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Emissions of material preservatives into the environment – realistic estimation of environmental risks through the improved characterisation of the leaching of biocides from treated materials used outdoors

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Emissions of material preservatives into the environment – realistic estimation of environmental risks through the improved characterisation of the leaching of biocides from treated materials used outdoors

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Abstract

This report supports the implementation of European regulations on biocidal products for the product types 7, 9 and 10. Emission of active substances from material preservatives into environmental compartments can occur due precipitation. Risk characterisations have to be based on estimations of environmental concentrations of target substances leached from material preservatives. Harmonised test procedures are required to predict environmental impact due to leaching. Seventeen treated articles, mainly paints, but also a textile, sealing tapes and sealing masses were investigated by intermittent contact to water to prove suitability of the proposed laboratory test procedure. Parameters that affect leaching of active substances were examined. Further development of a semi-analytical model to describe laboratory leaching data revealed that the model can be improved if changes of the leachability of substances during the test are supposed and integrated. Six paints and a textile were exposed to weathering to compare results from laboratory and field experiments. Similarities between leaching processes in both test approaches were observed. Generally, emissions of active substances are considerably higher in laboratory tests than from vertically installed test specimens exposed to weathering. Competing processes that cause losses of active substances can occur in both tests, but to a higher degree in field experiments. In addition, the influence of meteorological parameters on leaching processes was investigated. Factors besides the amount of driving rain were identified that effect leaching processes by complex interaction. Relations between laboratory and field data were analysed, and the applicability of the semi-analytical model was tested for field data. Guidance documents for leaching tests under laboratory and field conditions were drafted and discussed with experts on EU level (workshop 3./4. July 2014, BAM, Berlin), and are included in this report.

Kurzbeschreibung

Dieser Bericht unterstützt die Umsetzung europäischer Regelungen für Biozidprodukte der Produkttypen 7, 9 und 10. Die Freisetzung von Wirkstoffen aus Materialschutzmitteln in Umweltkompartimente kann bei Niederschlagsereignissen auftreten. Risikocharakterisierungen müssen auf Abschätzungen von Umweltkonzentrationen der betrachteten Stoffe basieren. Harmonisierte Testverfahren sind erforderlich, um eine Beeinflussung der Umwelt durch Auswaschung vorherzusagen. Siebzehn behandelte Waren, vor allem Farben, aber auch ein Textil, Dichtungsbänder und Dichtungsmassen wurden bei periodischem Wasserkontakt untersucht, um die Anwendbarkeit des vorgeschlagenen Laborverfahrens nachzuweisen. Faktoren, die Einfluss auf die Auswaschung von Wirkstoffen haben, wurden untersucht. Die Wieterentwicklung eines semi-analytischen Modells zur Beschreibung von Auswaschdaten aus Laborversuchen ergab, dass das Modell verbessert werden kann, wenn eine Änderung der Auswaschbarkeit von Substanzen während des Versuchs angenommen und einbezogen wird. Sechs Farben und ein Textil wurden der Witterung ausgesetzt, um Ergebnisse aus Labor- und Freilandversuchen zu vergleichen. Zwischen Auswaschprozessen in beiden Versuchsansätzen wurden Ähnlichkeiten beobachtet. Im Allgemeinen sind die Emissionen von Wirkstoffen im Laborversuch deutlich höher als bei vertikal installierten bewitterten Prüfkörpern. Konkurrierende Prozesse, die Verluste an Wirkstoffen bewirken, können in beiden Testverfahren auftreten, sind aber im Freilandversuch stärker ausgeprägt. Außerdem wurde der Einfluss von meteorologischen Parametern auf Auswaschprozesse untersucht. Es wurden Faktoren identifiziert, die zusätzlich zur Schlagregenmenge durch komplexe Interaktion auf Auswaschprozesse wirken. Beziehungen zwischen Labor- und Freilanddaten wurden analysiert und die Anwendbarkeit des semi-analytischen Modells für Freilanddaten getestet. Leitfäden für Auswaschversuche unter Labor- bzw. Freilandbedingungen wurden entworfen, mit europäischen Experten diskutiert (Workshop 3./4. Juli 2014, BAM, Berlin) und sind Bestandteil dieses Berichts.

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List of Abbreviations

ACN	acetonitrile
AS	active substance
BPR	Biocidal products regulation
CEN	European Committee for Standardization
Cum.	cumulative
DMSA	N,N-Dimethyl-N’-phenylsulfamide
DMST	N,N-dimethyl-N'-p-tolylsulfamide
ECHA	European Chemicals Agency
ESD	Emission Scenario Document
HPLC	high performance liquid chromatography
LC/MS	liquid chromatography - mass spectrometry
LC-MS/MS	liquid chromatography - tandem mass spectrometry
LOQ	limit of quantification
MC	microcapsules
NE	northeast
NW	northwest
PT	product type
PTFE	polytetrafluorethylen
RP	roof paint
SE	southeast
SM	sealing mass
SW	southwest
SSW	south to southwest
T	textile
THF	tetrahydrofuran
TOC	total organic carbon
Vs.	versus
WC	wood coating
UHPLC	ultra high performance liquid chromatography
ZnP	zinc pyrithione

Summary

The project is directed to support the implementation of European regulations on biocidal products that belong to product types 7 (film preservatives), 9 (fibre, leather, rubber and polymerised materials preservatives) and 10 (construction material preservatives). Risk characterisation of biocides includes 'the estimation of the incidence and severity of adverse effects likely to occur … in environmental compartments due to actual or predicted exposure to any active substances or substances of concern in a biocidal product' (BPR). These substances can migrate into environmental compartments during service life if materials like coatings, wood, fibres, polymers or construction materials contain preservatives, but. This transfer can be caused by water contact - so-called 'leaching' - and results in release of substances, possibly over a long period of time. Risk characterisation has to be based on predicted environmental concentrations, and its reliability depends on the quality of these predictions.

The aims of the current project where to improve knowledge on leaching processes and to provide proposals for leaching test procedures that can be applied for authorisation of biocidal products.

The project included laboratory leaching tests and field experiments on selected treated articles, preparation of guidance documents for leaching test procedures as well as mathematical processing of leaching test data including further development of a semi-analytical model for laboratory leaching test data and detailed analysis of the influence of weather conditions on leaching processes.

The applied laboratory method is based on EN 16105:2011, a leaching procedure that was developed to determine the release of substances from coatings in intermittent contact with water. Occasional water contact is assumed to apply for a number of treated articles including biocides of the investigated product types. Test specimens are exposed to immersion cycles under defined conditions. The procedure includes periods when the test specimens are allowed to dry to enable transport processes within the drying material.

Experiments under natural weathering conditions were performed according to NT build 509 (2005). This procedure was developed for treated wood and has been applied for about ten years to investigate leaching from treated wood under semi-field conditions. It is the basis for a procedure that is harmonised within CEN (CEN/TR 16663:2014). Rather small test specimens - compared to real constructions - are exposed to weathering. The test specimens are oriented towards a direction with high exposure to driving rain at a certain location.

Treated articles were selected that represent PT 7, PT 9 and PT 10 and contain active substances that belong to different chemical groups and, therefore, have different physico-chemical properties. It was intended to perform comparative studies on diuron, OIT and terbutryn. However, additional active substances, i.e. carbendazim, DCOIT, dichlofluanid, IPBC, tolylfluanid and zinc pyrithione had to be included to enable investigation of treated articles that differ in its area of application and chemical composition.

Eight wood coatings, four roof paints, an awning cloth, two PVC sealing tapes and two sealing masses were kindly provided by producers and represent marketed treated articles. Four paints were prepared by the producers based on biocide-free products and contained analogue mixtures of diuron, OIT and terbutryn.

Appropriate methods to prepare test specimens were developed. This includes comparison of different substrates, i.e. wood of different origin and glass for wood coatings, and fibre cement and glass for roof paints. The applicability of the proposed laboratory leaching test procedure was tested for all treated articles that were provided for the project. One product was also investigated according to CEN/TS 16637-2:2014, a leaching test that is based on permanent water contact. Active substances and selected transformation products were quantified in eluates, treated articles and residual test specimens by UHPLC and LC/MS methods. In addition, pH values of the eluates were monitored, and TOC and zinc were determined for selected eluates.

Laboratory experiments were not only performed to describe release of substances as such, but also to investigate properties of treated articles that can influence leaching, i.e. uptake of liquid water, water vapour sorption, hydrophilic properties of surfaces and desorption of active substances from the products matrices. Uptake of liquid water was calculated from mass data. Water vapour sorption was determined by isothermal measurement of the sorption of water vapour at solids according to DIN 66138. Desorption of active substances was investigated for four different paints by water exposure of dried and crushed paint films, that include different

concentrations of active substances, for a defined period of time and subsequent analysis of the active substances in the water phase.

Field experiments on selected treated articles were performed at three test sites, mainly at the headquarters of MPA Eberswalde. One experiment was performed at a second test site outside Eberswalde, and a few experiments were started later during the project at BAM in Berlin. The majority of the test specimens were exposed vertically and oriented to southwest. Test specimens from a textile were also oriented to northwest, northeast and southeast. One textile test specimen and a test specimen coated with one of the roof paints were exposed horizontally. Deviating from the NT build 509 procedure, runoff samples of single rain periods were analysed during the first months of each experiment at minimum. Later, samples were merged more frequently than defined in NT build 509. A number of experiments were performed for a longer duration of time. Field experiments with one of the wood coatings were performed in parallel at both test sites of MPA. Additional experiments were started three and six months later to compare leaching processes und different weather conditions at the beginning of outdoor exposure. Active substances were quantified in the runoff samples by a LC-MS/MS method at MPA Eberswalde and a UHPLC method at BAM. Conductivity, pH values and TOC concentrations were determined for selected runoff samples.

Selected test specimens were extracted to estimate residues of active substances after both test procedures. Mass balances were calculated using initial amounts of the target substances, the amounts found in either eluates or runoff samples and residues in the test specimens.

Results from laboratory tests

The proposed laboratory leaching test procedure proved to be suitable and repeatable for a series of active substances and treated articles.

Typical decreasing emission curves were observed for all investigated treated articles. Emissions are roughly related to physico-chemical properties of active substances, but also depend on properties of the treated articles and substrates.

Repeatability of parallel tests and standard deviation for repeated tests in the same laboratory indicate that the laboratory tests yield reliable results. It can be necessary to include data on transformation products to obtain repeatable results if transformation occurs already during the experiment. Sensitive analytical methods can be required to quantify target substances that are released at very low concentrations.

Emission curves provide information on the leaching process. Graphs in double logarithmic scaling indicate that diffusion mainly controls leaching from the investigated treated articles. In some cases, depletion of leachable target substances was observed during the experiments - usually distinctively below the original content of the active substances in the test specimens. Leaching was also controlled by dissolution of the target substances at the beginning of the leaching experiments for some treated articles. This was especially pronounced for leaching of the active substances from the impregnated textile.

Gaps in mass balances were observed when the sum of active substances in the eluates and residues in the test specimens were compared to the initial amount of active substances. This indicates further processes that cause losses of active substances.

Degradation, e.g. due to UV radiation is one possible reason for losses of active substances. However, not only active substances but also the matrix material of treated articles can be susceptible towards UV radiation as observations on increased leaching of carbendazim after UV exposure of the impregnated textile indicate.

Desorption experiments on paints confirm differences in the leachability of active substances of different physico-chemical properties, but do not result in the same ranging of treated articles as leaching experiments. That means that leaching is not only controlled by physico-chemical properties, but also by chemical bonds between active substances and treated articles.

All investigated treated articles and most of the substrates (despite of glass) absorbed water, i.e. water was available within the test specimens for solution and transport of substances. Substances were also transported from coatings into the substrate in case of test specimens from wood. It was demonstrated for two coatings and the impregnated textile that water vapour can be absorbed. That means that also air humidity might be involved in the mobilisation of substances from materials. It was also observed that the ability of the test specimens to take

up water changed in the course of the leaching experiments. The impregnated textile lost its water-repellent properties due to water contact during the laboratory experiments.

Comparison of materials in laboratory tests is mainly based on properties of the treated articles and the target substances that are related to water contact. Several parameters, like amount of water, duration of water contact, air humidity during the drying periods and temperature, are kept in a defined range. Other factors, like UV radiation, warming of surfaces, aging of materials, physical stress and influence of organisms, are either avoided or minimised.

Results from field experiments

The applied field test procedure was suitable to describe leaching of active substances from the selected treated articles.

Driving rain towards vertically installed test specimens is required to cause runoff. The amount and direction of driving rain depend on the local conditions at the test site. It is also known that the percentage of driving rain towards vertical surfaces is decreasing with increasing dimensions of the surfaces. In this respect, field experiments on relatively small test specimens represent severe exposure conditions. This fact is important to be considered if test results are extrapolated or used in models on leaching processes and means that area-related data from field experiments cannot be transferred to real surfaces without correction.

The number of parallel tests at the same experimental conditions was limited during the project. It has to be taken into account that it is impossible to repeat field tests under identical conditions when results of field experiments are compared. Even for test specimens that are investigated in parallel, the exposure conditions can vary and e.g. cause different amounts of runoff. Nevertheless, a few conclusions are possible. Maximum concentrations and cumulative losses of the target substances were in similar ranges for repeated experiments. This applies for parallel tests at the same site and a test site located in the proximity, tests that were started at different points in time and tests that were performed at another test site at another time. Variability between test results depends on properties of the target substances, e.g. its stability under the exposure conditions, among other things.

Presentations of cumulative emissions related to date and rain amount usually show step like curves since the results are not related to the actual exposure of the test specimens. Even emission curves related to the amount of runoff do not run completely smooth. This indicates further processes that determine the amount of leached substances in runoff samples. However, relation of cumulative emissions to the amount of runoff proved to be suitable to compare results from different tests. Depending on the target substance, emission curves from different experiments proceed more or less similar, especially during early stages of the experiments. Deviations become obvious mainly in the later stages of the experiments. Data on the test period as well as the amounts of rain and runoff during the experiment should always be given in reports since these parameters provide useful information on the experimental conditions during the experiment.

Concentrations of the target substances as well as the leached amounts per surface area differed considerably between runoff samples from single rain events or short rain periods. A tendency of decreasing values during the test period was observed. In many cases, the amounts of target substances in the runoff samples were low during summer, sometimes also during winter, and increased again in autumn and spring. It is supposed that degradation and possibly also evaporation of the target substances are increased during the summer. Extended availability of water under the weather conditions in autumn allow transport of the target substances to the materials surfaces again, and the substances are protected by lower temperatures and less UV dependent degradation on the surfaces and within the water film on the materials surfaces. Possibly, transport processes are rather slow at low temperatures during the winter.

In general, it is difficult to obtain leaching results for instable substances since it is impossible to either preserve or analyse these substances as soon as they occur in the collected runoff. During the project this was the case for zinc pyrithione from the impregnated textile and a wood coating. In such cases, it can be appropriate to analyse runoff samples for stable transformation products if these are relevant for risk assessments.

The emission curves of carbendazim from different experiments on an impregnated textile were almost identical if related to the amount of runoff even if oriented towards different directions. On the other hand, considerable

variation was observed for emission curves of OIT from different experiments. It is assumed that additional factors affecting the stability of OIT become relevant for the amounts of this substance in runoff samples.

A high percentage of rain is collected from horizontally exposed surfaces. It is supposed that a part of the rain water is either splashed or evaporated from wet surfaces depending on the surface properties. Only a part of the driving rain is collected from vertical surfaces, probably due to the same reasons. The concentrations of the target substances were lower whereas the total amounts of leached target substances were higher in runoff from horizontally exposed compared to vertically exposed test specimens. Leaching processes from horizontal surfaces were less affected by additional factors despite of the amount of rain than leaching processes from vertical surfaces.

Only a small percentage of the original amount of active substances was detected in runoff samples from the investigated treated articles. Analysis of residual amounts of these substances in the test specimens after the field experiment indicated large gaps in the mass balances. It was demonstrated that a part of the target substances can be transported into the substrate in case of coatings applied on wood. However, a considerable part of the target substances was lost due to other processes. Degradation and evaporation of target substances are supposed to cause these losses. However, no data are available that describe to what extend these processes influence the fate of substances in the investigated treated articles so far.

Area-related emissions from vertically installed test specimens of small dimensions are supposed to be higher than emissions from larger surfaces due to the stronger exposure to driving rain. However, field experiments provide better information to what extent leaching processes can occur under service conditions than data from laboratory tests.

The results of field experiments depend on properties of the target substances and the materials on the one hand and variable exposure conditions on the other hand. It is possible to compare leaching of certain substances as such and from different treated articles by means of field experiments. In any case, a certain degree of variability of the results has to be expected and considered.

The informative value of field experiments depends on the number and frequency of analysis of runoff samples. Results for merged runoff samples provide only general information on the amount of leached substances during certain periods of the experiment. If the last data from field experiments were obtained during the summer it cannot certainly be concluded that no further increase of emissions will occur. Estimations on the range of concentrations of target substances in runoff and conclusions on the dependency of leaching on actual exposure conditions is only possible, if the number of analysed samples is increased.

Comparison of laboratory and field experiments

Runoff samples from field experiments can contain considerably lower concentrations of the target substances than eluates from laboratory experiments. Therefore, estimation of target substances in runoff samples from field experiments can require more sensitive analytical procedures than analysis of eluates from laboratory experiments, especially if it is intended to observe single rain events.

Emissions tend to be higher in laboratory experiments compared to field studies on vertically installed test specimens. However, there is no constant ratio between results from both test procedures. Emissions from a horizontally installed test specimen were in the range of emissions during the laboratory tests for one example. Experiments with the impregnated textile indicate that emissions can be higher under field conditions if the material itself is not stable towards weathering.

It has to be kept in mind that lower emissions per surface area have to be expected for large vertical surfaces, e.g. facades from buildings, compared to small vertically installed test specimens because of the decreased amount of driving rain that impact large surface areas.

There are no comparative data for emissions from treated articles for small-area applications like sealing masses and sealing tapes under outdoor conditions. However, it is proposed to use laboratory data for risk assessments, and consider that emission can occur only from small surface areas. Emissions per surface area are probably overestimated, especially if e.g. joints are not exposed to the total amount of rain.

Differences between emissions of active substances and emissions from treated articles are indicated consistently by laboratory experiments and field experiments, i.e. if higher emissions of a substance compared to another one

are observed in the laboratory experiment, this can also be expected for the field experiment. However, actual ratios between results for active substances and emissions from different treated articles can vary. Additional parameters that are neglected in the laboratory test probably cause these differences. The following parameters seem to be important: (1) hydrophilic properties of surfaces, (2) degradation of active substances under weathering conditions, (3) evaporation of active substances from warmed-up surfaces. So far, there are experimental data that support assumptions on the influence of hydrophilic properties and degradation under UV radiation, but not on the relevance of increased evaporation.

Obviously, changes of material properties that influence leaching processes, e.g. hydrophilic properties, water vapour sorption and the chemical composition of treated articles, occur under laboratory as well as outdoor conditions.

The amount of water that is in contact with the test specimens seems to be a suitable parameter to compare laboratory and field test data, although the duration of water contact is neglected. Leaching processes appear to be controlled by similar parameters, i.e. diffusion and solution of target substances, under laboratory and field conditions. Therefore, it can be assumed that better understanding of the relevance of competing processes under outdoor conditions will improve the application of laboratory leaching data for risk assessments.

Modelling

The semi-analytical model (1) fits laboratory leaching data as closely as possible, (2) enables the extrapolation of emissions in laboratory tests and (3) describes the transport processes arising in laboratory tests according to EN 16105. In contrast to regression models, the semi-analytical model attempts to take into account the changing properties of the treated article (changing water absorption and changing chemical composition) as well as resulting changes in the desorption capability of the active substance.

The semi-analytical model fits the specific emission curves obtained in laboratory experiments for almost all active substances and treated articles well. Based on 9 immersion cycles the semi-analytical model predicts the emission curves for extended test series (up to 18 immersion cycles) very well. The semi-analytical model is well-suited to extrapolation. It can be used for the determination of emissions after any number of immersion cycles or experimental days. It can also be used for the determination of emissions after shorter immersion events, e.g. after an immersion time of 10 minutes. The model does not take into account degradation and evaporation of the active substances. This is justified on account of the fact that there are constant laboratory conditions and negligible environmental influences affecting the test specimens. Should the testing procedure according to EN 16105 be changed (UV-treatment, temperature changes), the model will need to be adapted.

The field test data is precise and reliable from a statistical point of view as the standard deviation of the relative cumulative emission after 10 l/m² runoff between the MPA and BAM test sites lies between 20 % and 40 % for each treated article - active substance - combination. Although the same weather conditions prevail, the observed emission after one single rain event can vary considerably between different test specimens. The differences can exceed 200 %.

Emission curves can be fitted well by means of linear weighted regression models. The observed emission [mg/m²] per amount of runoff [l/m²] can be explained by meteorological factors. Weather conditions play a crucial role for emissions. According to model calculations, the emission may vary by a factor of 10 or more. The analyses concluded that the runoff is the dominating factor affecting the emission. The amount of driving rain, the global radiation, the temperature and the air humidity proved to be the most important additional influencing factors. The cumulative emission can be described satisfactorily by means of the regression model taking into account all available meteorological factors.

For the prediction of total emissions in field tests, laboratory data cannot be used without further mathematical modelling and calibration. A direct comparison of field data and laboratory data reveals a significant overestimation based on laboratory data, especially in the case of vertical exposure. It is very likely that treated article- and active substance-dependent processes are important reasons for the low correlation observed between field data and laboratory data. Nevertheless, it was possible to perform a mathematical adjustment between the cumulative runoff in the field tests and the number of immersion cycles in the laboratory tests.

Furthermore, it is expected that appropriate laboratory tests together with an extended multivariate calibration model with time adjustment might allow reasonable predictions for treated articles and substances that have not been investigated in field experiments.

Guidance documents and leaching workshop

Proposals for a laboratory test and a semi-field test procedure were drafted based on EN 16105 for the laboratory test and NT build 509 and CEN/TR 16663 for the field experiment. Experiences from the project were considered as well.

A workshop 'Leaching behaviour of biocides from preservatives' was held in July 2014 at BAM in Berlin. About forty experts from ten European countries representing competent authorities, research and testing institutes and industry participated. Selected results of the project and experiences from leaching studied performed at other institutes were presented. The guidance proposals were discussed before and during the workshop. Further comments were collected after the workshop and after the Biocides WG-IV-2015 meeting of the Environment Working Group. These discussions are considered in the final versions of the guidance documents that are presented in this report. The final versions of the guidance documents are provided on the ECHA ESD website.

Conclusions

The laboratory test is based on an immersion scheme which was set arbitrarily taking into account commonly available analytical techniques, time and repeatability of test results. The main intention was to include drying phases to allow transport of water and target substances in treated articles and substrates. The laboratory procedure neglects some properties of target substances and treated articles that affect leaching, like stability of target substances and treated articles towards photolysis and hydrophilic properties of treated articles. In addition, the test procedure does not include temperature changes and is performed at rather constant relative humidity. Therefore, the test does not indicate variability of leaching processes. The proposed procedure is intended for treated articles that are exposed to occasional water contact. For treated articles that are in permanent contact to water, leaching tests according to CEN/TS 16637-2:2014, that was developed to assess the release of dangerous substances from construction products, should be an option.

The surface areas of the test specimens used for semi-field experiments are relatively small compared to large surface areas on real buildings, and the test specimens are oriented towards a direction that guarantees high exposure to driving rain at the test location. This results in relatively high availability of water from precipitation for leaching processes, and, consequently, relatively high amounts of runoff per surface area. Field test results cannot be reproduced since leaching processes under outdoor conditions are affected by complex interactions of several parameters. However, presentation of emissions per surface area in relation to the amount of runoff proved to be suitable to compare results from different experiments. Some variation of the test results has to be accepted.

As a consequence, the informal value of both test procedures in relation to service conditions is limited. Nevertheless, both procedures indicate consistent general differences between active substances and treated articles that can be expected to occur also during service life. The leaching processes from the investigated treated articles were mainly controlled by diffusion under laboratory and outdoor conditions. Solution control was also observed in some cases, again in a similar way for both test approaches.

The laboratory leaching experiments performed during the project revealed considerably higher emissions than the corresponding semi-field experiments on vertically installed test specimens. One exception was observed, i.e. enhanced leaching of carbendazim from an impregnated textile that can be caused by changes of the impregnation during outdoor exposure. However, the proposed laboratory procedure can be regarded as a leaching test under strong exposure conditions for materials under occasional water contact.

Differences between treated articles in laboratory and field tests are probably caused by certain properties of the treated articles. For instance, water drops remain on water repellent surfaces under outdoor conditions, and allow extended water contact for leaching, but also for photolysis of substances in the water film on surfaces. Different temperature on surfaces will affect diffusion within the material, but possibly also degradation of substances. It can be checked by supplementary laboratory tests whether these properties potentially impact either leaching of target substances or leachability of substances from treated articles. These tests can be rather simple, e.g. parallel

leaching tests at different temperatures and UV exposure of test specimens either prior to or during leaching experiments. The ability of treated articles to take up water and possible changes of this property can be observed during the laboratory leaching test if mass data of the test specimens are recorded. Observation of water drops on surfaces sprayed with water can indicate water repellency and changes of this property due to water contact.

