system of textured coating and paint in experiments with permanent immersion (Lab-PI, see Chapter 4.2.1 and Annex IV.1) and short-term immersion (Lab-ST, see Chapter 4.2.2 and Annex IV.2). The total amount of Terbutryn was 3000 mg/m². The graphs are parallel to a graph with a slope of 0.5 if leaching is controlled by diffusion. Flattened curves at the end of the leaching tests indicate depletion of the leachable active substance (see the curve for the Lab-PI experiment). [SCHOKNECHT ET AL. (2009)]

Leaching processes of inorganic ingredients from concrete based construction products have been extensively investigated including chemical reactions of inorganic substances in the leachates. Reactive mineralogical phases are a key factor controlling release of inorganic ingredients. It proved to be impossible to simply extrapolate laboratory leaching test results to field conditions. Therefore TIRUTA-BARNA (2008) and SCHIOPU ET AL. (2009) adapted the geochemical software PHREEQC to model leaching processes from concrete paving slabs. The model described by SCHIOPU ET AL. is based on the results of different laboratory tests, i.e. prCEN/TS 14429 (determines acid/base neutralisation capacity and pH-influence on release of substances of the test material), a dynamic leaching test (i.e.

continuous flow of leachant through a test assembly with a monolithic sample; eluate collected in separate fractions after fixed periods of time) and a multibatch test (i.e. leachant in test assemblies was completely renewed after fixed periods of time; similar to NEN 7345, see Annex IV.1). In addition, a thermodynamic database was involved, and rain water balance, water/material specific contact conditions, and uptake of atmospheric carbon dioxide were included into the model. The pH and concentrations of several inorganic substances (Ca, Na, K, Al, Si, Cr, Cu, Zn, Cl^-, $SO4^-$) were predicted for an acceptable range for leachates originating from different outdoor scenarios, i.e. a 'run-off' scenario (rain water run over a concrete block), and a 'stagnation' scenario (concrete block immersed in leachant in an open container; water could overflow during rain events).

WALDRON ET AL. (2005) modelled diffusion processes to predict long-term leaching of copper, chromium, arsenic and boron from treated wood.

Diffusion based models were also proposed to estimate migration of constituents of packaging materials into food [HELMROTH ET AL. (2002), SANCHES SILVA ET AL. (2007), CRUZ ET AL. (2008)].

5.3. Analytical Model

The parameters calculated by an arbitrary selected regression model can hardly be interpreted to describe driving forces of leaching processes. Besides, regression functions are highly dependent on the choice of the factor time, e.g. the number of cycles, the actual total time or the actual contact time etc. Furthermore, irregularities in the experimental process cannot be corrected. In addition, a lack of reproducibility exists since a better fitting implies worse reproducibility of the regression parameters from laboratory to laboratory. Extrapolation of leaching data is statistically not valid for regression models.

In order to overcome these shortcomings, a semi-analytical approach based on an idealised transport model of diffusion and leaching has been developed by UHLIG AND BALDAUF (for further details the reader is referred to pp 61).

This model is based on a simplified description of diffusion between layers of the material and leaching processes, using Fick's Laws. These processes are modelled non-stationary in time under the assumption of constant diffusion. Calculations have been carried out by means of the method of finite differences both in space and time. This procedure is closely related to the Crank-Nicholson procedure which is applying the finite differences technique solely in space.

The method has been applied to approximately 100 series of experimental data from leaching tests with façade coatings with either permanent or short-term immersions of test specimens (see Chapters 4.2.1 and 4.2.2 and Annex IV.1 and IV.2) and 20 series of leaching data with wood preservatives. The fit of the model was satisfying in all cases; the analytical approach outperformed in almost all cases the classical regression techniques such as the bi-phasic model.

Figure 12 represents the results for a façade-coating test series with discontinuous water contact for Irgarol 1051 (short-term immersions, see Chapter 4.2.2 and Annex IV.2). Apparently, the fit of the bi-phasic model is not satisfying as for several measurements there is no overlap between model and measured data. There are no discrepancies between measured data and the analytical model. This observation was confirmed for the other series considered in this report.

To examine the model for more variable test conditions (duration of test series, immersion periods, drying periods) another 14 series of experimental data were provided and statistically analysed. This analysis confirmed that the analytical model results in a satisfying fit also for longer test series with varying immersion and drying periods. Figure 13 illustrates a test series with several irregularities: at day 12 the test specimen was immersed for 6 hours instead of 2 times 1 hour; the subsequent drying period was extended from 3 days to 17 days. As the analytical model takes into account all these irregularities, the model fit is quite satisfying.

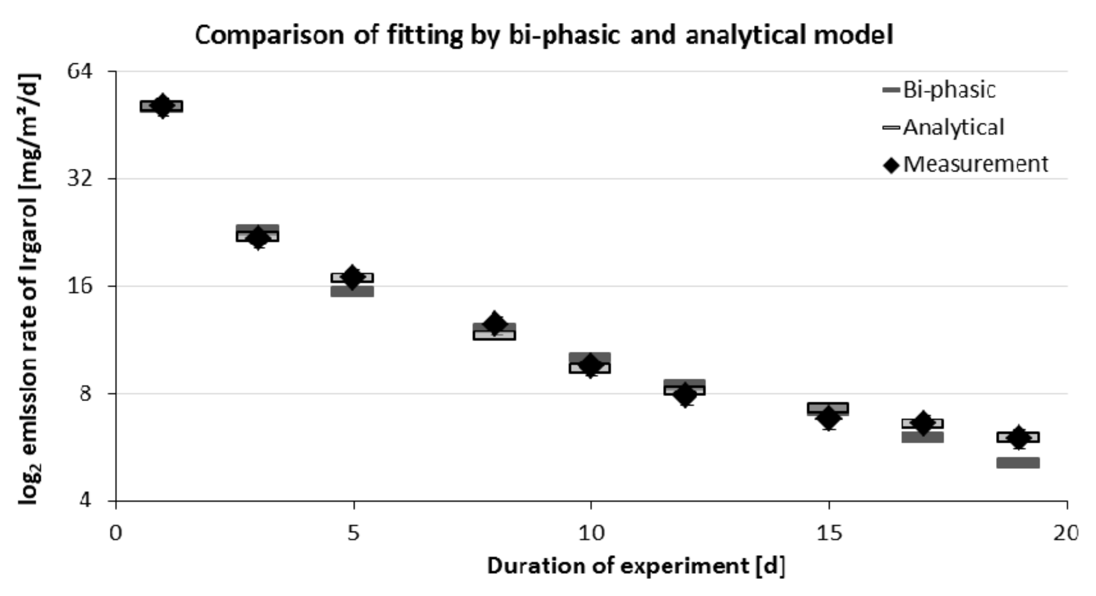

Figure 12: Comparison of fitting by bi-phasic and analytical model with data for Irgarol 1051 from an experiment with test specimens coated with a textured coating and exposed to short-term immersion (see Chapter 4.2.2 and Annex IV.2). The error bars represent the extended measurement uncertainty within the laboratory.

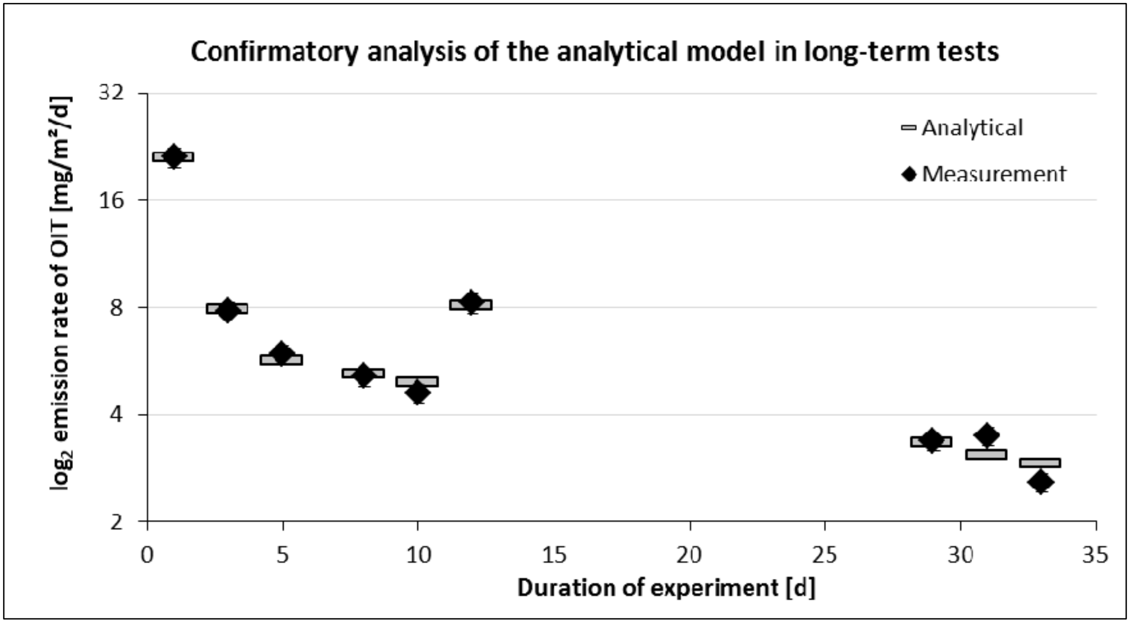

Figure 13: Confirmatory analysis for the analytical model with data for OIT from an experiment with test specimens coated with a façade coating (paint) and exposed to short-term immersions according to a modified time schedule. The error bars represent the extended measurement uncertainty within the laboratory.

In contrast to the pure mathematical fitting by a regression function the modeling with analytical models is deduced from physicochemical and deterministic processes of leaching. This has several advantages: As the analytical model is not only based on statistics, it is more appropriate for temporal extrapolation of leaching than common regression models. Irregularities in the experimental process can be corrected for by the analytical model, and it can easily be adapted to very different conditions and experimental processes. It is also easier to examine its predictive power for extrapolation purposes (within regression-based protocols the experimental schedule has to be continued strictly whereas the analytical approach allows simplifying the schedule). Due to an improved reliability, there is less risk of overestimating the total amount of leached active substance.

There are further **options** to develop and to extend the applicability of the model and to simplify the interpretability of parameters:

- The model could be improved by incorporating a very thin boundary layer and considering different transport mechanisms (transport/diffusion depends on temporal and spatial changes of humidity in the material).
- Improvement of the model by incorporating physico-chemical parameters (this could reduce the number of parameters to be estimated and would allow for reduced test protocols).
- The model could also be applied to the humidity gradient within the material. This would allow for better understanding of diffusion and transport of substances depending on transport of water. This could explain quantitatively why drying periods accelerate leaching processes.
- The model could also be extended for application under field conditions. A crucial element for the latter, however, is a comprehensive validation of model.
- Finally the model could be used to forecast the total amount of leached active substance with at least 2 or 3 data points on the basis of a comprehensive database of empirical data and physico-chemical parameters.

Further development of the model requires experimental data different from routine protocols, i.e.:

- Experimental series with more than 9 data points including varying experimental conditions
- Analytical results for each immersion event
- Concentration profiles of active substances within material
- Humidity profiles within material
- Diffusion and leaching coefficients for different active substances and materials

A tool for using the analytical model in practice can be developed.

6. Conclusions

Currently available **test approaches** (i.e. basic approaches to expose test specimens to water contact) should be sufficient to investigate leachability of biocidal active substances from preserved materials:

Permanent immersion tests including water exchanges allow general investigations of leaching processes and their driving forces to be undertaken.

Short-term immersion tests may be performed alternatively either to maintain integrity of materials, or when intermediate wetting and drying periods should be considered.

Semi-field tests may be performed to investigate leaching processes under outdoor conditions.

Publicly available data using these test designs are limited to certain product types (mainly wood preservatives and coatings). However, the applied test procedures should be adaptable to investigate other materials as well, i.e. polymerised materials like plastics and technical textiles. Adaptations may refer to the preparation, conditioning and handling of test samples rather than to the exposure scenarios themselves. These adaptations should be publicly available, e.g. as **material specific appendices for existing standardised procedures**. It is also probably necessary to adapt analytical methods to material specific co-elutants.

The development of a reasonable **horizontal approach** (i.e. a set of methods that generally applies to investigate leaching processes from different types of materials) should be followed, since the basic mechanisms of leaching are comparable for all combinations of active substances and materials. However, the horizontal approach for the investigation of leachability of organic substances from materials may differ to some extent from the horizontal approach for leaching studies on inorganic ingredients from waste and construction materials. Tests for **monolithic materials** should be more relevant than tests for granular matrices. In addition, speciation as well as chemical reactions (especially precipitation) depending on the composition of the leachant seem to be less important for organic than for inorganic ingredients. This especially applies for ‘pure’ rain water. **Binding to organic substances** within the surrounding compartment may have a severe influence on leaching processes if leaching occurs due to direct contact with soil, sediment or water containing high levels of organic substances (e.g. humic acids). Binding of active substances to the organic constituents of materials, and the amount of **dissolvable organic carbon** (DOC) belong to the ‘material-specific’ parameters. DOCs in materials can be constituents of materials from natural sources (e.g. wood), but also synthetic substances (e.g. binders in coatings). Although there are still limited data on coelution of DOC and biocides from materials, DOC has to be considered as a key parameter in explaining differences between materials, and to optimise leaching processes from materials. DOC might be a parameter for the classification of materials concerning their leachability. Additional key parameters for the leachability of organic substances from materials are their physico-chemical properties like **water solubility** and **n-octanol-water-partition coefficient**. The pH of the leachate may influence the stability of organic substances. However, **pH-dependency** tests seem to be crucial only if materials are intended for exposure to a wide range of pH, i.e. in contact to soil, sediment and surface water rather than to leaching due to precipitation. **Long-term studies** may be required to distinguish leachability at the beginning and during later periods of exposure, whereas **short tests** should be sufficient to prove **compliance** of a certain preserved material with materials that have been described in detail. This may concern composition and concentration of active substances as well as changes of the materials composition.

Options for the **interpretation of laboratory test data** as described in NEN 7345 should be utilised. Differentiation between emissions, either due to initial surface wash-off, or diffusion controlled transport to the materials surface, as well as indications for depletion - especially if depletion is observed at emissions that are considerably lower than the total amount of active substances - might be relevant for risk assessments, but also helpful if laboratory tests are applied to product development. **Simplified models on the transport of active substances within materials** are possibly an option to improve the interpretation of leaching test results.

Complex **analytical procedures** are necessary to detect organic substances in leachates. The concentrations may be low, and matrix effects due to material-specific co-elutants have to be excluded reliably. So far, chemical analysis has been performed mainly by in-house methods. Agreed analytical procedures proved to be applicable in different laboratories should increase trust in the results of leaching studies. In addition, analytical methods for active substances do not necessarily include metabolites and other degradation products.

Current **risk assessment** procedures require data on accumulated emissions within 30 days (time 1) and for a longer test period (time 2). It is intended to use leaching test results directly for calculations of PEC values. In certain cases, safety factors are applied. So far, the ranges of ratios between emissions in laboratory tests and average emissions under outdoor conditions have not been determined. Only a few observations are available, i.e. short-term leaching tests with one-minute immersion events seem to underestimate emissions in semi-field tests with treated wood; and a few immersion days with one-hour immersion events seem to represent much longer periods of semi-field tests with façade coatings if the data are related to the amount of water applied. The observed ratios differed for different active substances and during the course of the experiments. Risk assessments are based on calculations for model scenarios and only distinguish initial and later emission periods. Emission scenarios have to be regarded as simplified models that do not reflect variable exposure conditions. Transfer of the outcome of model calculations to dimensions that differ from the emission scenarios requires further considerations.

Laboratory data can only be reliably applied for risk assessments if knowledge of actual leaching during service life and further data on the relationship of emissions under different test conditions is available. Accumulated emission data should be compared rather than flux data, since in this way, variability of outdoor conditions is equalised to a certain extend. In addition, emission data should be related either to the amount of water applied (rain amount), or to the duration of water contact, instead of duration of the experiment. However, it has to be considered that the same amount of water causes different emissions depending on the duration of exposure, and a higher frequency of water exchanges during a certain period of time causes increased emissions.

Even if rough ranges of the ratios between different exposure conditions can be found for a number of materials in future, laboratory test data cannot be directly applied to describe leaching processes during service life. **Predictions** of emissions during service life **require complex models on leaching processes** considering variable conditions and interactions of exposure parameters with preserved materials. Knowledge on distribution and transport of water within the materials seems to be essential for modelling leaching phenomena. There are intentions to develop scientifically based leaching models for preserved materials. Valuable insight into leaching phenomena can be expected from these investigations. However, harmonised **routine risk assessments** cannot be based on complex models, but **require simplified approaches**.

First experiences with a so far **semi-analytical model for the description of leaching processes** of biocides from materials promise to overcome difficulties with regression functions. There are options for further improvement of the model and to develop a tool for routine application of this model by unspecialised users.

Uncertainty of the interpretation of laboratory test data and observed overestimation of emissions with current standard leaching tests and the use of test results for PEC calculations prompted applicants to perform higher tier semi-field studies to investigate the leachability of active substances from preserved materials rather than laboratory studies. Generally, results of semi-field experiments can be expected to correspond better with service life than laboratory tests. However, the test assemblies and exposure conditions do not necessarily represent service life conditions. In addition, the number of products that can be investigated within a certain period of time is limited.

So far, leaching data for organic biocidal active substances are rarely available, and only partly intended to develop test and assessment strategies. **Further research** is therefore required, aimed at investigating the circumstances and extent of leaching of biocidal active substances from preserved materials. **Coordinated, systematic studies** should be performed on well described ‘reference products’, representing different types of preserved materials under monitored service life conditions (in typical outdoor situations) or in well described and monitored field tests. The results should be compared with data from laboratory tests.

This way it should be possible to

- provide a database for comparison (‘compliance tests’) for products that have to pass risk assessments
- identify material components that considerably modulate leachability of active substances in order to classify similar materials to avoid exhaustive test series that will result in similar risk assessments
- support the application of experience from one active substance to other substances in the same formulation based on their physico-chemical characteristics (i.e. if comprehensive data on several active substances are available, a laboratory test should be sufficient to prove compliance for other active substances)
- transfer data for materials containing active substances at different concentrations
- investigate conditions to extrapolate between different exposure situations and for longer time periods.

Materials other than wood and coatings, i.e. plastics and technical textiles, must also be subject of these studies. Producers and applicants of active substances and biocidal products should be included in the studies to provide practical experience.

In addition to investigating leaching processes directly, available **monitoring** data for environmental compartments can be evaluated using location and time of occurrence of biocidal active substances - if these data can be related to certain locations or points in time that refer to the use of preserved materials. Uses of preserved materials that release relevant amounts of active substances into environmental compartments and may cause risks because of the ecotoxicological properties of the active substances may be identified in this way. Efficacy tests for material preservatives may provide indirect information on the leachability of active substances, e.g. failing of long-term studies or decreased efficacy after contact with water.

Science-based exchange of experience should be intensified as a basis for reasonable risk management.

Research on leaching processes and **development of leaching tests** as well as risk assessment strategies should be **coordinated** for the requirements of the **Biocidal Products Directive** as well as the **Construction Products Directive**, since both directives have to consider the same emission processes for materials during their service life.

7. Literature

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Coatings and Antifoulings

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DIN EN ISO 15181-3 (2007): Paints and varnishes - Determination of release rate of biocides from antifouling paints - Part 3: Calculation of the zinc ethylene-bis(dithiocarbamate) (zineb) release rate by determination of the concentration of ethylenethiourea in the extract (ISO 15181-3:2007); German Version EN ISO 15181-3:2007

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Summary

Materials that are used outdoors can be preserved by biocides to prevent disturbance by organisms, mainly colonisation by microorganisms. These applications may cause emissions of active substances into environmental compartments via leaching processes.

The European Biocidal Products Directive 98/8/EC (BPD) requires an assessment of environmental risks caused by the use of biocidal products. This report describes methods for characterisation of leaching of biocidal active substances from different materials under weathering conditions. Biocidal products used to preserve materials belong to main group 2 ‘preservatives’.

Uses of biocides in outdoor materials are briefly described. About 2,400 biocidal products (i.e. 15 % of the total number of biocidal products) are registered in Germany according to the ‘Biozid-Meldeverordnung’ for product types 6 (in-can preservatives), 7 (film preservatives), 9 (fibre, leather, rubber and polymerised materials preservatives) and 10 (masonry preservatives). The number of active substances - mainly organic substances - that are considered in the BPD review programme is between 30 and 55 for each of these product types. Preservatives (main group 2) contain about 20 to 25 % of the amount of active substances on the biocidal products market. Wood preservatives (PT 8) dominate within this group (10 to 15 % of the total amount of active substances on the market), whereas active substances for PT 6, 7, 9 and 10 account for about 0.3 up to 2 % each.

At present it is difficult to identify the use of preserved materials as sources of biocide emissions to the environment because of

- limited availability of production and use data
- simultaneous use of active substances for different purposes (e.g. agricultural uses, disinfection, preservation of different kinds of materials)
- different origins of pollutants in environmental samples (production, treatment and storage sites, service life of treated articles, air-borne pollution, e.g. run-off from roofs may contain biocides originating from air, but not from the roof material).

Outdoor materials that can contain biocidal products are building materials (like coatings, roofing tiles, concrete, masonry), wood and synthetic materials (like technical textiles and polymers). Leaching from the material into a water film on its surface is essential for biocidal activity for certain applications. In these cases leaching processes have to be optimised to guarantee long-term efficacy of the biocidal products.

Reports on emissions of active substances from preserved materials during service are rare, e.g. roof sealing membranes were identified as a source of the herbicide Mecoprop found in roof runoff waters, and the pathway from a building envelop to the receiving surface water was traced for the film preservative Irgarol 1051. Leachability of active substances from different materials was demonstrated in laboratory and/or fields studies, e.g. for outdoor paints, façade coatings, mortar, plastics and polymer sheets.

Leaching processes are based on complex interactions of substances with the material matrix and water. Different transport mechanisms are responsible for the transfer of constituents from the matrices into water, i.e. advection, diffusion and surface wash-off. After initial wash-off, diffusion to the materials surface is normally the limiting transport mechanism for compact materials having low permeability and porosity. So far, knowledge about leaching processes is less detailed for organic compounds compared to inorganic ingredients of materials.

Leaching processes are determined by properties of active substances and materials as well as the exposure conditions. Important parameters for leaching of organic substances from materials are concentration, distribution, water solubility, lipophilic versus hydrophilic properties, chemical structure and stability of the active substances as well as the composition of biocidal products on the one hand, and chemical composition, geometry, structure (porosity, internal pore structure, surface structure), water permeability, weathering resistance of the materials as well as the availability and distribution of water within the materials on the other hand.

Leaching processes are also determined by exposure conditions like precipitation, humidity, wind, temperature, UV radiation, orientation, composition and pH of the leaching water. These conditions are variable - changing with time and location. Local microclimates can be observed on material surfaces.

Leaching should be investigated as a process, at minimum tests should differentiate between early and later stages of this process. Either laboratory tests or experiments under outdoor exposure conditions - each approach having benefits and limitations - can be applied. Standardised leaching tests are available only for a limited number of materials (i.e. wood and antifoulings as well as a CEN standard proposal for coatings). The driving forces and factors that modulate leaching processes are universally valid. Experiences with mainly inorganic ingredients from construction products and waste have shown that dominant leaching factors can be identified and quantified in a limited number of different test procedures for a wide range of products and a wide range of application scenarios. Therefore, it is recommended to develop a set of leaching tests for preserved materials following a so-called ‘horizontal approach’. This means that a limited number of test procedures should apply to different materials (i.e. certain exposure procedures with appendices for handling of different materials).

Harmonised sets of leaching tests are currently developed for waste (CEN/TC 292) and construction products (CEN/TC 351). There are similar requirements to assess emissions from construction products in the Biocidal Products Directive and the Construction Products Directive.

It is also recommended to classify materials for risk assessments of biocides (i.e. certain types of coatings, certain polymers...), and to perform detailed investigation for well described reference products. ‘Compliance tests’ - i.e. based on a laboratory test procedure - might be sufficient for other materials of these classes.

Test procedures to investigate leaching processes from preserved materials include laboratory tests as well as field experiments. Laboratory test procedures designed for preserved wood under different conditions of use - either occasional or permanent contact with water (or soil) - should also apply to materials of other product types. The NT Build 509 procedure that was developed for treated wood might be the basis for semi-field studies with different materials.

Leaching tests generally describe the effect of water on leachable substances in a material as a process depending on either time, duration of water contact or the amount of water applied to test specimens.

Parameters that directly determine leaching test results are

- Chemical structure and physico-chemical properties of the active substance
- Actual formulation of the biocidal product
- Composition, structure and water permeability of the material.

Parameters that have to be defined in the test protocols to ensure repeatability are

- Size and structure of tests specimens (laboratory as well as field test)
- Matrix (in case that products have to be applied on a substrate, e.g. coatings)

Exposure conditions in laboratory tests can be permanent immersion, intermediate wetting and drying (short-term immersion) and artificial weathering.

Certain parameters have to be fixed and controlled:

- Water quality
- Duration of water contact
- Time schedule of water exchanges
- Temperature
- Relative humidity (for tests with drying periods)
- Amount of water per surface area of the test specimens

Specific test conditions may be applied to consider stability of the active substances or ‘aging’ of materials (e.g. UV radiation, pH and temperature changes). Wind, exposure orientation, local or regional conditions and change of the conditions are usually not considered in laboratory tests.

Laboratory tests are suitable to compare the leachability of active substances for different products and to characterise leaching processes and the influence of selected parameters.

The appropriateness of permanent immersion tests for risk assessments for materials with only occasional water contact is limited because of unrealistically high emission rates. In addition, transport processes within drying materials are not considered. Tests including intermediate wetting and drying periods are intended to mirror typical outdoor exposure conditions (short periods of water contact and transport of active substances in the materials during drying periods) and to protect materials from possible damage due to permanent water contact. The test conditions are more complex during artificial weathering, i.e. simulate rain or water condensation, interrupted by dry periods in combination with UV-irradiation of certain wavelength, intensity and duration, and changing temperature regimes. Controlled weathering conditions assure repeatable results, but do not represent service life conditions.

Field investigations describe the stability and functionality of materials under complex natural weather conditions.

Certain parameters have to be fixed:

- Construction, size and shape of test specimens
- Exposure orientation
- (Variable) local or regional conditions

The actual weathering conditions are more or less random.

Therefore, there are requirements to cope with the variability of weather conditions in field studies, mainly sufficient number of replicates and duration of tests, simultaneous exposure of known reference materials and monitoring of exposure conditions.

The Nordtest method ‘NT Build 509’ is aimed at investigating leaching of wood preservatives, but should be adaptable to other materials.

Field tests are suitable to investigate leaching processes closely related to service life conditions and to compare active substances in different products. However, results of independent weathering studies are difficult to compare.

Laboratory tests, field experiments and in-service situations differ not only in the ‘degree’ of exposure, but also in the ‘way’ of exposure. Consequently, there cannot be a scaling factor that balances results of different test approaches (e.g. laboratory tests vs. field tests), whereas more or less constant ratios between different protocols for laboratory experiments can be expected. Few experiences - mainly with preserved wood and coatings - confirm this assumption. The most reasonable basis to compare data from different tests is to relate accumulated emissions per surface area to the accumulated amount of applied water / rain. These leaching courses are modified by the duration of water contact and the exposure conditions between leaching events. Ratios between results of different experiments depend on the leached substance, the actual test conditions and the stage of the experiments.

So far, it has not been demonstrated, how leaching test data can fit into emission scenarios to provide realistic results for risk assessments. There are limitations to interpret and extrapolate regression functions as proposed in the OECD ESD for wood preservatives. The parameters determined in the regression functions do not describe leaching properties of the active substances in materials, but depend on the exposure conditions. Extrapolations derived from regression functions are questionable and apply only to the actual test parameters.

In this study a new, so far semi-analytical model for the assessment of leaching of biocides from treated materials is investigated (see contribution of UHLIG AND BALDAUF, pp 61). It is demonstrated that the analytical method outperforms common regression methods both in terms of prediction accuracy and in terms of flexibility and interpretability for different substances and surfaces. In addition, the model can be applied for continuous as well as discontinuous leaching processes (i.e. experiments with permanent water contact and short-term immersion).

Predictions of emissions during service life require complex models on leaching processes considering variable conditions and effects of exposure parameters on the preserved materials. Knowledge on distribution and transport of water within the materials seems to be essential for modelling leaching phenomena.

Coordinated research is necessary to get further information on the actual leaching during service life and relationship of emissions under different test conditions. Systematic studies should be performed on well described ‘reference products’, representing different types of preserved materials under monitored service life conditions (in typical outdoor situations) or in well described and monitored field tests. The results should be compared with data from laboratory tests.

This way it should be possible to

- provide a database for comparison (‘compliance tests’) for products that have to pass risk assessments
- identify material components that considerably modulate leachability
- support the application of experience from one active substance to other substances
- prove transferability of data for materials containing active substances at different concentrations
- investigate conditions to extrapolate between different exposure situations and for longer time periods.

Information from presentations given at a workshop on leaching tests for materials is included in the report. The presentations are listed in Annex V.

Overviews on literature - i.e. standards, regulations and guidelines, emission scenario documents and scientific reports - information sources, properties and use of selected active substances, emission scenarios that are related to service life of materials and leaching test methods are given at the end of the report.

Kurzfassung

Materialien können mit Bioziden ausgerüstet sein, um Schädigungen durch Organismen - hauptsächlich Ansiedlung von Mikroorganismen - zu verhindern. Bei Materialien, die im Außenbereich der Bewitterung ausgesetzt sind, können Leachingprozesse zu Wirkstoffemissionen in Umweltkompartimente führen.

Die Europäische Biozidproduktenrichtlinie 98/8/EG (BPD) verlangt eine Bewertung des Umweltrisikos, das durch die Anwendung von Biozidprodukten verursacht wird. Dieser Bericht beschreibt Methoden zur Charakterisierung des Leachings von bioziden Wirkstoffen aus verschiedenen Materialien unter Witterungsbedingungen. Biozidprodukte, die zum Schutz von Materialien verwendet werden, gehören zur Hauptgruppe 2 „Schutzmittel“.

Anwendungen von Bioziden in Materialien für den Außenbereich werden kurz beschrieben. Etwa 2400 Biozidprodukte (das sind 15 % der Gesamtzahl der Biozidprodukte) sind in Deutschland nach der „Biozid-Meldeverordnung“ für die Produkttypen 6 (Topf-Konservierungsmittel), 7 (Beschichtungsschutzmittel), 9 (Schutzmittel für Fasern, Leder, Gummi und polymerisierte Materialien) und 10 (Schutzmittel für Mauerwerk) registriert. Die Anzahl der Wirkstoffe - hauptsächlich organische Verbindungen -, die im Reviewprogramm zur BPD zu betrachten sind, liegt für die einzelnen Produkttypen zwischen 30 und 55. Schutzmittel (Hauptgruppe 2) umfassen etwa 20 bis 25 % der auf dem Markt befindlichen bioziden Wirkstoffe. Holzschutzmittel (PT 8) dominieren innerhalb dieser Gruppe (10 bis 15 % der auf dem Markt befindlichen Wirkstoffe), während die Wirkstoffe für PT 6, 7, 9 und 10 0,3 bis 2 % des Marktes ausmachen.

Die Anwendung von geschützten Materialien als Quelle von Biozidemissionen in die Umwelt zu identifizieren, ist gegenwärtig schwierig, weil

- Produktions- und Anwendungsdaten nur begrenzt verfügbar sind
- Wirkstoffe gleichzeitig für verschiedene Zwecke eingesetzt werden (z.B. Anwendungen in der Landwirtschaft, zur Desinfektion, zum Schutz unterschiedlicher Materialien)
- Kontaminationen unterschiedliche Quellen haben können (Produktions- und Lagerstandorte, Nutzungsphase, luftgetragene Schadstoffe, z.B. im Ablaufwasser von Dächern können Biozide enthalten sein, die aus der Luft stammen, und nicht aus dem Dachmaterial).

Materialien für den Außenbereich, die Biozidprodukte enthalten können, sind Bauprodukte (wie Beschichtungen, Dachziegel, Beton, Putz), Holz und synthetische Werkstoffe (wie technische Textilien und Polymere). Bei bestimmten Anwendungen ist das Auswaschen von Bioziden aus dem Material in einen auf der Oberfläche befindlichen Wasserfilm für die Wirkung erforderlich. In diesen Fällen sind Leachingprozesse zu optimieren, um eine lang anhaltende Wirkung des Biozidprodukts zu garantieren.

Berichte über Wirkstoffemissionen aus biozid ausgerüsteten Materialien während der Nutzungsphase sind selten, z.B. wurden Dachabdichtungsbahnen als Quelle des Herbizids Mecoprop in Dachablaufwasser identifiziert, und der Weg des Filmschutzmittelwirkstoffs Irgarol 1051 von einer Gebäudehülle bis zur Einleitungsstelle in den Vorfluter verfolgt. Für verschiedene Materialien (Farben für den Außenbereich, Fassadenbeschichtungen, Mörtel, Kunststoffe und Polymerfolien) wurde die Auswaschbarkeit von Wirkstoffen in Labor- und/oder Feldversuchen gezeigt.

Leachingprozesse basieren auf komplexen Wechselwirkungen von Substanzen mit dem Material und Wasser. Verschiedene Transportmechanismen sind für die Verlagerung von Bestandteilen aus Materialien in Wasser verantwortlich, das sind Advektion, Diffusion und Abwaschen der Oberfläche. Nach anfänglichem Abwaschen von der Oberfläche ist normalerweise Diffusion zur Materialoberfläche der bestimmende Transportmechanismus in kompakten Materialien mit geringer Durchlässigkeit und Porosität. Bisher ist das Wissen

über Leachingprozesse weniger detailliert für organische Verbindungen als für anorganische Bestandteile von Materialien.

Leachingprozesse werden sowohl durch Wirkstoff- und Materialeigenschaften als auch die Expositionsbedingungen bestimmt. Wichtige „Wirkstoffparameter“ sind deren Konzentration, Verteilung, Wasserlöslichkeit, lipohile im Vergleich zu hydrophilen Eigenschaften, chemische Struktur und Stabilität sowie die Zusammensetzung der Biozidprodukte; Wichtige „Materialparameter“ sind die chemische Zusammensetzung, Geometrie, Struktur (Porosität, interne Porenstruktur, Oberflächenstruktur), Wasserdurchlässigkeit und Witterungsbeständigkeit des Materials sowie Verfügbarkeit und Verteilung von Wasser im Material. Expositionsbedingungen wie Niederschlag, Feuchtigkeit, Wind, Temperatur, UV-Bestrahlung, Orientierung, Zusammensetzung und pH-Wert des Auswaschwassers bestimmen Leachingprozesse. Diese Bedingungen sind variabel und ändern sich mit Zeit und Ort. Auf Materialoberflächen können lokale Mikroklimata beobachtet werden.

Leaching sollte als Prozess untersucht werden. Als Minimum sollte zwischen frühen und späteren Stadien dieses Prozesses unterschieden werden. Sowohl Labortests als auch Versuche unter Freilandbedingungen - jeweils mit Vor- und Nachteilen - können angewandt werden. Standardisierte Leachingtests gibt es nur für eine begrenzte Anzahl an Materialien. Die Antriebskräfte und Faktoren, die Leachingprozesse beeinflussen, sind allgemein gültig. Erfahrungen, die hauptsächlich mit anorganischen Bestandteilen von Baustoffen und Abfällen gesammelt wurden, haben gezeigt, dass dominante Leachingfaktoren mit einer begrenzten Anzahl von verschiedenen Testverfahren für eine Vielzahl von Produkten und Anwendungsszenarien identifiziert und quantifiziert werden können. Deshalb wird empfohlen, ein Set an Leachingtests für biozid ausgerüstete Materialien gemäß einer sogenannten ‚horizontalen Herangehensweise‘ zu entwickeln. Das bedeutet, dass eine begrenzte Anzahl von Testverfahren für zur Untersuchung von Leachinprozessen aus unterschiedlichen Materialien anwendbar sind (d.h. bestimmte Expositionsverfahren mit Anhängen für die Handhabung verschiedener Materialien).

Harmonisierte Sets von Leachingtests werden gegenwärtig für Abfälle (CEN/TC 292) und Bauprodukte (CEN/TC 351) entwickelt. Es gibt ähnliche Anforderungen zur Bewertung von Emissionen aus Bauprodukten in der Biozidproduktenrichtlinie und der Bauproduktenrichtlinie.

Es wird auch empfohlen, Materialien für die Risikobewertung von Bioziden zu klassifizieren (d.h. bestimmte Typen von Beschichtungen, bestimmte Polymere, …) und detaillierte Untersuchungen für gut beschriebene Referenzprodukte durchzuführen. „Übereinstimmungstests“ - zum Beispiel auf der Basis von Laborversuchen - können dann ausreichend zur Risikobewertung für andere Produkte dieser Klassen sein.

Testverfahren zur Untersuchung von Leachingprozessen für biozid ausgerüstete Materialien umfassen Labortests und Freilandexperimente. Labortestverfahren, die für behandeltes Holz für verschiedene Anwendungsbedingungen entwickelt wurden - entweder gelegentliches Befeuchten oder ständigen Wasser- (oder Boden-)kontakt - sollten auch für andere Materialien anwendbar sein. Das NT Build 509-Verfahren für behandeltes Holz könnte die Basis für Freilandversuche mit anderen Materialien sein.

Prinzipiell beschreiben Leachingtests den Einfluss von Wasser auf auswaschbare Substanzen in einem Material als einen Prozess in Abhängigkeit von der Zeit, der Dauer des Wasserkontakts oder der Menge des Wassers, denen Prüfkörper ausgesetzt sind.

Parameter, die die Auswaschung direkt beeinflussen, sind

- Chemische Struktur and physikalisch-chemische Eigenschaften des Wirkstoffs
- Tatsächliche Formulierung des Biozidprodukts
- Zusammensetzung, Struktur und Wasserdurchlässigkeit des Materials.

Parameter, die im Testprotokoll festgelegt sein müssen, um die Reproduzierbarkeit zu sichern, sind

- Größe und Struktur der Prüfkörper (für Labor- und Freilanduntersuchungen)
- Matrix (falls Produkte auf einem Substrat aufzutragen sind, z.B. Beschichtungen)

Expositionsbedingungen in Labortests können sowohl dauerhafter Wasserkontakt, wechselndes Befeuchten und Trocknen (Kurzzeittauchen) bzw. künstliche Bewitterung sein.

Bestimmte Parameter müssen festgelegt und kontrolliert werden:

- Wasserqualität
- Dauer des Wasserkontakts
- Zeitschema für Wasserwechsel
- Temperatur
- Relative Luftfeuchtigkeit (für Tests mit Trocknungsphasen)
- Wassermenge je Oberfläche des Prüfkörpers

Spezifische Testbedingungen können angewandt werden, um die Stabilität der Wirkstoffe, oder „Alterung“ von Materialien zu berücksichtigen (z.B. UV-Bestrahlung, pH- und Temperaturänderungen). Wind, Ausrichtung nach der Himmelsrichtung, lokale oder regionale Bedingungen sowie deren Änderungen werden in Laborversuchen normalerweise nicht berücksichtigt.

Labortests sind geeignet, um die Auswaschbarkeit von Wirkstoffen für verschiedene Produkte zu vergleichen und Leachingprozesse sowie den Einfluss ausgewählter Parameter zu charakterisieren.

Leachingtests mit dauerhaftem Wasserkontakt sind für Risikobewertungen für Materialien mit gelegentlichem Wasserkontakt nur begrenzt geeignet, da die Emissionsraten unrealistisch hoch sind. Transportprozesse in trocknendem Material werden nicht berücksichtigt. Tests, bei denen Befeuchtungs- und Trockenphasen wechseln, sollen typische Bewitterungsbedingungen für Materialien im Außenbereich abbilden (kurze Phasen mit Wasserkontakt und Transport der Wirkstoffe im Material während der Trocknungsphasen) und außerdem Materialien vor möglichen Schäden durch dauerhaften Wasserkontakt schützen. Die Testbedingungen sind komplexer bei künstlichen Bewitterungsverfahren, in denen Regen oder Kondensation - unterbrochen durch trockene Perioden in Kombination mit UV-Bestrahlung definierter Wellenlänge, Intensität und Dauer - unter wechselndem Temperaturregime simuliert werden. Kontrollierte Bewitterungsbedingungen sichern reproduzierbare Ergebnisse, repräsentieren aber nicht die tatsächlichen Nutzungsbedingungen.

Feldversuche beschreiben die Stabilität und Funktionalität von Materialien unter komplexen natürlichen Witterungsbedingungen.

Bestimmte Parameter müssen festgelegt werden:

- Aufbau, Größe und Gestalt der Prüfkörper
- Orientierung der Prüfkörper
- (Variable) lokale und regionale Bedingungen

Die tatsächlichen Witterungsbedingungen sind mehr oder weniger zufällig.

Deshalb gibt es bestimmte Forderungen an Feldversuche, um den variablen Witterungsbedingungen gerecht zu werden, hauptsächlich genügende Anzahl an Parallelversuchen und ausreichende Testdauer, simultane Untersuchung von Referenzmaterialien und Aufzeichnen der Witterungsbedingungen.
Die Nordtest Methode „NT Build 509” dient der Untersuchung von Holzschutzmitteln, sollte aber auch für andere Materialien anpassbar sein.

Feldversuche sind geeignet, um Leachingprozesse unter Bedingungen zu untersuchen, die den Nutzungsbedingungen sehr nahe kommen, und um Wirkstoffe in verschiedenen Produkten zu vergleichen. Ergebnisse aus voneinander unabhängigen Bewitterungsstudien sind allerdings schwer zu vergleichen.

Unterschiede zwischen Labortests, Feldversuchen und Nutzungsbedingungen sind nicht einfach nur ein unterschiedlicher Grad der Bewitterung, sondern stellen auch eine unterschiedliche Art der Bewitterung dar. Daraus folgend kann es keinen einfachen Faktor geben, der die Ergebnisse unterschiedlicher Herangehensweisen (Labor- gegenüber Feldversuchen) ausgleicht, während mehr oder weniger konstante Verhältnisse zwischen verschiedenen Protokollen für Laborexperimente erwartet werden können. Einige wenige Erfahrungen - hauptsächlich mit behandeltem Holz und Beschichtungen - bestätigen diese Annahme. Am besten geeignet für den Vergleich von Daten aus unterschiedlichen Versuchen ist der Bezug zwischen kumulativen Emissionen je Flächeneinheit bezogen auf die kumulative Wasser-/Regenmenge. Diese Leachingverläufe werden durch die Dauer des Wasserkontakts und die Bewitterungsbedingungen zwischen Leachingereignissen modifiziert. Relationen zwischen Testverfahren sind abhängig von der ausgewaschenen Substanz, den tatsächlichen Versuchsbedingungen und dem Stadium der Experimente.

Bis jetzt wurde noch nicht gezeigt, wie Leachingtest-Daten so in Emissionsszenarien angewendet werden können, dass realistische Ergebnisse für Risikobewertungen erzeugt werden. Interpretationen und Extrapolationen von Regressionsfunktionen, wie sie im OECD ESD für Holzschutzmittel vorgeschlagen werden, sind nur begrenzt möglich. Die Parameter, die in den Regressionsfunktionen bestimmt werden, beschreiben nicht die Auswascheigenschaften von Wirkstoffen aus Materialien, sondern sind abhängig von den Bewitterungsbedingungen. Aus den Regressionsfunktionen abgeleitete Extrapolationen sind fragwürdig und gelten nur für die angewandten Testbedingungen.

In diesem Vorhaben wurde ein neues, bisher semi-analytisches Modell zur Bewertung des Leachings von Bioziden aus behandelten Materialien untersucht (siehe Beitrag von UHLIG UND BALDAUF, S. 61 ff). Es wird gezeigt, dass das analytische Modell übliche Regressionsmodelle hinsichtlich der Vorhersagegenauigkeit als auch hinsichtlich Flexibilität und Interpretierbarkeit für verschiedene Substanzen und Oberflächen übertrifft. Außerdem kann das Modell für kontinuierliche und diskontinuierliche Leachingprozesse (d.h. Experimente mit dauerhaftem und kurzzeitigem Wasserkontakt) eingesetzt werden.

Vorhersagen von Emissionen unter Nutzungsbedingungen erfordern komplexe Modelle von Leachingprozessen, die variable Bedingungen und Einflüsse der Witterungsbedingungen auf die biozid ausgerüsteten Materialien berücksichtigen. Kenntnisse über Verteilung und Transport von Wasser in den Materialien erscheint essentiell für die Modellierung von Leachingphänomenen.

Koordinierte Forschung ist erforderlich, um weitere Informationen über das tatsächliche Leaching in der Nutzungsphase und über Beziehungen von Emissionen unter verschiedenen Testbedingungen zu erhalten. Systematische Studien mit gut beschriebenen Referenzprodukten, die unterschiedliche Typen biozid ausgerüsteter Materialien repräsentieren, sollten unter dokumentierten Nutzungsbedingungen (unter Bedingungen, die für Außenanwendungen typischen sind) oder in gut beschriebenen und dokumentierten Feldversuchen durchgeführt werden. Die Ergebnisse sollten mit Daten aus Laborversuchen verglichen werden.

Dadurch sollte es möglich sein

- eine Datenbasis zur vergleichenden Risikobewertung für Produkte (‘Übereinstimmungstests’) zu erstellen
- Materialkomponenten mit wesentlichem Einfluss auf die Auswaschbarkeit zu identifizieren
- Erfahrungen mit einem Wirkstoff auf andere Wirkstoffe zu übertragen

- die Übertragbarkeit vorhandener Daten auf Materialien mit unterschiedlichen Wirkstoffgehalten nachzuweisen
- Bedingungen für Extrapolationen zwischen verschiedenen Expositionsbedingungen und auf längere Zeiträume zu untersuchen.