Mass balances including active substances in either eluates or runoff samples and residual amounts in test specimens compared to the initial amounts indicate that competing processes can occur under laboratory conditions, and to a higher extend under outdoor conditions. Degradation, e.g. due to photolysis, and evaporation are supposed to be important processes to explain the fate of active substances. These processes can exceed emissions due to leaching considerably. Results from the field experiments indicate that competing processes mainly occur during summer, and increased amounts of target substances can be observed in runoff samples during autumn again.

Further steps that are necessary to implement the proposed leaching test methods in the authorisation procedure for biocidal products have to be discussed and decided. It remains a challenging task to develop procedures to apply leaching test data for risk assessments. Preferably, this should be a joint activity including interested experts from several European member states.

A model has been developed which predicts the measured emission in the laboratory tests. This model can be used for extrapolation, as it takes into account the physicochemical processes which play a role in leaching.

The analyses of the field test data have shown that the runoff is the most crucial influence factor on the emission in field experiments. The analyses have also shown that the temperature and the global radiation have a crucial influence as well.

There is a systematic difference between the laboratory test data and the vertically exposed field test data. The cumulative emission results as measured in the laboratory experiments are significantly higher than those measured in the vertically exposed field experiments. Accordingly, laboratory experiments can be seen as representing a worst case scenario. In the first couple of weeks of the field experiments there is good agreement between field data and laboratory data. After this period there is an increasing difference due to higher emissions in the laboratory tests. The difference could be caused by long-term processes such as degradation and evaporation.

The total emission results in the field experiments are subject to considerable variability. The total emission measured in a field experiment depends on the weather conditions that prevail during the experimental period. Necessary actions are proposed in order to make reasonable predictions for treated articles and substances that have not been investigated.

Zusammenfassung

Das Forschungsvorhaben soll die Umsetzung europäischer Regelungen zu Biozidprodukten der Produkttypen 7 (Beschichtungsschutzmittel), 9 (Schutzmittel für Fasern, Leder, Gummi und polymerisierte Materialien) und 10 (Schutzmittel für Baumaterialien) unterstützen.

Laut Biozid-VO beinhaltet eine Risikocharakterisierung eine 'Abschätzung der Häufigkeit und Schwere schädlicher Wirkungen … die in einem Umweltkompartiment infolge einer tatsächlichen bzw. vorhergesagten Exposition gegenüber einem Wirkstoff oder bedenklichen Stoff in einem Biozidprodukt wahrscheinlich auftreten'. Diese Substanzen können während der Nutzungsphase in die Umwelt gelangen, wenn Materialien wie Beschichtungen, Holz, Fasern, Polymeren oder Baumaterialien nicht direkt in die Umwelt freigesetzt werden. Dieser Transfer kann durch Wasserkontakt - sogenanntes ‚Leaching' (Auswaschung) - erfolgen und über einen langen Zeitraum, zur Freisetzung von Substanzen führen. Eine Risikocharakterisierung muss auf vorhergesagten Umweltkonzentrationen basieren, und ihre Verlässlichkeit hängt von der Güte der Vorhersage ab.

Ziel dieses Forschungsvorhabens war es, das Wissen über Auswaschungsprozesse zu vertiefen und Vorschläge für Auswaschungstestverfahren, die bei der Zulassung von Biozidprodukten angewandt werden können, bereitzustellen. Im Vorhaben wurden Auswaschversuche im Labor und Freilandversuche an ausgewählten behandelten Waren (hier: mit Biozidprodukten ausgerüstete Materialien) durchgeführt, Leitfäden für Auswaschversuche erstellt sowie die Versuchsdaten mit mathematischen Verfahren ausgewertet. Dazu wurde ein semi-analytisches Modell für Daten aus Laborversuchen weiterentwickelt, und detailliert betrachtet, wie Witterungseinflüsse auf Auswaschprozesse wirken.

Das verwendete Laborverfahren basiert auf der EN 16105:2011, einem Auswaschtest, der entwickelt wurde, um die Freisetzung von Substanzen aus Beschichtungen durch periodischen Wasserkontakt zu ermitteln. Es wird davon ausgegangen, dass eine Vielzahl von behandelten Waren mit den hier betrachteten Biozidprodukten eher gelegentlichem als dauerhaftem Wasserkontakt ausgesetzt ist. Im Test werden Prüfkörper, unter definierten Bedingungen, festgelegten Tauchzyklen ausgesetzt. Es gibt Phasen, in denen die Prüfkörper abtrocknen können, um Transportprozesse innerhalb des trocknenden Materials zu ermöglichen.

Experimente bei natürlicher Bewitterung wurden in Anlehnung an das in NT build 509 (2005) beschriebene Verfahren durchgeführt. Dieses Verfahren wurde für behandeltes Holz entwickelt und wird seit etwa 10 Jahren angewandt, um Auswaschung aus behandeltem Holz unter Freilandbedingungen zu untersuchen. Es ist Basis für ein Verfahren, das innerhalb des CEN harmonisiert wird (CEN/TR 16663:2014). Im Vergleich zu realen Bauwerken eher kleine Prüfkörper werden der Witterung ausgesetzt. Die Prüfkörper werden so ausgerichtet, dass sie am jeweiligen Standort einer relativ hohen Schlagregenmenge ausgesetzt sind.

Für Anwendungen von Biozidprodukten aus PT 7, PT 9 und PT 10 wurden repräsentative behandelte Waren ausgewählt. Die enthaltenen Wirkstoffe gehören zu unterschiedlichen chemischen Gruppen und haben folglich unterschiedliche physikalisch-chemische Eigenschaften. Es war beabsichtigt, vergleichende Untersuchungen mit Diuron, OIT und Terbutryn durchzuführen. Weitere Substanzen, nämlich Carbendazim, DCOIT, Dichlofluanid, IPBC, Tolylfluanid und Zinkpyrithion wurden ebenfalls betrachtet, um behandelte Waren mit unterschiedlichen Anwendungsbereichen und unterschiedlicher chemischer Matrix in die Untersuchungen einzubeziehen. 8 Farben für Holz, 4 Farben für Dächer, ein Markisenstoff, 2 PVC-Dichtungsbänder zum Abdichten von Fensterrahmen und 2 Dichtungsmassen, die jeweils marktübliche Produkte repräsentieren, wurden von Herstellern freundlicherweise zur Verfügung gestellt. Bei 4 Farben wurde bei den Herstellern ein analoges Gemisch von Diuron, OIT und Terbutryn zu jeweils biozidfreien Produkten zugefügt.

Geeignete Methoden zum Herstellen von Prüfkörpern wurden entwickelt. Das beinhaltet auch den Vergleich von verschiedenen Untergrundmaterialen, d.h. Holz verschiedenen Ursprungs und Glas für Holzfarben, sowie Faserzement und Glas für Dachfarben. Für alle Produkte, die für das Forschungsvorhaben zur Verfügung gestellt wurden, wurde geprüft, ob das vorgeschlagene Laborverfahren anwendbar ist. Ein Produkt wurde zusätzlich nach CEN/TS 16637-2:2014 untersucht, einem Auswaschtest, der auf dauerhaftem Wasserkontakt basiert. Wirkstoffe und ausgewählte Abbauprodukte in Eluaten, den behandelten Waren und nach Versuchsende aus ausgewählten Prüfkörpern wurden durch UHPLC- und LC/MS-Methoden quantifiziert. Zusätzlich wurden die pH-Werte der Eluate erfasst und für ausgewählte Eluate der TOC- und Zink-Gehalt bestimmt.

Laborversuche wurden nicht nur durchgeführt, um die Freisetzung von Substanzen zu beschreiben, sondern auch Eigenschaften der behandelten Waren zu untersuchen, die die Auswaschung beeinflussen. Das betrifft die Aufnahme von flüssigem Wasser, Wasserdampfsorption, Hydrophilie und Desorption von Wirkstoffen aus den Matrizes. Die Aufnahme von flüssigem Wasser wurde aus den aufgezeichneten Prüfkörpermassen berechnet. Wasserdampfsorption wurde durch ein isothermes Messverfahren für die Aufnahme von Wasserdampf durch Feststoffe nach DIN 66138 bestimmt. Für 4 Farben wurde die Desorption von Wirkstoffen untersucht. Dazu wurden Proben der getrockneten Farbfilme mit unterschiedlichen Wirkstoffgehalten zerkleinert und unter definierten Bedingungen in Wasserkontakt gebracht. Anschließend wurden die Wirkstoffkonzentrationen in den wässrigen Überständen bestimmt.

Freilandversuche wurden für ausgewählte behandelte Waren an 3 Standorten durchgeführt, hauptsächlich am Stammsitz der MPA Eberswalde. Ein Experiment wurde an einem zweiten Standort außerhalb von Eberswalde durchgeführt, und einige Experimente wurden im späteren Verlauf des Projekts bei der BAM in Berlin gestartet. Die Mehrzahl der Prüfkörper war vertikal installiert und nach Südwesten ausgerichtet. Weitere Prüfkörper des Textils wurden auch nach Nordwesten, Nordosten und Südosten ausgerichtet. Ein Prüfkörper des Textils und ein mit einer Dachfarbe beschichteter Prüfkörper wurden horizontal installiert. Abweichend vom NT build 509-Verfahren wurden mindestens für die ersten Versuchsmonate Ablaufwasserproben von einzelnen Regenphasen analysiert. Später wurden Proben gesammelt und vereinigt, aber häufiger als nach NT build 509 vorgesehen. Einige Experimente wurden auch über einen längeren Zeitraum durchgeführt. Für eine Holzfarbe wurden Versuche an beiden Freilandstandorten der MPA Eberswalde durchgeführt. Weitere Experimente wurden nach 3 bzw. 6 Monaten gestartet, um Auswaschprozesse zu vergleichen, die unter verschiedenen Witterungsbedingungen begonnen wurden. Die Wirkstoffe in den Ablaufwasserproben wurden bei der MPA Eberswalde mittels LC-MS/MS und bei der BAM mittels UHPLC quantifiziert. Für ausgewählte Ablaufwasserproben wurden die Leitfähigkeit, pH-Werte und TOC-Gehalte bestimmt.

Nach Abschluss der Versuche wurden ausgewählte Prüfkörper aus Labor- und Freilandexperimenten extrahiert und die verbliebenen Wirkstoffgehalte bestimmt. Anhand der Ausgangsmengen, Wirkstoffmengen in Eluaten bzw. Ablaufwasserproben und den Restgehalten der Prüfkörper wurden Massenbilanzen berechnet.

Ergebnisse aus Laborversuchen

Das vorgeschlagene Laborverfahren war für eine Reihe von behandelten Waren geeignet und reproduzierbar.

Für alle untersuchten Produkte wurden abfallende Emissionsverläufe beobachtet. Emissionen sind grundsätzlich abhängig von physikalisch-chemischen Eigenschaften der Wirkstoffe, aber auch von Eigenschaften der behandelten Waren und Untergrundmaterialien.

Abweichungen zwischen Parallelversuchen und Standardabweichungen für wiederholte Versuche im selben Labor zeigen, dass die Laborversuche zuverlässige Ergebnisse liefern. Falls Umsetzungsprozesse bereits während der Versuche auftreten, kann es erforderlich sein, Daten zu Transformationsprodukten einzubeziehen, um wiederholbare Ergebnisse zu erhalten. Besonders empfindliche Analysenverfahren können erforderlich sein, um Zielsubstanzen zu identifizieren, die nur in sehr geringen Konzentrationen freigesetzt werden.

Emissionsverläufe liefern auch Informationen über den Auswaschprozess an sich. Doppelt logarithmische Darstellungen weisen darauf hin, dass die Auswaschung aus den untersuchten Materialien vor allem durch Diffusion kontrolliert wird. In einigen Fällen wurde Verarmung an auswaschbaren Zielsubstanzen beobachtet – üblicherweise deutlich unterhalb der Ausgangsmenge an Wirkstoffen in den Prüfkörpern. Bei einigen Materialien war zu Beginn der Versuche auch das Lösen der Zielsubstanzen geschwindigkeitsbestimmend für die Auswaschung. Besonders ausgeprägt war das für die Wirkstoffe im imprägnierten Textil.

Bilanzlücken wurden festgestellt, wenn die Summe der Wirkstoffe in den Eluaten und Restgehalte in den Prüfkörpern den Ausgangsmengen für die Wirkstoffe gegenüber gestellt wurden. Das weist auf weitere Prozesse hin, die zu Wirkstoffverlusten führen.

Abbau, zum Beispiel durch UV-Bestrahlung, ist eine mögliche Ursache für Wirkstoffverluste. Aber nicht nur Wirkstoffe, sondern auch die Materialmatrix von behandelten Waren kann empfindlich gegenüber UV-Strahlen sein, wie Beobachtungen über erhöhte Auswaschung von Carbendazim nach UV-Beanspruchung des behandelten Textils zeigen.

Desorptionsversuche mit Farben bestätigen Unterschiede in der Auswaschbarkeit von Wirkstoffen mit unterschiedlichen physikalisch-chemischen Eigenschaften, ergeben aber nicht die gleiche Reihung der behandelten Waren wie die Auswaschversuche. Das bedeutet, dass die Auswaschung nicht nur von physikalisch-chemischen Eigenschaften, sondern auch von chemischen Bindungen zwischen Wirkstoffen und behandelten Waren bestimmt wird.

Alle untersuchten behandelten Waren und die meisten Untergrundmaterialien (außer Glas) nahmen Wasser auf. Das bedeutet, dass innerhalb der Prüfkörper Wasser zum Lösen und zum Transport von Substanzen verfügbar war. Im Falle von Prüfkörpern aus Holz wurden Substanzen aus Beschichtungen auch in das Untergrundmaterial transportiert. Für 4 Farben und das imprägnierte Textil wurde gezeigt, dass Wasserdampf aufgenommen wird. Das bedeutet, dass auch Luftfeuchtigkeit zur Mobilisierung von Substanzen aus Materialien beitragen kann. Es wurde auch beobachtet, dass sich die Fähigkeit zur Wasseraufnahme im Laufe von Auswaschversuchen ändert. Bei dem Textil gingen die wasserabweisenden Eigenschaften durch Wasserkontakt im Laborversuch verloren.

Vergleiche von Materialien in Laborversuchen basieren hauptsächlich auf Eigenschaften von behandelten Waren und Zielsubstanzen, die sich unter Wasserkontakt auswirken. Verschiedene Parameter wie Wassermenge, Dauer des Wasserkontakts, Luftfeuchte während der Trocknungsphasen und Temperatur sind festgelegt und bleiben während der Versuche gleich. Andere Faktoren, wie UV-Strahlung, Aufwärmen von Oberflächen, Alterung von Materialien, physikalischer Stress und Beeinflussung durch Mikroorganismen werden vermieden oder minimiert.

Ergebnisse von Freilandversuchen

Das angewandte Verfahren war geeignet, um Auswaschung von Wirkstoffen aus den ausgewählten behandelten Waren zu beschreiben.

Schlagregen muss auf vertikal installierte Flächen auftreffen, damit sich Ablaufwasser bildet. Menge und Richtung des Schlagregens sind von lokalen Bedingungen am Versuchsort abhängig. Es ist auch bekannt, dass der prozentuale Anteil des Schlagregens auf vertikale Flächen mit zunehmender Größe dieser Flächen abnimmt. Freilandversuche mit relativ kleinen Prüfkörperoberflächen bedeuten in dieser Hinsicht strenge Expositionsbedingungen. Diese Tatsache ist wichtig, wenn Versuchsdaten extrapoliert und in Modellen für Auswaschprozesse verwendet werden, und bedeutet, dass flächenbezogene Daten aus Freilandversuchen nicht ohne Korrekturfaktor auf reale Flächen bezogen werden können.

Die Anzahl von Parallelversuchen bei gleichen Versuchsbedingungen war im Rahmen des Forschungsvorhabens begrenzt. Wenn Daten aus Freilandversuchen verglichen werden, ist zu beachten, dass es nicht möglich ist, diese unter identischen Bedingungen zu wiederholen. Selbst für Prüfkörper, die parallel untersucht werden, können die Expositionsbedingungen variieren und z.B. unterschiedliche Mengen an Ablaufwasser verursachen. Trotzdem sind einige Schlussfolgerungen möglich. Die maximalen Konzentrationen und kumulativen Verluste der Zielsubstanzen lagen für wiederholte Experimente in ähnlichen Bereichen. Das gilt für parallele Versuche am gleichen Ort und einem nahegelegenen Standort, Versuche die zu unterschiedlichen Zeitpunkten gestartet wurden sowie für Versuche, die zu einem anderen Zeitpunkt an einem anderen Ort durchgeführt wurden. Die Variabilität zwischen den Ergebnissen hängt, neben anderen Faktoren, von Eigenschaften der Zielsubstanzen ab, wie z.B. ihrer Stabilität unter den Versuchsbedingungen.

Darstellungen von kumulativen Verlusten mit Bezug auf Datum und Regenmenge zeigen üblicherweise abgestufte Kurven, da die Ergebnisse nicht auf die tatsächliche Exposition mit Wasser zurückgeführt sind. Auch Kurven, die auf die Ablaufwassermenge bezogen sind, verlaufen nicht völlig gleichförmig. Das ist ein Hinweis auf weitere Prozesse, die die Menge an ausgewaschenen Substanzen in Ablaufwasserproben bestimmen. Allerdings haben sich Darstellungen kumulativer Emissionen mit Bezug auf die Ablaufwassermenge als tauglich erwiesen, um Ergebnisse verschiedener Tests zu vergleichen. Je nach Zielsubstanz verlaufen Emissionskurven verschiedener Experimente mehr oder weniger ähnlich, vor allem in frühen Versuchsstadien. Unterschiede werden vorwiegend in späteren Versuchsstadien deutlich. Angaben zum Versuchszeitraum, den Regen- und Ablaufwassermengen sollten in Berichten zu Freilandversuchen enthalten sein, weil diese Parameter nützliche Informationen zu den Versuchsbedingungen liefern.

Die Konzentrationen der Zielsubstanzen und die ausgewaschenen Mengen je Fläche unterschieden sich beträchtlich für Ablaufwasserproben von einzelnen Regenereignissen oder kurzen Regenperioden. Es wurde eine Tendenz zu abnehmenden Werten beobachtet. Häufig waren die Mengen der Zielsubstanzen in Ablaufwasserproben im Sommer - und gelegentlich auch im Winter - gering, und stiegen dann im Herbst und im Frühjahr wieder an. Es wird vermutet, dass Abbau, und eventuell auch Verdunstung der Zielsubstanzen im Sommer besonders hoch sind. Wenn unter herbstlichen Witterungsbedingungen wieder mehr Wasser zur Verfügung steht, können Zielsubstanzen wieder an die Materialoberflächen transportiert werden. Darüber hinaus sind die Substanzen in den Oberflächen und dem darauf befindlichen Wasserfilm durch geringere Temperaturen und weniger UV-Strahlung geschützt. Bei geringen Temperaturen im Winter sind vermutlich Transportprozesse verlangsamt.

Grundsätzlich ist es schwierig, Auswaschdaten für instabile Verbindungen zu erhalten, weil es nicht möglich ist, diese Substanzen zu konservieren oder zu analysieren, sobald sie im Ablaufwasser auftreten. In diesem Forschungsvorhaben war das der Fall für Zinkpyrithion aus dem imprägnierten Textil und einer Holzfarbe. In derartigen Fällen kann es hilfreich sein Es kann angebracht sein, stabile Transformationsprodukte in den Ablaufwasserproben zu bestimmen, wenn diese für die Risikocharakterisierung von Bedeutung sind.

Die Emissionsverläufe für Carbendazim aus dem imprägnierten Textil waren in Bezug auf die Ablaufwassermenge aus verschiedenen Versuchen nahezu identisch, auch wenn die Prüfkörper aus verschiedenen Richtungen exponiert waren. Andererseits wurden beträchtliche Unterschiede für OIT aus verschiedenen Versuchsansätzen beobachtet. Es wird vermutet, dass die OIT-Menge in den Ablaufwasserproben durch Faktoren beeinflusst wird, die seine Stabilität beeinträchtigen.

Von horizontal ausgerichteten Proben wird ein hoher Prozentanteil des Regenwassers als Ablaufwasser gewonnen. Sicherlich spritzt ein Teil des Regenwassers in Abhängigkeit von den Oberflächeneigenschaften ab oder

verdunstet von feuchten Flächen. Nur ein Teil des Schlagregens wird von vertikal ausgerichteten Oberflächen gesammelt, vermutlich aus denselben Gründen. In den Ablaufwasserproben von horizontal ausgerichteten Prüfkörpern waren die Konzentrationen der Zielsubstanzen geringer, die insgesamt ausgewaschenen Mengen aber höher als von vertikal ausgerichteten Prüfkörpern. Auswaschprozesse von horizontalen Flächen wurden neben der Regenmenge weniger durch zusätzliche Faktoren beeinflusst als Auswaschprozesse von vertikalen Flächen.

Für die untersuchten behandelten Waren wurde nur ein geringer prozentualer Anteil der Ausgangmenge an Wirkstoffen in Ablaufwasserproben nachgewiesen. Analysen der Restmengen dieser Substanzen in den Prüfkörpern im Anschluss an Freilandversuche ergaben große Lücken in den Massenbilanzen. Für beschichtete Holzproben wurde gezeigt, dass ein Teil der Zielsubstanzen in das Untergrundmaterial (Holz) transportiert werden kann. Ein beträchtlicher Anteil der Zielsubstanzen geht aber durch andere Prozesse verloren. Es wird vermutet, dass Abbau und Verdunstung diese Verluste verursachen. Bisher gibt es aber keine Daten, die das Ausmaß der einzelnen Prozesse auf den Verbleib der Substanzen in den untersuchten behandelten Waren zeigen.

Es wird angenommen, dass flächenbezogene Emissionen von vertikal ausgerichteten Prüfkörpern mit relativ geringen Dimensionen höher sind als Emissionen von größeren Flächen, da sie in stärkerem Maße Schlagregen ausgesetzt sind. Allerdings zeigen Freilanduntersuchungen besser, welche Größenordnung Auswaschprozesse unter Nutzungsbedingungen haben können, als Daten aus Laborversuchen.

Die Ergebnisse von Freilandversuchen werden einerseits durch Eigenschaften der Zielsubstanzen und Materialien bedingt, und andererseits durch variable Witterungsbedingungen beeinflusst. Es ist möglich, die Auswaschung bestimmter Substanzen untereinander bzw. aus verschiedenen behandelten Waren anhand von Freilanduntersuchungen zu vergleichen. Auf jeden Fall muss eine gewisse Variabilität der Versuchsergebnisse erwartet und berücksichtigt werden.

Die Aussagefähigkeit von Freilandversuchen hängt von der Anzahl und Häufigkeit der Analysen von Ablaufwasserproben ab. Ergebnisse für Sammelproben geben nur eine allgemeine Information über die Menge an ausgewaschenen Substanzen in bestimmten Versuchsphasen. Falls die letzten Daten eines Freilandversuchs während des Sommers gewonnen wurden und ein Plateau aufweisen, kann man nicht sicher schließen, dass kein weiterer Anstieg auftreten wird. Nur wenn eine höhere Anzahl von Proben analysiert wird, können Konzentrationsbereiche für Zielsubstanzen in Ablaufwasser abgeschätzt und Rückschlüsse auf die Abhängigkeit der Auswaschmengen von tatsächlichen Expositionsbedingungen gezogen werden.

Vergleich von Labor- und Freilandversuchen

Die Bestimmung von Zielsubstanzen in Ablaufwasserproben erfordert empfindlichere Analysenverfahren als die Analyse von Eluaten aus Laborversuchen, insbesondere wenn einzelne Regenereignisse beobachtet werden sollen.

Emissionen sind in Laborversuchen tendenziell höher als in Freilandversuchen an vertikal ausgerichteten Prüfkörpern. Es gibt aber kein festes Verhältnis zwischen den Resultaten der beiden Versuchsvarianten. Bei einem horizontal installierten Prüfkörper waren die Emissionen im Bereich der Werte, die im Laborversuch bestimmt wurden. Versuche mit dem imprägnierten Textil weisen darauf hin, dass Emissionen unter Freilandbedingungen höher sein können, wenn das Material selbst nicht witterungsstabil ist.

Vergleichsdaten für Emissionen von behandelten Waren für kleinflächige Anwendungen, wie Dichtungsmassen und Dichtungsbänder, die der Witterung ausgesetzt sind, stehen nicht zur Verfügung. Es wird vorgeschlagen, Labordaten zur Risikocharakterisierung zu nutzen, und dabei zu berücksichtigen, dass Freisetzung nur von kleinen Flächen erfolgt. Die Freisetzung je Flächeneinheit wird dabei vermutlich überschätzt, vor allem wenn z.B. Fugen nicht der gesamten Regenmenge ausgesetzt sind.

Unterschiede bei Emission von Wirkstoffen bzw. aus behandelten Waren werden in Labor- und Freilandversuchen übereinstimmend angezeigt, d.h. wenn im Laborversuch relativ hohe Mengen einer Substanz im Vergleich zu einer anderen ausgewaschen werden, kann das auch im Freilandversuch erwartet werden. Die tatsächlichen Verhältnisse zwischen Ergebnissen für verschiedene Wirkstoffe oder unterschiedliche behandelten Waren können aber für beide Verfahren variieren. Vermutlich verursachen zusätzliche Parameter, die im Laborversuch vernachlässigt werden, diese Unterschiede. Folgende Parameter erscheinen wichtig: hydrophile Eigenschaften von Oberflächen, Abbau von Substanzen unter Witterungsbedingungen und Verdunstung von Wirkstoffen aus erwärmten Oberflächen. Bisher gibt es experimentelle Daten, die die Vermutung unterstützen, dass hydrophile Eigenschaften

und Abbau unter UV-Bestrahlung einen Einfluss haben. Zur Relevanz von erhöhter Verdunstung liegen keine Daten vor.

Offensichtlich treten sowohl unter Labor- als auch Freilandbedingungen Veränderungen von Materialeigenschaften auf, die einen Einfluss auf Auswaschprozesse haben, z.B. hydrophile Eigenschaften, Wasserdampfsorption und die chemische Zusammensetzung von behandelten Waren.

Die Wassermenge, mit der Prüfkörper in Kontakt sind, scheint eine brauchbare Bezugsgröße zu sein, um Labor- und Freilanddaten zu vergleichen, obwohl die Dauer des Wasserkontakts dabei ignoriert wird. Auswaschung scheint unter Labor- und Freilandbedingungen durch die gleichen Prozesse, nämlich Diffusion und Lösen der Zielsubstanzen, kontrolliert zu sein. Ein vertieftes Verständnis der zusätzlich im Freiland auftretenden Prozesse kann helfen, Daten aus Laborversuchen besser zur Risikocharakterisierung zu nutzen.

Modellierung

Das semi-analytische Modell entspricht den Labordaten so genau wie möglich, ermöglicht Extrapolationen von Emissionen in Laborversuchen und beschreibt die Transportprozesse, die in Laborversuchen nach EN 16105 ablaufen. Im Gegensatz zu Regressionsmodellen wird im semi-analytischen Modell versucht, sich ändernde Eigenschaften der behandelten Waren (sich ändernde Wasseraufnahme und chemische Zusammensetzung) und resultierende Änderungen der Desorptionsfähigkeit der Wirkstoffe zu berücksichtigen.

Das semi-analytische Modell bildet die einzelnen in den Laborversuchen erhaltenen Emissionsverläufe für fast alle Wirkstoffe und behandelten Waren gut ab. Ein auf der Basis von 9 Tauchzyklen erstelltes semi-analytisches Modell sagt die Ergebnisse für verlängerte Versuchsserien (bis zu 18 Tauchzyklen) sehr gut vorher. Das semi-analytische Modell ist für Extrapolationen gut geeignet. Es kann für die Bestimmung von Emissionen nach einer beliebigen Anzahl von Tauchzyklen oder Versuchstagen genutzt werden. Es kann auch angewandt werden, um Emissionen nach kürzeren Tauchphasen, z.B. nach einer Tauchzeit von 10 Minuten zu bestimmen. Abbau oder Verdunstung von Substanzen werden im Labormodell nicht berücksichtigt. Das ist gerechtfertigt vor dem Hintergrund, dass bei konstanten Laborbedingungen gearbeitet wird und die auf die Prüfkörper wirkenden Umwelteinflüsse vernachlässigbar sind. Falls das Testverfahren nach EN 16015 variiert wird (UV-Behandlung, Temperaturänderungen), muss das Modell angepasst werden.

Die Daten aus den Freilandversuchen sind präzise und verlässlich aus der Sicht einer statistischen Betrachtung, da die Standardabweichung zwischen Versuchen an den MPA- und BAM-Standorten für alle Kombinationen aus behandelten Waren und Wirkstoffen zwischen 20 und 40 % liegen, wenn die relativen kumulativen Emissionen für einen Zeitraum, in dem 10 l/m² Ablaufwasser angefallen waren, verglichen werden. Obwohl dieselben Witterungsbedingungen herrschen, können aber die Emissionen, die für einzelne Regenereignisse beobachtet werden, zwischen verschiedenen Prüfkörpern erheblich variieren. Die Unterschiede können 200 % erreichen.

Emissionskurven können mit linear gewichteten Regressionsmodellen gut abgebildet werden. Die beobachteten Emissionen [mg/m²] je Ablaufwassermenge [l/m²] können durch die meteorologischen Bedingungen erklärt werden. Wetterbedingungen spielen eine entscheidende Rolle für Emissionen, die nach den Modellberechnungen um einen Faktor von 10 und mehr variieren können. Die Analysen zeigen, dass die Ablaufwassermenge der dominierende Einflussfaktor auf die Emissionen ist. Schlagregenmenge, Globalstrahlung, Temperatur und Luftfeuchte haben sich als wichtigste zusätzliche Einflussfaktoren erwiesen. Kumulative Emissionen können zufriedenstellend mit einem Regressionsmodell beschrieben werden, das alle verfügbaren meteorologischen Faktoren einbezieht.

Zur Vorhersage von Gesamtverlusten in Freilandversuchen können Labordaten nicht ohne weitere mathematische Modellierung und Kalibrierung genutzt werden. Ein direkter Vergleich von Freiland- und Labordaten ergibt signifikante Überschätzung durch Labordaten, insbesondere bei vertikaler Exposition. Die geringe Korrelation zwischen Freiland- und Labordaten ist sehr wahrscheinlich durch Prozesse bedingt, die für die behandelten Waren und Wirkstoffe charakteristisch sind. Trotzdem war es möglich, eine mathematische Beziehung zwischen der kumulativen Menge an Ablaufwasser und der Anzahl der Tauchzyklen im Laborversuch herzustellen. Außerdem wird erwartet, dass durch geeignete Labortests zusammen mit einem erweiterten multivariaten Kalibriermodell mit einer zeitlichen Anpassung sinnvolle Vorhersagen für im Freiland nicht untersuchte behandelte Waren und Substanzen möglich sind.

Leitfäden und Leaching-Workshop

Vorschläge für ein Laborverfahren basierend auf EN 16105 und ein Freilandverfahren in Anlehnung an NT build 509 und CEN/TR 16663 wurden erstellt. Dabei wurden auch Erfahrungen aus dem Forschungsvorhaben berücksichtigt.

Im Juli 2014 wurde an der BAM in Berlin der Workshop 'Leaching behaviour of biocides from preservatives' durchgeführt. Etwa 40 Experten von Zulassungsbehörden, Forschungs- und Prüfinstituten und der Industrie aus 10 europäischen Ländern und von der ECHA nahmen teil. Ausgewählte Projektergebnisse und Erfahrungen aus Auswaschstudien an anderen Instituten wurden präsentiert. Die Herangehensweise zur Modellierung von Auswaschdaten aus Laborversuchen und zur Interpretation von Daten aus Freilandversuchen wurde erläutert. In Vorbereitung und während des Workshops wurden die Entwürfe der Leitfäden mit Experten diskutiert. Weitere Kommentare zu den offenen Fragen wurden im Anschluss an den Workshop und ein Treffen der Arbeitsgruppe Umwelt anlässlich des Biocides WG-IV-2015 meetings bei der ECHA gesammelt. Diese Diskussionen sind in den Endversionen der Leitfäden berücksichtigt. Die Leitfäden sind Bestandteil dieses Berichts.

Schlussfolgerungen

Der Labortest basiert auf einem Tauchschema für definierte Prüfkörper, das unter Berücksichtigung üblicherweise verfügbarer Analysentechnik, Zeitaufwand und Reproduzierbarkeit der Testergebnisse willkürlich festgelegt wurde. Hauptanliegen war es, Trocknungsphasen einzubeziehen, um Transport von Wasser und Zielsubstanzen in den behandelten Waren und Untergrundmaterialien zu ermöglichen. Das Laborverfahren ignoriert einige Eigenschaften von Zielsubstanzen und behandelten Waren, die Einfluss auf die Auswaschung haben, wie die photolytische Stabilität der Zielsubstanzen und behandelten Waren sowie hydrophile Eigenschaften der behandelten Waren. Das Verfahren beinhaltet außerdem keine Temperaturänderungen und wird bei etwa konstanter relativer Luftfeuchte durchgeführt. Dadurch zeigt der Versuch die Variabilität von Auswaschprozessen nicht an. Das vorgeschlagene Verfahren ist für behandelte Waren vorgesehen, die gelegentlichem Wasserkontakt ausgesetzt sind. Für behandelte Waren, die in ständigem Wasserkontakt sind, sollte der Test nach CEN/TS 16637:2014 in Frage kommen, der entwickelt wurde, um die Freisetzung gefährlicher Stoffe aus Bauprodukten zu bestimmen.

Die Oberflächen von Prüfkörpern für Freilandversuche sind relativ klein im Vergleich zu großen Fassadenflächen an realen Gebäuden, und die Prüfkörper sind so orientiert, dass am jeweiligen Standort ein hoher Anteil an Schlagregen auftreffen kann. Das führt zu relativ hohen Wassermengen, die für Auswaschprozesse verfügbar sind, und folglich auch zu relativ hohen Mengen an Ablaufwasser je Flächeneinheit. Freilandversuche können nicht reproduziert werden, weil Auswaschprozesse unter Witterungsbedingungen durch das komplexe Zusammenwirken verschiedener Faktoren beeinflusst werden. Die Darstellung von flächenbezogenen Emissionen in Bezug auf die Ablaufwassermenge hat sich aber als brauchbar erwiesen, um Ergebnisse aus verschiedenen Versuchen zu vergleichen. Eine gewisse Variation der Versuchsergebnisse muss dabei in Kauf genommen werden.

In der Konsequenz ist die Aussagefähigkeit beider Testverfahren mit Bezug auf Nutzungsbedingungen begrenzt. Trotzdem zeigen beide Verfahren übereinstimmende grundsätzliche Unterschiede zwischen Wirkstoffen und behandelten Waren an, von denen erwartet werden kann, dass sie so auch unter Anwendungsbedingungen auftreten. Bei den untersuchten behandelten Waren wurden Auswaschprozesse sowohl unter Labor- als auch Freilandbedingungen vor allem durch Diffusion kontrolliert. In einigen Fällen wurde beobachtet, dass die Auswaschung durch das Lösen der Zielsubstanzen kontrolliert wird, auch das in ähnlicher Weise in beiden Versuchsvarianten.

Die während des Forschungsvorhabens durchgeführten Laborversuche ergaben deutlich höhere Verluste als die entsprechenden Freilandversuche an vertikal installierten Prüfkörpern. Eine Ausnahme wurde beobachtet, nämlich erhöhte Freisetzung von Carbendazim aus einem imprägnierten Textil, die durch Veränderungen der Imprägnierung unter Witterungsbedingungen verursacht sein kann. Trotzdem kann das vorgeschlagene Labortestverfahren für Materialien, die gelegentlichem Wasserkontakt ausgesetzt sind, als ein Auswaschversuch unter strengen Expositionsbedingungen angesehen werden.

Unterschiede zwischen behandelten Waren, die in Labor- und Freilandversuchen verschieden ausgeprägt sind, werden vermutlich durch bestimmte Eigenschaften der behandelten Waren verursacht. Zum Beispiel verbleiben unter Freilandbedingungen Wassertropfen länger auf wasserabweisenden Oberflächen. Das ermöglicht verlängerten Wasserkontakt für Auswaschvorgänge, aber auch für erhöhte Photolyse von Substanzen im Wasserfilm auf Oberflächen. Verschiedene Oberflächentemperaturen beeinflussen die Diffusion im Material, und möglicherweise

auch den Abbau von Substanzen. Durch ergänzende Laborversuche kann geprüft werden, ob diese Eigenschaften möglicherweise einen Einfluss auf die Auswaschung von Zielsubstanzen an sich oder auf die Auswaschbarkeit von Substanzen aus einer behandelten Ware haben. Das können einfache Tests sein, z.B. parallele Auswaschversuche bei verschiedenen Temperaturen und UV-Behandlung von Prüfkörpern vor oder während der Auswaschversuche. Die Fähigkeit von behandelten Waren, Wasser aufzunehmen, und mögliche Veränderungen dieser Eigenschaft können beobachtet werden, indem die Prüfkörpermassen im Versuchsverlauf erfasst werden. Wasserabweisende Eigenschaften und deren Veränderungen können beobachtet werden, indem Oberflächen mit Wasser besprüht, und die Tropfen beobachtet werden.

Massenbilanzen, für Wirkstoffe in Eluaten bzw. Ablaufwasserproben und Restmengen in Prüfkörpern im Vergleich zu den Ausgangsmengen zeigen, dass unter Laborbedingungen und in größerem Ausmaß unter Freilandbedingungen, konkurrierende Prozesse ablaufen. Abbau, z.B. durch Photolyse, und Verdunstung werden als wichtige Prozesse vermutet, um den Verbleib von Wirkstoffen zu erklären. Diese Prozesse können Emissionen durch Auswaschung deutlich übertreffen. Ergebnisse von Freilandversuchen zeigen, dass konkurrierende Prozesse vor allem im Sommer auftreten, und im Herbst wieder höhere Mengen an Zielsubstanzen in Ablaufwasserproben beobachtet werden können.

Weitere Schritte, die erforderlich sind, um die vorgeschlagenen Testverfahren in das Zulassungsverfahren für Biozidprodukte einzubeziehen, müssen diskutiert und beschlossen werden. Es bleibt eine Herausforderung, Verfahren zu entwickeln, um Leachingdaten zur Risikocharakterisierung zu nutzen. Vorzugsweise sollte das eine gemeinsame Aktivität von interessierten Fachleuten aus verschiedenen europäischen Ländern sein.

Ein Modell wurde entwickelt, das die im Laborversuch gemessenen Emissionen vorhersagt. Es kann für Extrapolationen genutzt werden, da es physikalisch-chemische Prozesse berücksichtigt, die beim Leaching eine Rolle spielen.

Die Analyse von Freilanddaten hat gezeigt, dass die Ablaufwassermenge der wichtigste Einflussfaktor auf Emissionen in Freilandversuchen ist. Die Analyse hat auch ergeben, dass Temperatur und Globalstrahlung wesentlichen Einfluss haben.

Es gibt einen systematischen Unterschied zwischen Labor- und Freilanddaten für vertikal exponierte Prüfkörper. Die im Labor bestimmten kumulativen Emissionen sind signifikant höher als die für vertikal exponierte Prüfkörper im Freilandversuch. Folglich können diese Laborversuche als worst-case-Szenario angesehen werden. Für die ersten Wochen während der Freilandversuche gibt es eine gute Übereinstimmung zwischen Freiland- und Labordaten. Danach gibt es eine zunehmende Differenz mit höheren Emissionen im Laborversuch. Diese Differenz könnte durch langfristige Prozesse wie Abbau und Verdunstung bedingt sein. Die Gesamtemissionen in Freilandversuchen können beträchtlich schwanken. Sie sind abhängig von den während des Versuchs herrschenden Witterungsbedingungen. Notwendige Schritte werden vorgeschlagen, um verlässliche Vorhersagen für nicht untersuchte behandelte Waren bzw. Stoffe treffen zu können.

1. Introduction

The project was intended and designed to support the implementation of European regulations on biocidal products, i.e. the Biocidal Products Directive (98/8/EC) and later the Regulation (EU) No 528/2012 concerning the making available on the market and use of biocidal products. It is directed to biocidal products of the product types 7 (film preservatives), 9 (fibre, leather, rubber and polymerised materials preservatives) and 10 (construction material preservatives) that belong to main group 2 'preservatives'.

Risk characterisation of biocides includes *'the estimation of the incidence and severity of adverse effects likely to occur in … environmental compartments due to actual or predicted exposure to any active substances or substances of concern in a biocidal product'* (BPR). These substances are not directly released into environmental compartments, if materials like coatings, wood, fibres, polymers or construction materials contain preservatives, but can migrate into environmental compartments during service life. This transfer can be caused by water contact – so-called 'leaching' - and results in release of substances, possibly over a long period of time. Risk characterisation has to be based on predicted environmental concentrations, and its reliability depends on the quality of these predictions.

Leaching of biocidal active substances of main group 2 under weathering conditions was subject of a former research project funded by the Federal Environment Agency (UBA, Umweltbundesamt) (Schoknecht et al. 2012) that serves as basis for the current project. The aims of the current project where to improve knowledge on leaching processes and to provide proposals for leaching test procedures that can be applied for authorisation of biocidal products.

The following work packages were performed during the project:

- Literature survey and selection of active substances and treated articles for testing
- Laboratory tests
- Field experiments
- Preparation and discussion of leaching test proposals
- Mathematical processing of leaching test data and further development of a semi-analytical model
- Workshop 'Leaching behaviour of biocides from preservatives'

Leaching is affected by complex interaction of parameters that cannot be described in detail for the assessment of each biocidal product. Reasonable simplifications of test procedures and interpretation of results are required and have to be agreed among authorities, test laboratories and producers. Reliability of test results will increase if simplifications are based on deep understanding of leaching processes.

It was intended to use the general design of already harmonised test procedures for the development of test methods as much as possible to avoid a number of different procedures for different treated articles. The applicability of these procedures was proven and preparation of suitable test specimens was tried for different types of treated articles during the project.

The applied laboratory method was based on EN 16105:2011, a leaching procedure that was developed to determine the release of substances from coatings in intermittent contact with water. Occasional water contact is assumed to apply for a number of treated articles including biocides of the investigated product types rather than permanent water contact. Test specimens are exposed to immersion cycles under defined conditions. The procedure includes periods when the test specimens are allowed to dry to enable transport processes within the drying material. An equivalent procedure is described in an OECD Guidance document for treated wood (OECD GD 107, 2009). CEN/TS 15119-1:2008 was also developed for treated wood, but defines a different immersion scheme. Laboratory experiments were not only performed to describe release of substances as such, but also to investigate properties of treated articles that can influence leaching, i.e. uptake of liquid water, water vapour sorption, hydrophilic properties of surfaces and desorption of active substances from the products matrices.

Experiments under natural weathering conditions were performed according to NT build 509 (2005). This Nordtest procedure was developed for treated wood and has been applied for about ten years to investigate leaching from treated wood under semi-field conditions. A harmonised procedure for investigation of treated wood that is based on NT build 509 is also under development within CEN and was published as CEN/TR 16663:2014.

Smaller test specimens – compared to real constructions – are exposed to weathering. The test specimens are oriented towards a direction with high exposure to driving rain at a certain location. Field studies performed during this project were designed to improve knowledge on leaching processes under natural weathering. Therefore, deviating from the NT build 509 procedure, runoff samples of single rain periods were analysed during the first months of each experiment at minimum. Later, samples were merged more frequently than defined in NT build 509. A number of experiments were performed for a longer duration of time. Residues of active substances were determined in selected test specimens from both test procedures to allow mass balances.

Proposals for a laboratory test and a semi-field test procedure were drafted based on the cited documents and experiences from the project, and were discussed with experts from EU competent authorities, research and testing institutes, and industry.

A semi-analytical model for the mathematical processing of laboratory leaching data was developed during a previous UBA research project (Uhlig and Baldauf in Schoknecht et al. 2012). It was intended to improve this model during the current project and to check whether this approach is also applicable for leaching experiments under natural weathering conditions. This required detailed mathematical investigations on the influence of parameters that are effective under outdoor conditions on leaching processes performed by QuoData GmbH.

Leaching of biocides from facade coatings

Recent research on leaching of biocides from materials was mainly directed to facade coatings. A number of research activities were initiated by reports that active substances migrate from facades into surface waters (Burkhardt et al. 2011) and the fact, that large surface areas can be affected. Leaching processes of active substances from façade coatings were investigated by laboratory tests (Schoknecht et al. 2009) and under natural weather conditions (Burkhardt et al. 2012). A laboratory leaching test (EN 16105:2011) was developed for coatings, and its reliability proven by an inter-laboratory comparison (Schoknecht et al. 2013). Styszko et al. (2014) and Bollmann et al. (2015) compared biocide partitioning between water and solid phase for different active substances and binders to explain leachability on the basis of chemical properties of active substances and matrix components. As a consequence of increasing knowledge on leaching of active substances, industry introduced microencapsulated active substances into coatings with the intention to avoid unnecessary high concentrations of active substances in water films on coatings surfaces at the beginning of service life and increase the stability of active substances in coatings. Experiments reported by Burkhardt and Vonbank (2011) and Breuer et al. (2012) proved this effect. In addition, models were developed to estimate actual exposure of facades (Blocken et al. 2013) and buildings in urban environments (Coutu et al. 2013) towards driving rain. Coutu et al. (2012) also tried to model leaching of biocides from facades on city-scale. Bollmann et al. (2014) described the dynamics of biocide emissions from buildings in a suburban storm water catchment in Denmark. Bester et al. (2014) report on investigations on the mobility of active substances in coating materials, semi-field experiments on renders as well as observations in storm water sewers in a Danish settlement and surface waters from a number of sites in the Greater Copenhagen area. This research was funded by the Danish EPA to support the implementation of European biocides regulations. Current knowledge on leaching from facades was summarised by Schoknecht and Bagda (2014).

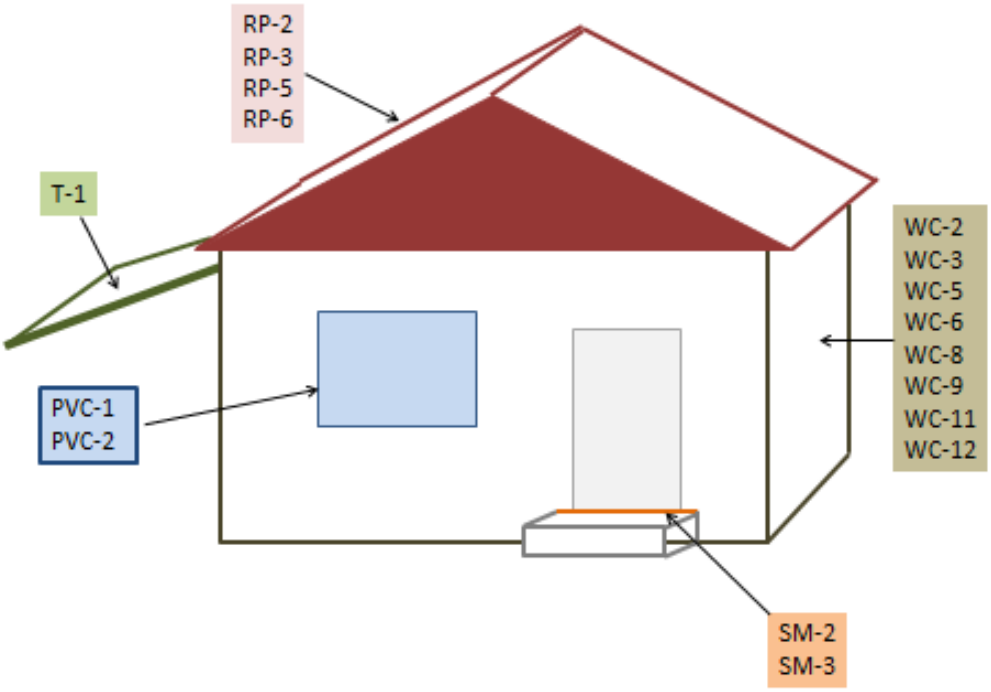
2. Selection of active substances and treated materials

It was intended to investigate treated articles that

- contain active substances for product types PT 7, PT 9 or PT 10, preferably substances to be used in more than one product type,
- contain active substances from different chemical groups that possess different water solubility and lipophilic properties, expressed as octanol-water partition coefficients (Kow),
- represent basic materials of different chemical composition
- are applied to either large or small surface areas that are exposed to precipitation to different extent.

Figure 1 illustrates possible applications of the selected treated articles. Diuron, OIT and terbutryn were chosen to represent active substances with different properties (see Annex I). However, these substances are not intended to be used in all of the selected materials. Therefore, DCOIT, carbendazim and zinc pyrithione were included in the test programme. Wood coatings containing IPBC, dichlofluanid and tolylfluanid were included to cover additional active substances used in commercial products.

Figure 1: Example of applications of the investigated treated articles



All treated articles were thankworthy provided by manufacturers (see overview in Table 1). Most articles were provided as commercially available. Some of the commercial paints contain microencapsulated active substances. A mixture of selected active substances was added to four different biocide-free, commercial paints at concentrations that are commonly used in commercial products. The corresponding commercial paints were also provided. Samples of the sealing tapes and the textile were produced for this project by the manufacturers according to common industrial procedures.

Table 1: Treated articles included in the test programme

Treated article		Basic material	Active Substances
Type	**Code**		
Wood coating	WC-1	oil based wood varnish, brown	None
	WC-2	oil based wood varnish, brown	Dichlofluanid
	WC-3	oil based wood varnish, brown	Tolylfluanid
	WC-4	dispersion of acrylate and alkyd resin, brown	None
	WC-5	dispersion of acrylate and alkyd resin, brown	IPBC and OIT
	WC-6	dispersion of acrylate and alkyd resin, brown	IPBC
	WC-7	acrylate-based, water-dilutable, white	None
	WC-8*	acrylate-based, water-dilutable, white	0.1 % diuron, 0.053 % OIT, 0.1 % terbutryn
	WC-9	acrylate-based, water-dilutable, white	OIT, terbutryn, ZnP (MC)
	WC-10	water-dilutable polymer dispersion, white	None
	WC-11*	water-dilutable polymer dispersion, white	0.1 % diuron, 0.05 % OIT, 0.1 % terbutryn
	WC-12	water-dilutable polymer dispersion, white	carbendazim, OIT, terbutryn (MC)
Roof paint	RP-1	acrylate-based, water-dilutable, black	None
	RP-2*	acrylate-based, water-dilutable, black	0.053 % OIT, 0.1 % terbutryn
	RP-3	acrylate-based, water-dilutable, black	OIT, terbutryn, ZnP (MC)
	RP-4	acrylate-based, water-dilutable, red	None
	RP-5*	acrylate-based, water-dilutable, red	0.05 % OIT, 0.1 % terbutryn
	RP-6	acrylate-based, water-dilutable, red	OIT, terbutryn, ZnP (MC)
Awning cloth	T-1	impregnated synthetic textile, green	carbendazim, ZnP
Sealing tape for window frames	PVC-1-B	polyvinyl chloride (PVC, tape), grey	OIT
	PVC-2-B	polyvinyl chloride (PVC, tape), grey	DCOIT
Sealing mass	SM-2	silicone, transparent	Carbendazim
	SM-3	silicone, transparent	Carbendazim

*A mixture of active substances was added to biocide-free commercial paints to obtain WC-8, WC-11, RP-2 and RP-5. The basic formulation is the same in WC-1 to WC-3, WC-4 to WC-6, WC-7 to WC-9, WC-10 to WC-12, RP-1 to RP-3 and RP-4 to RP-6, respectively; MC: microcapsules.