Informationen aus Präsentationen, die anlässlich eines Workshops über Leachingtests mit Materialien gehalten wurden, sind im Bericht enthalten. Autoren und Titel der Präsentationen sind in Anhang V gelistet.

Übersichten über Literatur (Standards, Regelungen und Richtlinien, Emissionsszenario-Dokumente und wissenschaftliche Berichte), Informationsquellen, Eigenschaften und Anwendungen ausgewählter Wirkstoffe, Emissionsszenarien mit Bezug auf die Nutzungsphase von Materialien und Leachingtests werden am Ende des Berichts gegeben.

Leaching of Biocides – Mathematical Modelling

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1 Introduction

A crucial element of the determination of leaching rates is the underlying mathematical model. Non-linear regression models are quite popular and can be applied easily. However, they do not apply properly for discontinuous water contact, and long-term extrapolation of results is highly depending on the model applied and cannot be considered valid.

In association with the working group „Materials Protection against Fungi and Insects" (Dr. Ute Schoknecht) of the Federal Institute for Materials Research and Testing (BAM), emission courses of biocidal active substances - measured in test procedures in accordance with OECD Documents[1] [2] - were analyzed statistically by the quo data GmbH.

Quo data received from BAM several series of experimental data, examined several mathematical models and explored options to improve them. In the first step different regression models were examined. These results are presented in chapter 2. The underlying data - discussed in a first meeting on the 13th October 2009 in Dresden – were obtained in the project "Urban Biocides" and an EU project for preservative-treated wood. In the project "Urban biocides" emissions of biocides in façade renders and façade paints were determined by the BAM. Thereby the following 9 biocides were investigated in leaching tests with discontinuous (OECD TG107) and continuous water contact (OECD G313). In this report biocides and biocidal active substances are understood to be synonymous.

Table 1: Investigated biocides in façade-coatings within the project "Urban Biocides"

Benzisothiazolinone (BIT)
Carbendazim
Dichlorooctylisothiazolinone (DCOIT)
Diuron
Iodopropynylbutylcarbamate (IPBC)
Irgarol
Isoproturon
Octylisothiazolinone (OIT)
Terbutryn

The EU project for preservative-treated wood comprised discontinuous (OECD TG107) and continuous leaching tests (OECD G313) for the following 3 wood preservatives.

Table 2: Investigated wood-preservatives within an EU project

Copper-triazole
Copper from Copper-Chrome-Borate compounds
Propiconazole

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[1] OECD Guidelines for the Testing of Chemicals Test No. 313: Estimation of Emissions from Preservative - Treated Wood to the Environment: Laboratory Method for Wooden Commodities that are not Covered and are in Contact with Fresh Water or Seawater.

[2] OECD Guidance in the Series on Testing and Assessment No. 107: on the Estimation of Emissions from Wood Preservative-Treated Wood to the Environment: for Wood held in Storage after Treatment and for Wooden Commodities that are not covered and are not in Contact with Ground.

None of the regression models analysed in step 1 allowed an adequate fitting of the leaching data. In addition, long-term extrapolation of results was considered critical. Therefore in the second step an analytical model approach was established. This analytical approach takes into account the processes of diffusion, evaporation and dissolving by applying the finite-difference method. It is explained in chapter 3. In chapter 4 the fitting by the analytical model is compared to the fitting by the regression models.

The outcome of these analyses was discussed in a second project meeting in Dresden on the 18th December 2009. Results were also presented to the international leaching workshop on 21st January 2010 organized by BAM in Berlin.

In order to assess the performance of the analytical model with long-term data, BAM conducted another leaching test series over a period of two months. Quo data received these data on 15th March 2010. The data included measurement results of 5 biocides (Carbendazim, DCOIT, Diuron, OIT and Terbutryn) for the façade coatings render and paint as well as 2 wood preservatives (Copper and Tebuconazole) for treated wood, each for discontinuous and continuous water contact.

It turned out that the analytical model established in step 2 allows a fairly adequate fitting also to the long-term leaching data. In case of discontinuous water contact a modification of the analytical model was required. Results of the analysis are presented in chapter 5. The resulting analytical model has the potential to characterize leaching of biocidal active substances from different materials under varying test conditions.

2 Regression models

2.1 Differential equation models

The process of emission can be approximately described by time-dependent functions. An overview of several models describing the leaching tests has been compiled by Roel Fleuren[3]. The bi-phasic model was proven to be the best model fitting experimental leaching data. Therefore all regression models presented in this report are compared to this type of function.

There are two main approaches for extrapolating the leaching data measured in a laboratory. One is focusing on the average daily Flux-rate, i.e. the average quantity of an active ingredient that is daily leached out of 1 m² of a test specimen during a certain period. The other approach is focusing on the cumulative quantity of an active ingredient that is leached out after a certain period of time.

The following regression models describe the concentration of the active ingredient in the test specimen as result of a linear differential equation. Two points of time t_1 and t_2 ($t_1 < t_2$) are considered with the corresponding concentrations $C(t_1)$ and $C(t_2)$ assuming that the time-related changes of the concentration within the time interval $t_2 - t_1$ are given by a linear function of time-dependent parameters, i.e.

$$\frac{C(t_2) - C(t_1)}{t_2 - t_1} = \alpha(t_1) \cdot C(t_1) + \beta(t_1)\,.$$

2.1.1 Model 1

The first model assumes constant parameters a and b, respectively for α and β, respectively, i.e.

$$\frac{C_1(t_2) - C_1(t_1)}{t_2 - t_1} = a \cdot C_1(t_1) + b\,.$$

The resulting differential equation has the solution

$$C_1(t) = -\frac{a}{b} + \frac{a}{b} \cdot \exp(-b \cdot t) + C(0) \cdot \exp(-b \cdot t)\,.$$

Thereby $C(0)$ denotes the initial concentration of the active ingredient in the test specimen. The unknown parameters a and b have to be estimated by minimising the residual standard deviation.

Residual standard deviation

The residual standard deviation (ressd) can be considered as a goodness-of-fit measure, i.e. the lower the residual standard deviation, the closer is the fitting to the data.

It is calculated by

$$\text{ressd} = \sqrt{\frac{\sum_{i=1}^{n} (y_i - \hat{y}_i)^2}{n - p}}\,.$$

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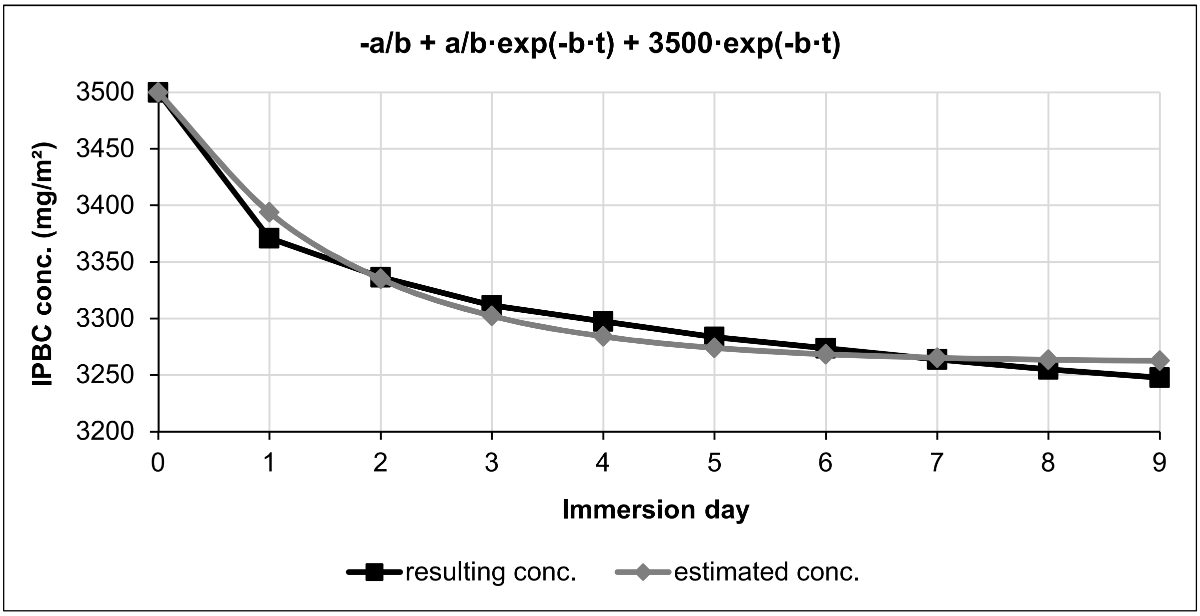
[3] Proposal for the interpretation of leaching study data for wood preservatives (biocides), Factsheets for the (eco)toxicological risk assessment strategy of the National Institute for Public Health and the Environment NL, Part VI, 2006

In this context n denotes the number of measurements and p the number of parameters to be estimated. y_i and $\hat{y}_i$ denote the i-th measured and estimated value, respectively.

Figure 1 illustrates an example for fitting of experimental data by a function of type C_1.

Figure 1: Fitting by function of type C_1 (biocide: IPBC, project: "Urban Biocides", test: OECD TG107)



This example originates from the project "Urban Biocides" of the Federal Institute for Materials Research and Testing (BAM). The numerical values are based on leaching data of the biocide Iodopropinylbutylcarbamat (IPBC) in discontinuous tests (OECD Test Guideline 107). The initial concentration of IPBC in the test specimen was specified by 3500 mg/m².

The following Table 3 shows the determined concentrations due to optimised parameters of type C_1 and the deviations of the resulting concentrations obtained from the measured emission.

Table 3: Fitting by function of type C_1 (biocide: IPBC, project: "Urban Biocides", test: OECD TG107)

Immersion Day	**Measured Emission** [mg/m²]	**Resulting Conc. R** [mg/m²]	**Estimated Conc. E** [mg/m²]	**Deviation R-E** [mg/m²]	**Squared Deviation** [(mg/m²)²]
0		3500.00	3500.00	0.00	
1	129.1	3370.87	3393.85	-22.98	528.12
2	34.4	3336.45	3334.93	1.52	2.30
3	24.8	3311.61	3302.24	9.37	87.87
4	14.2	3297.37	3284.09	13.28	176.30
5	13.8	3283.56	3274.02	9.54	90.94
6	10.0	3273.59	3268.43	5.15	26.55
7	9.7	3263.90	3265.33	-1.43	2.05
8	8.8	3255.13	3263.61	-8.48	71.94
9	7.4	3247.74	3262.66	-14.92	222.48
				ressd:	**13.14 mg/m²**

2.1.2 Model 2

The residual standard deviation of 13.14 mg/m² in model 1 is not satisfying. A better fitting can be obtained by using the following differential approach:

$$\frac{C_2(t_2)-C_2(t_1)}{t_2-t_1}=\alpha(t_1)\cdot C_2(t_1).$$

In contrast to the first model the decrease of the concentration is time-dependent and the constant b is not considered. The function $\alpha(t_1)$ can be chosen arbitrarily, but the lower decrease of the concentration as time t increases has to be taken into account by $\alpha(t)$. An appropriate example may be $\alpha(t)=t^{\tilde{b}}$, where $-1<\tilde{b}<0$. The solution of the resulting differential equation is

$$C_2(t)=C(0)*\exp(-a\cdot t^b).$$

This model is applied to the example mentioned above; the results are shown in Figure 2 and Table 4.

Figure 2: Fitting by function of type C_2 (biocide: IPBC, project: “Urban Biocides”, test: OECD TG107)

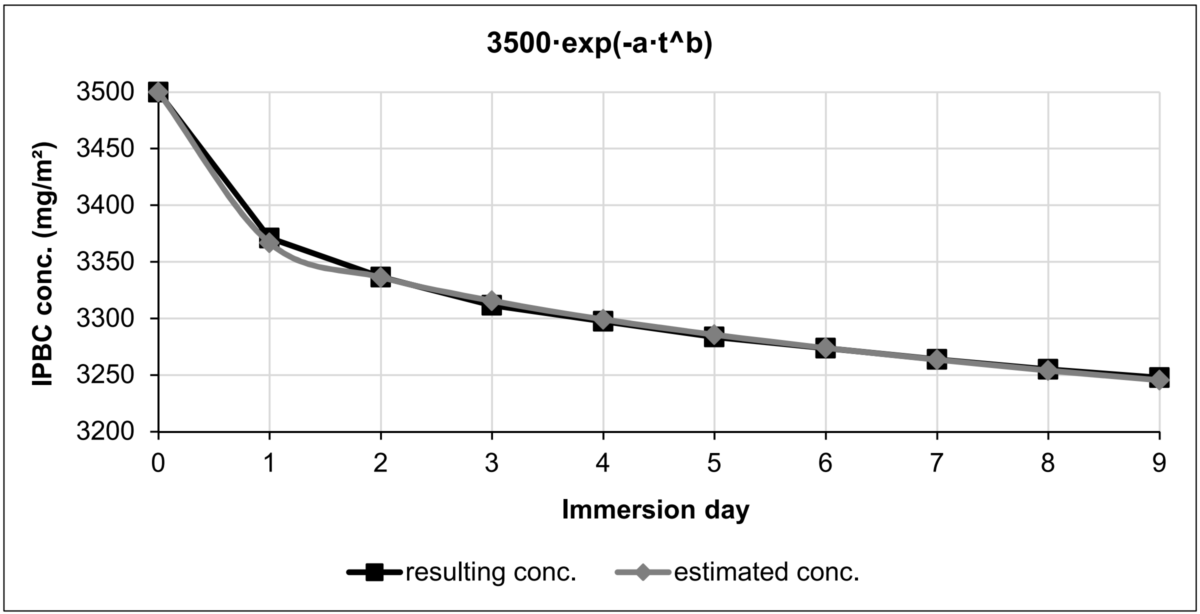


Table 4: Fitting by function of type C_2 (biocide: IPBC, project: “Urban Biocides”, test: OECD TG107)

Immersion Day	**Measured Emission** [mg/m²]	**Resulting Conc. R** [mg/m²]	**Estimated Conc. E** [mg/m²]	**Deviation R-E** [mg/m²]	**Squared Deviation** [(mg/m²)²]
0		3500.00	3500.00	0.00	
1	129.13	3370.87	3366.64	4.23	17.86
2	34.41	3336.45	3336.27	0.19	0.03
3	24.84	3311.61	3315.47	-3.86	14.89
4	14.24	3297.37	3299.18	-1.81	3.28
5	13.81	3283.56	3285.60	-2.04	4.15
6	9.97	3273.59	3273.84	-0.25	0.06
7	9.69	3263.90	3263.42	0.48	0.23
8	8.77	3255.13	3254.02	1.11	1.24
9	7.39	3247.74	3245.43	2.31	5.36
				ressd:	**2.59 mg/m²**

2.1.3 Model 3

The residual standard deviation with a value of 2.59 mg/m² in model 2 can be reduced considerably by a further improvement. In contrast to model 2 a lower bound for the concentration is added, i.e.

$$\frac{C_3(t_2) - C_3(t_1)}{t_2 - t_1} = \alpha(t_1) \cdot \left[C_3(t_1) - \tilde{c}\right].$$

In consequence the quantity which can be theoretically leached for an infinite period of time is bounded by the factor $\tilde{c}$.

Assuming the same function $\alpha(t)$ as mentioned above, the following class of function

$$C_3(t) = \left(C(0) - c\right) + c * \exp(-a \cdot t^b)$$

is obtained as solution. The results of fitting are presented in Figure 3 and Table 5.

Figure 3: Fitting by function of type C_3 (biocide: IPBC, project: "Urban Biocides", test: OECD TG107)

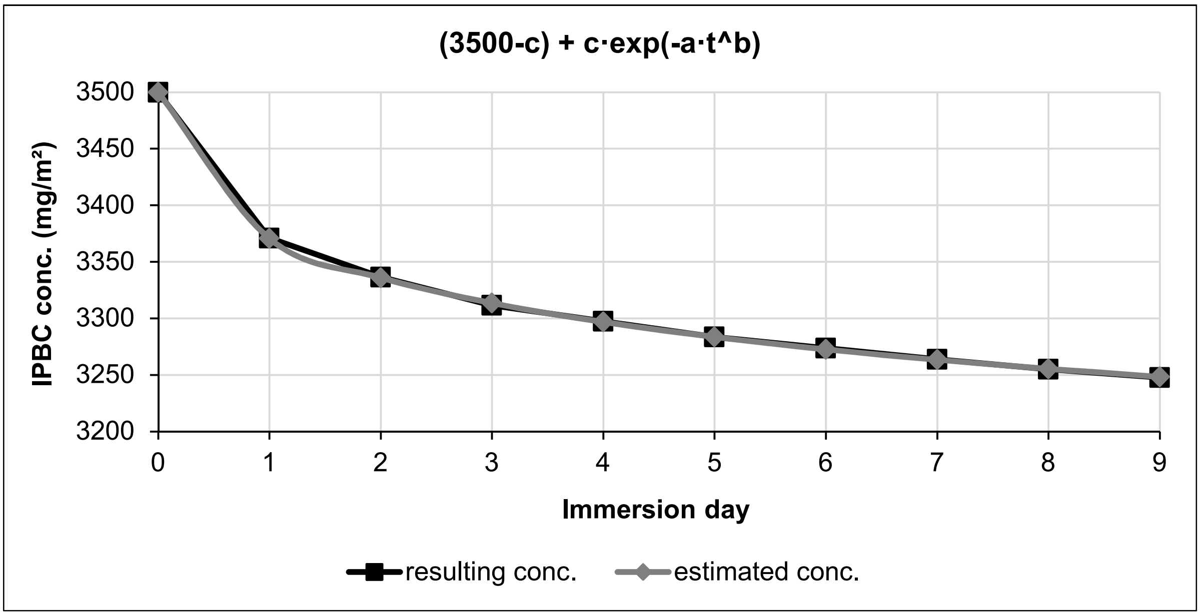


Table 5: Fitting by function of type C_3 (biocide: IPBC, project: "Urban Biocides", test: OECD TG107)

Immersion Day	Measured Emission [mg/m²]	Resulting Conc. R [mg/m²]	Estimated Conc. E [mg/m²]	Deviation R-E [mg/m²]	Squared Deviation [(mg/m²)²]
0		3500.00	3500.00	0.00	0.00
1	129.13	3370.87	3370.63	0.24	0.06
2	34.41	3336.45	3335.98	0.47	0.22
3	24.84	3311.61	3313.50	-1.89	3.57
4	14.24	3297.37	3296.80	0.57	0.32
5	13.81	3283.56	3283.56	0.00	0.00
6	9.97	3273.59	3272.63	0.96	0.92
7	9.69	3263.90	3263.37	0.53	0.28
8	8.77	3255.13	3255.37	-0.24	0.06
9	7.39	3247.74	3248.36	-0.62	0.38
				ressd:	**0.98 mg/m²**

2.1.4 Model 4

The relatively good fitting in model 3 can also be attained by applying the function

$$\alpha(t) = \frac{\exp(-\tilde{b} \cdot t)}{1 - \exp(-\tilde{b} \cdot t)} .$$

In this case the following function type solves the corresponding differential equation

$$C_4(t) = a \cdot \left(1 - \exp(-b \cdot t)\right)^c + C(0) .$$

For 5 out of 9 biocides the residual standard deviation can be reduced by the application of this model compared to the application of model 3 (see Table 8 on p.72). For IPBC the residual standard deviation in model 4 (1.15 mg/m²) is slightly greater than in model 3 (0.98 mg/m²). The resulting fitting by C_4 based on the leaching data of IPBC is shown in Figure 4 as well as in Table 6.

Figure 4: Fitting by function of type C_4 (biocide: IPBC, project: "Urban Biocides", test: OECD TG107)

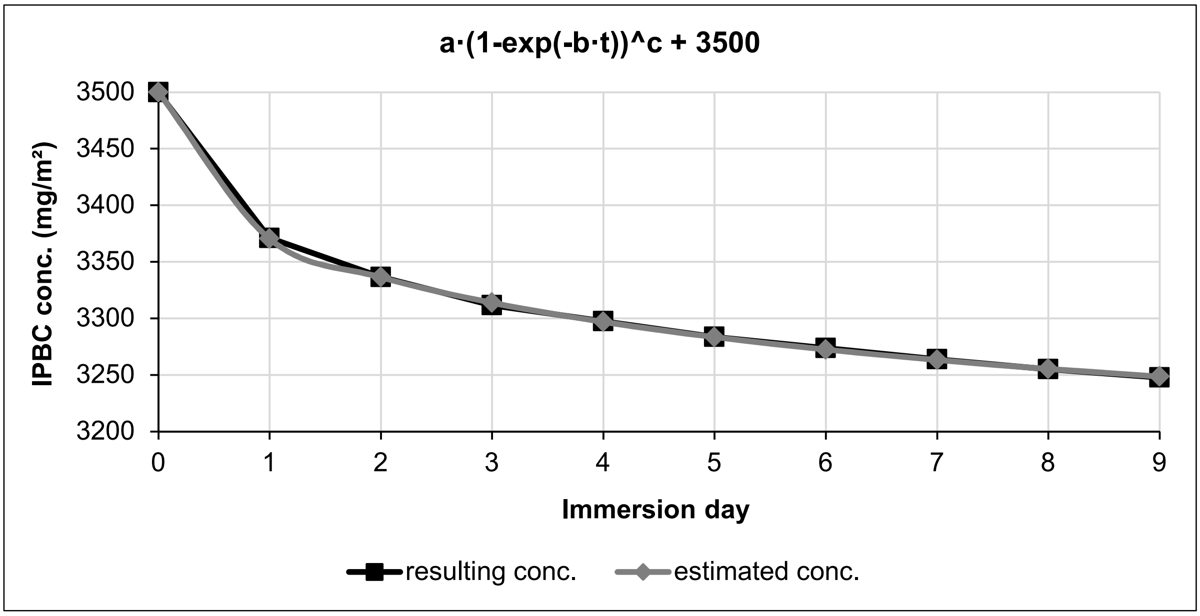


Table 6: Fitting by function of type C_4 (biocide: IPBC, project: "Urban Biocides", test: OECD TG107)

Immersion Day	**Measured Emission** [mg/m²]	**Resulting Conc. R** [mg/m²]	**Estimated Conc. E** [mg/m²]	**Deviation R-E** [mg/m²]	**Squared Deviation** [(mg/m²)²]
0		3500.00	3500.00	0.00	0.00
1	129.13	3370.87	3370.27	0.60	0.36
2	34.41	3336.45	3336.33	0.12	0.01
3	24.84	3311.61	3313.78	-2.17	4.71
4	14.24	3297.37	3296.86	0.51	0.26
5	13.81	3283.56	3283.43	0.13	0.02
6	9.97	3273.59	3272.41	1.17	1.38
7	9.69	3263.90	3263.18	0.72	0.51
8	8.77	3255.13	3255.33	-0.20	0.04
9	7.39	3247.74	3248.58	-0.84	0.71
				ressd:	**1.15 mg/m²**

2.2 Bi-phasic model

The bi-phasic model mentioned in the beginning of this section refers to following class of function

$$C_{bi}(t) = C(0) - a - c + a \cdot \exp(-b \cdot t) + c \cdot \exp(-d \cdot t).$$

The model is based on the assumption that two phases of diffusion are occurring, on the one hand the relatively fast diffusion through water on the boundary layer of the material and on the other hand the slower diffusion due to biocides located deeper in the material. The results of fitting by the bi-phasic model for the leaching data of the biocide IPBC are presented in Figure 5 and Table 7.