3. Methods

3.1 Laboratory experiments

3.1.1 Preparation of test specimens

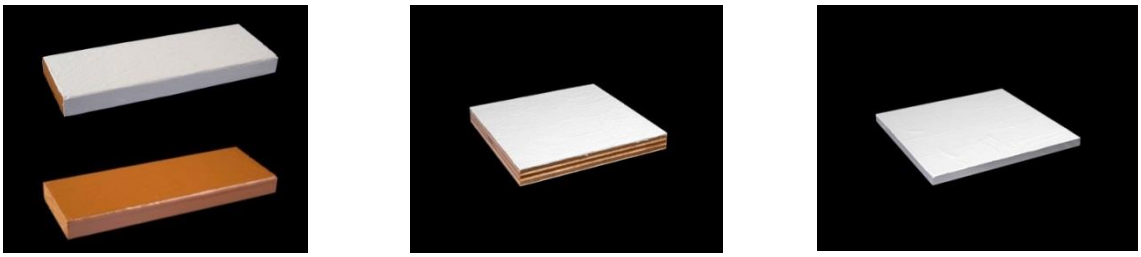
3.1.1.1 Wood coatings

Wood coatings (paints) were applied to different substrates, i.e.:

- Pine sapwood (*Pinus sylvestris*), 11 × 4 × 1 cm³, longitudinal edges rounded to avoid rupture of paint films on sharp edges, end grain sealed using a 1 : 1 mixture of Sigillon I and II
- Birch plywood (*Betula* spec.), 10 × 10 × 1 cm³, side faces sealed using a 1 : 1 mixture of Sigillon I and II
- Glass 10 × 10 × 0.5 cm³, one of the 10 × 10 cm² surfaces was roughened to improve adhesion of paints

Pine sapwood is commonly used for laboratory experiments with wood preservatives, especially for biological tests on the efficacy of wood preservatives, since wood preservatives can be well distributed into this substrate. Boards of birch plywood were used for the field experiments. Parallel tests with this substrate were performed to indicate possible differences between these wood species. Tests of wood coatings on glass specimens were included to avoid chemical interaction with wood matrix components, water uptake of wood and transport of substances into wood.

Figure 2: Wood coatings applied on pine sapwood, birch plywood and glass



Left: pine sapwood, middle: birch plywood, right: glass

3.1.1.2 Roof paints

Roof paints were applied to different substrates, i.e.:

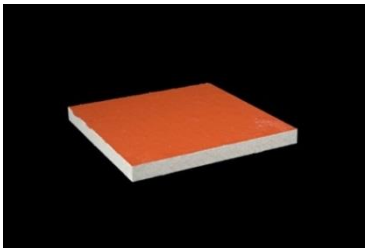
- Fibre cement, 10 × 10 × 0.8 cm³, side faces sealed using a 1 : 1 mixture of Sigillon I and II
- Glass 10 × 10 × 0.5 cm³, one of the 10 × 10 cm² surfaces was roughened to improve adhesion of paints

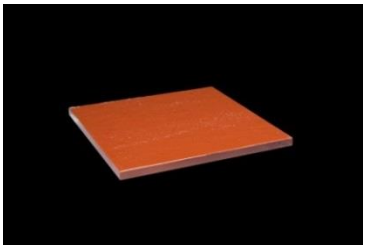
Tests of roof paints on glass specimens were included to avoid chemical changes caused by fibre cement matrix (e.g. increase of pH), water uptake of fibre cement and transport of substances into the fibre cement matrix.

Wood coatings and roof paints were applied according to the manufacturer's instructions. This refers to the amount of paint per surface area, application of ground coats and the duration of drying phases. The paints dried under laboratory conditions, and the test specimens were stored for a period of three to four days at 20 ± 2 °C and 65 ± 5 % relative humidity until the leaching tests were started.

Test specimens were also prepared with corresponding biocide-free paints, if available, to check for contamination of the eluates and matrix effects during the quantification of active substances.

Figure 3: Roof paints applied on fibre cement and glass



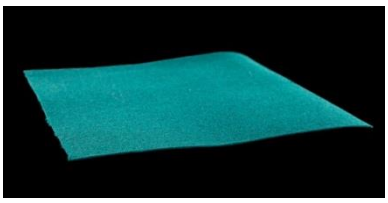


Left: fibre cement, right: glass

3.1.1.3 Textile

Test specimens of 10 × 10 cm² were cut from the original textile sample.

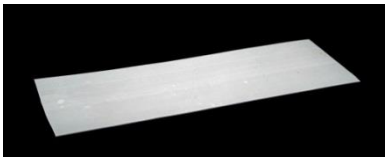
Figure 4: Textile test specimen



3.1.1.4 Sealing tape

Strips of 12.5 cm length were cut from the original tape to obtain test specimens of 12.5 × 4 × 0.2 cm³.

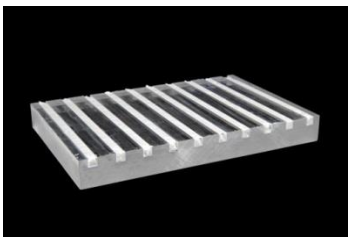
Figure 5: Test specimen of PVC sealing tape



3.1.1.5 Sealing mass

Sealing masses (joint sealers) were applied to joints of 5 mm × 5 mm cross sections of a custom-built shaped part of acryl glass to obtain a total area of 50 cm² exposed surface.

Figure 6: Joints on a shaped part filled with sealing mass



3.1.2 Pretreatment of test specimens

Some textile test specimens were exposed to UV-A light in an accelerated weathering machine (QUV, Pausch Messtechnik) for seven days with six cycles of 3 h irradiation and 1 h of darkness per day to investigate the influence of UV on leaching of carbendazim and zinc pyrithione. The procedure results in a dosage of 22 J/m² (irradiance

48.6 W/m², i.e. 0.89 W/m² at 340 nm) that was applied prior to the leaching experiments. UV-A lamps produce a light spectrum similar to the conditions at noon. The temperature within the QUV was 40 - 45 °C. In deviation from the original protocol described in EN 152, the specimens were not wetted during the UV exposure. The leaching experiments were started directly after finishing UV exposure.

3.1.3 Leaching test

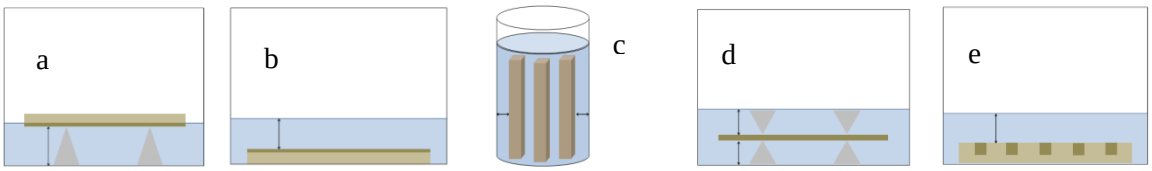
3.1.3.1 Intermittent water contact

The laboratory leaching tests followed the main parameters defined in EN 16105. Test specimens were arranged either in polystyrene containers or in beaker glasses and covered with water at a defined ratio of 25 l/m² water volume per area of exposed surface as illustrated in Figure 7. The minimum water layer above or below the exposed surface was 1 cm. The test assemblies were covered to avoid evaporation. It was checked that the target substances do not adhere to the polystyrene containers during the immersion periods. Control experiments were performed with the corresponding biocide-free product, if available.

Immersion cycles were defined to consist of 1 h immersion, 4 h drying and 1 h immersion. Nine immersion cycles were performed within three weeks, i.e. experiments were started on Monday, and immersion cycles were performed every Monday, Wednesday and Friday. The tests were performed at 20 ± 2 °C. The test specimens dried at relative humidity of 65 ± 5 % between the immersion events. The eluates of the two immersion events of each immersion cycle were merged and analysed. Masses of the test specimens were recorded before and after each immersion event to measure water uptake.

Some experiments were extended to eighteen immersion cycles within six weeks, and in some cases the eluates from the first two immersion cycles were analysed every ten minutes (see Table A II-1).

Figure 7: Variations of test assemblies applied



a) test specimens of fibre cement, b) test specimens of glass and birch plywood, c) test specimens of pine sapwood, d) test specimens from textile and sealing tape, d) shaped part containing sealing mass; dark: treated articles, bright: substrates

3.1.3.2 Permanent water contact

The PVC sealing tape containing DCOIT was exposed to permanent water contact according to CEN/TS 16637-2. Test stripes were arranged in polystyrene containers and covered with water at a defined ratio of 25 l/m² water volume per area of exposed surface as illustrated in Figure 7d. The minimum water layer above or below the exposed surface was 1 cm. The test assemblies were covered to avoid evaporation. Water was exchanged and analysed after 6 h, 1 d, 2.25 d, 4 d, 9 d, 16 d, 36 d and 64 d.

An overview of all laboratory leaching experiments is given in Annex II.

3.1.4 Analysis of eluates

Eluates were analysed for pH and target substances, and in some cases also for total organic carbon (TOC) and zinc.

Target substances were analysed by liquid chromatography of the eluates without preconcentration. External standards were used for calibration. See Table 2 for details.

Eluates from control experiments on biocide-free products were used to check for contamination of eluates and matrix influence on sensitivity of mass spectrometry.

Table 2: Liquid chromatography of target substances in eluates

	UHPLC			LC/MS		
Equipment	Agilent 1290 Infinity including DAD			Agilent 1100 coupled to a 6130 Quadrupole LC/MS		
Column	Luna 3 µm C18(2) 100 Å, 2 × 50 mm and guard column (Phenomenex)			Luna 3 µm C18(2) 100 Å, 2 × 50 mm and guard column (Phenomenex)		
Temperature	35 °C			20 °C		
Flow	0.5 ml/min			0.5 ml/min		
Elution	Time	Eluent A	Eluent B	Time	Eluent A	Eluent B
		H_2O	Aceto-nitrile		H_2O + 0.2 % acetic acid	Acetonitrile + 0.2 % acetic acid
	min	[%]	[%]	min	[%]	[%]
	0 - 3	90	10	0-1	70	30
	9.5 - 10.5	25	75	3	50	50
	11	90	10	7	25	75
	12	90	10	10 - 12.5	70	30
Target substance	Signal	Calibration range	LOQ	Signal	Calibration range	
	nm	µg/l	µg/l	m/z	µg/l	
DCOIT	280	5 - 500	6	282	50 – 1000	
OIT	280	2 - 500	5	214	50 – 1000	
Carbendazim	280	3 – 1000	3	192		
Diuron	254	1 - 1000	1	233		
Terbutryn	225	2 - 250	3	242		
IPBC				282	50 – 1000	
Dichlofluanid	225	10 - 1000		-		
DMSA	225	10 - 1000		-		
Tolylfluanid	225	10 - 1000		-		
DMST	225	10 - 1000		-		

Zinc pyrithione was determined in eluates according to the procedure described under 3.1.5 for the analysis of the textile. DMSA and DMST are metabolites of dichlofluanid and tolylfluanid, respectively.

The eluates for selected experiments were analysed for TOC by catalytic combustion and non-dispersive infrared (NDIR) detection according to EN 1484:1997 using a Shimadzu TOC-VCPH-Analyzer.

Zinc was either quantified by ICP-MS iCAP Q or ICP-OES iCAP7400 Duo (Thermo Fisher Scientific).

3.1.5 Analysis of treated articles

3.1.5.1 Paints (wood coatings and roof paints)

About 1 g of the solvent-based paints (WC-1, WC-2, WC-3) was weighed, diluted 1/1000 with acetone, filtered through 0.2 µm PTFE syringe filter and analysed by the UHPLC method described under 3.1.4.

About 1 g of the wet water-based paints were applied to glass plates and dried until constant weights were obtained. The dry paints were removed from the plates and crashed using a scalpel. Dry weights were determined. 50 ml methanol was added to three parallel samples of about 0.3 g (dry weight) for each paint. Deviating from the other paints, 50 ml acetone was added to samples of WC-12. The samples were sonicated for 1 h at 40 °C (Sonorex, 100 % performance), and kept overnight at 8 °C to allow precipitation of particles. Supernatants were filtered through 0.2 µm PTFE syringe filters if necessary, diluted (methanol extracts: 1:10 with methanol; acetone extracts from WC-12: 1:20 with acetone) and analysed by the UHPLC method described under 3.1.4.

In addition, dry paints were removed from surface areas of 4 cm² of the test specimens (using a microtome if possible). 15 ml methanol were added to the particles / chips (about 100 to 200 mg) followed by ultrasonic extraction for 1 h at 40 °C (Sonorex, 100 % performance). Extracts were filtered through 0.2 µm PTFE syringe filters, diluted 1:10 with methanol and analysed by the UHPLC method described under 3.1.4. Thin blades were cut from the underlying layers of the wood test specimens. The blades were collected for the layers 0-1, 1-2 and 2-3 mm from the surface, crushed and extracted and analysed as the paint samples. The LC/MS method described under 3.1.4 was applied for samples with relatively low contents of the target substances to better differentiate between signals from target substances and matrix components.

3.1.5.2 Sealing mass

About 1 g of the sealing masses were applied to glass plates and dried for several days until constant weight was obtained. The dry films of the sealing masses were removed from the plates and crushed using a scalpel. Dry weights were determined. 50 ml acetone was added to three subsamples of about 0.3 g (air dried mass) each. The samples were sonicated for 1 h at 40 °C (Sonorex, 100 % performance), and kept overnight at 8 °C to allow precipitation of particles. Supernatants were filtered through 0.2 µm PTFE syringe filters if necessary, 1:20 diluted with acetone and analysed by the UHPLC method described under 3.1.4.

3.1.5.3 Sealing tape

Samples of the PVC sealing tape in the original state and obtained after leaching experiments were cut into strips of 1 mm width. Three subsamples of about 0.2 g were solved in 4 ml tetrahydrofuran (THF) each and sonicated for 30 min (Sonorex, 100 % performance). Afterwards, 12 ml of the HPLC eluent (acetonitrile/H_2O/THF - 38/38/24 - v/v/v) was added. The samples were kept in the fridge for 2 h to enable all PVC to precipitate. 1 ml of the supernatant were filtered through 0.45 µm PTFE syringe filters into HPLC vials and analysed according to the UHPLC method described in Table 3.

3.1.5.4 Textile

The textile was cut into strips of 1 mm width. 50 ml acetone was added to three subsamples of about 0.3 g. The samples were sonicated for 1 h at 40 °C (Sonorex, 100 % performance), and kept overnight at 8 °C to allow precipitation of particles. Supernatants were filtered through 0.45 µm PTFE filters if necessary and diluted 1:20 with acetone. Carbendazim was analysed according to the UHPLC method described under 3.14. Zink pyrithione was analysed according to the procedures described in Table 4. The extraction procedure was repeated to detect any residues that remained in the textile during the first extraction.

Table 3: Liquid chromatography of OIT and DCOIT in extracts from PVC sealing tapes

	UHPLC		
Equipment	Agilent 1290 Infinity including DAD		
Column	Luna 3 µm C18(2) 100 Å 3.6 × 75 mm and guard column (Phenomenex)		
Temperature	30 °C		
Flow	1.0 ml/min		
Elution	Time	Eluent A	Eluent B
		ACN : H_2O : THF = 38 : 38 : 24	Acetonitrile
	min	%	%
	0 - 5	100	0
	5 - 9	20	80
	10 -12	100	0
Target substance	Signal		Calibration range
	nm		mg/l
OIT	280		1-10
DCOIT	280		1-10

Table 4: Liquid chromatography of zinc pyrithione in eluates and extracts from the textile

	UHPLC		HPLC
Equipment	Agilent 1290 Infinity including DAD		Agilent 1100 Series including DAD
Column	Onyx Monolithic C18 3 x 100 mm (Phenomenex)		
Temperature	30 °C		
Flow	2.0 ml/min		
Elution	Time	Eluent A	Eluent B
		0.037 g EDTA + 0.035 g oxalic acid in 1 l H_2O, pH 4	Acetonitrile
	min	%	%
	0	85	15
	1	67.5	32.5
	2	20	80
	3	85	15
Target substance	Signal		Calibration range
	nm		mg/l
Zinc pyrithione	340		0.01 -1.0

3.1.6 Desorption of active substances from paints (wood coatings and roof paints)

Desorption of active substances was investigated for the wood coatings WC-7 and WC-8 as well as WC-10 and WC-11 and for the roof paints RP-1 and RP-2 as well as RP-4 and RP-5. Commercial products of formulated active substances were added to the biocide free paints WC-7, WC-9, RP-1 and RP-4 to obtain concentrations of 100 µg of each active substance per g wet paint. The mixtures were stirred with an ULTRA-TURRAX T 25. Additional amounts of biocide-free paints were added to these mixtures to obtain active substance concentrations of 0.3, 1, 3, 10 and 30 µg/g. The wet paints were applied on glass plates and dried until constant weight was obtained. The dried films were scraped off the glass plates and crushed to particles of about 2 mm in diameter.

Desorption experiments:

10 ml of ultrapure water were added to 6 samples á 200 mg of each of the paints containing 100 µg/g active substances. These mixtures were stirred for 1, 3, 6, 18, 24 and 28 h to determine the required contact time to obtain equilibrium (i.e. constant concentrations of active substances in the supernatant). The supernatants were filtered into vials for quantification of the active substances. Stirring for 24 h proved to be the optimum duration to obtain equilibrium for all paints investigated. Therefore stirring for 24 h was applied for the experiments using samples with different concentrations of active substances. The pH of these samples was adjusted to pH 7.3 by H_3PO_4 and NaOH. In addition, desorption experiments were performed for paints of the correspondent formulations that were prepared by manufacturers and contained active substances, i.e. WC-8, WC-11, RP-2, RP-5. The concentrations of active substances in the paint materials were compared to concentrations of active substances in the supernatants to check whether linear desorption isotherms are obtained. Since this was the case desorption constants (K_d) were calculated according to equation 1.

Equation (1): $$K_d = \frac{c_S}{c_W}$$

with

K_d Desorption constant [l/kg]
c_S Concentration of active substance in the original material [µg/kg]
c_w Concentration of active substance in the water phase [µg/l]

3.1.7 Isothermal measurement of the sorption of water vapour at solids

Sorption of water vapour was measured according to DIN 66138 using a DVS-1 System (Surface Measurement Systems).

Samples of the textile and dry paint films were investigated to compare water vapour sorption of different materials and of materials before and after leaching experiments. The materials were crushed, and subsamples of about 20 mg were used in the experiments.

3.1.8 Wettability of surfaces

Test specimens were sprayed with water. Pictures of the surfaces were taken according to defined time schedules, and the occurrence of water drops was visually examined on the basis of these series of photographs. This test was performed to compare water repellency of wood coatings and the influence of weathering on water uptake of the impregnated textile.

3.2 Field experiments

3.2.1 Preparation of test specimens

3.2.1.1 Wood coatings

Wood coatings (paints) were applied to birch plywood boards (*Betula* spec.), 76 × 74 × 1 cm³, side faces were sealed using 'Pyrotect Lack'.

3.2.1.2 Roof paints

Roof paints were applied to fibre cement boards, 76 × 74 × 1 cm³. The roof paints were also applied to the side faces.

Wood coatings and roof paints were applied according to the manufacturer's instructions. This refers to the amount of paint per surface area, application of ground coats and the duration of drying phases. The paints dried at room temperature protected from direct radiation for a period of five days until the field experiments were started.

3.2.1.3 Textile

Textile samples were fixed to wooden frames of 76 cm × 74 cm lateral lengths.

3.2.2 Experiments according to NT build 509

3.2.2.1 Installation of test specimens

Field experiments were mainly performed at the test ground of MPA Eberswalde at its headquarters in Eberswalde. One experiment was performed at a test ground about 1 km away from MPA headquarters on a crest above Eberswalde (Drachenkopf).

Test specimens were installed either vertically or horizontally directed to southwest (see Figure 8). Equipment to determine driving rain was installed besides vertically installed test specimens at both sites (see left side of Figure 8a). Two textile test specimens were installed back-to back to obtain exposure to four cardinal directions (SW / NE and NW / SE, respectively).

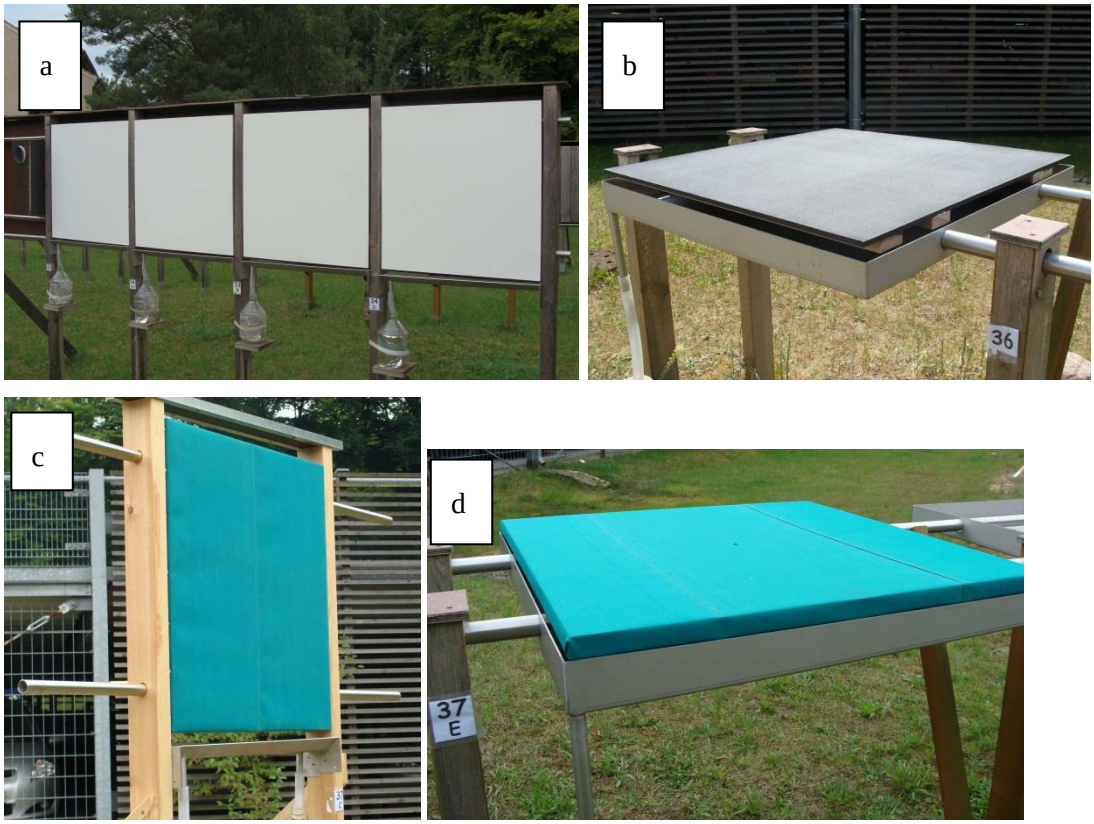
Subsequently in the project, additional experiments were started at BAM headquarters in Berlin, Unter den Eichen. Test specimens were vertically installed on the house wall of a single-storey building directed to south-southwest (see Figure 9).

Both sites belong to areas that are only moderately affected by driving rain according to DIN 4108-3.

3.2.2.2 Sampling of runoff water

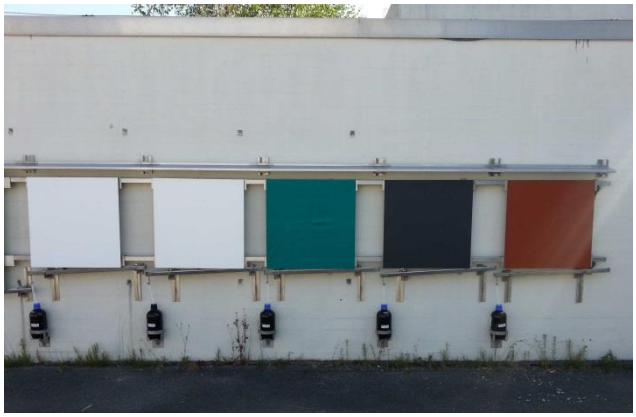
Runoff water was sampled after rain events, at minimum once a week in case of rain events during this period. Each runoff sample was analysed for the active substances during the first 4.5 to 8 months of the experiments in Eberswalde and for the whole duration of the experiments performed at BAM. Later, aliquots of the runoff samples from the experiments performed at MPA Eberswalde were stored and combined for analysis. The sampling scheme followed the specification given in NT build 509. One additional sample was analysed between the given sampling periods.

Figure 8: Test assemblies for field experiments at MPA Eberswalde



a) wood coatings on birch plywood, vertically installed, b) roof paint on fibre cement, horizontally installed, textile installed vertically (c) and horizontally (d; the bottles were covered with aluminium foil during the experiments to avoid photochemical effects

Figure 9: Test specimens at BAM



3.2.2.3 Meteorological data

Actual amounts of rain and driving rain were measured at both test sites in Eberswalde. In addition, data sets including data on temperature, global radiation, precipitation, wind velocity and wind direction were kindly provided by the Faculty of Wood Science and Technology (Hochschule für Nachhaltige Entwicklung Eberswalde).

Meteorological data collected by a weather station in the immediate vicinity of the BAM test site were provided by the Deutscher Wetterdienst Potsdam. The data sets include temperature, precipitation, relative humidity, wind velocity and

wind direction. Data on global radiation were provided by the Institute of Meteorology of the Free University Berlin (FU) from the weather station 'Botanischer Garten' located about 2.5 km away from the BAM test site.

An overview of the field experiments is given in Annex III.

3.2.3 Analysis of runoff samples

The target substances in the runoff samples from the BAM experiments were analysed according to the UHPLC method that was applied for the eluates from the laboratory tests (see Table 2 under 3.1.4). The pH values and conductivity were determined if sufficient volume of the samples was available.

The target substances in the runoff samples from the MPA experiments were analysed by liquid chromatography (LC-MS/MS) after filtration (0.25 µm). Samples were partially diluted. External standards were used for calibration (see Table 5 for details).

Table 5: Liquid chromatography of target substances in runoff samples

	LC-MS/MS			
Equipment	Agilent 1200 HPLC Liquid Chromatography System 320 MS/MS Triple Quadropol Agilent Technologies			
Column	Phenomenex C18 aqua, 3 µm and 125 Å, 150 mm * 2 mm			
Temperature	30 °C			
Flow	0.2 ml/min			
Elution	Time		Eluent A H_2O + 0.1% formic acid	Eluent B Acetonitrile + 0.1% formic acid
	min		[%]	[%]
	0.0		99.5	0.5
	0.5		99.5	0.5
	10.0		0.5	99.5
	20.0		0.5	99.5
Target substance	Signal (m/z)		Calibration range	LOQ
	Precursor	Product	µg/l	µg/l
OIT (Quantifier)	214.0	57.1	0.5 – 250.0	1.0
OIT (Qualifier)	214.0	101.9		
Carbendazim (Quantifier)	192.0	160.0	1.0 – 250.0	2.0
Carbendazim (Qualifier)	192.0	132.0		
Diuron (Quantifier)	233.0	72.0	0.5 – 250.0	1.0
Diuron (Qualifier)	233.0	160.0		
Terbutryn (Quantifier)	242.0	186.0	0.25 – 250.0	0.3
Terbutryn (Qualifier)	242.0	90.9		

4. Results and Discussion

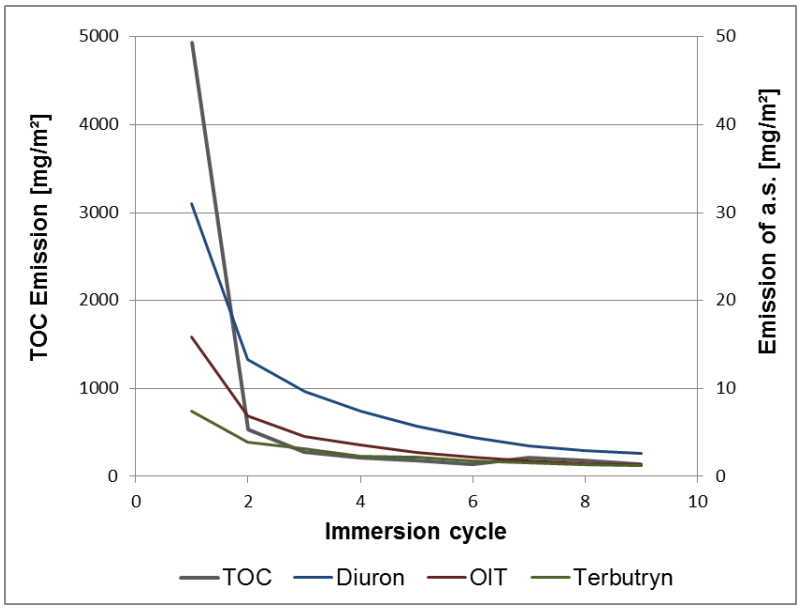
4.1 Laboratory experiments

4.1.1 Experiments according to EN 16105

Emissions during immersion cycles decreased with the number of immersion cycles for all treated articles and active substances tested. Typical emission curves were obtained as demonstrated in Figure 10 for the wood coating WC-11 as an example. The complete data set obtained in the laboratory tests is given in Annex II. Cumulative emissions are summarised in Table A II-3. Figures A II-1 to A II-20 demonstrate emissions during immersion cycles and cumulative emission curves.

The amount of organic carbon was considerably higher than the amount of active substances analysed in the eluates from all investigated treated articles (see Figure 10 for an example, additional data are presented in Table A II-3). This does not only indicate a number of additional substances in the eluates but can also be a sign for possible changes of the chemical composition of the material as well as the leachate. It has to be assumed that chemical processes influence the leaching process.

Figure 10: Emissions per immersion cycle of TOC and active substances from WC-11

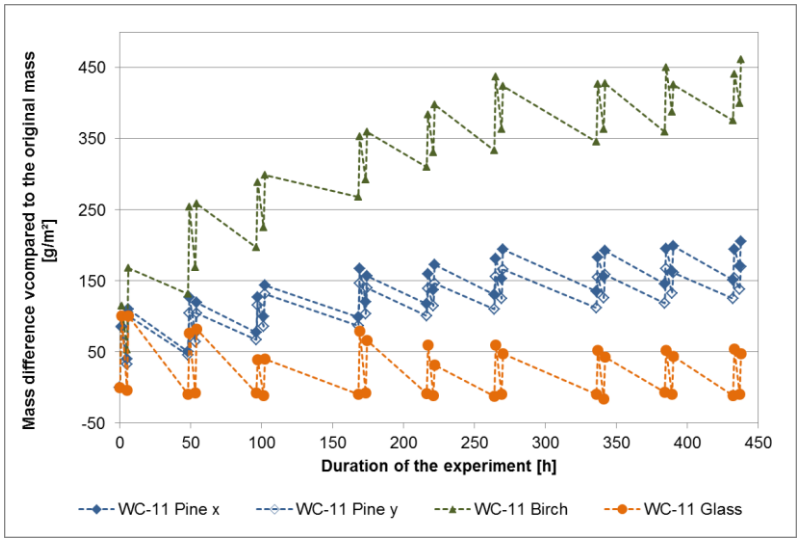


The investigated treated articles absorbed water during the immersion cycles. The substrates for wood coatings and roof paints - despite of glass - also absorbed water. Test specimens of birch plywood took up more water than test specimens prepared from pine sapwood. Uptake of water by PVC was mainly observed during long term exposure. Water uptake was increasing with the number of immersion cycles at the beginning of the leaching experiment on the impregnated textile. It is assumed that the swellability of the impregnated textile was increased.

An example for water uptake of test specimens during the leaching test is shown in Figure 11. The data for all treated articles are summarised in Table A II-4 in Annex II.

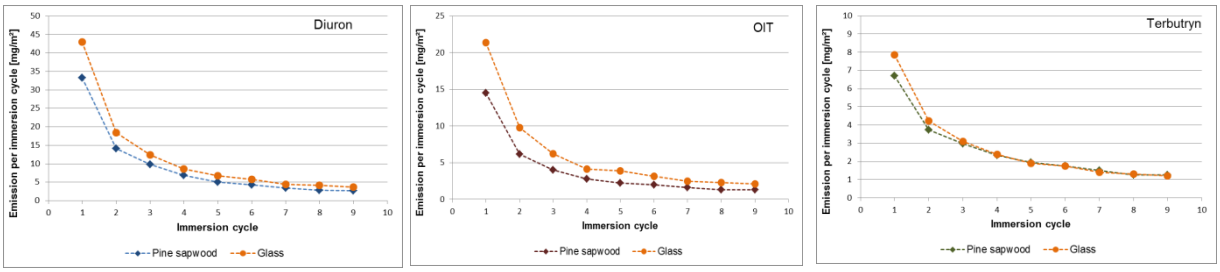
Analysis of test specimens of *Pinus silvestris* demonstrated that uptake of water caused transport of active substances into the substrate (see Table 6). This affected the amount of leached substances from wood coatings on wood compared to glass, i.e. the amounts of leached substances were slightly higher if transport to the substrate was impossible in case of glass (see Figure 12 and Figures A II-9 to A II-12 in Annex II).

Figure 11: Water uptake of test specimens during leaching experiments



Mass differences compared to the original mass observed during leaching experiments using WC-11 on pine sapwood ('Pine x' and 'Pine y'), birch plywood ('Birch') and glass ('Glass').

Figure 12: Emission curves for active substances from WC-11 on pine sapwood and glass

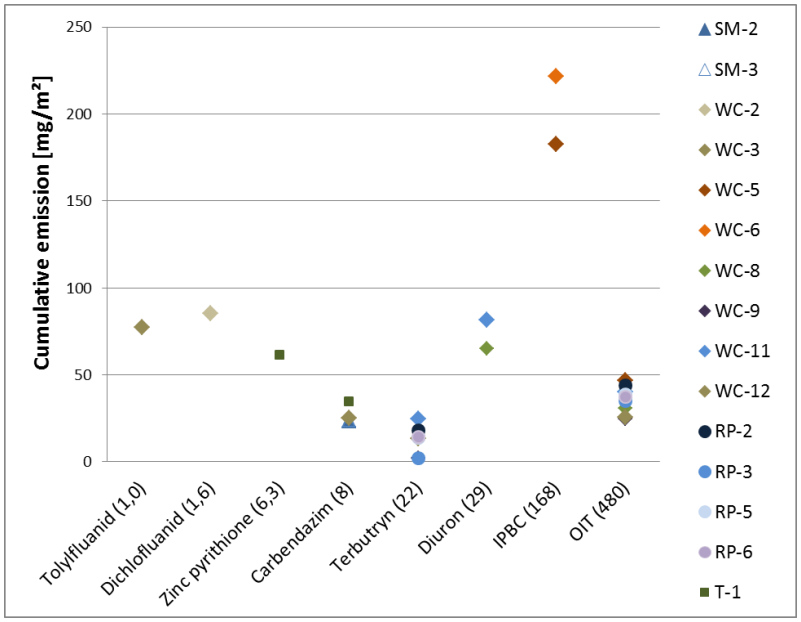


Unexpectedly, the amounts of active substances leached from roof paints on fibre cement were higher than from roof paint on glass, although water was also absorbed by test specimens of fibre cement, i.e. transport of active substances into the substrate was also possible for these test specimens. It is assumed that higher emission from fibre cement is caused by relatively high pH of eluates from this substrate. High pH values have been described to increase leaching of organic substances in general, and this may enhance leaching of active substances due to co-elution with other organic substances.

The pH of eluates from coated wood depends on the coating and ranged between about pH 5 and pH 7, whereas the pH of the eluates from coated fibre cement ranged between about 7.5 and pH 8 at the beginning of the experiments. Later, the pH tends to be in the range of the pH of the eluent (deionised water). The sealing masses, PVC sealing tapes and impregnated textile did not have big influence on the pH of the eluates. The ranges of pH-values measured in the eluates are summarised in Annex II, Table A II-5.

Total amounts of leached substances during the whole leaching tests were in similar ranges for the investigated active substances for different matrices, e.g. carbendazim from a silicone sealing mass, an impregnated synthetic textile and a wood coating. Data are summerised in Figure 13 and Table A II-3 in Annex II.

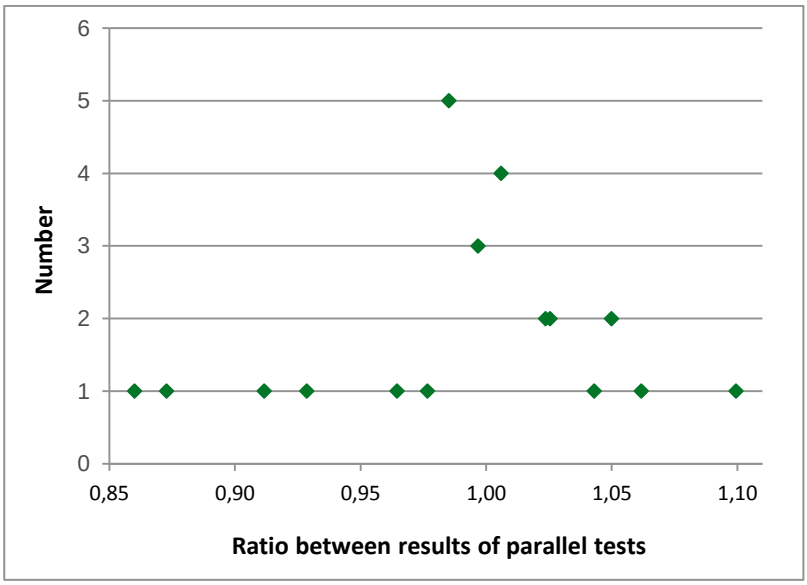
Figure 13: Summary of total emissions during the leaching experiments



Summary of total emissions of active substances from different materials during the nine immersion cycles of experiments according to EN 16105. Water solubility of the substances is given in brackets after its name. Product codes are explained in Table 1 in the Materials section.

Data from parallel tests within one test series and data from different test series were used to examine repeatability of laboratory experiments according to the EN 16105 procedure. The ratios of cumulative emissions were between 0.95 and 1.05 in 21 out of 27 data series from parallel tests (see Figure 14). Higher deviations between parallel tests were observed in case of low emissions and for unstable substances.

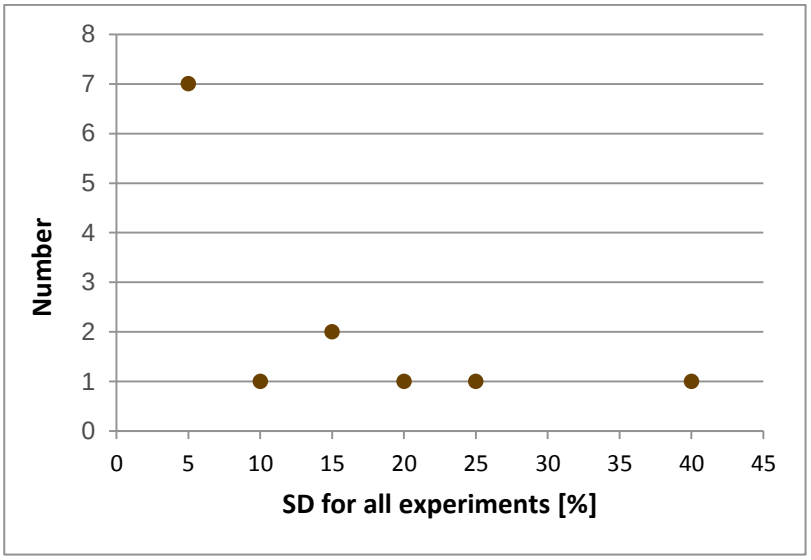
Figure 14: Repeatability of parallel tests



The graph represents the number of test results that correspond to a certain ratio between cumulative emissions during nine immersion cycles in parallel tests on all investigated active substances and treated articles.

Relative standard deviations between cumulative emissions in repeated experiments in one laboratory were below 15 % for 10 out of 13 data series (see Figure 15). Again, higher values were observed in case of low emissions and for unstable substances.

Figure 15: Standard deviations from repeated experiments

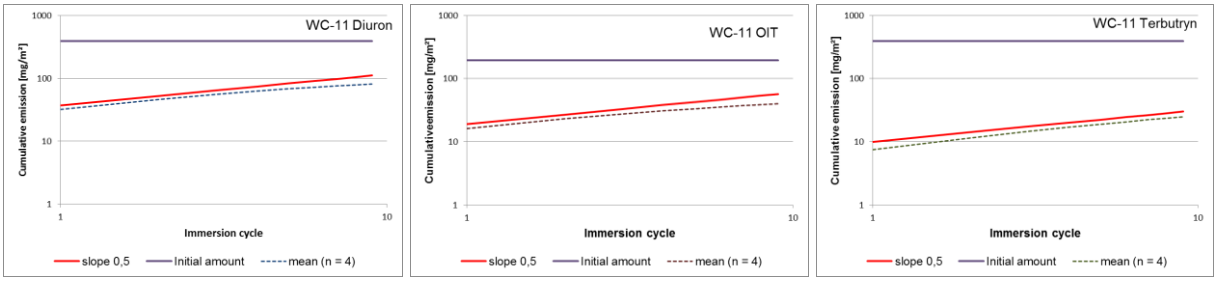


The graph represents the number of test results that correspond to a certain range of standard deviation (0 % to 5 %, 5 % to 10 % and so on) between cumulative emissions during nine immersion cycles in repeated experiments within one laboratory on the treated articles that were investigated in repeated test series.

Mechanisms that control the leaching process during the laboratory experiments were investigated using double logarithmic graphs of either cumulative emissions or emissions during immersion cycles versus the number of immersion cycles. Immersion cycles represent certain duration of water contact during the test, i.e. time. Lines with a slope of 0.5 indicate diffusion controlled processes in the graphs for cumulative emissions since diffusion is proportional to the square root of time (i.e. exponent 0.5). This exponent becomes factor 0.5 in logarithmic functions. In the double logarithmic graphs for decreasing emissions during immersion cycles diffusion is indicated by a line with a slope of -0.5, accordingly.

Diffusion control appears important for many of the investigated active substances and treated articles (see Figure 16 and Annex II, Figures A II-1 to A II-6 and A II-9 to A II-20).

Figure 16: Cumulative emission of active substances from WC-11 in double logarithmic graphs



Lines with a slope of 0.5 indicate diffusion-controlled leaching.

Decrease of the line for cumulative emissions during later periods of the experiments in double logarithmic graphs indicates depletion of active substances that are available for leaching. This was observed for diuron and OIT emissions from several wood coatings, and in extended experiments also for terbutryn. It has to be noted that depletion starts far below the level of the initial amount of active substances.

Leaching processes can also be controlled by dissolution of the target substances on the surface of materials. In this case leached amounts are directly proportional to time, which is indicated by lines with a slope of 1 in double logarithmic graphs for cumulative results. Leaching curves for carbendazim from T-1 and OIT from PVC-1 run parallel to lines with a slope of 1. During extended experiments the curves start to run parallel to lines with a slope of 0.5. Dissolution

controlled leaching is also indicated for other treated articles at the beginning of the leaching experiments, e.g. OIT from the wood coatings WC-5 and from PVC sealing tape and IPBC from the wood coatings WC-5 and WC-6.

A semi-analytical model that describes leaching processes under laboratory conditions was developed on the basis of the test results and is explained in Chapter 5.1.

Special cases

- Fast transformation

Some active substances can be degraded either during the experiments or during storage of eluates before analysis. Examples are dichlofluanid, tolylfluanid and IPBC. Transformation products have to be quantified, and the results both for the active substance and transformation products have to be reported in these cases. DMSA as a metabolite of dichlofluanid and DMST as a metabolite of tolylfluanid were quantified in addition to the active substances to investigate leaching from wood coatings.

- Difficult analysis and fast transformation

Zinc pyrithione was observed to be instable. In addition, quantification was impossible using the available analytical method in a few paints and eluates from the paints. Eluates from textiles had to be analysed immediately to obtain results. Analysis of zinc is not suitable to replace analysis of zinc pyrithione because of additional sources of zinc in the treated articles.

- Low concentrations of target substances in eluates

Analysis has to be performed with more sensitive methods, e.g. for DCOIT.

An alternative laboratory leaching test that has been developed to investigate leaching of substances from construction products, i.e. CEN/TS 16637-2:2014, was performed with PVC sealing tape containing DCOIT since longer duration of water contact is assumed to increase the amounts of DCOIT leached and this way also the concentrations that have to be estimated (see chapter 4.1.2 below).

4.1.2 Experiments according to CEN/TS 16637-2:2014 on PVC sealing tape

A dynamic surface leaching test (DSLT) was developed for monolithic construction products by CEN/TC 351. The test protocol includes permanent contact of the material to water for 64 days. The leachate is changed and analysed for the target substances according to a defined time schedule that includes immersion periods that increase from 6 h up to 36 d during the experiment.

It was observed that DCOIT is not stable in the leachates from PVC-2, but degraded within two to three days. However, low emissions were confirmed by analysis of DCOIT in the PVC sealing tape before and after the leaching test (see Figures A II-21 to A II-23 in Annex II).

4.1.3 Concentration of active substances in treated articles

Analysis of active substances confirmed that the concentrations were in the range given in the recipes in most cases (see Table A II-2 in Annex II).

The results obtained for diuron concentrations in wood coating materials were lower than expected. This observation is probably caused by matrix effects of additional substances in the products. It was impossible to confirm the content of zinc pyrithione in most cases with the available analytical method. The amounts of zinc determined in WC-9 and RP-3 were in the range of the amount corresponding to the expected amount of zinc pyrithione at minimum. The contents of carbendazim and zinc pyrithione in T-1 were lower than expected from the recipe. This observation was confirmed by a second laboratory. It is not known if these substances are stable during the industrial impregnation procedure. It has to be considered that analytical methods could not be optimised to determine the content of active substances in the treated article within this project.

A part of the test specimens was analysed for the active substances after the leaching experiments. The wood coatings and the substrate (pine sapwood) were analysed for experiments on WC-8 and WC-11. Only the coating was analysed for experiments on RP-2 since it was impossible to cut samples from the fibre cement. The tests specimens from the textile were analysed as such.

Summation of the residual contents and the amounts determined in the eluates indicates gaps in the mass balances for the active substances in the investigated treated articles (see Table 6).

Table 6: Mass balance of active substances in test specimens and eluates from leaching tests

Treated article	Active substance	n	Residual content		Content in eluates	Gap
			Total	In wood*		
			%	%	%	%
WC-8	Diuron	2	58; 59	3	27	14 - 15
	OIT	2	60; 68	16	21	11 - 19
	Terbutryn	2	94; 109	1.0	5	
WC-11	Diuron	2	47; 59	1	21	20 - 32
	OIT	2	38; 59	7	18	23 - 44
	Terbutryn	2	39; 59	0.4	6	35 - 55
RP-2	OIT	2	11; 27		14	59 - 75
	Terbutryn	2	52; 73		3	24 - 45
T-1	Carbendazim	4	75 +/- 1		5	20
	Zinc pyrithione	4	86 +/- 4		4	10

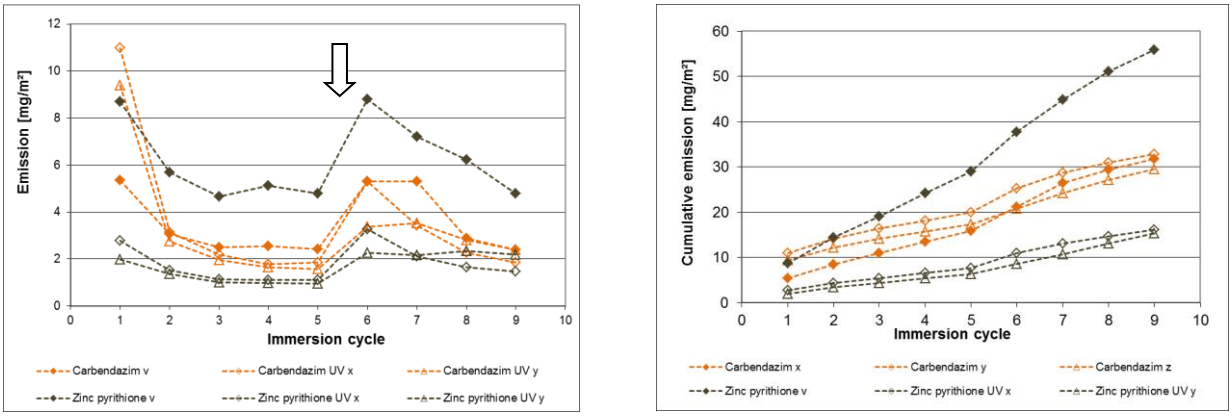
The data for WC-8, WC-11 and RP-2 are related to the recipes, and the data for T-1 are related to the analysed content of active substance.

4.1.4 Effect of UV radiation on leaching from the textile

The effext of UV radiation on leaching of active substances was investigated to explain unexpected high emissions of carbendazim from the textile under field conditions compared to laboratory tests. UV exposure in an accelerated weathering machine had different effects on the amounts of carbendazim and zinc pyrithione in the eluates. The amount of carbendazim in the eluates was enhanced at the beginning of the experiment, while the amount of zinc pyrithione was diminished during the whole experiment compared to test specimens that were not exposed to UV radiation (see Figure 17). Lower amounts of zinc pyrithione were probably caused by degradation of this substance, while damage of the textile impregnation is assumed to cause the increased amounts of carbendazim.

Carbendazim was stable towards the same kind of UV exposure in former experiments on façade paints and renders, whereas other active substances, i.e. cybutryn (Irgarol 1051), DCOIT, diuron, IPBC, isoproturon, OIT and terbutryn were sensitive to this treatment (Schoknecht et al. 2009).