Figure 5: Fitting by bi-phasic model (biocide: IPBC, project: "Urban Biocides", test: OECD TG107)

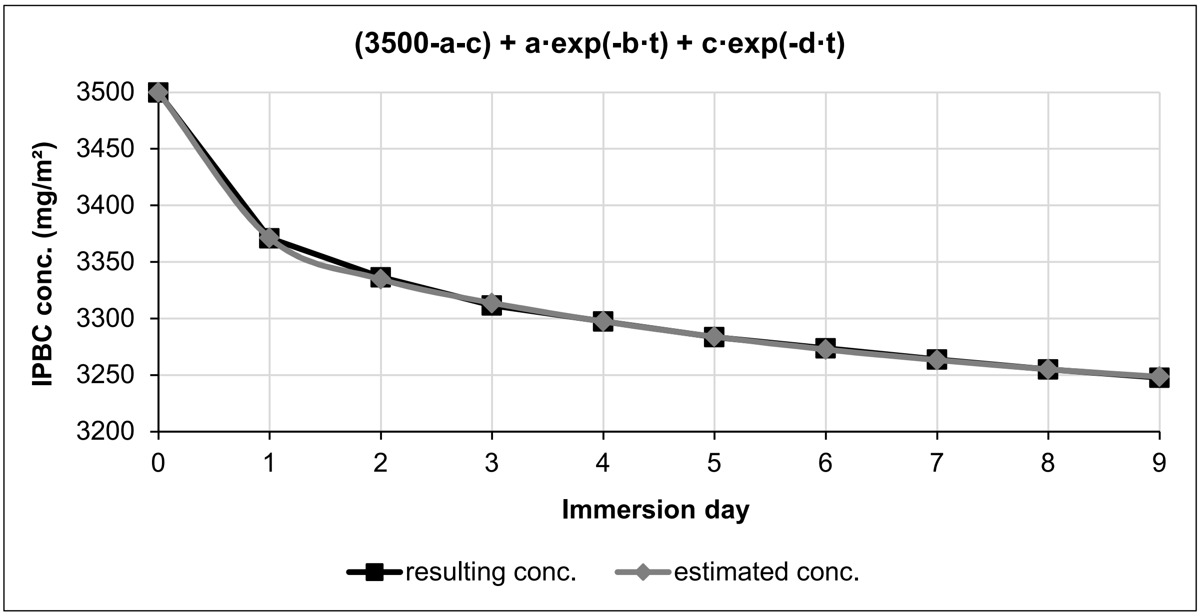


Table 7: Fitting by bi-phasic model (biocide: IPBC, project: "Urban Biocides", test: OECD TG107)

Immersion Day	**Measured Emission** [mg/m²]	**Resulting Conc. R** [mg/m²]	**Estimated Conc. E** [mg/m²]	**Deviation R-E** [mg/m²]	**Squared Deviation** [(mg/m²)²]
0		3500.00	3500.00	0.00	0.00
1	129.13	3370.87	3371.24	-0.38	0.14
2	34.41	3336.45	3334.65	1.81	3.26
3	24.84	3311.61	3313.68	-2.07	4.29
4	14.24	3297.37	3297.41	-0.04	0.00
5	13.81	3283.56	3283.92	-0.36	0.13
6	9.97	3273.59	3272.62	0.97	0.94
7	9.69	3263.90	3263.12	0.78	0.60
8	8.77	3255.13	3255.15	-0.02	0.00
9	7.39	3247.74	3248.45	-0.71	0.50
				ressd:	**1.41 mg/m²**

The residual standard deviation in bi-phasic model with a value of 1.41 mg/m² is higher than the respective figures in model 3 and 4. The deviations between estimated values of the regression models and measured values are shown in connection with the analytical model in Figure 14 (section 4.1) on p.84.

2.3 Comparison of differential equation models with the bi-phasic model

Within the project "Urban Biocides", 9 biocides were determined in leaching tests with discontinuous and continuous water contact. The fittings of the measured leaching rates by means of the differential equation models and by means of the bi-phasic model are compared exemplarily for render-coatings in discontinuous tests. In the following all data refer to these leaching tests for which the initial concentration of each active ingredient on the test specimens was specified by 3500 mg/m².

The following Table 8 lists the residual standard deviations - based on the leaching data of the discontinuous tests - for model 3 and 4 corresponding to the functions of type C_3 and C_4, respectively, and the bi-phasic model corresponding to C_{bi}.

Table 8: Residual standard deviations [in mg/m²] of fitting by 3 regression models (9 different biocides, project: "Urban Biocides", test: OECD TG107); the lowest value for each biocide is highlighted in bold

Biocide	**Model 3**	**Model 4**	**Bi-phasic model**
	$3500 - c + c \cdot e^{-a \cdot t^b}$	$3500 + a \cdot (1 - e^{-b \cdot t})^c$	$3500 - a - c + a \cdot e^{-b \cdot t} + c \cdot e^{-d \cdot t}$
BIT	4.02	3.42	**3.34**
Carbendazim	0.46	**0.41**	**0.41**
DCOIT	**0.30**	0.33	0.31
Diuron	2.20	**1.95**	2.07
IPBC	**0.98**	1.15	1.41
Irgarol	**0.52**	0.59	0.79
Isoproturon	2.13	1.93	**1.80**
OIT	1.56	**1.32**	**1.32**
Terbutryn	**0.65**	0.74	1.01
Mean	1.42	**1.32**	1.38

The differences for these 3 regression models are negligible, e.g. the number of lowest residual standard deviation (highlighted in bold) is almost equal. The lowest mean value over all biocides has the model 4 with a value of 1.32 mg/m². It should be noted that model 4 consists of only 3 parameters instead of 4 parameters in the bi-phasic model.

The good fitting by the regression model 4 is confirmed by considering the absolute deviation between the measured and estimated value of each immersion day. The following Table 9 shows the mean relative deviation between the observation and the estimation with respect to the observation over the 9 immersion days; values highlighted in bold specify the lowest mean relative deviation.

Table 9: Mean value of the absolute deviation between measured and estimated value relative to the measured one of fitting of leaching data by 3 regression models (9 different biocides, project: "Urban Biocides", test: OECD TG107); the lowest value for each biocide is highlighted in bold

Biocide	**Model 3**	**Model 4**	**Bi-phasic model**
BIT	10.7 %	**8.3 %**	11.8 %
Carbendazim	4.4 %	4.2 %	**3.8 %**
DCOIT	10.6 %	11.2 %	**9.9 %**
Diuron	7.7 %	**6.8 %**	7.7 %
IPBC	**6.6 %**	7.4 %	8.1 %
Irgarol	**4.8 %**	5.2 %	6.6 %
Isoproturon	5.6 %	**4.9 %**	5.6 %
OIT	5.8 %	**5.2 %**	7.2 %
Terbutryn	**4.3 %**	4.7 %	6.0 %
Mean	6.7 %	**6.4 %**	7.4 %

Although the differences between the 3 regression models are relatively low, the lowest deviation shows model 4 with a mean value 6.4 %.

The theoretical cumulative quantity which can even be totally leached over an infinite period of time is given in Table 10. Thereby the time-parameter t in the regression models is set to infinite.

Table 10: Estimation of the total leaching quantity [in mg/m²] (9 different biocides, project: "Urban Biocides", test: OECD TG107)

Biocide	**Model 3**	**Model 4**	**Bi-phasic model**
BIT	561.44	536.23	520.92
Carbendazim	168.83	158.60	149.04
DCOIT	44.44	43.05	42.13
Diuron	339.52	333.15	328.29
IPBC	365.34	304.94	286.73
Irgarol	195.20	173.87	165.58
Isoproturon	583.04	551.82	542.65
OIT	384.58	343.84	323.17
Terbutryn	295.45	265.21	252.47

The total leaching quantity of model 3 exceeds the one of model 4, whereas model 4 exceeds the one of bi-phasic model. It should be noted that it cannot be guaranteed that the true total leaching quantity is in the range of the three figures obtained.

3 Analytical Model

3.1 Physical processes

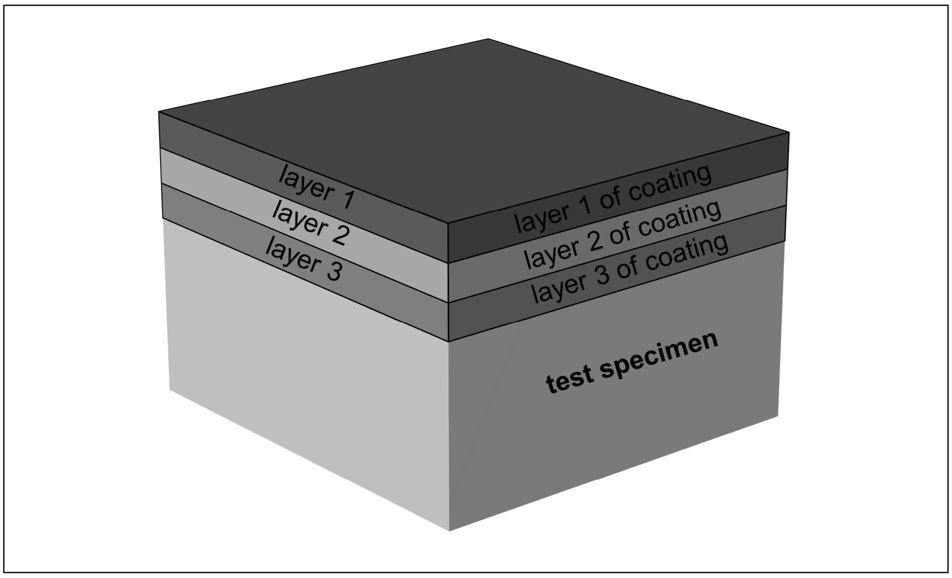
Although the regression models provide a mathematical estimation of the leaching rate, the physicochemical processes of leaching cannot be described, and regression parameters can hardly be interpreted in a physicochemical sense. In the following chapter an analytical approach is presented which takes into account the diffusion and the leaching process as well as the dissolving in continuous water tests and the process of drying in discontinuous water tests.

At the beginning, the total quantity of biocides in the material (façade-coating or treated wood) is to be analysed. Consequently, the initial biocide concentration is "0" in the water of the glass jar in which the specimens are immersed. During immersion, a part of biocide is emitted from the material into the water, whereby the distribution of the biocide within the material is changed. Biocide molecules are leached primarily on the surface and the exchange of molecules within the material proceeds due to the changed concentration gradients. To find a reasonable mathematical model for the leaching behaviour of biocides, the various dynamic processes have to be discretized appropriately.

3.2 Modelling of diffusion

To model the diffusion process, the material to be examined is divided into layers. For simplicity, 3 layers may be accepted as sufficient. A graphical representation of this 3-layer-approach is illustrated for façade-coating in Figure 6.

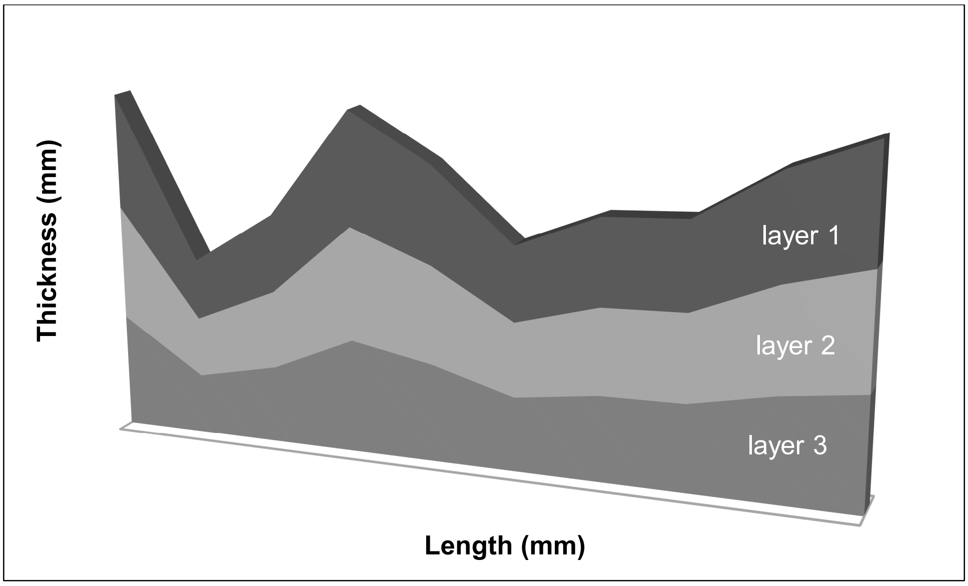
Figure 6: 3-layer-model of the façade-coating



Layer 1 is regarded as the contact area between material and water. The second layer can be regarded as medial layer and the third one can be considered as interface between specimen and material (e.g. coating) or as inner core of the material (e.g. wood), respectively. An equal-sized thickness of all 3 layers can be guaranteed by dividing the thickness of the entire material by 3.

Thus, despite the unevenness of the surface of material, equal-sized layers can be considered. Besides it is assumed that the flow between layers is constant over time.
Figure 7 illustrates this step for an arbitrary façade-coating.

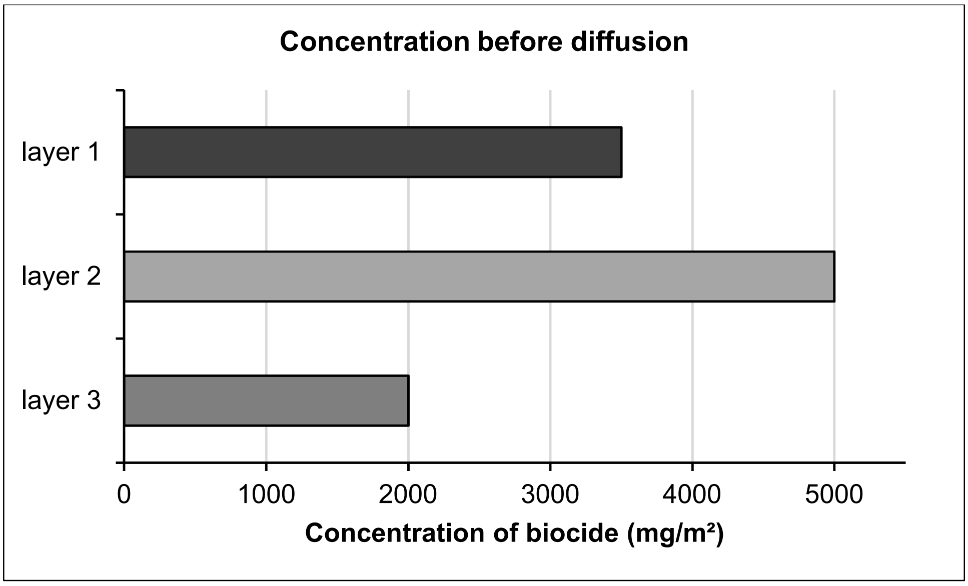
Figure 7: Arrangement of layers for any uneven façade-coating in cross-section



According to Fick's first law of diffusion, the particle transport in isothermal case is proportional to the concentration gradient. Furthermore, the diffusion flow proceeds in direction of decreasing concentration.

This time-constant particle transport is illustrated by means of an example. Figure 8 shows an arbitrary concentration of biocide in the 3 layers at any point of time with values of 3500 mg/m² in layer 1, 5000 mg/m² in layer 2 and 2000 mg/m² in layer 3.

Figure 8: Concentration of biocide in the 3 layers before diffusion process



The transport of biocide diffused between the layers is expressed by the difference between the concentration of layer 1 and the concentration in layer 2 as well as of layer 2 and layer 3.

These differences may be interpreted as concentration gradients. A certain percentage of the concentration gradient – which simulates the diffusion constant – is emitted to the layer with the lower concentration of biocide.

For an illustration the numerical example mentioned above is considered. Based on numerical values of Figure 8, the absolute difference between layer 1 and layer 2 is 1500 mg/m² and between layer 2 and layer 3 3000 mg/m². When a diffusion coefficient of 0.2 m²/time unit is assumed,

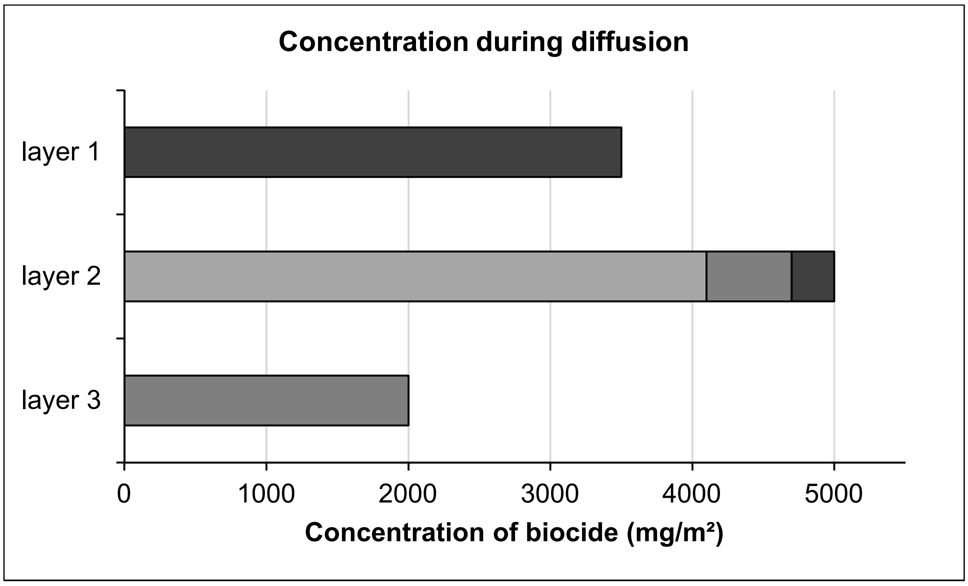
$$0.2\ m^2/\text{time unit} \cdot 1500\ mg/m^2/m^2 = 300\ mg/m^2/\text{time unit}$$

are transported from layer 2 to 1 and

$$0.2\ m^2/\text{time unit} \cdot 3000\ mg/m^2/m^2 = 600\ mg/m^2/\text{time unit}$$

from the second to the third layer as demonstrated in Figure 9.

Figure 9: Concentration of biocide in the 3 layers during diffusion process



The following Figure 10 shows the concentration of biocide in the 3 layers after the diffusion. Then layer 1 shows a value of

$$3500\ mg/m^2 + 300\ mg/m^2 = 3800\ mg/m^2,$$

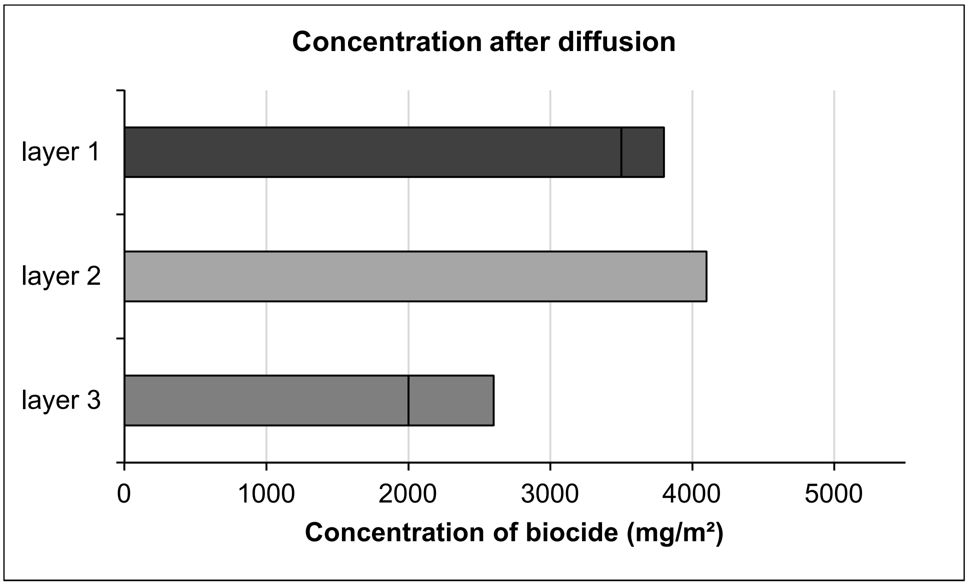
layer 2 shows a concentration of

$$5000\ mg/m^2 - 300\ mg/m^2 - 600\ mg/m^2 = 4100\ mg/m^2$$

and layer 3 a value of

$$2000\ mg/m^2 + 600\ mg/m^2 = 2600\ mg/m^2.$$

Figure 10: Concentration of biocide in the 3 layers after diffusion process within one time unit



Although this discrete time observation of substance transport represents a simplification of the continuous diffusion process, it still results in an efficient calculation of the emitted amount of biocide. In modelling the process of leaching, a distinction has to be made between continuous and discontinuous water contact.

3.3 Modelling of leaching

3.3.1 Continuous water contact

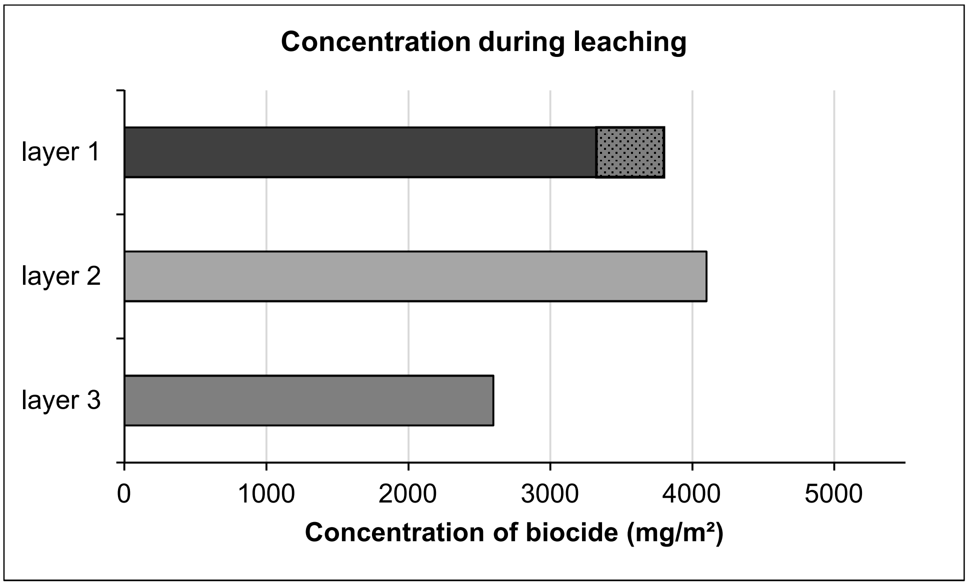
In experiments with continuous water contact the water is replaced according to a fixed timetable. After replacing the water, the concentration of biocide in water is "0". For simplicity it is assumed that only a certain percentage of the biocide concentration of layer 1 – the interface between material and water - is emitted. The practically simultaneous processes of diffusion and leaching are modelled in sequence: the process of leaching is determined after the calculation of the diffusion step.

Based on the numerical example mentioned above, the concentration of biocide in layer 1 is 3800 mg/m² after the diffusion. If a leaching factor of 0.125 is applied,

$$0.125 \cdot 3800\ \mathrm{mg/m^2} = 475\ \mathrm{mg/m^2}$$

are released by water and the concentration in layer 1 decreases to 3325 mg/m². This is reflected by the following Figure 11.

Figure 11: Change of the concentration of biocide in 3 layers during leaching



After leaching, diffusion is calculated once again. In the case of subsequent calculations of leaching it has to be taken into account that the concentration of biocide in the water does not amount “0“ any longer. Additionally, the water solubility of the biocide is limited. Therefore the total quantity of biocide leached of layer 1 after a substitution of water is considered. The concentration of biocide in water is related to the one in layer 1 by considering the absolute difference between them. Multiplying the concentration in water by a fixed factor will improve the fitting of leaching data.

When the concentration in layer 1 is higher than the corrected concentration in water, the leaching factor will be multiplied by the difference between them to calculate the quantity of leaching. When concentration in layer 1 is lower, no leaching flux is determined.

3.3.2 Discontinuous water contact

In experiments with discontinuous water contact the specimens are immersed on each test day with the same frequency and same length of time in clean water. Additionally, the redistribution in the materials is influenced by its drying. The water evaporates out of material and thereby the transport of active ingredients to the surface is carried out.

The modelling of discontinuous water contact is similar to the continuous one from the previous section. However, the concentration of biocide in water during the step of leaching in the stage of water contact has been considered negligible since the time of this water contact is only one hour. The potential loss of substance during the drying process, i.e. the potential transport of biocide molecules due to evaporating water, is implemented by removing a certain percentage of layer 1 after each step of diffusion in stages of drying.

Hence two stages are considered in experiments with discontinuous water contact. On the one hand stages with water contact, where the leaching is ensued through the water and on the other hand stages without water contact, where the evaporation of water ensues.

3.4 Calculation of fitting

3.4.1 Number of calculation steps

The number of diffusion as well as leaching steps in experiments with continuous water contact and the number of diffusion as well as leaching or evaporation steps in experiments with discontinuous water contact can be derived from the general experimental design.

3.4.1.1 Continuous water contact

In OECD Guideline 313 the water is substituted at the following points of time:

6 hours, 1 day, 2 days (BAM often 3 days), 4 days, 8 days, 15 days, 22 days and 29 days.

For modelling it is assumed that the trial period is split into 6-hour intervals. Thus, in total

$$29 \cdot 4 \text{ (6-hour intervals)} = 116 \text{ points of time}$$

are considered, each with a step of diffusion and leaching. Deviating trial periods from OECD Guideline 313 can be easily comprised.

3.4.1.2 Discontinuous water contact

The time intervals between stages of leaching and evaporation for the calculation result from OECD TG 107. There are 2 immersion events on each test day, both lasting 1 h with an interim drying period of 4 hours. The immersion events ensue on the following days:

day 1, day 3, day 5, day 8, day 10, day 12, day 15, day 17 and day 19.

Meanwhile, the specimens are dried. Because of the hourly immersion stage, a division into hourly intervals is meaningful and for that reason

$$19 \text{ days} \cdot 24 \text{ hours} = 456 \text{ points of time}$$

are considered. Deviating trial periods from OECD TG 107 can be easily comprised.

3.4.2 Calculation formulae

The modelled quantities of emission leached from layer 1 are referred to the measured FLUX-rates (= emitted quantity of biocide per day). Therefore in continuous tests the modelled emission quantities of all points of time of one immersion event are cumulated and divided by the number of days of the immersion event. In discontinuous tests the water samples of both immersion events per experimental day are combined to one sample. Thus the modelled emission quantities of these both points of time are added.

The equations for determination the estimated Flux-rate in the analytical model are given in the following Table 11. Thereby F(i) denotes the FLUX-rate at point of time i.

Table 11: Determination of the estimated Flux in the analytical model

	Continuous water contact		Discontinuous water contact	
Points of time	116 = 29 days · 4(= 6-hour-interval)		456 = 19 days · 24 hours	
Characteristics	timing of water exchange [· 0.25 days]: 1;4;12;16;32;60;88;116		stages of immersion [hour]: 1;6;49;54;97;102;169;174;217;222; 265;270;337;342;385;390;433;438	
Estimation	Day 0.25	$4 \cdot F(1)$	Day 1	F(1)+F(6)
	Day 1	$\frac{4}{3} \cdot \sum_{i=2}^{4} F(i)$	Day 3	F(49)+F(54)
	Day 3	$\frac{1}{2} \cdot \sum_{i=5}^{12} F(i)$	Day 5	F(97)+F(102)
	Day 4	$\sum_{i=13}^{16} F(i)$	Day 8	F(169)+F(174)
	Day 8	$\frac{1}{4} \cdot \sum_{i=17}^{32} F(i)$	Day 10	F(217)+F(222)
	Day 15	$\frac{1}{7} \cdot \sum_{i=33}^{60} F(i)$	Day 12	F(265)+F(270)
	Day 22	$\frac{1}{7} \cdot \sum_{i=61}^{88} F(i)$	Day 15	F(337)+F(342)
	Day 29	$\frac{1}{7} \cdot \sum_{i=89}^{116} F(i)$	Day 17	F(385)+F(390)
			Day 19	F(433)+F(438)

3.4.3 Influence parameters

In Table 12 the parameters to be examined are summarised for both experimental arrangements.

Table 12: Influence parameters in tests with continuous and discontinuous water contact

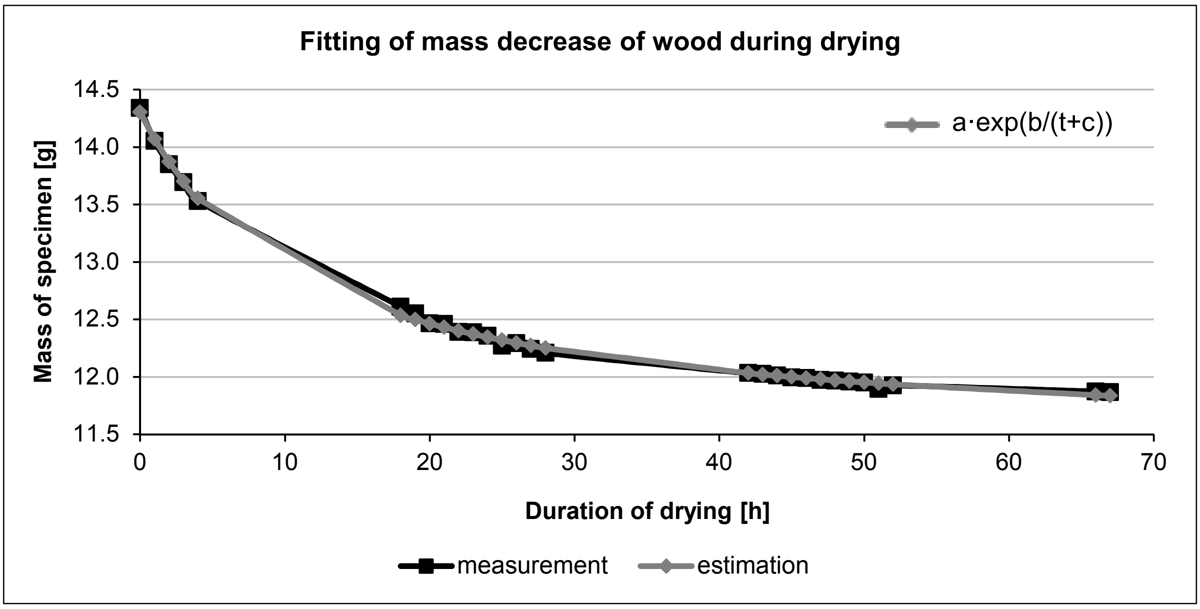
Continuous water contact	Discontinuous water contact
• **Constant of diffusion** for modelling the change of biocide concentration between the different layers	
• **Constant of leaching** for modelling the emission of biocide through the water out of the contact area material/water	
• **Constant** for modelling the dependence **of** the **concentration** of biocide **in water** and in material	• **Constant of evaporation of water** for modelling the stage of drying

These parameters are determined by minimising the residual standard deviation as measure of the deviation between observed and estimated emissions according to the calculations in Table 11.

3.4.4 Constant of evaporation of water

The process of drying is modelled in the analytical model by withdrawing a fixed percentage of layer 1 in stages without water contact. The modelling of a time-dependent factor of evaporation is more realistic since the process of evaporation of water decreases with increasing duration of drying. Data of the mass of wood during the process of drying are recorded by the BAM. The loss of mass can be described by a specific exponential function for example as it is shown in the following Figure 12.

Figure 12: Fitting of mass of wood during process of drying after 1 hour immersion



However, there are no data for migration of biocides to the materials surface due to evaporating water. An exponential decrease of the evaporation factor in the model does not result in a reduction of the residual standard deviation in contrast to a fixed constant. The reciprocal of the root of duration of drying multiplied with the constant of evaporation E proves to be a better estimation in some cases, i.e. drying for 5 hours implies an evaporation factor of E/√5.

Nevertheless this simplifying assumption of the process of evaporation cannot be confirmed. In order to address this issue another test series would be required.

3.4.5 Additional parameters

Besides estimating the parameters in Table 13, the initial concentration of biocide in each layer can be estimated to improve the fitting of leaching data. Only the concentration of layer 1 and layer 2 has to be estimated since the third layer can be calculated as difference of the triple initial concentration measured before experiment and the concentration in layer 1 and layer 2. The reason is that the total concentration results from the mean of the 3 layers.

In continuous laboratory tests an additional normalization of the calculated quantity of emissions results in a further improvement of the estimation by multiplying the output with a further constant.

Table 13 summarizes the parameters which have to be estimated to fit the leaching data.

Table 13: Parameters to be optimized in the analytical model

Continuous water contact	Discontinuous water contact
• Constant of diffusion • Constant of leaching • Constant of concentration in water • Initial concentration in layer 1 • Initial concentration in layer 2 • Normalization	• Constant of diffusion • Constant of leaching • Constant of evaporation of water • Initial concentration in layer 1 • Initial concentration in layer 2

3.5 Calculation software

The numerical implementation of this optimization model was realised by means of the software package GAUSS. GAUSS is a matrix programming language for mathematics and statistics, developed and marketed by Aptech Systems.

4 Comparison of regression models with analytical model

In this section the results of fitting of the leaching data are presented for the project “Urban Biocides” both for discontinuous water contact in section 4.1, and for continuous water contact in section 4.2. Exemplarily the following conditions in the project are considered:

- Initial concentration of each biocide on the test specimens: 3500 mg/m²
- Coating: Render
- Treatment without ultra-violet radiation.

4.1 Results for discontinuous tests

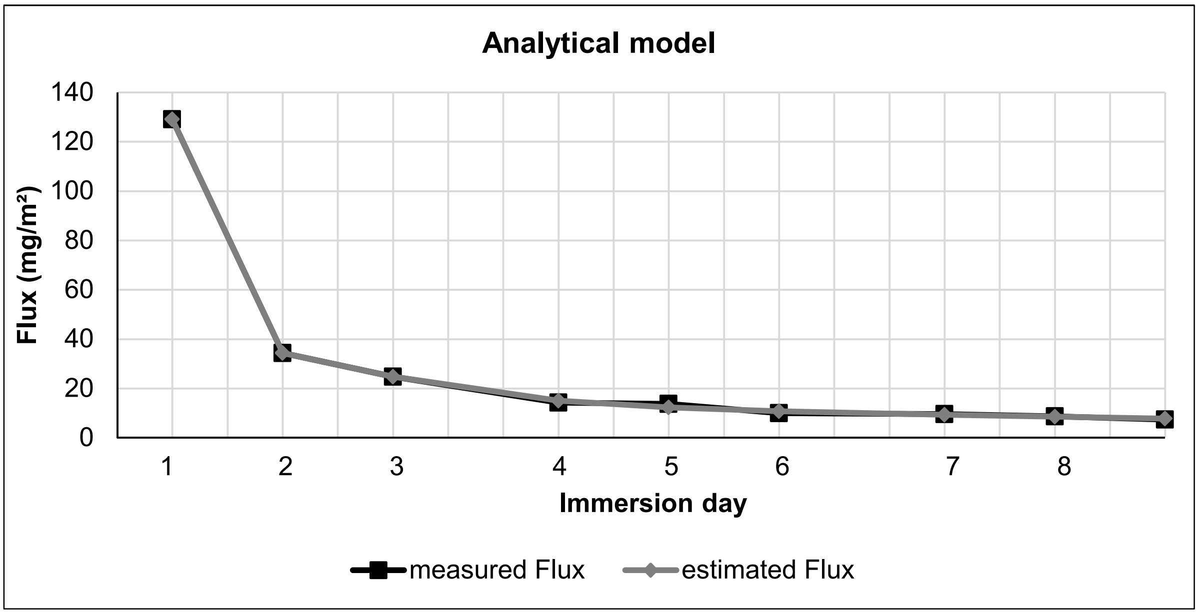
As an instance of tests with discontinuous water contact the leaching data of IPBC is examined more precisely. The best fitting could be obtained by assuming a time-indepedent rate of evaporation of water and the same initial concentration in layer 1 and 2.

The following Table 14 and Figure 13 display the goodness-of-fit according to the 3 regression models mentioned in chapter 2. The residual standard deviation in the analytical model with a value of 0.87 mg/m² is lower than the lowest one of the 3 regression models with a value of 0.98 mg/m².

Table 14: Fitting by analytical model (biocide: IPBC, project: “Urban Biocides”, test: OECD TG107)

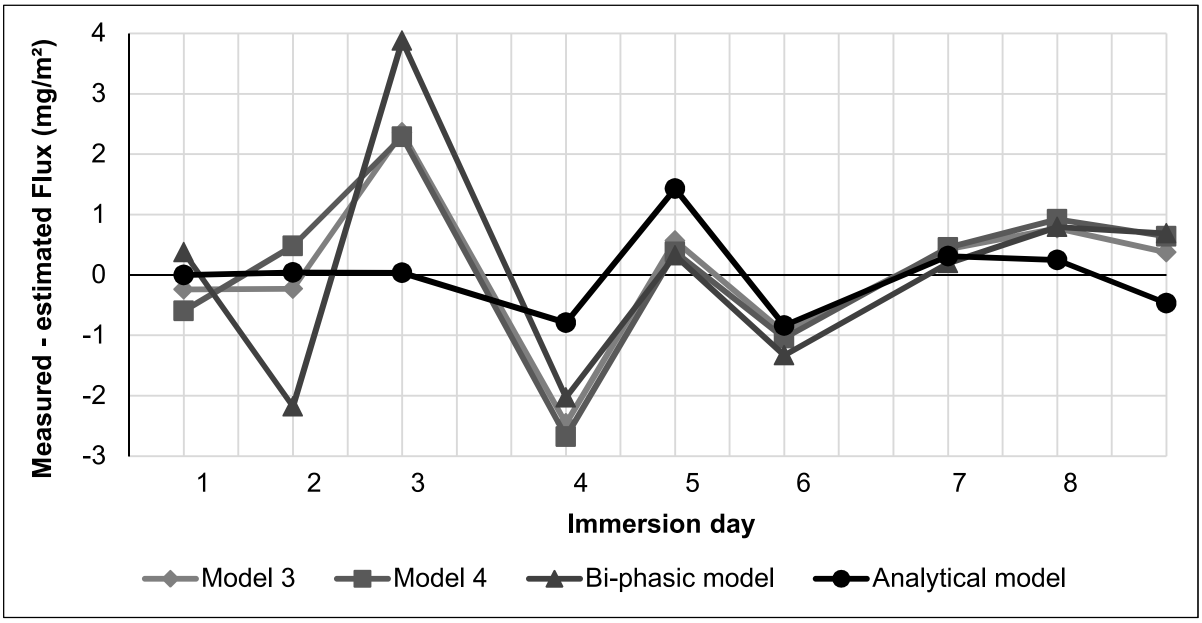
Immersion Day	**Measured Flux M** [mg/m²]	**Estimated Flux E** [mg/m²]	**Deviation M-E** [mg/m²]	**Squared Deviation** [(mg/m²)²]
1	129.13	129.14	0.00	0.00
2	34.41	34.37	0.04	0.00
3	24.84	24.81	0.03	0.00
4	14.24	15.03	-0.79	0.62
5	13.81	12.38	1.43	2.04
6	9.97	10.81	-0.84	0.70
7	9.69	9.37	0.31	0.10
8	8.77	8.52	0.25	0.06
9	7.39	7.86	-0.47	0.22
			ressd:	**0.87 mg/m²**

Figure 13: Fitting by analytical model (biocide: IPBC, project: "Urban Biocides", test: OECD TG107)



The course of the leaching process is described well. Particularly the problem of longer stages of drying between the 3rd and 4th immersion day can be reflected well by the analytical model. The deviation between measurement and estimation of the 3 regression models and the analytical model is illustrated in the following Figure 14.

Figure 14: Deviation between measured and estimated Flux of regression models and analytical model (biocide: IPBC, project: "Urban Biocides", test: OECD TG107)



The high deviations on the 3rd and 4th immersion day are conspicuous. The analytical model reproduces the Flux-rate in the beginning extremely well, whereas the regression models cannot distinguish the different durations between the test days. On the one hand in all regression models the estimated 3rd Flux is much smaller than the measured one and on the other hand the 4th estimated value is much higher. So the estimation of the Flux-rate fails before a longer stage of drying (immersion day 3 and 6) in the regression models.

The fitting by the analytical model is slightly worse regarding the regression models for immersion day 5 which can be based on an emission of a small deposit potentially. The change of the leaching rate from high decreasing in the beginning to the progressive slower flux as time passes has to be reproduced slightly better in an appropriately modified model. The deviations for immersion day 7, 8 and 9 are not yet quite satisfying. However, it should be considered that the measurement uncertainty of the analytical data is higher in low concentrations.

In the following Table 15 the residual standard deviations of fitting of the leaching data are listed for each 3 regression models and the analytical model for each of the 9 biocides examined in render coatings with discontinuous water contact.

Table 15: Residual standard deviation [in mg/m²] of fitting by regression models and analytical model (9 different biocides, project: "Urban Biocides", test: OECD TG107)

Biocide	**Model 3**	**Model 4**	**Bi-phasic model**	**Analytical model**
BIT	4.02	3.42	3.34	**2.77**
Carbendazim	0.46	**0.41**	**0.41**	0.51
DCOIT	0.30	0.33	0.31	**0.28**
Diuron	2.20	1.95	2.07	**1.01**
IPBC	0.98	1.15	1.41	**0.87**
Irgarol	**0.52**	0.59	0.79	0.54
Isoproturon	2.13	1.93	1.80	**1.33**
OIT	1.56	**1.32**	**1.32**	1.45
Terbutryn	**0.65**	0.74	1.01	1.04
Mean	1.42	1.32	1.38	**1.09**

For 5 out of 9 biocides the minimal value for the residual standard deviation is obtained by the analytical model. For the biocides Irgarol and OIT the analytical model shows the second lowest value, whereas it has the highest one for Carbendazim and Terbutryn. The mean residual standard deviation of the analytical model with a value of 1.09 mg/m² is significantly lower than the respective figures for the regression models.

Table 16: Mean absolute deviation between measured and estimated value relative to measured one of fitting of leaching data by regression models and analytical model (9 different biocides, project: "Urban Biocides", test: OECD TG107)

Biocide	**Model 3**	**Model 4**	**Bi-phasic model**	**Analytical model**
BIT	10.7 %	8.3 %	11.8 %	**8.1 %**
Carbendazim	4.4 %	4.2 %	3.8 %	**2.9 %**
DCOIT	10.6 %	11.2 %	9.9 %	**7.2 %**
Diuron	7.7 %	6.8 %	7.7 %	**6.0 %**
IPBC	6.6 %	7.4 %	8.1 %	**4.1 %**
Irgarol	4.8 %	5.2 %	6.6 %	**2.4 %**
Isoproturon	5.6 %	4.9 %	5.6 %	**4.8 %**
OIT	5.8 %	**5.2 %**	7.2 %	6.3 %
Terbutryn	4.3 %	4.7 %	6.0 %	**4.0 %**
Mean	6.7 %	6.4 %	7.4 %	**5.1 %**

The preceding Table 16 confirms the goodness of the fitting by the analytical model in contrast to the regression functions. Therein the mean absolute deviation between the measured and estimated value relative to the measured one over the 9 immersion days is listed; values highlighted in bold specify the lowest absolute deviation.

For 8 out of 9 biocides the mean absolute deviation has the lowest value (highlighted in bold) for the analytical model. The average percentage deviation in the analytical model is only 5.1 % over all biocides. This value is approximately 20 % lower than the lowest corresponding value of the regression models.

4.2 Results for continuous tests

The project "Urban Biocides" also included tests with discontinuous water contact. The corresponding measurements are fitted by the regression models and the analytical model. The results are listed in the following Table 17.