Figure 17: Leaching of carbendazim and zinc pyrithione from the textile T-1 without and after exposure to UV radiation

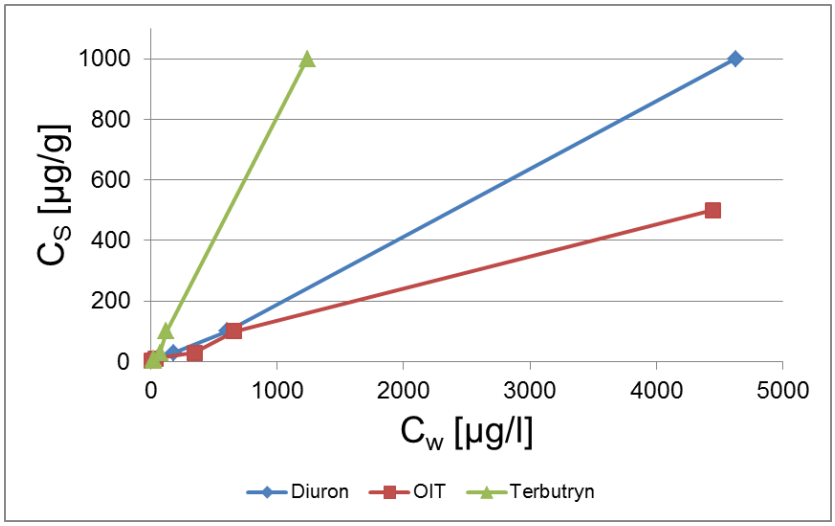


The water was removed, but the test assemblies remained covered after immersion cycle 5. The test specimens stayed wet, and this caused an increase of leached active substances during the following immersion cycles.

4.1.5 Desorption of active substances from paints

Desorption of active substances from solid matter into the water phase is part of leaching processes. The equilibrium of the distribution of a substance between solid matter and water phase depends on its water solubility and the chemical composition of the material, i.e. lipophilic properties and the availability of binding sites. The distribution between solid matter and water phase was investigated for a range of concentrations of the target substances in the treated articles. The slopes of the graphs represent desorption constants (K_d) if the relation between the concentrations of the substances in solid matter (c_S) and the water phase (c_W) is linear (see Figure 18 and Table 7).

Figure 18: Desorption isotherms of active substances from WC-10 and WC-11



Decreasing K_d-values indicate increased tendency of a substance to move into the water phase. The desorption experiments using different paints yielded highest K_d-values for terbutryn that differed between the investigated products. Differences between products were also observed for diuron, the K_d-values of OIT differed only slightly. Styszko et al. (2014) reported somewhat lower K_d-values for diuron from similar experiments with acrylic and silicone modified renders.

It was checked whether emissions observed in the leaching experiments correlate with desorption constants (see Table 7). Generally, negative correlation of -0.90 was observed for the whole set of data. Correlation was strong for active

substances from the same matrix, i.e. experiments using either WC-7 and WC-8, or WC-10 and WC-11. However, no correlation between K_d-values and emissions was observed if either OIT or terbutryn originate from different paints. Despite of the limited amount of data, there seem to be additional controlling parameters for leaching from coatings of the investigated paints besides the factors that control desorption of the target substances.

Table 7: Relation between results of desorption and leaching experiments

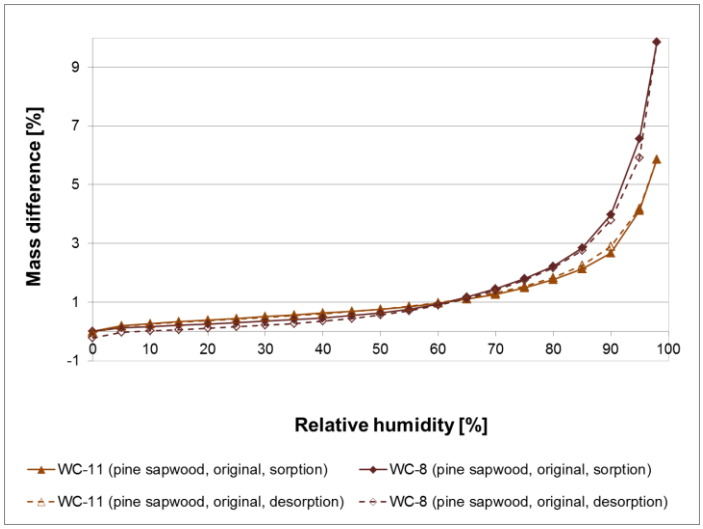
Paint	Active substance	K_d l/kg	R^2	Emission during laboratory leaching experiments %
WC-7/8	Diuron	123	0.997	26.2
	OIT	124	0.984	23.4
	Terbutryn	1139	0.998	5.4
WC-10/11	Diuron	215	0.999	20.9
	OIT	113	0.996	20.7
	Terbutryn	805	0.999	6.3
RP-1/2	OIT	121	1.000	14.8
	Terbutryn	887	0.993	3.3
RP-4/5	OIT	102	0.994	18.5
Correlation coefficient between K_d-values and emission		All data		-0.90
		WC-7/8		-0.99
		WC-10/11		-0.99
		OIT		0.16
		Terbutryn		-0.01

*Correlation between desorption constants (K_d) and emission during leaching experiments according to EN 16105 for active substances from different wood coatings and roof paints. R^2 refers to the linear regression of the desorption isotherms.

4.1.6 Water vapour sorption of treated articles

Water vapour sorption experiments indicate that the investigated materials (WC-8, WC-11, RP-2, RP-5 and T-1) take up water vapour at relative humidity commonly observed under outdoor conditions (see Table A II-6 and Figures A II-24 to 29 in Annex II). Water vapour sorption curves differed between products (see Figure 19 and Table A II-6 in Annex II), and changed if the materials were exposed to either laboratory leaching tests or weathering. The ability of materials to take up liquid water is not necessarily correlated to the ability to take up water vapour. However, the ability to take up water decreased during the leaching experiment using WC-11, while it increased for the impregnated textile. The same tendency was observed for the ability to take up water vapour (see Table A II-7). It has to be considered that the coatings and the textile were crushed, i.e. the surface area was enlarged for the water vapour sorption experiments. As a consequence, higher amounts of water can be sorbed, and longer periods of time are required to obtain equilibrium masses if compared to water vapour sorption of undisturbed materials. However, these observations indicate that air humidity at ranges that are commonly observed under outdoor conditions can contribute to the mobilisation of substances within materials.

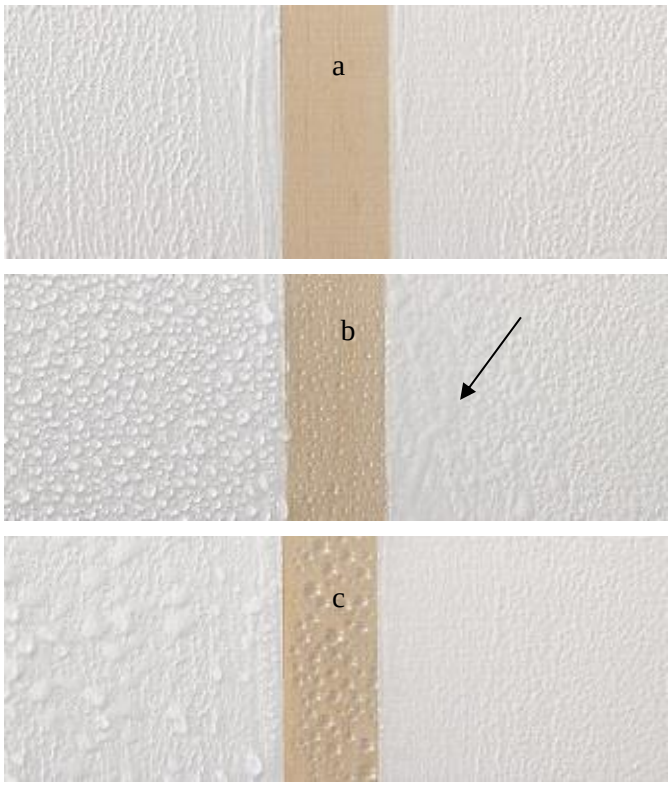
Figure 19: Water sorption curves for crushed samples from coatings of WC-8 and WC-11



4.1.7 Wettability of surfaces

Water drops stayed for longer periods of time on surfaces of the wood coating WC-8 compared to WC-11 in a laboratory test (see Figure 20) as well as on the test specimens installed in the MPA and BAM test sites. This means that the surfaces of WC-8 were exposed to water contact for longer periods of time than those of WC-11 in the field experiments.

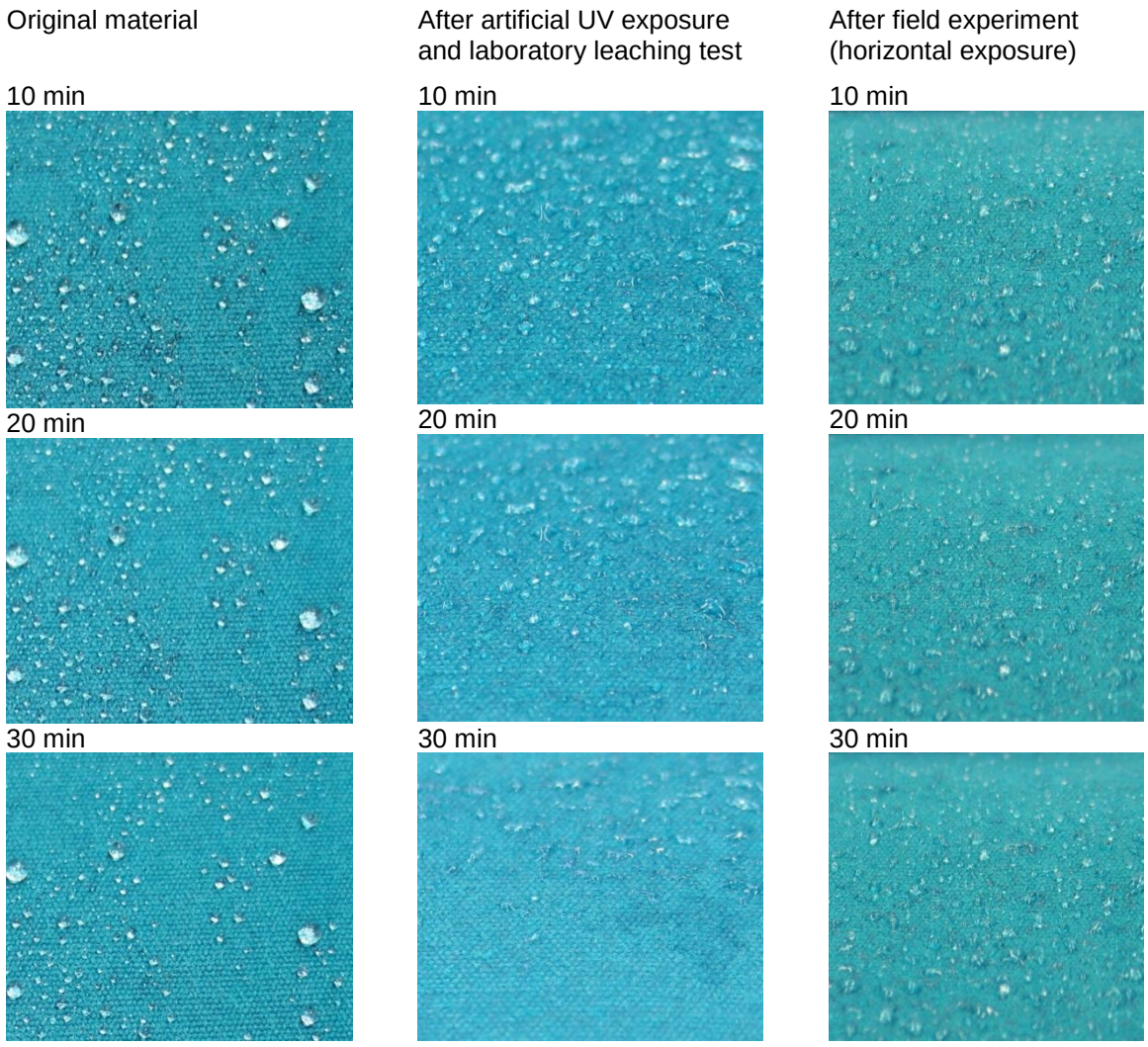
Figure 20: Water drops on surfaces of WC-8 and WC-11



Photographs were taken from the same sector of a birch plywood board coated with WC-8 (left site) and WC-11 (right site) (a) before, (b) 8 s and (c) 4 min after spraying with water. The arrow indicates water running down on the WC-11 coating. After 4 minutes no more water is visible on the surface of WC-11, while merged drops with lower contact angles are still visible on the surface of WC-8.

Remaining globular water drops were observed on the original impregnated textile T-1 for at least thirty minutes. Contact angles were smaller, and the drops almost disappeared within thirty minutes if the textile was exposed to either laboratory leaching or weathering (see Figure 21). Similar observations were made if the leached test specimen was exposed to UV- radiation as described under 3.1.2 prior to the leaching test.

Figure 21: Changes of water repellency of the textile T-1 due to water exposure



Stability of water drops on the impregnated textile T-1 without and after the laboratory leaching experiment at different duration after spraying.

4.1.8 Summary of results from laboratory leaching experiments

The proposed laboratory leaching test procedure proved to be suitable and repeatable for a series of active substances and treated articles.

Typical decreasing emission curves were observed for all investigated treated articles. Emissions are roughly related to physico-chemical properties of active substances, but also depend on properties of the treated articles and substrates.

Repeatability of parallel tests and standard deviation for repeated tests in the same laboratory indicate that the laboratory tests yield reliable results. It can be necessary to include data on transformation products to obtain repeatable results if transformation occurs already during the experiment. Sensitive analytical methods can be required to quantify target substances that are released at very low concentrations (e.g. below 0.01 mg/l).

Emission curves provide information on the leaching process. Graphs in double logarithmic scaling indicate that diffusion mainly controls leaching from the investigated treated articles. In some cases, depletion of leachable target substances was observed during the experiments – usually distinctively below the original content of the active substances in the test specimens. Leaching was also controlled by dissolution of the target substances at the beginning of the leaching experiments for some treated articles. This was especially pronounced for leaching of the active substances from the impregnated textile.

Gaps in mass balances were observed when the sum of active substances in the eluates and residues in the test specimens were compared to the initial amount of active substances. This indicates further processes that cause losses of active substances.

Degradation, e.g. due to UV radiation is one possible reason for losses of active substances. However, not only active substances but also the matrix material of treated articles can be susceptible towards UV radiation as observations on increased leaching of carbendazim after UV exposure of the impregnated textile indicate.

Desorption experiments on paints confirm differences in the leachability of active substances of different physico-chemical properties, but do not result in the same ranging of treated articles as leaching experiments.

All investigated treated articles and most of the substrates (despite of glass) absorbed water, i.e. water was available within the test specimens for solution and transport of substances. Substances were also transported from coatings into the substrate in case of test specimens from wood. It was demonstrated for four coatings and the impregnated textile that water vapour can be absorbed. That means that also air humidity might be involved in the mobilisation of substances from materials. It was also observed that the ability of the test specimens to take up water changed in the course of the leaching experiments. The impregnated textile lost its water-repellent properties due to water contact during the laboratory experiments.

Comparison of materials in laboratory tests is mainly based on properties of the treated articles and the target substances that apply under water contact. Several parameters, like amount of water, duration of water contact, air humidity during the drying periods and temperature, are kept in a defined range. Other factors, like UV radiation, warming of surfaces, aging of materials, physical stress and influence of organisms, are either avoided or minimised.

4.2 Field experiments according to NT build 509

4.2.1 Rain, driving rain and runoff from test specimens at the test sites

The monthly amounts of rain and driving rain at the test sites are demonstrated for the duration of the experiments in Figures 22 and 23. The amount of rain from different directions at the BAM test site is illustrated in Annex III, Figure A III-16. The amount of driving rain was directly measured at the Eberswalde test sites. Driving rain was not measured for the BAM test site, but estimated using a procedure described in EN ISO 15927-3. The 'airfield index' (see Equation 2) describes exposure to driving rain at a certain location. Two deviations from the described procedure were applied: (a) the meterorological data obtained during the experiment were used instead of mean data from at least 10 years; (b) data for 10 min periods were used instead of data on an hourly basis.

Equation (2) $$I_A = \frac{2}{9}\sum \upsilon r^{\frac{8}{9}}\cos(D-\theta)$$

with

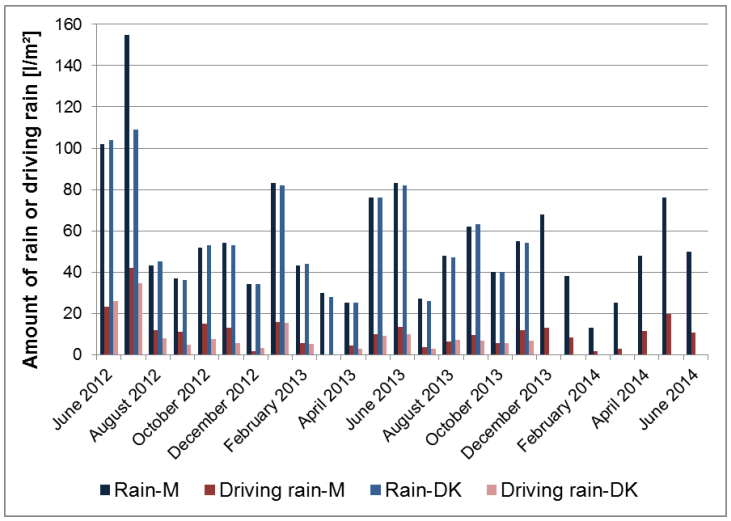
I_A annual airfield index (i.e. quantity of driving rain that would occur on a vertical wall of given orientation per square meter of wall during a certain time period)
r hourly rain amount
υ hourly mean of wind velocity
D hourly mean of wind direction
θ direction of the wall towards north

Driving rain

Driving rain depends on the amount of rain and wind (direction and velocity), that causes deflection of raindrops towards vertical surfaces. In addition, it is influenced by topographic, urban, building and material factors. For detailed information on calculation of wind-driven rain and rainwater runoff from facades see Blocken et al. 2010, Blocken and Carmeliet 2010 and Blocken et al. 2013.

About 18 % (mean value) of the monthly rain amount reached the test specimens at the test site Eberswalde, Möllerstraße, and about 14 % of the monthly rain amount reached the test specimens at Eberswalde, Drachenkopf. Maximum amounts of driving rain were about 30 % of the monthly rain amount for both test sites. The amounts of driving rain estimated according to the procedure given in EN ISO 15927-3 for the BAM test site were lower, i.e. 10 % of the monthly rain amount as mean, and 25 % as maximum values.

Figure 22: Monthly rain amounts and driving rain during the field experiments at MPA Eberswalde



Test sites: M: Möllerstraße, DK: Drachenkopf; driving rain was measured.

Figure 23: Rain and calculated airfield index during the field experiments at BAM, Berlin

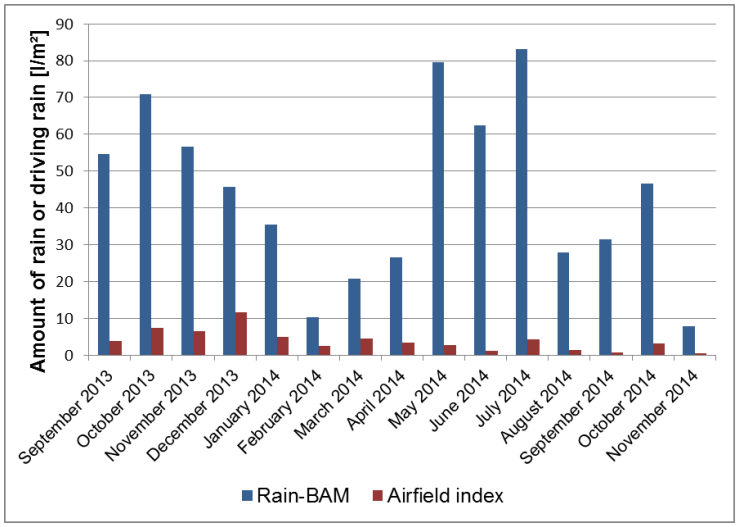


Table 8: Runoff from the test specimens at the test sites

Treated article	Location	Orientation	Experiment No.	Duration Months	Runoff/rain amount %
WC-8	MPA, Möllerstraße	vertical	1	25	2.7
	BAM	vertical	2	15	3.1
WC-9	BAM	vertical	3	8	2.2
WC-11	MPA, Möllerstraße	vertical	4	25	3.1
	MPA, Möllerstraße	vertical	5	25	3.8
	MPA, Drachenkopf	vertical	6	18	4.7
	MPA, Möllerstraße	vertical	7	22	3.5
	MPA, Möllerstraße	vertical	8	19	2.7
	BAM	vertical	9	15	3.6
WC-12	BAM	vertical	10	8	2.7
RP-2	MPA, Möllerstraße	horizontal	11	18	78
	BAM	vertical	12	15	3.2
RP-5	BAM	vertical	13	15	2.2
T-1	MPA, Möllerstraße	horizontal	14	15	87
	MPA, Möllerstraße	vertical (SW)	15	15	3.0
	MPA, Möllerstraße	vertical (NE)	16	15	4.5
	MPA, Möllerstraße	vertical (NW)	17	15	3.2
	MPA, Möllerstraße	vertical (SE)	18	15	4.9
	BAM	vertical (SSW)	19	7	3.0

Data on rain amounts and runoff volumes for the single experiments are given in Annex III, Tables A III-2 to 17.

Only about 2 to 5 % of the total amount of rain, which is also only a part of the driving rain, was collected as runoff samples from the vertically exposed test specimens. About 80 to 90 % of the total amount of rain was collected from horizontally exposed surfaces. A part of the rain water was probably either evaporated from wet surfaces or splashed. Reduced runoff is expected if test specimens absorb high amounts of water. The amounts of collected runoff varied

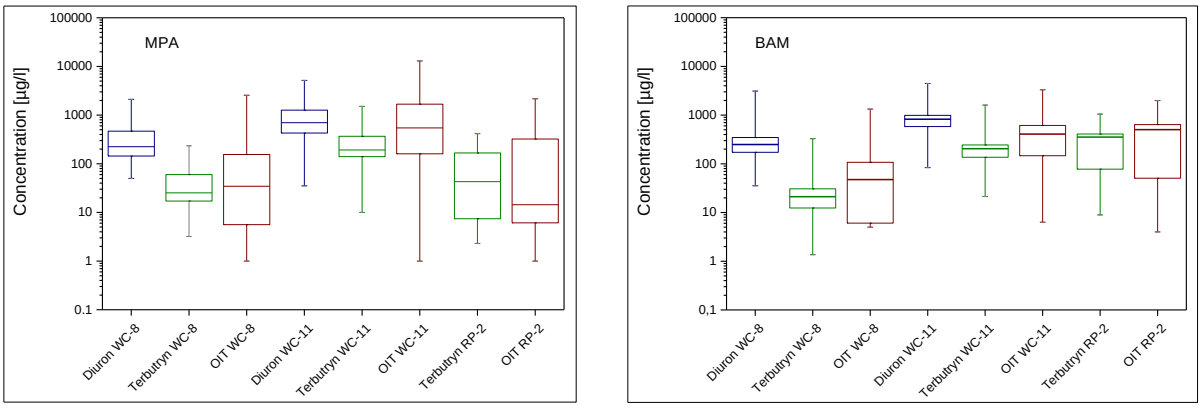
between test specimens from the same treated article at the same test site (see the data for WC-11), but were in similar ranges for experiments at MPA and BAM. Slightly higher runoff volumes were obtained from test specimens coated with WC-11 compared to WC-8. (see Table 8)

4.2.2 Concentration of active substances in runoff-samples

The concentrations of the target substances in runoff samples vary considerably and can differ by several orders of magnitude. In general, the values tend to decrease during the experiments. The results obtained during the first 4.5 months of exposure are presented as box-and-whisker diagrams in Figures 24 and 25 (see also Annex III, Tables A III-2 to A III-17).

Maximum and mean concentrations are similar for active substances in runoff samples from vertically exposed test specimens for the wood coatings WC-8 and WC-11 from MPA and BAM experiments (Figure 24). The tendency of slightly higher concentrations for the BAM experiments can be explained by the fact that the tests at MPA were started at the end of May 2012 whereas the tests at BAM were started at the end of August 2013. As a consequence, the test specimens were exposed to higher temperatures and UV degradation during the beginning of the MPA experiments. The mean concentrations of terbutryn and OIT and the maximum concentrations of terbutryn were higher in the runoff samples of vertically compared to horizontally exposed RP-2, whereas the maximum concentrations of OIT were similar for both experiments.

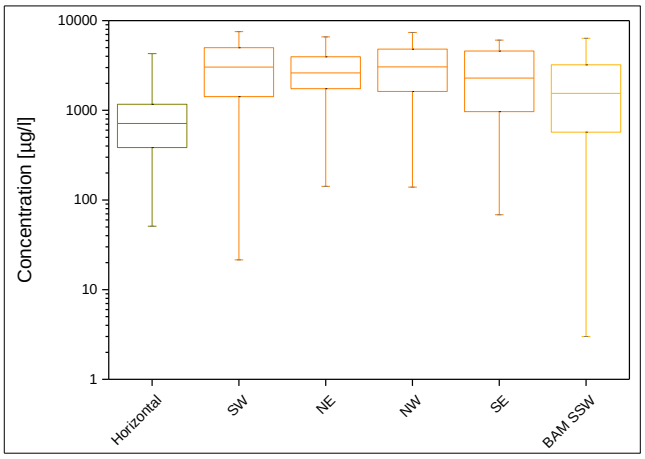
Figure 24: Concentration of active substances in runoff samples from coatings during the first 4.5 months of exposure



Left side: MPA experiments on WC-8 and WC-11 (vertical exposure) and RP-2 (horizontal exposure). Right side: BAM experiments on WC-8, WC-11 and RP-2 (all vertically exposed). The boxes represent median values, 25th and 75th percentiles, the whiskers indicate minimum and maximum values. LOQs were inserted if the target substance was not detected in a sample. The median values (right diagram, bold lines) are in the range of the 25th percentile in some cases due to a number of samples with very low concentrations of active substances from the BAM experiments.