Table 17: Residual standard deviation [in mg/m²/d] of fitting by regression models and analytical model (9 different biocides, project: "Urban Biocides", test: OECD G313)

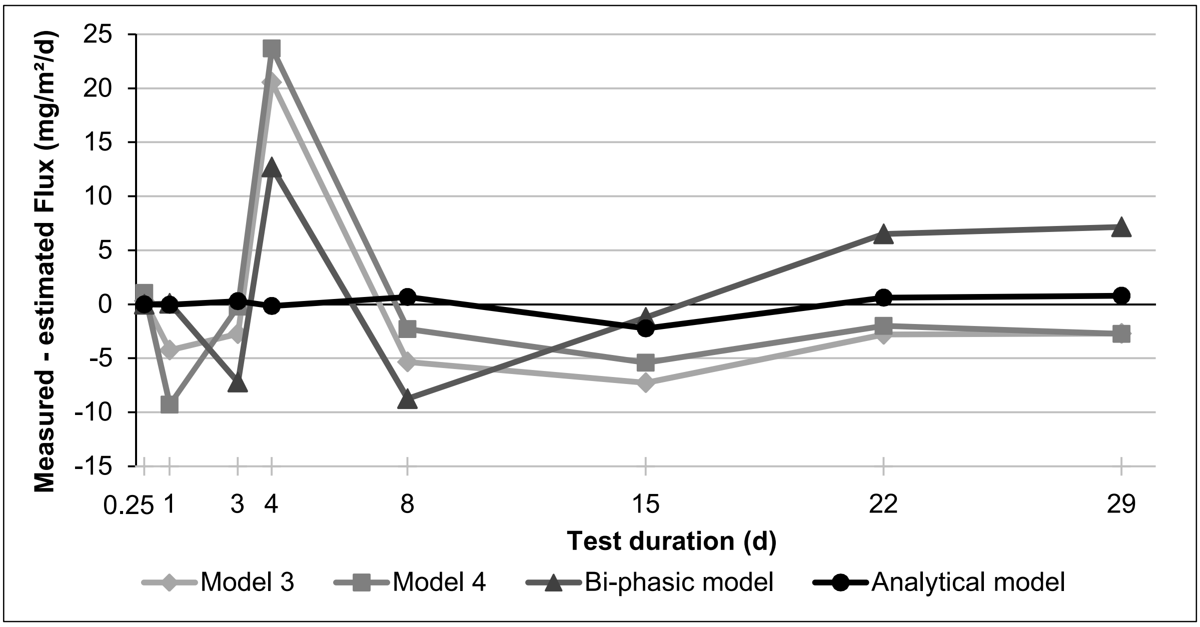
Biocide	**Model 3**	**Model 4**	**Bi-phasic model**	**Analytical model**
BIT	23.26	17.52	14.30	**11.88**
Carbendazim	25.34	24.62	19.37	**3.76**
DCOIT	1.33	1.39	1.18	**0.20**
Diuron	10.04	12.12	9.79	**3.58**
IPBC	16.54	16.88	13.43	**2.31**
Irgarol	6.88	6.81	6.88	**1.07**
Isoproturon	16.49	19.93	12.40	**3.83**
OIT	10.44	11.79	9.81	**1.48**
Terbutryn	11.06	10.74	10.20	**1.07**
Mean	13.49	13.53	10.82	**3.24**

The analytical model shows the best fitting for all 9 examined biocides. The average residual standard deviation of the analytical model is approximately 3.3 times lower than the one of the bi-phasic model and even 4 times lower than the ones of model 3 and 4. The following Table 18 and Figure 15 illustrate the discrepancy between measurement and estimation using the example of biocide Octylisothiazolinone (OIT).

Table 18: Fitting by regression models and the analytical model [in mg/m²/d] (biocide: OIT, project: "Urban Biocides", test: OECD G313)

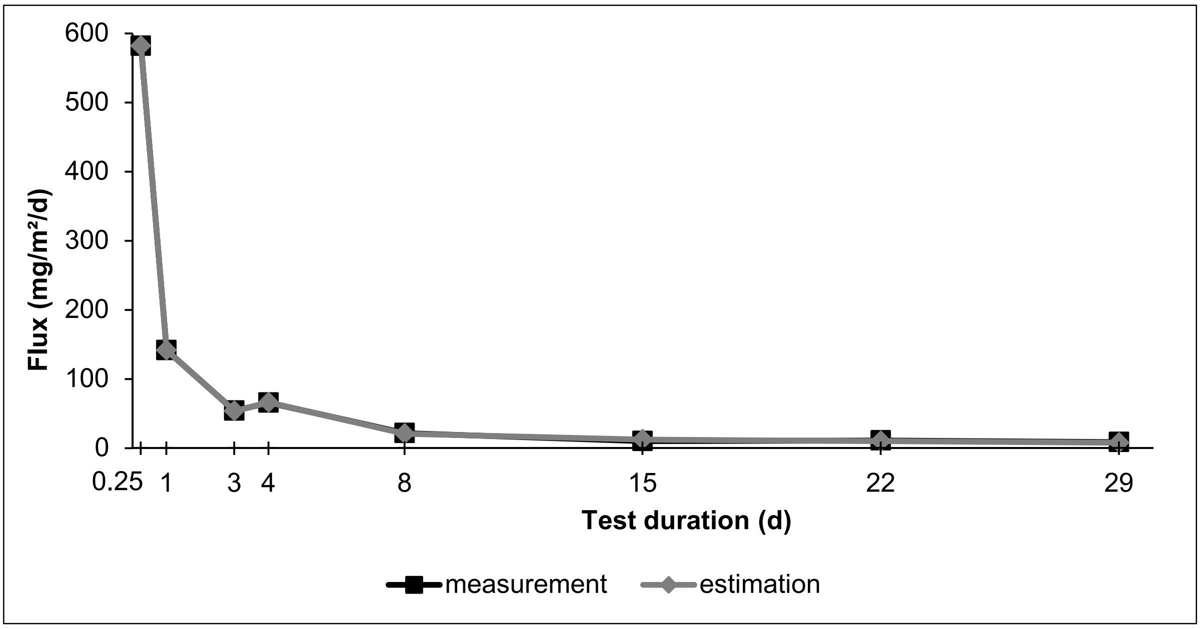
Day	**Measurement**	**Model 3**	**Model 4**	**Bi-phasic model**	**Analytical model**
0.25	582.12	581.80	581.07	582.13	582.12
1	141.80	146.06	151.08	141.71	141.82
3	54.07	56.81	54.28	61.28	53.79
4	65.81	45.26	42.12	53.11	65.98
8	21.64	26.99	23.92	30.40	20.96
15	10.23	17.49	15.64	11.46	12.46
22	10.84	13.64	12.83	4.32	10.21
29	8.79	11.48	11.52	1.63	8.00

Figure 15: Deviation between measured and estimated Flux of regression models and analytical model (biocide: OIT, project: "Urban Biocides", test: OECD G313)



The analytical model reproduces the first 4 measurements of the Flux extremely well. The estimated Flux on the 8th experimental day differs slightly, whereas the highest deviation is noted on the 15th experimental day after the first immersion period of 7 days. The model overestimates this 6th measurement. In contrast the following 2 measured Flux-rates are underestimated. However, the highest deviation between measured and estimated is only 2.3 mg/m²/d and the following Figure 16 demonstrates this relatively good fitting by the analytical model.

Figure 16: Fitting by analytical model (biocide: OIT, project: "Urban Biocides", test: OECD G313)



5 Confirmatory analyses of the analytical model in long-term tests

Several long-term test series were carried out by the BAM in order to examine the analytical model for a longer period of time.

Tests with treated wood were extended from 29 to 77 days total immersion time for OECD G313 and from 9 to 25 experimental days for OECD TG107 (from 19 to 78 days in total). In the OECD G313 test a leaching stage of 14 days was carried out at the end. In the OECD TG107 test the specimens were once immersed for 1 week after the 73rd experimental day.

Another experiment derived from OECD TG107 was carried out for façade coatings over a period of 33 days (9 immersion days). In this experiment, on the 6th immersion day the specimens were immersed for 6 hours, whereas in the other immersion days the immersion time was 2 hours in agreement with the scheme in OECD TG107.

These series of measurements with different immersion and drying stages were to be used for testing the analytical model in several versions with 5 to 7 parameters.

5.1 Wood

5.1.1 Discontinuous tests

In the long-term tests with discontinuous water contact after the 73rd experimental day a high peak (see Figure 17 and Figure 19) was observed. This peak can be explained by a long immersion time – and it has to be estimated by the analytical model. The high peak is based on the 7 days immersion of the specimen. This continuous water contact of 7 days is fulfilled in the analytical model by combining both approaches in section 3.3 (3.3.1 for continuous water contact and 3.3.2 for discontinuous one). So the constant of concentration in water described in subsection 3.3.1 is included in the stage of 7 days immersion. Therefore the following 7 parameters are optimized:

- Constant of diffusion
- Constant of leaching
- Constant of evaporation of water
- Constant of concentration in water
- Initial concentration in layer 1
- Initial concentration in layer 2
- Normalization.

The results for Copper as well as Tebuconazole look promising since the residual standard deviations with values of 1.40 mg/m² for Copper (see Table 18) and 0.10 mg/m² for Tebuconazole (see Table 19), respectively, are very small. The deviation between the measured and estimated quantity leached after the 78 experimental days totally is 0.06% for Copper and 0.23% for Tebuconazole, respectively. Furthermore the estimated curves in Figure 17 and Figure 18 proceeds smooth. The contingent peaks in the measured data which are not reproduced by the smooth model can be based on measurement errors or random leaching events reasoned by releasing of a secondary depot due to the long water contact. The relatively good fitting shows the goodness of the analytical model. The parameters mentioned above expresses a sufficient reproduction of the measured values.

Table 19: Fitting by analytical model (biocide: Copper, long-term test: OECD TG107 modified)

Experimental Day	Measured Flux M [mg/m²]	Estimated Flux E [mg/m²]	Deviation M-E [mg/m²]	Squared Deviation [(mg/m²)²]
1	1164.43	1164.40	0.03	0.00
3	258.51	259.14	-0.63	0.40
5	114.91	112.34	2.57	6.59
8	70.27	71.36	-1.10	1.20
10	47.61	50.07	-2.46	6.03
12	40.21	40.99	-0.78	0.60
29	22.45	22.75	-0.30	0.09
31	18.18	16.44	1.74	3.02
33	15.55	14.26	1.29	1.65
36	15.33	13.72	1.61	2.60
38	12.45	11.19	1.26	1.58
40	11.62	9.96	1.66	2.74
43	10.91	9.67	1.24	1.54
45	7.49	7.91	-0.42	0.17
47	7.29	7.05	0.24	0.06
50	6.30	6.83	-0.54	0.29
52	5.21	5.63	-0.42	0.18
54	3.75	5.00	-1.24	1.54
57	3.04	4.86	-1.82	3.31
59	2.37	3.95	-1.57	2.48
61	3.16	3.53	-0.38	0.14
64	3.40	3.43	-0.03	0.00
73	21.14	21.34	-0.20	0.04
75	1.58	1.51	0.07	0.01
78	0.71	1.60	-0.90	0.80
			ressd:	**1.40 mg/m²**

Figure 17: Fitting by analytical model (biocide: Copper, long-term test: OECD TG107 modified)

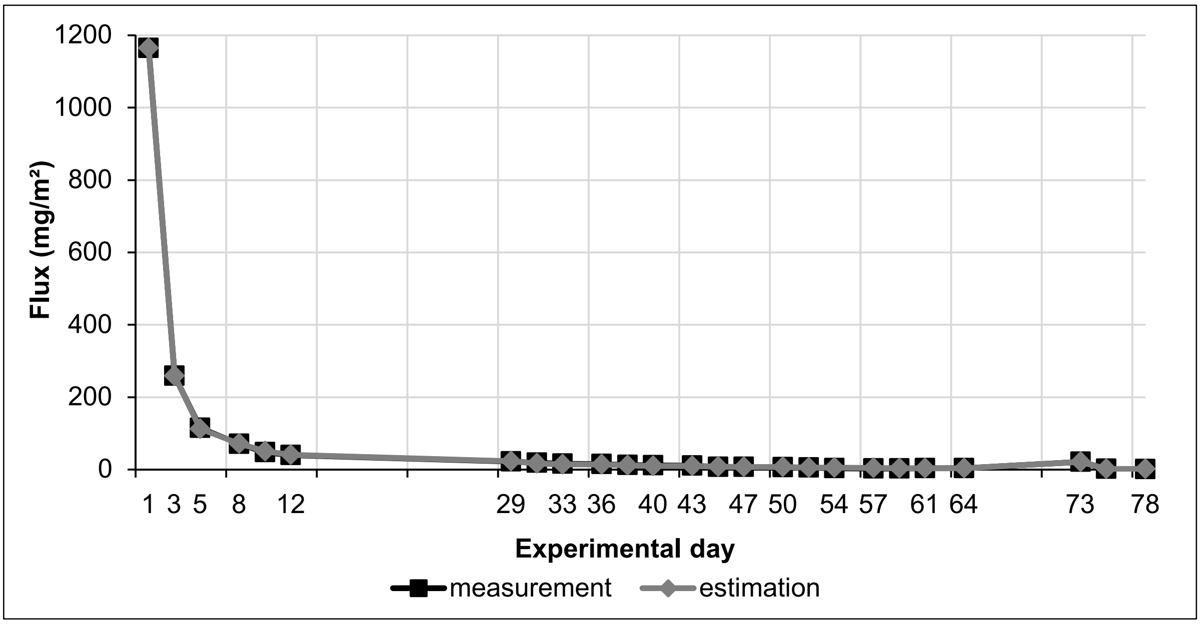


Figure 18: Deviation between measured and estimated Flux of analytical model (biocide: Copper, long-term test: OECD TG107 modified)

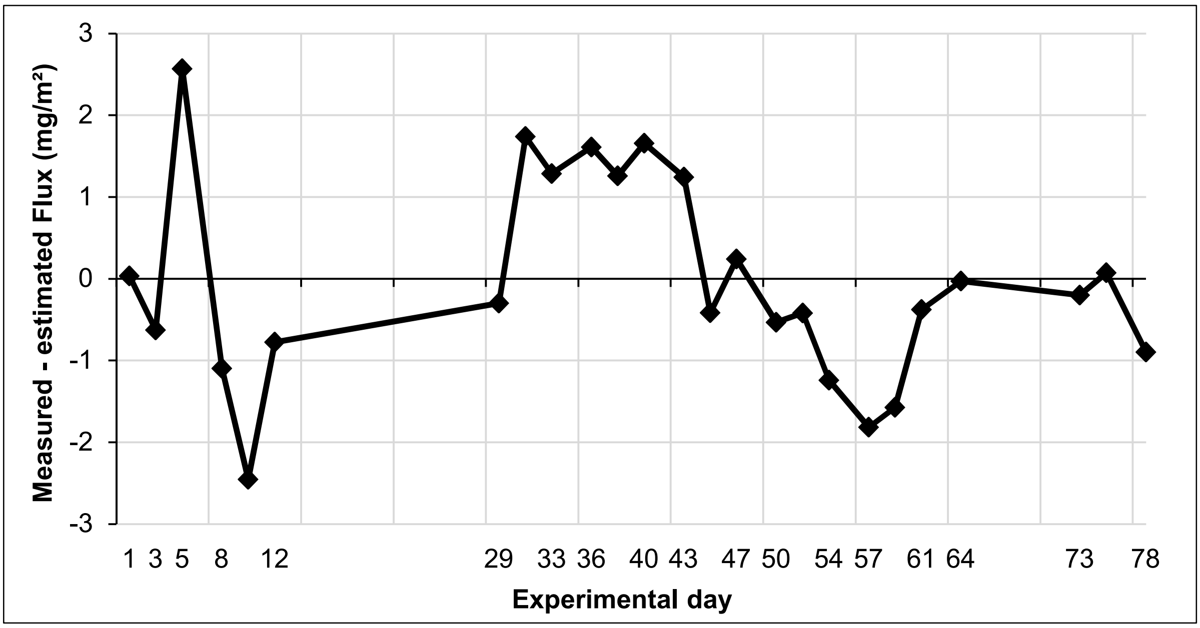


Table 20: Fitting by analytical model (biocide: Tebuconazole, long-term test: OECD TG107 modified)

Experimental Day	Measured Flux M [mg/m²]	Estimated Flux E [mg/m²]	Deviation M-E [mg/m²]	Squared Deviation [(mg/m²)²]
1	2.88	2.80	0.08	0.01
3	2.38	2.46	-0.08	0.01
5	2.09	2.17	-0.08	0.01
8	1.75	1.86	-0.11	0.01
10	1.83	1.66	0.17	0.03
12	1.54	1.49	0.05	0.00
29	1.01	0.96	0.05	0.00
31	0.91	0.89	0.02	0.00
33	0.80	0.83	-0.03	0.00
36	0.81	0.78	0.03	0.00
38	0.72	0.74	-0.02	0.00
40	0.69	0.70	-0.01	0.00
43	0.71	0.67	0.04	0.00
45	0.56	0.64	-0.08	0.01
47	0.60	0.62	-0.02	0.00
50	0.55	0.60	-0.05	0.00
52	0.50	0.59	-0.09	0.01
54	0.63	0.57	0.06	0.00
57	0.72	0.57	0.15	0.02
59	0.42	0.55	-0.13	0.02
61	0.44	0.54	-0.10	0.01
64	0.47	0.54	-0.07	0.00
73	1.36	1.35	0.01	0.00
75	0.88	0.71	0.17	0.03
78	0.64	0.67	-0.03	0.00
			ressd:	**0.10 mg/m²**

Figure 19: Fitting by analytical model (biocide: Tebuconazole, long-term test: OECD TG107 modified)

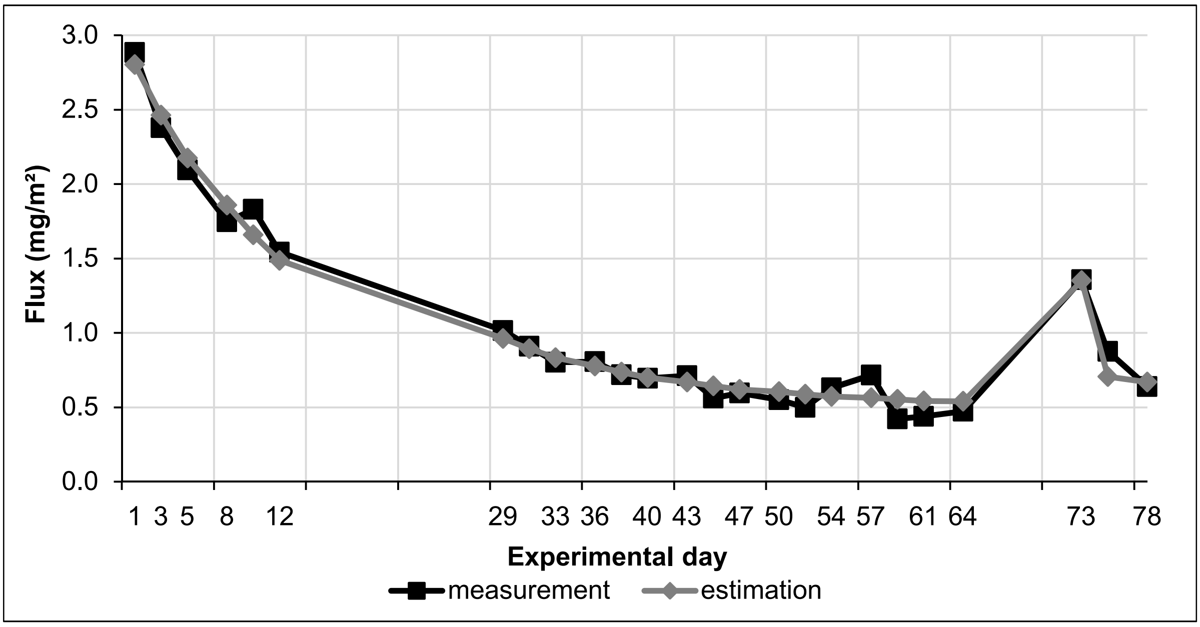
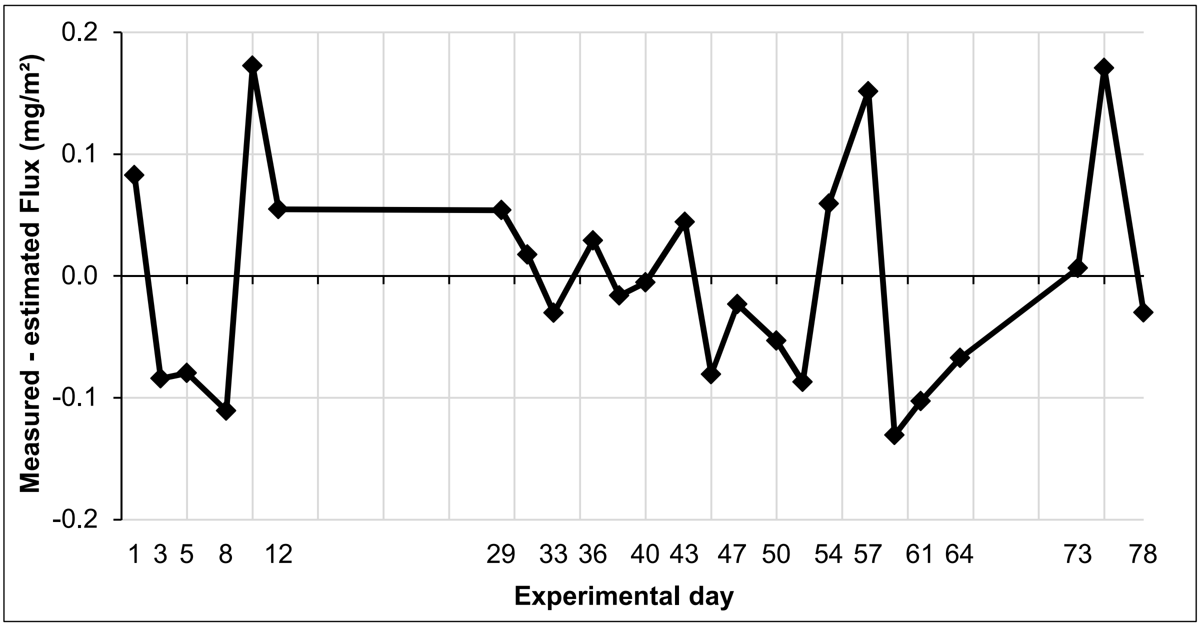


Figure 20: Deviation between measured and estimated Flux of analytical model (biocide: Tebuconazole, long- term test: OECD TG107 modified)



5.1.2 Continuous tests

The residual standard deviations with values of 0.84 mg/m² for Copper (see Table 21) and 0.20 mg/m² for Tebuconazole (see Table 22) show the goodness of the fitting by the analytical model also in continuous tests.

Table 21: Fitting by analytical model (biocide: Copper, long-term test: OECD G313 modified)

Experimental Day	**Measured Flux M** [mg/m²/d]	**Estimated Flux E** [mg/m²/d]	**Deviation M-E** [mg/m²/d]	**Squared Deviation** [(mg/m²/d)²]
0.25	534.61	534.61	0.00	0.00
1	129.56	129.57	0.00	0.00
3	60.48	60.48	0.00	0.00
7	32.56	32.81	0.25	0.06
14	18.46	17.24	-1.22	1.49
21	9.79	10.74	0.95	0.89
28	6.09	7.27	1.18	1.40
35	6.26	4.96	-1.30	1.69
42	3.21	3.39	0.18	0.03
49	1.85	2.32	0.47	0.22
56	1.60	1.58	-0.02	0.00
63	1.53	1.08	-0.45	0.20
77	1.17	0.62	-0.54	0.30
			ressd:	**0.84 mg/m²**

Figure 21: Fitting by analytical model (biocide: Copper, long-term test: OECD G313 modified)

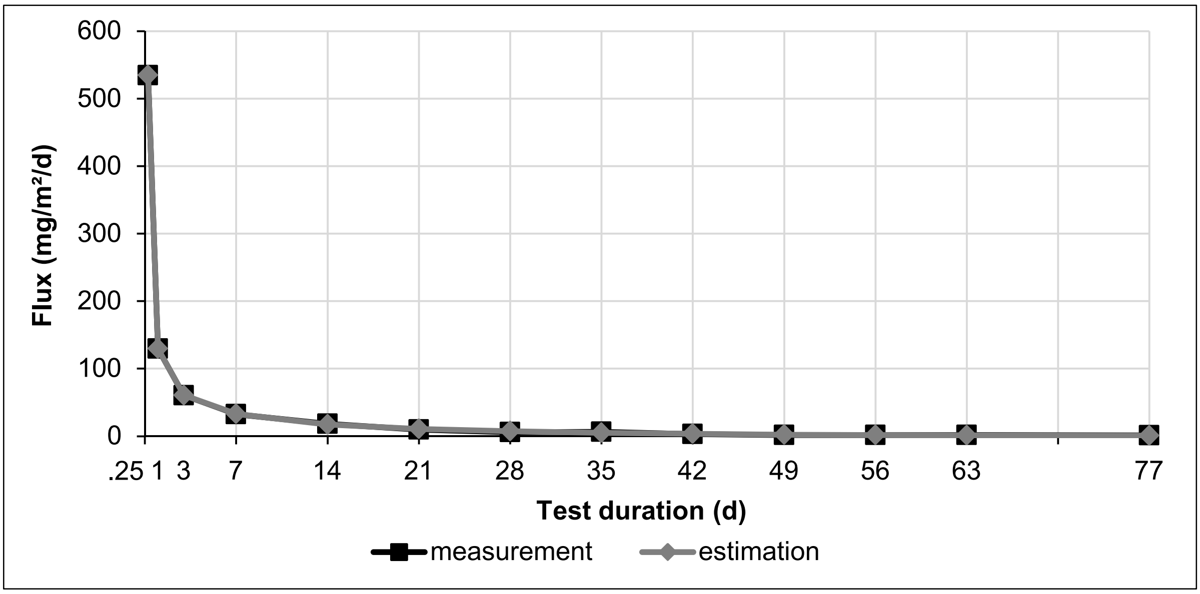


Figure 22: Deviation between measured and estimated Flux of analytical model (biocide: Copper, long-term test: OECD G313 modified)

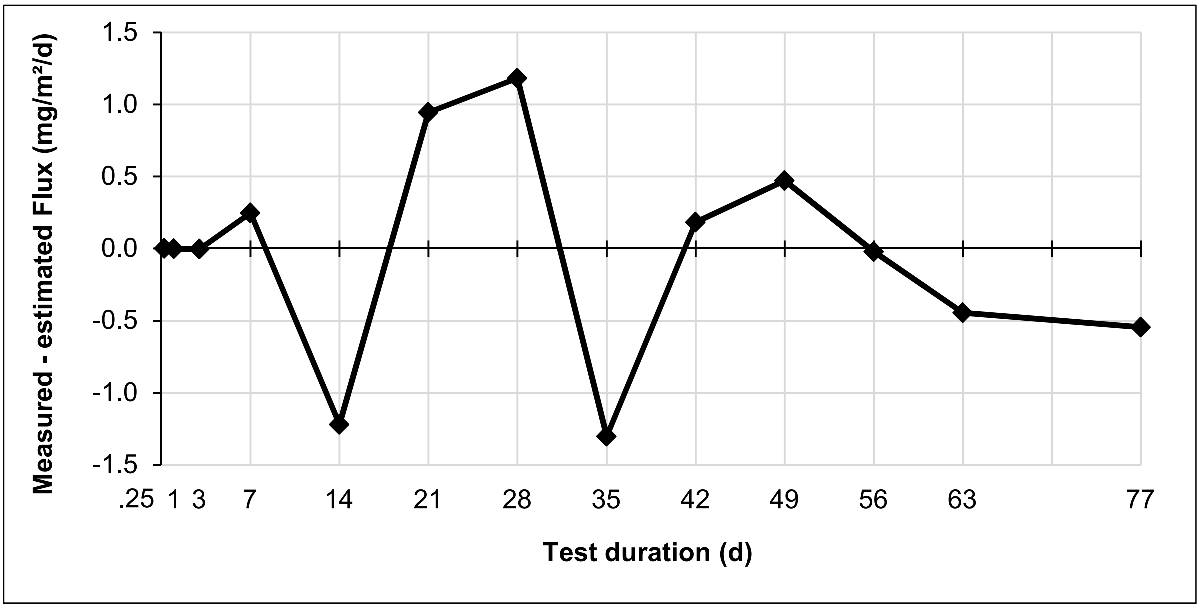


Table 22: Fitting by analytical model (biocide: Tebuconazole, long-term test: OECD G313 modified)

Experimental Day	**Measured Flux M** [mg/m²/d]	**Estimated Flux E** [mg/m²/d]	**Deviation M-E** [mg/m²/d]	**Squared Deviation** [(mg/m²/d)²]
0.25	18.14	18.14	0.00	0.00
1	6.76	6.76	0.00	0.00
3	2.81	2.84	0.03	0.00
7	1.57	1.49	-0.08	0.01
14	0.97	0.78	-0.19	0.03
21	0.33	0.68	0.35	0.12
28	0.35	0.59	0.24	0.06
35	0.80	0.51	-0.29	0.09
42	0.46	0.44	-0.02	0.00
49	0.38	0.38	0.00	0.00
56	0.34	0.33	-0.01	0.00
63	0.30	0.28	-0.01	0.00
77	0.14	0.12	-0.02	0.00
			ressd:	**0.20 mg/m²**

Figure 23: Fitting by analytical model (biocide: Tebuconazole, long-term test: OECD G313 modified)

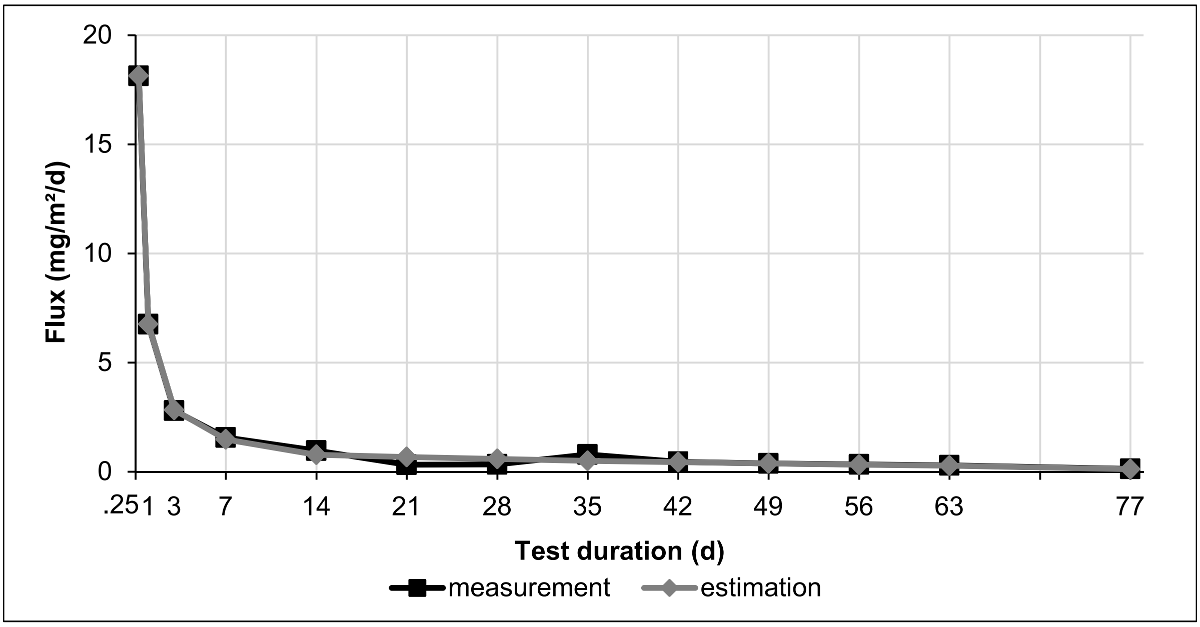
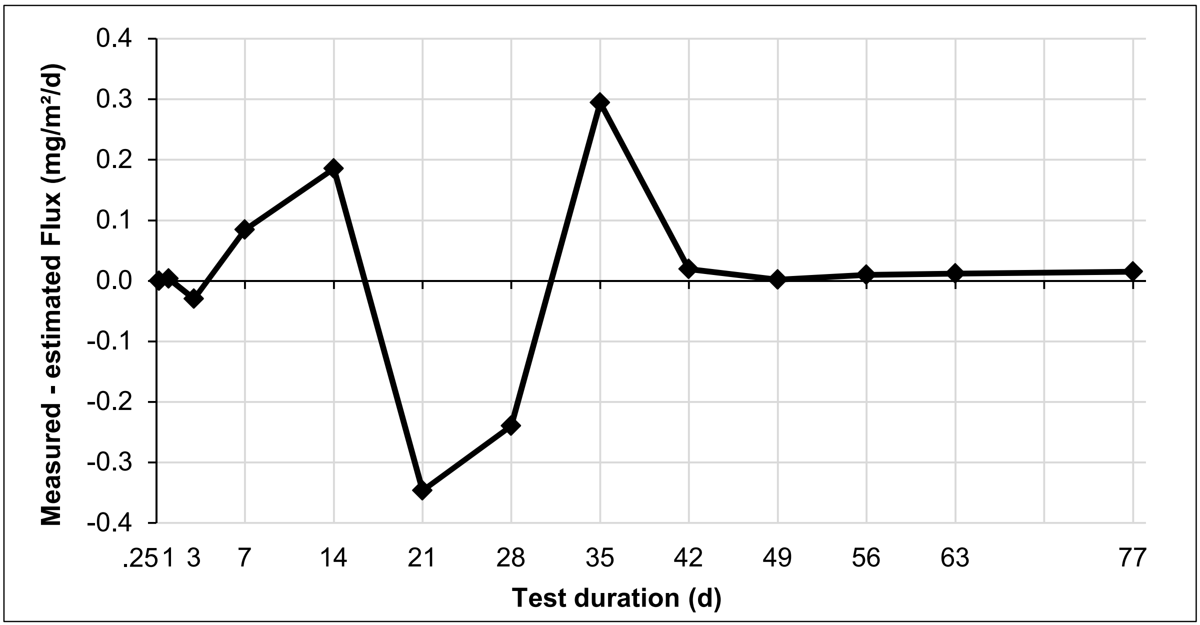


Figure 24: Deviation between measured and estimated Flux of analytical model (biocide: Tebuconazole, long- term test: OECD G313 modified)



5.2 Façade-coating

In total, 10 series of experimental data of discontinuous tests (5 different biocides in façade renders and façade paints) were provided and statistically analysed. Exemplarily the results of the fitting are shown in the following Table 23 and the both subsequent figures Figure 25 and Figure 26 for the biocide OIT in façade paint.

Table 23: Fitting by analytical model (biocide: OIT, long-term test: OECD TG107 modified)

Experimental Day	**Measured Flux M** [mg/m²]	**Estimated Flux E** [mg/m²]	**Deviation M-E** [mg/m²]	**Squared Deviation** [(mg/m²)²]
1	21.06	21.05	0.01	0.00
3	7.80	7.89	-0.08	0.01
5	5.89	5.67	0.23	0.05
8	5.10	5.20	-0.09	0.01
10	4.60	4.91	-0.31	0.10
12	8.21	8.08	0.13	0.02
29	3.37	3.34	0.03	0.00
31	3.47	3.08	0.39	0.15
33	2.57	2.92	-0.35	0.12
			ressd:	**0.34 mg/m²**

The 6 hours immersion events on the 12th experimental day as well as a stage of drying of 14 days are reproduced by the analytical model. Longer time series were not available.

Figure 25: Fitting by analytical model (biocide: OIT, long-term test: OECD TG107 modified)

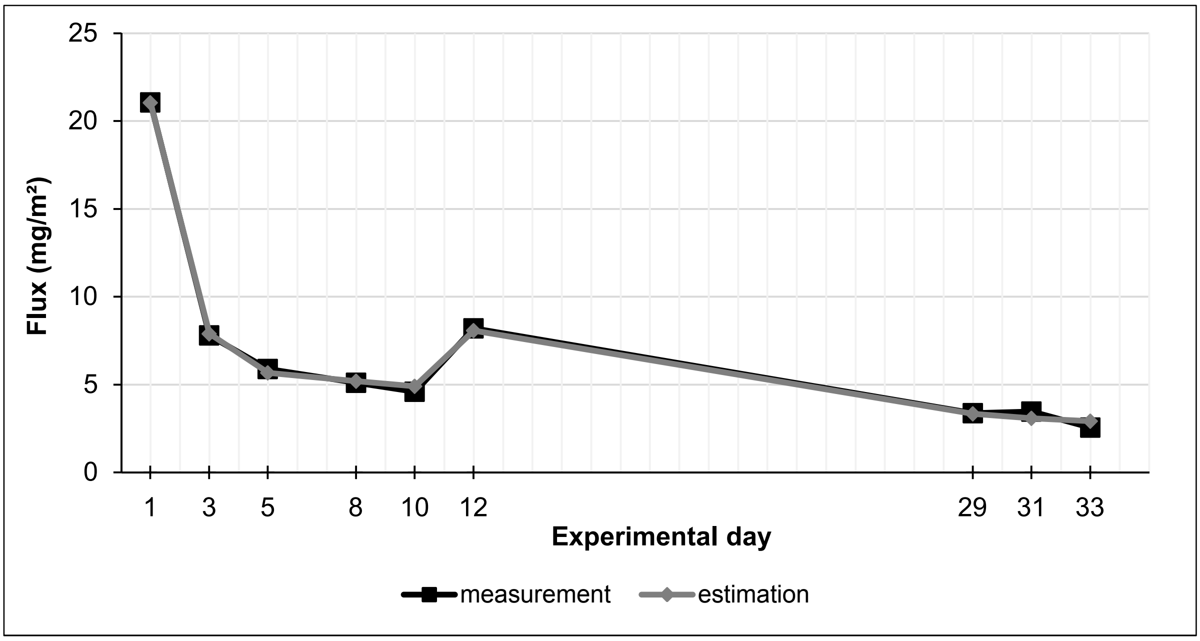
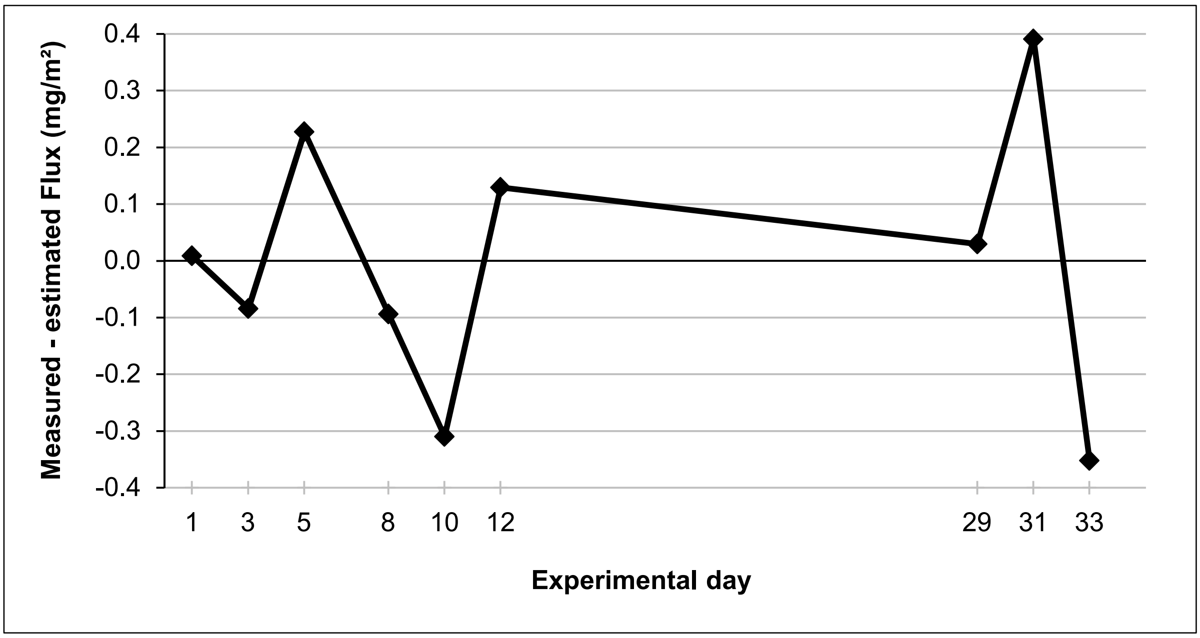


Figure 26: Deviation between measured and estimated Flux of analytical model (biocide: OIT, long-term test: OECD TG107 modified)



The examination of all 10 data sets resulted in a residual standard deviation from 0.11 for Terbutryn in façade paint to 0.65 for OIT in façade render.

Annex I - Information sources

Source	Content
European Commission http://ec.europa.eu/environment/biocides/	Biocidal Products Directive 98/8/EC (BPD) and related regulations
European Commission Joint Research Center, Institute for Health and Consumer Protection http://ecb.jrc.ec.europa.eu/biocides/	Emission scenario documents, Technical guidance documents, Workshop reports
European Chemicals Agency http://echa.europa.eu/	REACH guidance documents
Beuth Verlag http://www.beuth.de/	German, European and international (DIN, CEN and ISO) standards
OECD http://www.oecd.org/department/0,2688,en_-2649_32159259_1_1_1_1_1,00.html	Biocide documents Emission scenario documents Guidelines
Bundesamt für Arbeitsschutz und Arbeitsmedizin (BAuA) http://www.baua.de/	Biocide documents (e.g. Biocidal products registered according to Biozid-Meldeverordnung)
Leaching.Net http://www.leaching.net/	Information about leaching, literature and links
Industry associations	Specific information on products and product types
Scientific publications	See Chapter 7, Literature
Experts from scientific institutes	Reports and experience in own scientific work on biocides

Annex II - Properties and use of selected active substances

Substance class	Active substance	Molecular mass	Water solubility [mg/l]	Vapour pressure	log K_{OW}	Stability	Product type	Use concentration [%]	Number of products*
Isothiazolinones	DCOIT	282,2	14	6.6 hPa	4.9	Stable to light and increased temperature, stable at pH 3 to 9, sensitive to primary and secondary amines, thiols in addition to oxidizing or reducing agents	7, 8, 9,10, 11, 12, 21	0.1-2	179
	CMIT	149,6	5000	$3.6 * 10^5$ mPa (20 °C)	0.4	decomposition starts at 55 °C, sensitive to amines, alkaline solutions, SH compounds	not notified	--	--
	MIT	115,2	30,000	$5.85 * 10^3$ mPa	0.5	stable to light, stable at temp. up to 80 °C, stable at pH 2 to 10 in aqueous solution, sensitive to oxidizing and reducing agents and electrophiles, degradation and evaporation within 3 weeks at 18-20 °C, 4 weeks at 6-12 °C	2, 4, 6, 7, 9, 10, 11, 12, 13, 22	--	359
	combination CMIT/MIT		completely soluble in water			decomposition starts at 50 °C	2, 3, 4, 6, 7, 9, 10, 11, 12, 13	0.02-0.3	1645
	BIT	151,2	1000		0.64	stable and effective at pH 4 to 12, incompatible with some oxidizing and reducing agents	2, 6, 7, 9, 10, 11, 12, 13, 22	0.02-0.5	766
	OIT	213,3	480	4.9 mPa (25 °C)	2.45 (24 °C)	stable to light, stable at temperatures up to 200 °C, stable at pH 2 to 10 in aqueous solution at room temperature, sensitive to oxidizing and reducing agents and electrophiles	4, 6, 7, 9, 10, 11, 12, 13	0.015-4	997

Annex II - Properties and use of selected active substances *continued*

Substance class	**Active substance**	**Molecular mass**	**Water solubility [mg/l]**	**Vapour pressure**	**log K_{OW}**	**Stability**	**Product type**	**Use concentration [%]**	**Number of products***
Benz-imidazoles	Carbendazim	191,2	8	0.09 mPa (20 °C)	1.6	stable 7 d at 20,000 lux, slowly decomposed in alkaline solution; decomposed in water with half-live between 2 and 25 months	7, 9, 10, 11, 12	0.05-4	236
Urea derivatives	Diuron	233,1	42	$1.1 * 10^{-3}$ mPa (25 °C)	2.85 - 3.95	stable in neutral media at normal temperature, hydrolysed at elevated temperatures, by acids and alkalis; demethylation of N-atom, active in soil for 4-8 months; DT_{50} 90-180 d	7, 10	0.2-3	109
	Isoproturon	206,3	65	0.0033 mPa (20 °C)	2.5 (pH 7, 22 °C)	very stable to light, acids and alkalis; DT_{50} in soil 6-28 d; degradation increases 10 times in organic soil between 10 °C and 30 °C	7, 9, 10, 11, 12, 13	--	15
Triazines	Irgarol 1051, Cybutryne	253,4	7	$8.8 * 10^{-2}$ mPa (20 °C)	3.95	not readily biodegradable, stable against hydrolysis, photolysis in fresh water DT_{50} 36 d	7, 9, 10, 21	0.2-2	147
	Terbutryn	241,4	22	0.225 mPa (25 °C)	3.65 (25 °C)	stable under normal conditions, methylthio group is hydrolysed in the presence of strong acids or alkalis; DT_{50} in soil 14-28 d	7, 9, 10	0.2-2	225
Carbamates	IPBC, 3-Iod-2-propinyl butylcarbamate	281,1	168	$1.04 * 10^{3}$ mPa (20 °C)	2.4	stable at acidic and neutral conditions, decomposed in the presence of amines	6, 7, 8, 9, 10, 11, 13	0.003-6	953

Annex II - Properties and use of selected active substances *continued*

Substance class	Active substance	Molecular mass	Water solubility [mg/l]	Vapour pressure	log K_{OW}	Stability	Product type	Use con-centration [%]	Number of products*
Azoles	Propiconazole	342,2	100	56 µPa (25 °C)	3.72	no significant hydrolysis; half life in aerobic aquatic systems is 25-85 d	1, 2, 4, 7, 8, 9, 10, 12, 20	0.05-15	418
	Tebuconazole	307,8	32	1.3 µPa (20 °C)	3.7	stable to hydrolysis in the absence of light under sterile conditions	7, 8, 9, 10	0.3-1.5	85
Phenyl sulfamides	Dichlofluanid	333,2	1.3	2.09 * 10-5 kPa	2.72	decomposed by alkaline media, sensitive to light; unstable in soil	7, 8, 10, 21	--	193
Pyridine derivatives	Zn-pyrithione	317,7	8	negligible	0.93	stable at pH 4 to 8.5; sensitive against oxidizing and reducing agents and light	2, 6, 7, 9, 10, 21	0.05-4	347
Activated halogen atom	Bronopol, 2-Bromo-2-nitro-1,3-propanediol	165,1	2.5 x 10^5	1.68 * 10-3 Pa	0.18	stable at pH 4, sensitive to light and alkaline media (yellow or brown colour), fast degradation in the environment	2, 6, 9, 11, 12, 22	0.001-0.03	728
Quaternary ammonium compounds	Benzyl-C_{12-16}-alkyldimethyl-, chloride; Benzalkonium chloride	variable	2.5 x 10^5			stable at normal conditions (pH 1-12)	1, 2, 3, 4, 7, 8, 9, 10, 11, 12	--	1495

[Data on active substances from TOMLIN, 1994; PAULUS, 2005 and BÜRGI ET AL. 2007]
* registered in Germany according to Biozid-Meldeverordnung

Annex III - Emission scenarios related to service life of materials

Annex III.1: Emission scenarios for in-can preservatives (PT 6)

Application	Emission into water during service life of materials	Models for service life situations	References
Production of paints and coatings	Emissions may occur during service life due to weathering, e.g. from metal surfaces (motor vehicles, metal frames), wooden surfaces (construction elements), concrete, façade coatings, road-marking paints.	See PT 7, 8 and 10	TGD IV (2003), IC 14 Paints, lacquers and varnishes industry, VAN DER AA ET AL. (2004), EA-UK (2002)
Paper production	Not expected to be exposed to weathering (exception: posters may be exposed to weathering)		TGD IV (2003), IC 12 Pulp, paper and board industry, VAN DER AA ET AL. (2004)
Leather production	Not expected to be exposed to weathering, applied active substances may be leached during washing (applies to waste water treatment)		TGD IV (2003), IC-7 Leather processing industry, VAN DER AA ET AL. (2004)
Textile production	Emissions may occur during service life due to weathering from technical textiles, e.g. tents, textile roofs, sails, tarpaulins. Active substances used in clothing and shower curtains are expected to be leached mainly during washing and/or use (applies to waste water treatment).	See PT 9	TGD IV (2003) IC-13 Textile processing industry, VAN DER AA ET AL. (2004),
Intermediate products, e.g. additives for mortar or concrete	Emissions may occur during service life due to weathering and/or direct contact to water and/or soil from construction materials.	See PT 10	MIGNÉ (2002)
Glues and adhesives	Small surface areas in contact with environmental compartments in many cases Plywood is mainly used in indoor-situations	See PT 8 and 10	

Annex III.2: Emission scenarios for film preservatives (PT 7)

Application	Emission into water during service life of materials	Models for service life situations	References
Paints and coatings	Emissions may occur during service life due to weathering, e.g. from metal surfaces (motor vehicles, metal frames), wooden surfaces (construction elements), concrete, façade coatings, road-marking paints.	See PT 8 and 10 Calculation of regional emissions from decorative paints for private and professional use	TGD IV (2003), IC 14 Paints, laquers and varnishes industry. VAN DER AA ET AL. (2004a),

Annex III.3: Emission scenarios for wood preservatives (PT 8)*

Application	Emission into water during service life of materials	Models for service life situations	References
Treated wood	Emissions may occur during service life due to weathering and/or direct contact to water and/or soil.	Fence with receiving soil compartment, Noise barrier with receiving soil compartment and sewage treatment plant (STP), Timber cladded house with receiving soil compartment, Transmission pole with receiving soil compartment, Fence post with receiving soil compartment, Jetty in lake, Bridge over pond, Sheet piling in a waterway, Harbour wharf. Calculation of local concentrations in water and soil based on $Q_{leach,time}$ derived from leaching tests	OECD ESD (2003)

* Emission scenario documents for wood preservatives were included since assessments for other materials refer to models for wood preservatives.