The concentrations of carbendazim were lower in case of horizontally compared to vertically exposed textile T-1 (Figure 25). The ranges of carbendazim concentrations in runoff samples from vertically exposed T-1 were similar for the four exposure directions of the MPA experiment. The carbendazim concentrations in the runoff samples from the BAM experiment are slightly lower than those from the MPA experiment. The BAM experiments on the textile T-1 were started exactly one year after the MPA experiments. In both experiments single runoff samples were analysed from September until April of the following year.

Figure 25: Concentration of carbendazim in runoff samples from the impregnated textile T-1



Data originate from MPA and BAM experiments. The boxes represent median values, 25th and 75th percentiles, the whiskers indicate minimum and maximum values. LOQs were inserted if the target substance was not detected in a sample.

The pH-values and conductivity data for the runoff samples from BAM experiments are summarised in Annex III, Table A III-18 and Figures A III-10 to A III-15. The pH-values of runoff samples from the coated wood test specimens ranged between pH 8.5 and 6.0 and decreased during the experiment. The pH-values of runoff samples from coated fibre cement increased during the early stages of the experiments up to values of about pH 9.5 and decreased later to values between pH 6.5 and 7.5. The pH-values of runoff samples of the impregnated textile ranged between pH 6.0 and 8.0. Conductivity of runoff samples varies between the single rain events with relatively high values for distinct rain periods.

4.2.3 Cumulative emissions of active substances

There are different ways to present cumulative data from field experiments, each having its own informative value:

Presentation of cumulative emissions versus

- calendar date (see Figure 26) allows to relate observations to seasons and actual weather conditions,
- the amount of rain (see Figure 27) relates data to a parameter of the actual weather conditions, i.e. availability of water, that is generally required for leaching,
- the amount of runoff (see Figure 28) relates data to the actual amount of driving rain that is in fact responsible for the transport of substances from materials into the environment. Additional information on the amount of rain allows conclusions on the local exposure conditions during the experiments.

The latter type of presentation was preferably used for comparison of results from different experiments in this report.

Observations from the field experiments are described for selected treated articles. The diagrams for all experiments are presented in Annex III, Figures A III-1 to A III-9.

Figure 26: Emission of diuron (D), terbutryn (T) and OIT (O) from WC-8 vs. calendar date

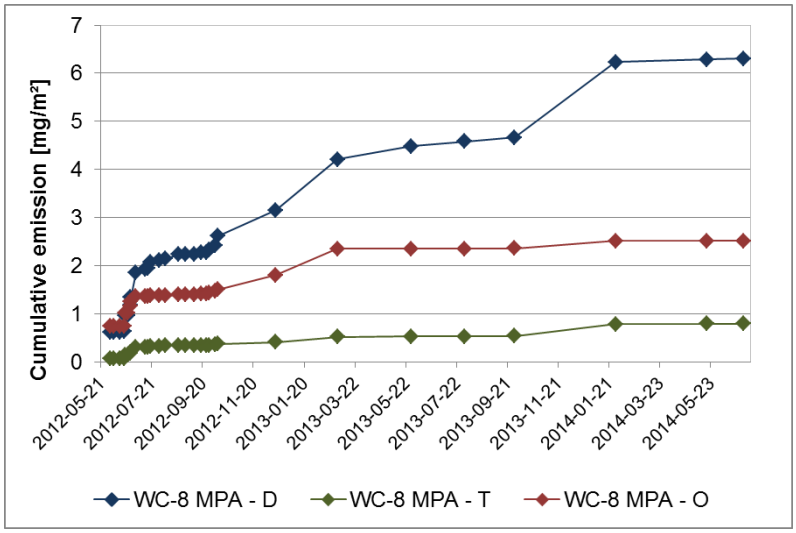


Figure 27: Emission of diuron (D), terbutryn (T) and OIT (O) from WC-8 vs. the amount of rain

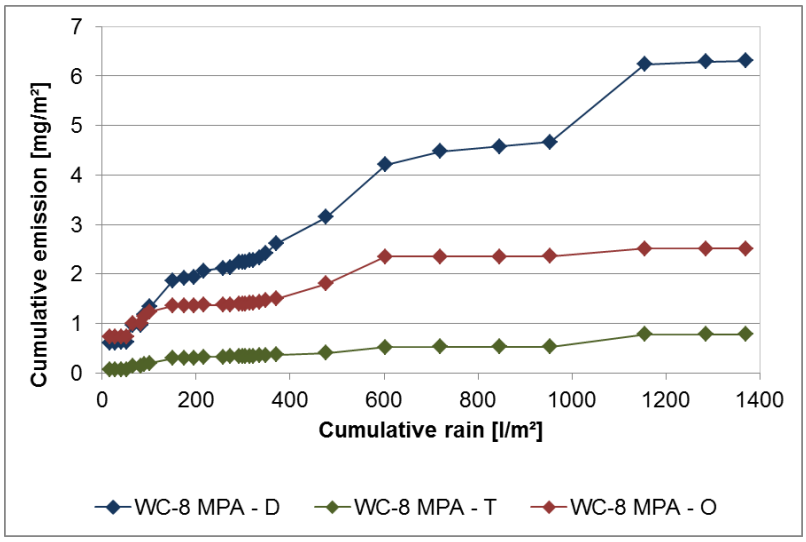
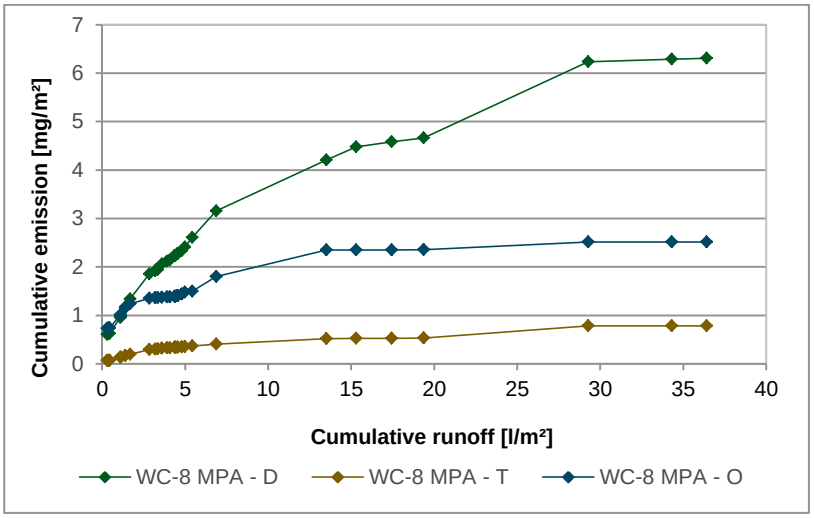


Figure 28: Emission of diuron (D), terbutryn (T) and OIT (O) from WC-8 vs. the amount of runoff

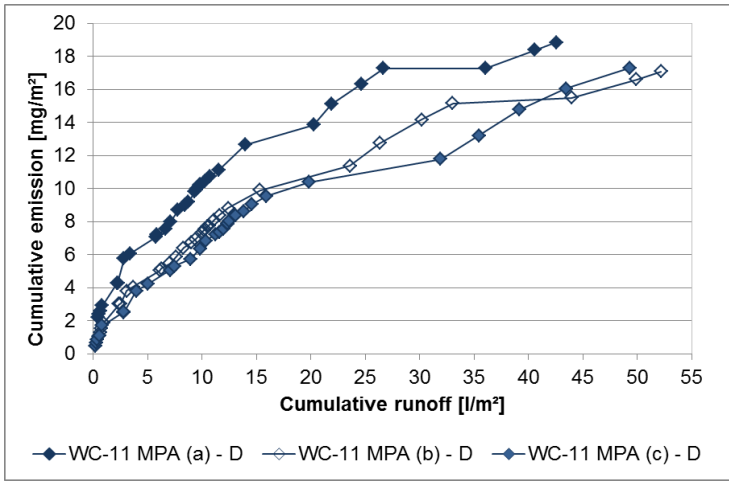


The influence of several factors was investigated during the field experiments: Three test specimens for the wood coating WC-11 were investigated at the same time. Two test specimens were installed at the MPA test site 'Möllerstrasse'. The third test specimen was installed about 1 km away at the MPA test site 'Drachenkopf'. The results are presented in Figures 29 to 31. Deviation between the results differs for the investigated active substance. Similar emission curves related to cumulative runoff were obtained for terbutryn, especially during the early stages (three to four months) of the experiment. This applies also for diuron with some restrictions. Differences between parallel tests at the same site can be caused by different amounts of obtained runoff. The emission curves of OIT were similar during the early stages (about three to four months) of the experiment at the same test site, but differ considerably between the two test sites. The emission curves were also similar for the early stages of the experiments on WC-11 if they were performed at the same site, but started with a time lag of three and six months (see Figures 32 to 33). Differences in the courses of the emission curves occurred mainly during later stages of the experiments. However, the total emissions were in similar ranges for all active substances.

About 2.5 % of the original amounts of diuron, 0.3 % of terbutryn and 2 % of OIT were found in runoff samples from field experiments on the wood coating WC-8 during about two years. About 5 % of the original amount of diuron, 1.2 % of terbutryn and 10 % of OIT were detected in case of WC-11.

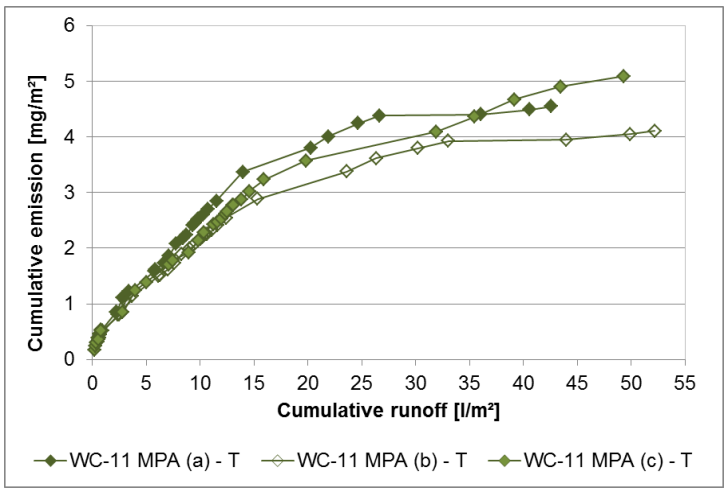
Experiments on vertically exposed tests specimens coated with the wood coatings WC-8 and WC-11 were performed in Eberswalde and Berlin. The experiments in Berlin were started fifteen months later than the experiments in Eberswalde, and are intended to run until the end of 2016 depending on the observed results. Data until the end of November 2014 were considered for this report.

Figure 29: Emission of diuron (D) from WC-11 during parallel experiments at different test sites



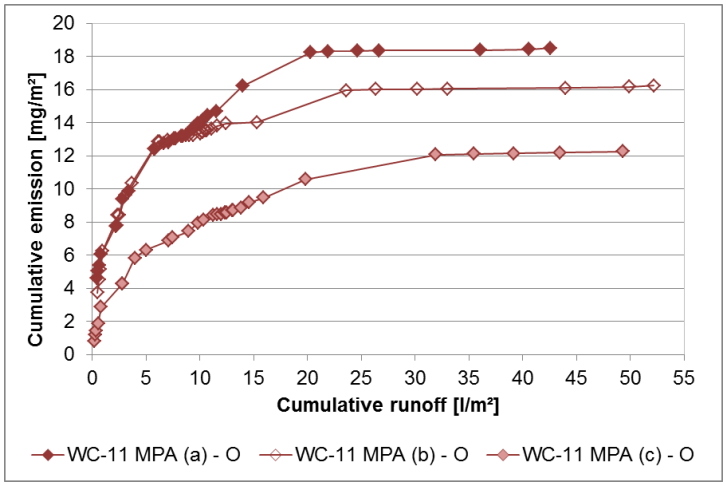
Parallel experiments at the same location (a, b) and at a different test site (c)

Figure 30: Emission of terbutryn (T) from WC-11 during parallel experiments at different test sites



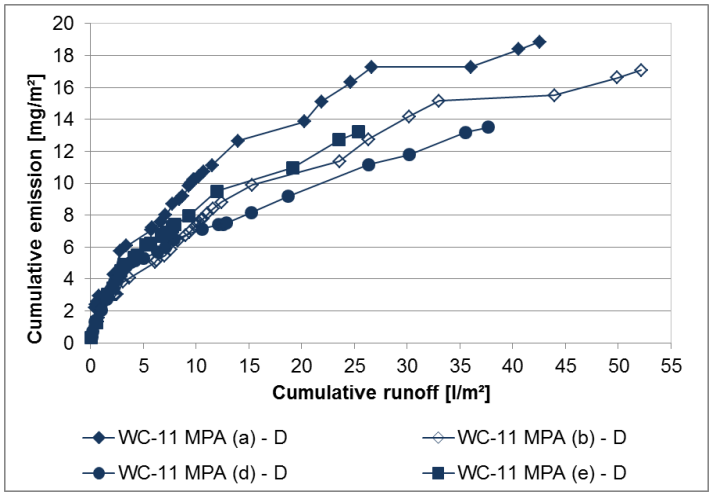
Parallel experiments at the same location (a, b) and at a different test site (c)

Figure 31: Emission of OIT (O) from WC-11 during parallel experiments at different test sites



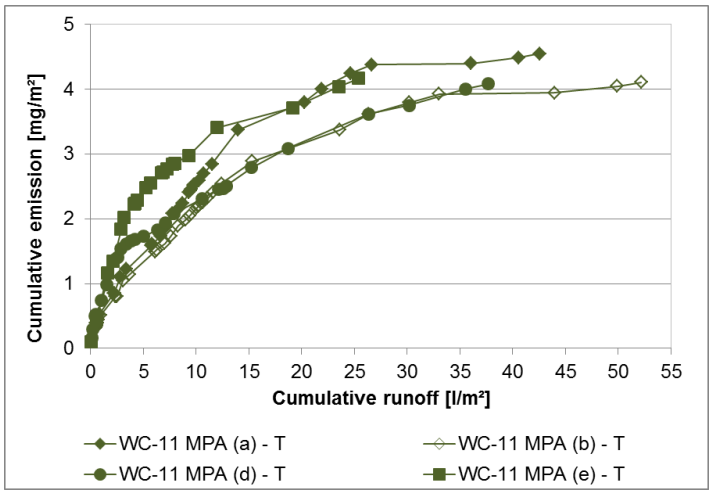
Parallel experiments at the same location (a, b) and at a different test site (c)

Figure 32: Emission of diuron (D) from WC-11 during experiments at different test periods



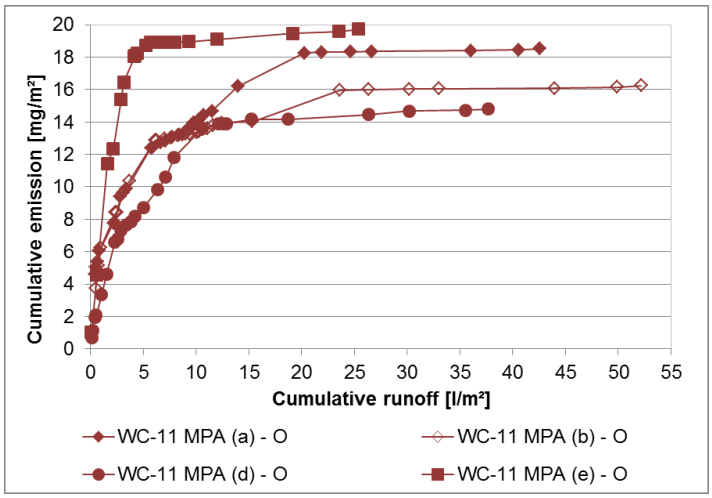
Parallel experiments (a, b) and experiments started three months (d) and six months (e) later, all at the same location

Figure 33: Emission of terbutryn (T) from WC-11 during experiments at different test periods



Parallel experiments (a, b) and experiments started three months (d) and six months (e) later, all at the same location

Figure 34: Emission of OIT (O) from WC-11 during experiments at different test periods



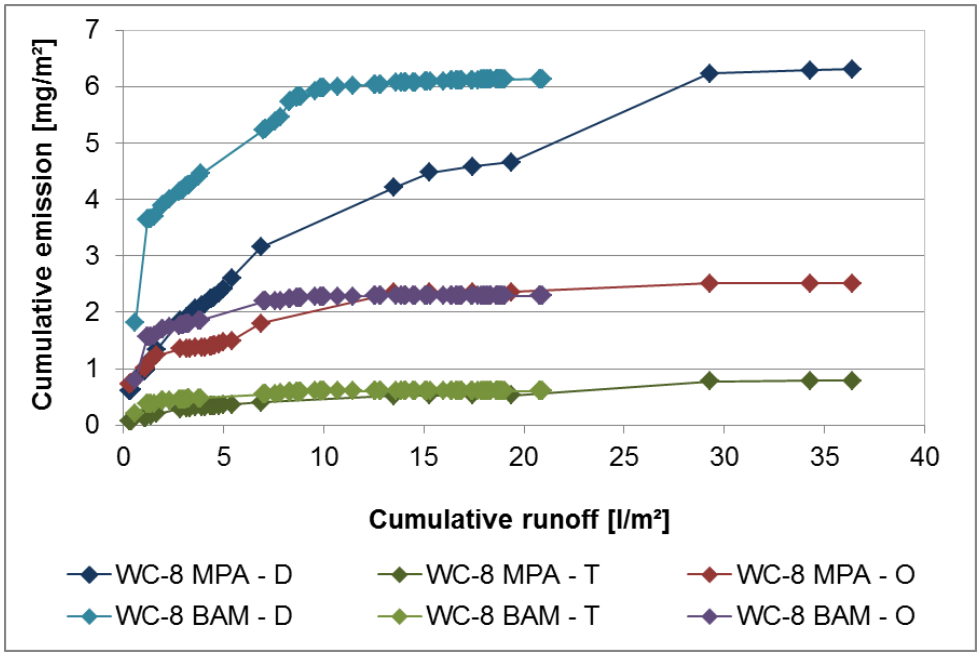
Parallel experiments (a, b) and experiments started three months (d) and six months (e) later, all at the same location

The data for WC-8 are related to the cumulative runoff for comparison of experiments at MPA and BAM (Figure 35). The courses of the emission curves ran steeper for all active substances at the beginning of the BAM compared to the MPA experiment. The very first data point for diuron is considerably high for the BAM experiment. The total emissions for all active substances are on similar levels at the end of both experiments, i.e. after 25 months for the MPA experiment and 15 months for the BAM experiment.

Emission in relation to the dates was chosen to compare the data for experiments on WC-11. This provides information on the seasons instead of the exposure to rain. The emission curves for diuron and terbutryn (Figure 36 and 37) run steeper at the beginning of the BAM experiments compared to the MPA experiments. However, there are also differences between the MPA experiments that were started at different points in time. The total emissions are similar for the first series of MPA experiments and the BAM experiment, but slightly lower for the MPA experiments that were started later. The emission curves for OIT (Figure 38) were steep at the beginning of all experiments. After several months the cumulative emissions remain at a certain level, i.e. either very small amounts or no more OIT was found in the runoff samples. The differences between the total emissions during the experiments are higher for OIT than for the other investigated substances. In addition, OIT emission was observed to be very low during the three included summer seasons. The amounts of OIT found in the runoff samples increased during autumn. This was also observed for diuron and terbutryn, but less pronounced than for OIT. Similar observations were also made for vertically installed test specimens for the other investigated coatings (see Figures A III-1, A III-6 to A III-8). Probably, degradation of OIT on the materials surfaces can occur relatively fast, but further amounts of OIT can be transported from deeper layers of the treated article to its surface when OIT is less affected.

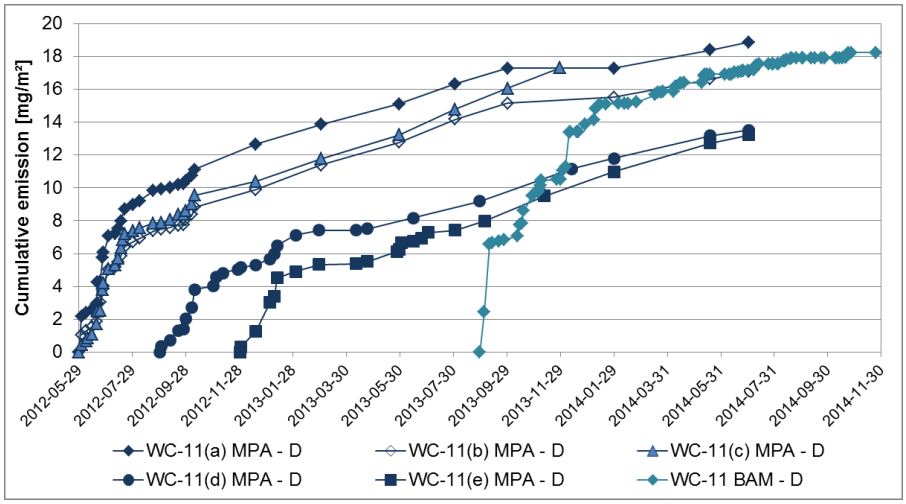
Amendment: During December 2014 and January 2015 further emissions were observed for (a) diuron from WC-11, and to a limited extend also from WC-8, (b) terbutryn from W-11, WC-9, WC-12, RP-2 and RP-5, (c) OIT from WC-9, WC-12, and to a limited extend from RP-5, and (d) carbendazim from WC-12. No emissions were detected for terbutryn and OIT from WC-8 and OIT from RP-2. These data are not included in this report.

Figure 35: Emission of diuron (D), terbutryn (T) and OIT (O) from WC-8 vs. the amount of runoff



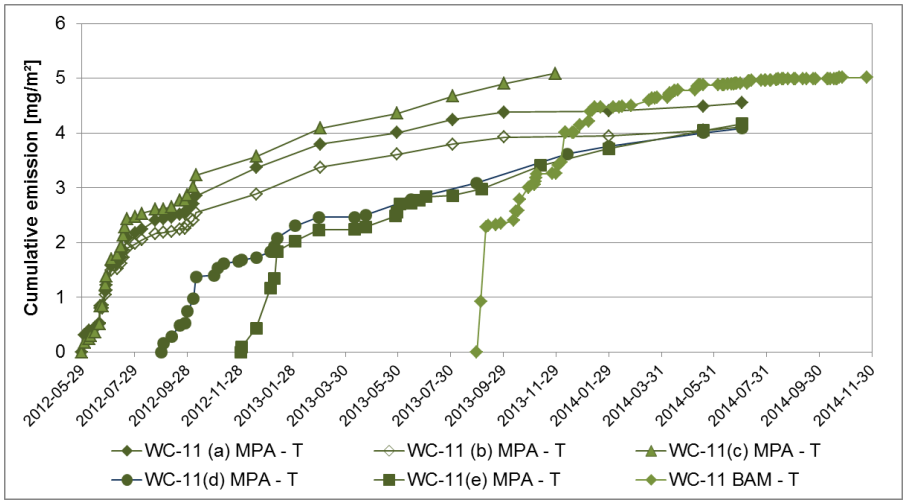
Experiments at different locations (MPA and BAM) that were started at different points in time

Figure 36: Emission of diuron (D) from WC-11 vs. the calendar date



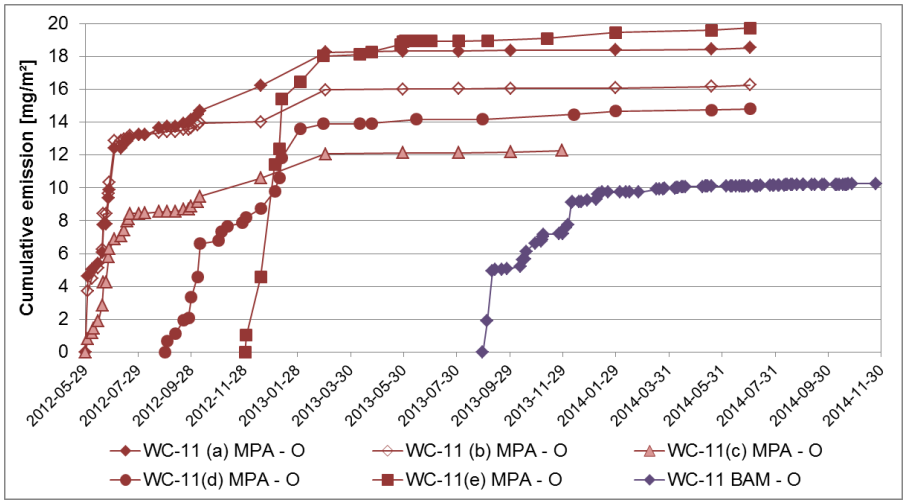
Experiments at different locations that were started at different points in time

Figure 37: Emission of terbutryn (T) from WC-11 vs. the calendar date



Experiments at different locations that were started at different points in time

Figure 38: Emission of OIT (O) from WC-11 vs. the calendar date



Experiments at different locations that were started at different points in time

The impregnated textile T-1 was chosen to investigate the influence of the exposure direction on leaching of active substances. Four test specimens were installed vertically and oriented towards south-west, north-east, north-west and south-east. A fifth test specimen was installed horizontally. The textile impregnation included carbendazim and zinc pyrithione. However, zinc pyrithione was not stable in the runoff samples and could therefore not be detected in these samples.