Annex III.4: Emission scenarios for preservatives for fibre, leather, rubber and polymerised materials (PT 9)

Application	Emission into water during service life of materials	Models for service life situations	References
Textiles	Emissions may occur during service life due to weathering from technical textiles, e.g. tents, textile roofs, sails, tarpaulins. Active substances used in clothing and shower curtains are expected to be leached mainly during washing and/or use (applies to waste water treatment).	Calculation of regional emissions based on duration of service life, concentration of active substances in products, and default values for fractions released into waste water and soil	TGD IV (2003) IC-13 Textile processing industry, TISSIER ET AL. (2001)
Rubber	Emissions may occur during service life due to weathering and/or direct contact to water and/or soil.	Calculation of regional emissions based on used tonnage, concentration of active substances in products and default values for fractions released into water	TGD IV (2003) IC 15 Others (Rubber industry), TGD II (2003), § 2.3.3.5 VAN DER AA ET AL. (2004b)
Plastics	Emissions may occur during service life due to weathering and/or direct contact to water and/or soil.	Calculation of regional emissions based on used tonnage, concentration of active substances in products and default values for fractions released into water	TGD IV (2003) IC 11 (Polymers Industry), TGD II (2003), § 2.3.3.5, VAN DER AA ET AL. (2004b)

Annex III.5: Emission scenarios for masonry preservatives (PT 10)

Application	Emission into water during service life of materials	Models for service life situations	References
Cement, concrete, mortar, stone, baked clay	Emissions may occur due to weathering during service life and/or direct contact to water and/or soil due to rinsing (cleaning of treated surfaces, often performed with high pressure sprayer)	House with receiving soil compartment (rural) or run-off to STP (urban), Calculation of emissions due to rinsing based on default values, Calculation of local concentrations in soil based on $Q_{leach,time}$ derived from leaching tests, Calculation taking into account removal processes (i.e. degradation, volatilisation, leaching from soil to ground water)	MIGNÉ (2002)

Annex IV - Test methods

Annex IV.1 - Laboratory tests, permanent immersion

Reference	PT	Procedure	Assessment	
			Advantages	Limitations
OECD Guideline 313 (2007)	8	Test specimens are exposed to permanent contact with water which is replaced during the test: Sampling intervals: 6 h, 1 day, 2, 4, 8, 15, 22 and 29 days Defined ratio of surface area of specimens per water volume: 0,4 $cm^2 * 1 cm^{-3}$ [or 25 l/m²] Minimum surface area of specimens: 200 cm² Temperature: 20 +/- 2 °C Water quality: de-ionised water, pH 5 – 7 or synthetic seawater Leachates are collected after each leaching interval and analysed for active substances.	Tests - result in emission curves that describe leaching as a process - are reproducible - are transferable to other materials	Emission curves are only valid for the applied test conditions.
DIN CEN/TS 15119-2 (2008)	8	Test specimens are exposed to permanent contact with water which is replaced during the test: Minimum of 7 leaching intervals of a minimum of 1 and a maximum of 7 days within 19 days Defined ratio of surface area of specimens per water volume: 0,4 $cm^2 * 1 cm^{-3}$ [or 25 l/m²] Minimum surface area of specimens: 200 cm² Temperature: 20 +/- 2 °C Water quality: de-ionised water, pH 5 – 7 Leachates are collected after each leaching interval and analysed for active substances.	Tests - result in emission curves that describe leaching as a process - are reproducible if the same sampling schedule is applied - are transferable to other materials	Emission curves are only valid for the applied test conditions. Extrapolation of the test results only applies for continuation of the test itself, not for service life conditions. Applicability of the data for soil contact has not been shown. Limited repeatability for organic substances since the time schedule is not defined.

Annex IV.1 - Laboratory tests, permanent immersion*, continued*

Reference	PT	Procedure	Assessment	
			Advantages	Limitations
EN ISO 15181 Parts 1, 2, 3 (2007) Part 4 (2009) Part 5 (2008)	21	Coated test cylinders rotate in a tank with synthetic seawater and are transferred into test vessels for defined time periods: Test periods at days 1, 3, 7, 10, 14, 21, 24, 28, 31, 35, 38, 42 and 45 Temperature: 25 +/- 2 °C Water quality: synthetic seawater Leachates are collected after each test interval and analysed for active substances.	Tests - result in emission curves that describe leaching as a process	The test procedure was developed for the specific use conditions of antifoulings.
NEN 7345 (1995)		Test specimens are exposed to permanent contact to water which is replaced during the test ('tank test'): Sampling intervals: 6 h, 1 day, 2.25, 4, 9, 16, 36 and 64 days Range of water volume is defined depending on either volume or surface area of the test specimens Smallest dimension of test specimens: 40 mm, or a minimum surface area of 75 cm² Temperature: 20 +/- 2 °C Water quality: demineralised water, acidified with nitric acid to pH 4 +/- 1 Successively eluted fractions are analysed for leached components.	This standard includes a procedure to determine the leaching mechanism in the diffusion test.	The test was designed for inorganic substances from monolithic materials. Certain organic substances may not be stable at pH 4. The water volume per surface area has to be defined more precisely to ensure repeatability of tests for organics. Microorganisms may grow in the tanks during long leaching periods - especially if emissions of potentially toxic substances decrease during the later sampling intervals.

Annex IV.1 - Laboratory tests, permanent immersion, *continued*

Reference	PT	Procedure	Assessment	
			Advantages	**Limitations**
CEN/TC 351		A series of test procedures, including a dynamic surface leaching test, are under development.	The dynamic surface leaching test may also apply for preserved materials that are in permanent contact with water.	
EN 12457 Parts 1 - 4 (2003) prCEN/TS 14405 (2004) 14429 (2006) 14997 (2007)		Several 'one stage batch tests' and 'column percolation tests' are available. A 'dynamic surface leaching test' for monolithic waste is under development.	Selection of appropriate leaching tests and methodology for the characterisation of waste are described in EN 12902 (2008).	Available tests were developed for granular materials which is not typical for materials that are considered here.
AWPA E 20-04 (2004)	8	Test procedure for wood in <u>permanent contact to wet soil</u>: Size of test specimens: 14 mm * 14 mm * 150 mm Temperature: 26 °C +/- 3 °C Soil: two soils representing different geographical areas, saturated with distilled water for 24 h and drained for 16 h Moisture control: test containers are weighed and water is added to maintain the initial weight Duration: 12 weeks Exposed and unexposed test specimens are analysed for active substances.		Single data point does not represent emission process. Uncertainty of analytical data for active substances in wood may be higher than the actual emissions (comparison of analytical results for exposed and unexposed test specimens compensates for limited recovery rate of the analytical method or stability of the active substance)

Annex IV.1 - Laboratory tests, permanent immersion*, continued*

Reference	**PT**	**Procedure**	**Assessment**	
			Advantages	**Limitations**
LINDNER (1997)	7	Experimental study: Calcium silicate specimens coated with paints were exposed to running tap water. Dimension of specimens: 100 mm * 75 mm * 6 mm Flux: 1 l/h Temperature: about 15 °C Samples were taken after 48 and 96 h (corresponds to 1500 and 3000 l/m², respectively), and analysed for Diuron in the paint film.	Comparison with data from a semi-field test (see also Annex IV.4) Proposal for a simple migration model based on time scales.	Two data points provide only limited information about the leaching process.
JUNGNICKEL ET AL. (2008)	7	Experimental study: Glass plates coated with roof paints were exposed to periods of permanent water contact and intermediate drying periods. Duration of water contact periods: 24 or 72 h (plates were gently shaken in the test chambers) Drying: 24 h at room conditions Duration of the test: 40 days, i.e. about 600 h of water contact Exposed surface area per water volume: 190 * 100 mm plates in 1 l water Water quality: synthetic rain water Leachates of each period of water contact were collected and analysed for active substances	Comparative emission data for 'real' products from the market. Proposal for modelling biocide concentrations in runoff and receiving rain barrels depending on rain intensity.	Time schedule was not defined, but dependent on test results. Exposure conditions are severe compared to natural weathering.

Annex IV.1 - Laboratory tests, permanent immersion*, continued*

Reference	PT	Procedure	Assessment	
			Advantages	**Limitations**
SCHOKNECHT ET AL. (2009)	7	Experimental study: Test specimens with different facade coatings (four renders and two systems of render and paint) were leached in a procedure similar to OECD 313. deviation: coated surface area: 82.5 cm^2	Experimental data for different products and nine active substances. Comparison of different laboratory leaching tests (see also Annex IV.2 for short-term immersion tests and Annex IV.3 for artificial weathering).	Experimental data have not been related to field data or data from actual service life conditions.

Annex IV.2 - Laboratory tests, short-term immersion

Reference	PT	Procedure	Assessment	
			Advantages	Limitations
DIN CEN/TS 15119-1 (2008)	8	Test specimens are exposed to intermediate wetting and drying by a dipping procedure: Time schedule: 9 immersion days with 3 dipping events of 1 min each per immersion day, drying periods of 3 h between dipping events of an immersion day Schedule of immersion days: minimum of 1 day without dipping between immersion days, e.g. immersions on days 1, 3, 5, 8, 10, 12, 15, 17 and 19 Defined ratio of surface area of specimens per water volume: 0,4 cm^2 * 1 cm^{-3} [or 25 l/m²] Minimum surface area of specimens: 200 cm² Temperature: 20 +/- 2 °C (applies to water and air) Relative humidity: 65 +/- 5 % Water quality: de-ionised water, pH 5 - 7 Leachates are collected per immersion day and analysed for active substances.	Tests - result in emission curves that describe leaching as a process - are reproducible because of definite test parameters - simulate wet and dry cycles which occur under outdoor conditions (use class 3 conditions for treated wood) - prevent e.g. coatings on test specimens from damage by long duration of water contact (which does not occur under service life conditions) - are transferable to other materials	Emission curves are only valid for the applied test conditions. It has not been shown that one immersion day corresponds to a ‘typical’ day of rainfall. It has not been shown if water penetrates as deep into the wood as rain water does under service life conditions to allow transport of active substances from deeper layers to the surface.

Annex IV.2 - Laboratory tests, short-term immersion*, continued*

Reference	PT	Procedure	Assessment	
			Advantages	**Limitations**
OECD Guidance Document No. 107 (2009)	8	Test specimens are exposed to intermediate wetting and drying by a dipping procedure: Different time schedules: Schedule 1: 9 immersion days with 3 dipping events of 1 min each per immersion day, drying periods of 3 h between dipping events of an immersion day Schedule 2: 9 immersion days with 2 dipping events of 60 min each per immersion day, drying periods of 4 h between dipping events of an immersion day Schedule 3: 9 immersion days with one dipping event of 2 h Immersion days are set to days 1, 3, 5, 8, 10, 12, 15, 17 and 19 Defined ratio of surface area of specimens per water volume: 0,4 cm^2 * 1 cm^{-3} [or 25 l/m²] Minimum surface area of specimens: 200 cm² Temperature: 20 +/- 2 °C (applies to water and air) Relative humidity: 65 +/- 5 % Water quality: de-ionised water, pH 5 – 7 Leachates are collected per immersion day and analysed for active substances. Artificial rain regime: general recommendations	Tests - result in emission curves that describe leaching as a process - are reproducible because of definite test parameters - simulate wet and dry cycles which occur under outdoor conditions (use class 3 conditions for treated wood) - prevent e.g. coatings on test specimens from damage by long duration of water contact (which does not occur under service life conditions) - are transferable to other materials	Emission curves are only valid for the applied test conditions. It has not been shown that one immersion day corresponds to a 'typical' day of rainfall. It has not been shown if water penetrates as deep into the wood as rain water does under service life conditions (especially for schedule 1) to allow transport of active substances from deeper layers to the surface. Schedules 2 and 3 are intended to mimic vertical and horizontal exposure, respectively. This has not been demonstrated yet.

Annex IV.2 - Laboratory tests, short-term immersion*, continued*

Reference	PT	Procedure	Assessment	
			Advantages	**Limitations**
prEN 16105 (2010) under discussion within CEN/TC 139	7	Test specimens are exposed to intermediate wetting and drying by a dipping procedure: Time schedules: 9 immersion days with 2 dippings of 60 min each per immersion day, drying periods of 4 h between dipping events of an immersion day Immersion days are proposed to be day 1, 3, 5, 8, 10, 12, 15, 17 and 19 Defined ratio of water volume per surface area of specimens: 25 l/m² Minimum surface area of specimens: 100 cm² Temperature: 23 +/- 2 °C (applies to water and air) Relative humidity: 50 +/- 5 % Water quality: de-ionised water, pH 6 +/- 1 Leachates are collected per immersion day and analysed for target substances	Tests - result in emission curves that describe leaching as a process - are reproducible because of definite test parameters - simulate wet and dry cycles which occur outdoors - prevent coatings from damage by long duration of water contact (which does not occur under service life conditions) - are transferable to other substances and other materials	Emission curves are only valid for the applied test conditions.
SCHOKNECHT ET AL. (2009)	7	Experimental study: Test specimens with different facade coatings (six renders and four systems of render and paint) were leached in a procedure similar to prEN 16105. deviations: coated surface area: 82.5 cm^2, temperature: 20 +/-2 °C, relative humidity: 65 +/- 5 %	Experimental data for different products and nine active substances. Comparison of different laboratory leaching tests (see also Annex IV.1 for permanent immersion tests and Annex IV.3 for artificial weathering).	Experimental data have not been related to field data or data from actual service life conditions.

Annex IV.3 - Laboratory tests, artificial weathering

Reference	PT	Procedure	Assessment	
			Advantages	Limitations
Burkhardt et al. (2009a)	7	Experimental study: Façade panels (structured as ETICS in real buildings) were investigated in weathering chambers. Test specimens: 2 m * 0.75 m, vertically installed Exposure: 3 phases of 28 cycles within 7 days, each cycle included a 1-h-spray interval with tap water (80 l/m$^{2)}$, amount of water applied within 21 days: 6720 l/m² Maximum temperatures on the façade surfaces: 30, 40 and 50 °C during phase 1, 2 and 3, respectively, UV radiation and relative humidity (60 to 100 %) were controlled Runoff water was collected and analysed for active substances.	Comparative study of different active substances in a series of products. Subsequent change of test parameters allows investigation of the influence of different parameters (e.g. temperature changes, rain amount, wetting and drying) on leaching processes.	Test conditions are designed to accelerate the influence of weathering, e.g. rain amount per hour is higher than under natural weathering conditions.
Schoknecht et al. (2009)	7	Experimental study: Test specimens with different facade coatings (four renders and two systems of render and paint) were exposed to spray events. Surface area of specimens: 700 cm² (angled 60°) Spay events: 2.5 l/m² within 2 min (10 times over 10 days) Temperature: 20 +/- 2 °C Water quality: de-ionised water, pH 5 - 7 Runoff water was collected after each spray event and analysed for active substances.	Experimental data for different products and nine active substances. Comparison of different laboratory leaching tests (see also Annex IV.1 for short-term and Annex IV.2 for permanent immersion tests).	Rain amount per minute was higher than under natural weathering conditions. Total amount of rain was to low to describe emission processes. Experimental data have not been related to field data or data from actual service life conditions.

Annex IV.4 - Semi-field and field tests

Reference	PT	Procedure	Assessment	
			Advantages	Limitations
NT Build 509 (2005)	8	Treated wood is exposed to natural weathering: Dimension of specimens: 7 panels (100 mm * 25 * 760 mm) are arranged to one test set-up Installation: Test racks can be exposed horizontally or vertically (to the south or southwest) Duration: at least one year, but most likely 2 years if long-term leaching data are required Leachates are sampled after each significant rain event, bulked and analysed for active substances according to a previously planned time schedule (e.g. 0-60 mm, 60-120 mm, 120-240 mm, 480-720 mm, 720-960 mm of rain and so on)	The procedure can be adapted for other materials.	
LINDNER (1997)	7	Experimental study: Calcium silicate specimens coated with paints were exposed to natural weathering. Dimension of specimens: 100 mm * 75 mm * 6 mm Installation of specimens: exposed northwards, angled 60°, 1 m above ground, site near Hanover (Germany) Test period: 05/1992 until 10/1994 (ca. 860 d) Climate: moderately cold winters, moderately warm summers, 700 mm rainfall and about 1200 h sunshine per year (average data) Specimens were taken periodically (4 points of time) and analysed for Diuron in the paint film.	Comparison with data from a laboratory test (see also Annex IV.1) Proposal for a simple migration model based on time scales.	

Annex IV.4 - Semi-field and field tests, *continued*

Reference	**PT**	**Procedure**	**Assessment**	
			Advantages	**Limitations**
BURKHARDT ET AL. (2009A)	7	Experimental study: Façade panels (structured as ETICS in real buildings) were exposed to natural weathering. Dimension of specimens: 1.80 m * 0,75 m Installation of specimens: wall of a model house, exposed westwards, lower edge about 0.5 m above ground, site in Zurich (Switzerland) Test period: January 2008 until January 2009 (372 d) Total amount of rainfall: about 550 l/m² Runoff water was collected after each rain event with runoff and analysed for active substances.	Emission data are related to actual exposure conditions. Comparative study of different active substances in different products.	
BORHO (Workshop 2010, see Annex V)	7	Experimental Study: Ongoing semi-field study with façade coatings to investigate field test parameters and compare results from laboratory tests and experiments under natural weathering conditions.		
SCHERER AND SCHWERD (Workshop 2010, see Annex V)	7	Experimental Study: Comparative study for different façade coatings at two different sites in Germany.		

Annex IV.4 - Semi-field and field tests, *continued*

Reference	**PT**	**Procedure**	**Assessment**	
			Advantages	**Limitations**
KLAMER (Workshop 2010, see Annex V)	6 7 9 10	Experimental Study: Semi-field studies have been started to investigate product type specific adaptations of NT Build 509 and compare laboratory tests and experiments under natural weathering conditions. Procedure has to be adopted to characteristics of materials (e.g. textiles with certain structure of inner and outer layers) and exposure conditions (e.g. exposition angle).		

Annex V - Workshop 'Leaching tests for materials'

21st January 2010 in Berlin, BAM Federal Institute for Materials Research and Testing

Current activities of research institutes and producers to describe leaching of biocides from materials and approaches to provide and use information for risk assessments were presented. Open questions and requirements were identified and discussed.

The content of the presentations and the discussion are considered in the report.

Presentations

Ute Schoknecht and Antje Töpfer, BAM Federal Institute for Materials Research and Testing, Berlin (Germany)

The project 'Characterisation of leaching of biocidal active substances of main group 2 'preservatives' from different materials under weathering conditions'

Christian Scherer and Regine Schwerd, Fraunhofer Institut for Building Physics (IBP), Holzkirchen (Germany)

Experiences with emissions of biocides from facade coatings under real weathering conditions

Nicole Borho, Dr.-Robert-Murjahn-Institute, Ober-Ramstadt (Germany)

Leaching of biocides from coatings - Laboratory test method compared to field studies

Henning Baldauf and Steffen Uhlig, quo data Gesellschaft für Qualitätsmanagement und Statistik mbH, Dresden (Germany)

Leaching of Biocides – Mathematical Modelling – An analytical approach

Michael Burkhardt, University of Applied Science, Institute of Environmental and Process Engineering UMTEC, Rapperswil (Switzerland)

How real is lab and how real is "real" world?

David Cantrell, Arch Timber Protection, Castleford (UK)

Environmental Emission of Wood Preservatives: data interpretation and the relationship between laboratory and field tests

Morton Klamer, Danish Technological Institute, Taastrup (Denmark)

Adaption of practical leaching study designs to emission scenarios in PT 6, 7, 9 and 10

Torsten Groth, LANXESS Deutschland GmbH, Leverkusen (Germany)

Options for a refinement of the environmental risk assessment for the PTs 7, 8 and 10