Results for the vertically exposed test specimens are presented in Figures 39 and 40. Emissions of carbendazim from textile specimens that were exposed to different directions decreased in the following order: SE > NE > NW ~ SW. However, the cumulative emissions were very similar if related to the cumulative runoff. Even the experimental data from the BAM experiment that was started one year later fit very well. This strong dependency of the emissions on the amount of runoff cannot be expected if the target substance is either less stable towards UV degradation or is evaporated to a larger proportion.

Figure 39: Emission of carbendazim from T-1 exposed to different directions versus calendar date

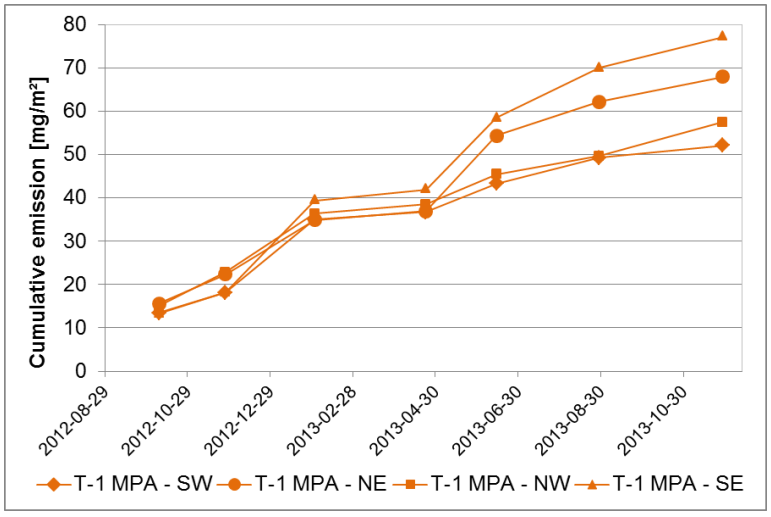
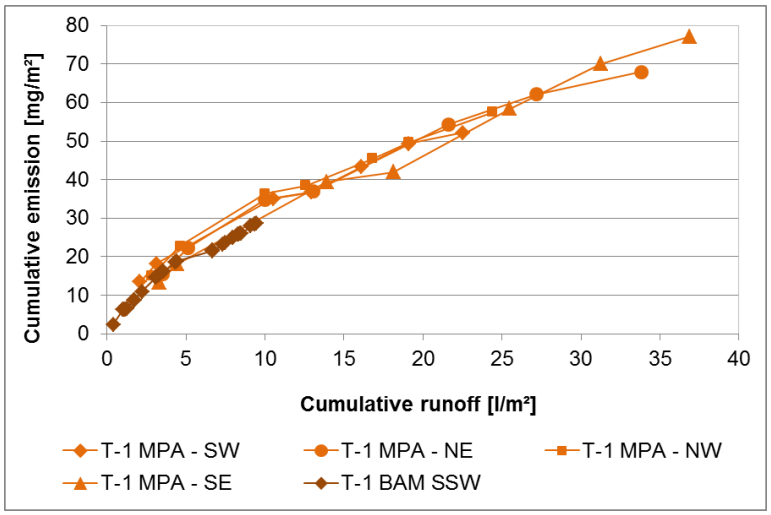
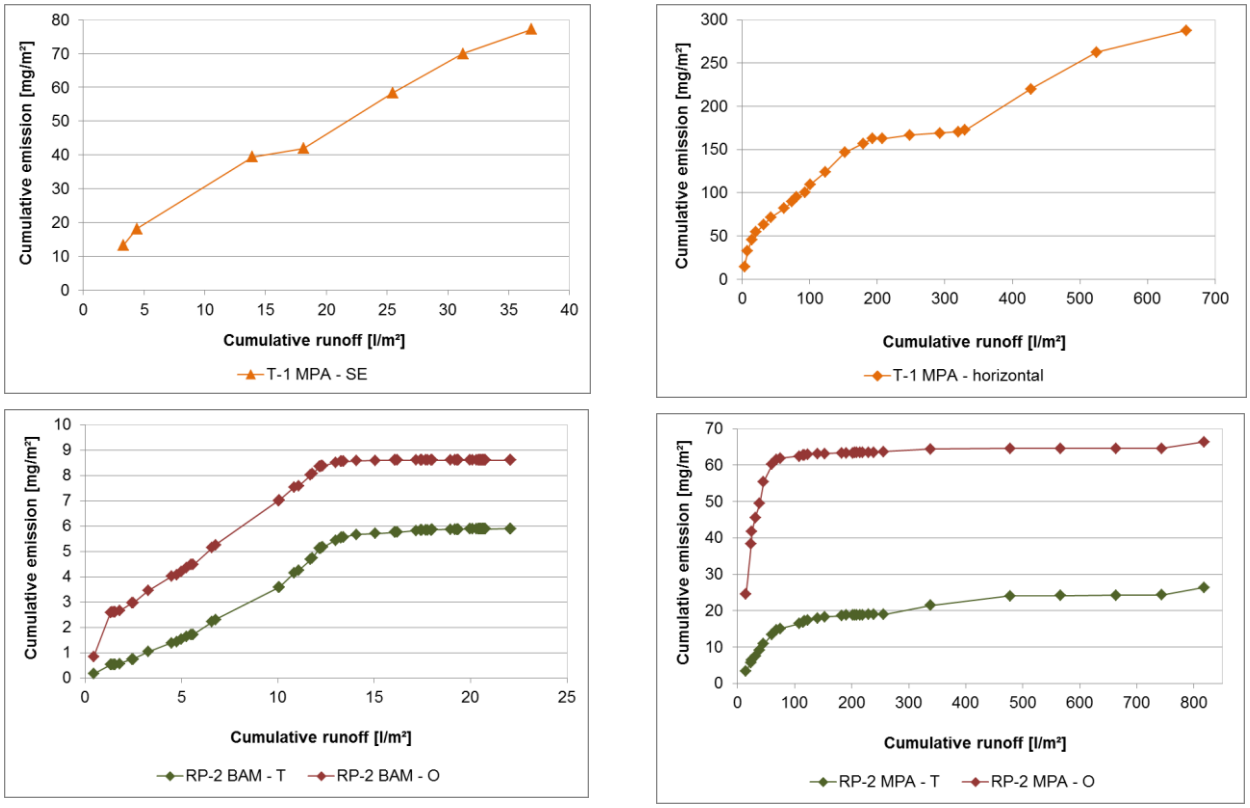


Figure 40: Emission of carbendazim from T-1 exposed to different directions vs. runoff



Vertical and horizontal exposure of test specimens can be compared for parallel MPA experiments on the textile T-1. In addition, independent experiments on the roof paint RP-2 were performed at MPA and BAM. One test specimen was installed horizontally at MPA. Another test specimen was installed vertically at BAM fifteen months later. As expected, the proportions of runoff from the amount of rain and the leached amounts of target substances were considerably higher for horizontally compared to vertically exposed test specimens (see Figure 41).

Figure 41: Comparison of horizontal and vertical exposure of test specimens



Emission of active substances from test specimens that were installed either vertically (left side) or horizontally (right side). The duration of the experiments was 15 months for the experiments on the textile (graphs show data for carbendazim), 18 months for the horizontally exposed roof paint RP-2 (all at MPA Eberswalde), and 15 months for the vertically exposed RP-2 at BAM.

About 6 to 11 % of the amount of carbendazim that was analysed in the textile samples was detected in the runoff samples from vertically exposed test specimens, and about 40 % were detected in runoff samples from the horizontally exposed test specimen. The percentages are 1 to 2 % and 8 %, respectively, if the results are related to the carbendazim concentration in the recipe. Damage of the impregnation is assumed to be a cause of relatively high emissions. Possibly, the textile is not intended to be used under continuous weathering.

4.2.4 Mass balances for active substances

Residual concentrations of active substances in treated articles after field experiments and the amounts that were detected in runoff samples are summarised in Table 9. Transport of active samples from coatings into subjacent wood was also observed under field test conditions (see Table 6 for the results from the laboratory tests). The amount of active substance detected in wood was highest for OIT which has the highest water solubility (480 mg/l) and lowest for terbutryn (22 mg/l), both in the laboratory and field experiments. Water solubility seems to affect transport of substances from coatings into wood. Considerable gaps occur between residual amounts of the target substances in the test specimens and the amounts detected in the runoff samples from the coated materials. Only small gaps were observed for carbendazim from the textile. The gaps seem to be higher for the wood coating WC-8 compared to WC-11. It was observed that water drops remain longer on surfaces from WC-8 than on surfaces from WC-11 during the field experiments at MPA as well as at BAM (see Chapter 4.1.7, Figure 20 for this effect under laboratory conditions). Possibly, this enables increased degradation of active substances due to longer duration of exposure, e.g. towards UV radiation.

Table 9: Mass balance of active substances in test specimens and runoff samples from field experiments

Treated article	Orientation	Active substance	Residual content (mean)			Content in eluates	Gap
			n*	Total	In wood		
				%	%	%	%
WC-8	Vertical	Diuron	1	25	5	2.6	73
		OIT		20	10	1.7	79
		Terbutryn		8	0.3	0.3	92
WC-11	Vertical	Diuron	4	40	6	4.4	55
		OIT		26	14	4.7	70
		Terbutryn		28	0.7	1.3	71
RP-2	Horizontal	OIT	1	n.d.		8.2	92
		Terbutryn		10.8		4.1	85
T-1	Vertical	Carbendazim	4	75		9.0	16
		Zinc pyrithione		11		unknown	
	Horizontal	Carbendazim	1	40		46.0	14
		Zinc pyrithione		n.d		unknown	

The data for WC-8, WC-11 and RP-2 are related to the recipes, and the data for T-1 are related to the analysed content of active substance. *n is the number of test specimens. Three subsamples were analysed for each test specimen. The amounts of active substances detected in wood represent a part of the total residual content.

4.2.5 Emission of active substances during rain events

It is interesting to note that the emissions during rain events or short-term periods of only a few days show maxima and minima for all investigated treated articles and active substances at the same time. This was observed for the BAM experiments (see Figures 42 and 43) as well as for the MPA experiments (see Annex III, Figure A III-17). Generally, emissions during 'high emission rain events' tend to decrease with the course of the experiments - except for emissions of carbendazim from the impregnated textile. Apparently, further amounts of carbendazim were mobilised during the winter seasons, possibly by damage of the impregnation (see Figure 42 and results for the MPA experiments in Figures 44 and 45).

Leaching of active substances from the horizontally exposed roof paint RP-2 seems to decrease rather steadily with a few less distinctive periods of increased emissions. However, higher emissions were detected later in a merged sample (see Figure 41, last data points for terbutryn and OIT from horizontally exposed RP-2).

Simultaneous minimum and maximum emissions at the same time were also observed for test specimens from the textile that were exposed vertically towards different directions. Only the relation between the emissions from test specimens oriented to different directions is slightly changing, probably caused by the actual exposure to driving rain.

The simultaneous occurrence of minimum and maximum emission events cannot be related only to the amount of rain or driving rain to the test specimens. Additional parameters of the weathering conditions affect leaching similarly for all parallel experiments. Therefore the dependency of leaching processes on several weathering parameters was studied in detail to identify crucial factors (see Chapter 5.2).

Figure 42: Emission during rain periods (BAM experiments) vs. calendar date

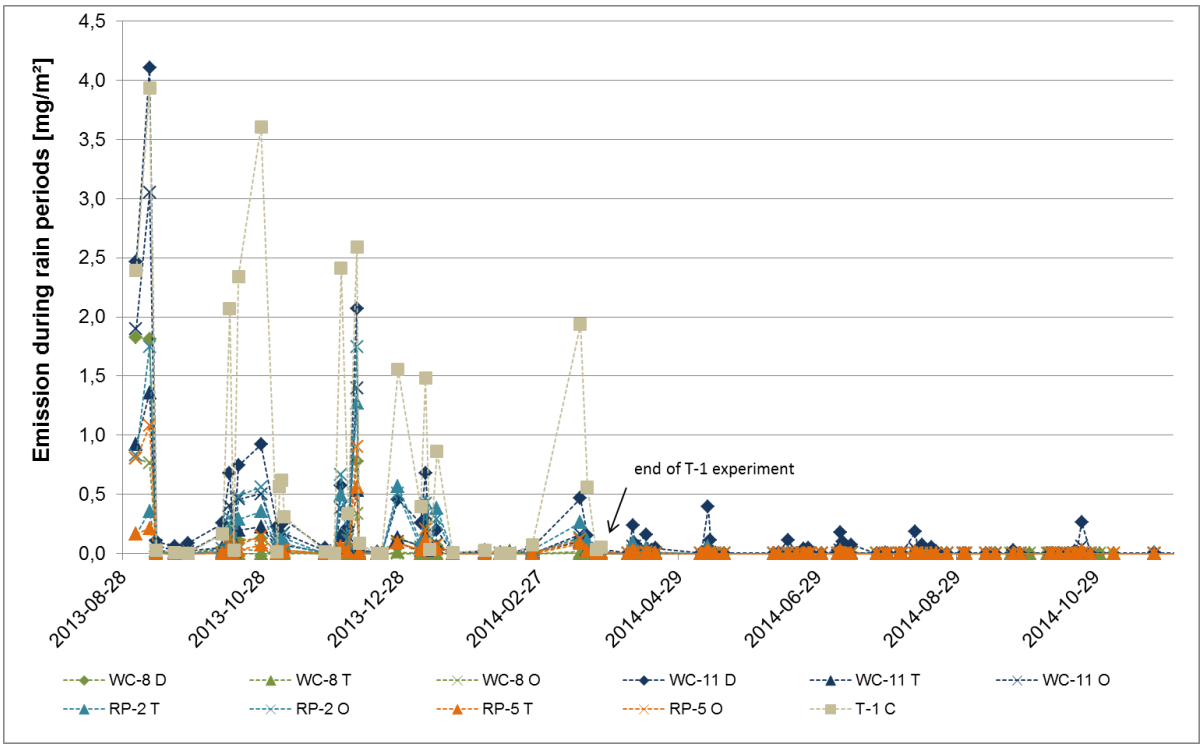


Figure 43: Picture detail of Figure 42

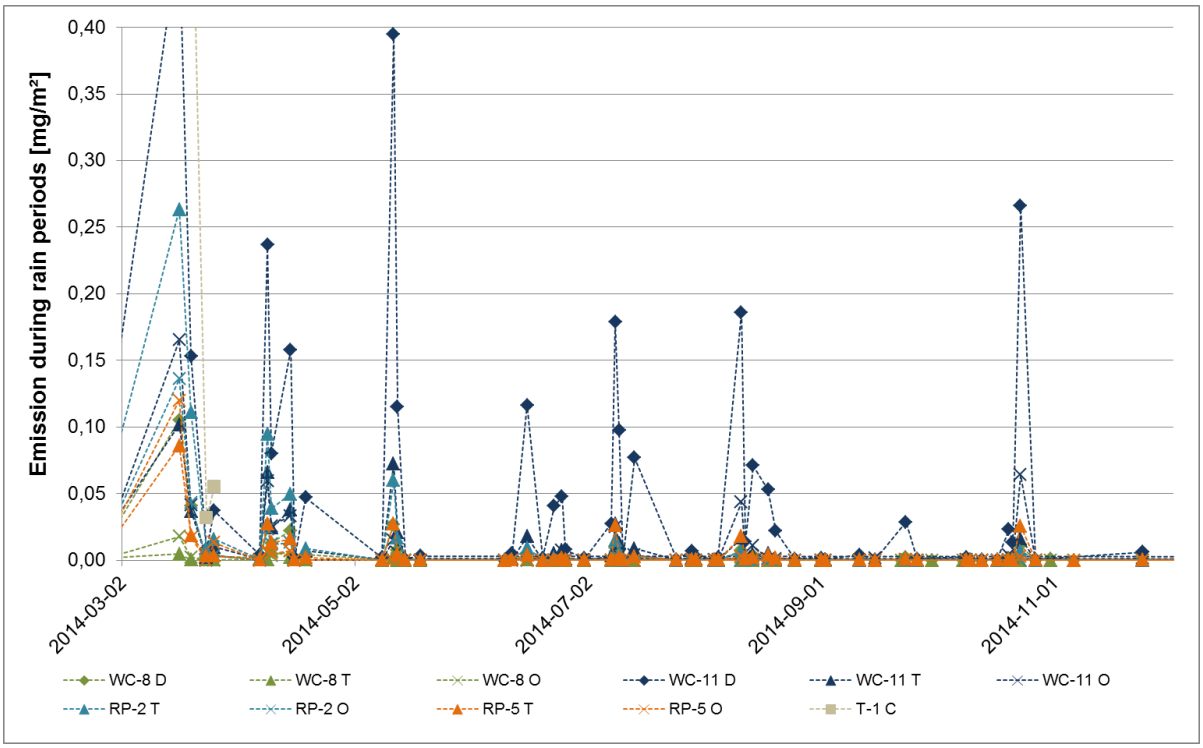
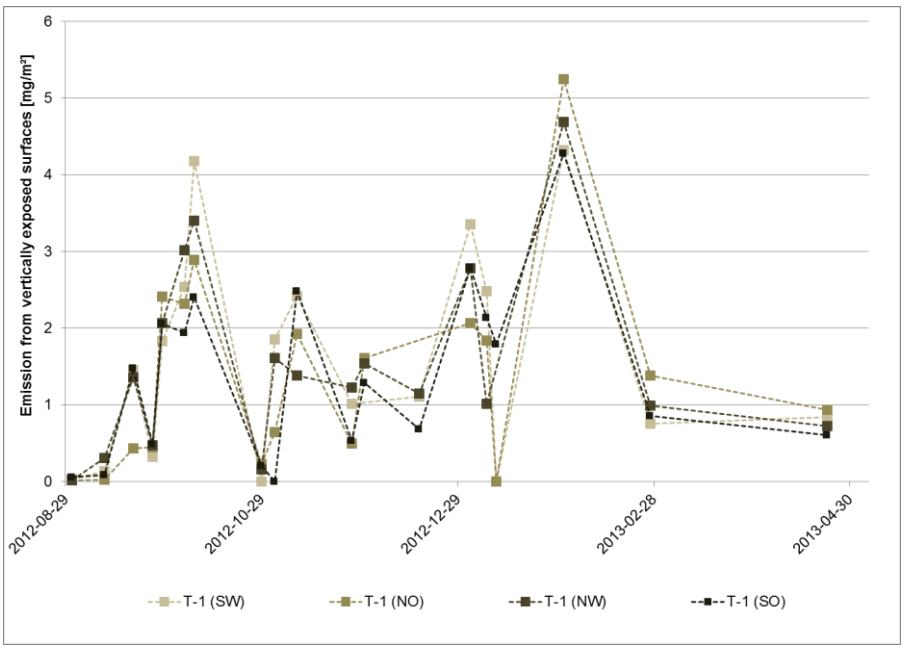
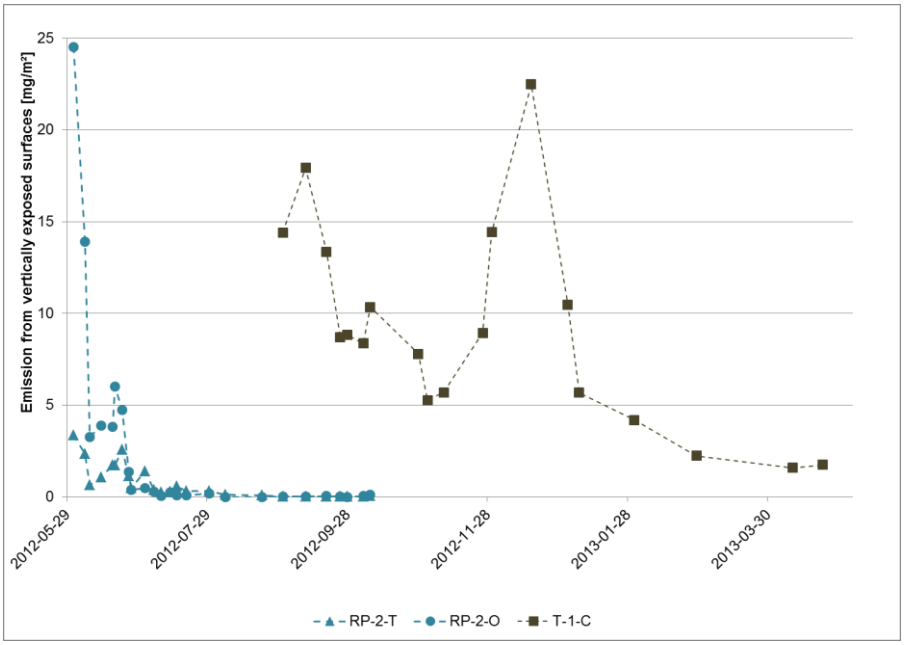


Figure 44: Emission of carbendazim during rain periods from T-1 test specimens vs. calendar date



The test specimens were installed vertically and oriented towards different directions. Data originate from MPA experiments.

Figure 45: Emission of active substances during rain periods from horizontally installed test specimens vs. calendar date



Data originate from MPA experiments.

4.2.6 Summary of results from the field experiments

The applied field test procedure was suitable to describe leaching of active substances from the selected treated articles.

Driving rain towards vertically installed test specimens is required to cause runoff. The amount and direction of driving rain depend on the local conditions at the test site. It is also known that the percentage of driving rain towards vertical surfaces is decreasing with increasing dimensions of the surfaces. In this respect, field experiments on relatively small test specimens represent severe exposure conditions. This fact is important to be considered if test results are extrapolated or used in models on leaching processes, and means that area-related data from field experiments cannot be transferred to real surfaces without correction.

The number of parallel tests at the same experimental conditions was limited during the project. It has to be taken into account that it is impossible to repeat field tests under identical conditions when results of field experiments are compared. Even for test specimens that are investigated in parallel, the exposure conditions can vary and e.g. cause different amounts of runoff. Nevertheless, a few conclusions are possible. Maximum concentrations and cumulative losses of the target substances were in similar ranges for repeated experiments. This applies for parallel tests at the same site and a test site located in the proximity, tests that were started at different points in time and tests that were performed at another test site at another time. Variability between test results depends on properties of the target substances, e.g. its stability under the exposure conditions, among other things.

Presentations of cumulative emissions related to date and rain amount usually show stepwise curves since the results are not related to the actual exposure of the test specimens. Even emission curves related to the amount of runoff do not run completely smooth. This indicates further processes that determine the amount of leached substances in runoff samples. However, relation of cumulative emissions to the amount of runoff has proved to be suitable to compare results from different tests. Depending on the target substance, emission curves from different experiments proceed more or less similar, especially during early stages of the experiments. Deviations become obvious mainly in the later stages of the experiments. Data on the test period as well as the amounts of rain and runoff during the experiment should always be given in reports since these parameters provide useful information on the experimental conditions during the experiment.

Concentrations of the target substances as well as the leached amounts per surface area differed considerably between runoff samples from single rain events or short rain periods. A tendency of decreasing values during the test period was observed. In many cases, the amounts of target substances in the runoff samples were low during summer, sometimes also during winter, and increased again in autumn and spring. It is supposed that degradation and possibly also evaporation of the target substances are increased during the summer. Extended availability of water under the weather conditions in autumn allow transport of the target substances to the materials surfaces again, and the substances are protected by lower temperatures and less UV radiation onto the surfaces and the water film on the materials surfaces.

In general, it is difficult to obtain leaching results for instable substances since it is impossible to either preserve or analyse these substances as soon as they occur in the collected runoff. During the project this was the case for zinc pyrithione from the impregnated textile and a wood coating. It can be an option to analyse runoff samples for stable transformation products if these are known and relevant for risk assessments.

The emission curves of carbendazim from different experiments on an impregnated textile were almost identical if related to the amount of runoff even if oriented towards different directions. On the other hand, considerable variation was observed for emission curves of OIT from different experiments. It is assumed that additional factors affecting the stability of OIT become relevant for the amounts of this substance in runoff samples.

A high percentage of rain is collected from horizontally exposed surfaces. It is supposed that a part of the rain water is either splashed or evaporated from wet surfaces depending on the surface properties. Only a part of the driving rain is collected from vertical surfaces, probably due to the same reasons. The concentrations of the target

substances were lower whereas the total amounts of leached target substances were higher in runoff from horizontally exposed compared to vertically exposed test specimens. Leaching processes from horizontal surfaces were less affected by additional factors despite of the amount of rain than leaching processes from vertical surfaces.

Only a small percentage of the original amount of active substances was detected in runoff samples from the investigated treated articles. Analysis of residual amounts of these substances in the test specimens after the field experiment indicated large gaps in the mass balances. It was demonstrated that a part of the target substances can be transported into the substrate in case of coatings applied on wood. However, a considerable part of the target substances was lost due to other processes. Degradation and evaporation of target substances are supposed to cause these losses. However, no data are available that describe to what extend these processes influence the fate of substances in the investigated treated articles so far.

Area-related emissions from vertically installed test specimens of small dimensions are supposed to be higher than emissions from larger surfaces due to the stronger exposure to driving rain. However, field experiments provide better information to what extent leaching processes can occur under service conditions than data from laboratory tests.

The results of field experiments depend on properties of the target substances and the materials on the one hand and variable exposure conditions on the other hand. It is possible to compare leaching of certain substances as such and from different treated articles. In any case, a certain degree of variability of the results has to be expected and considered.

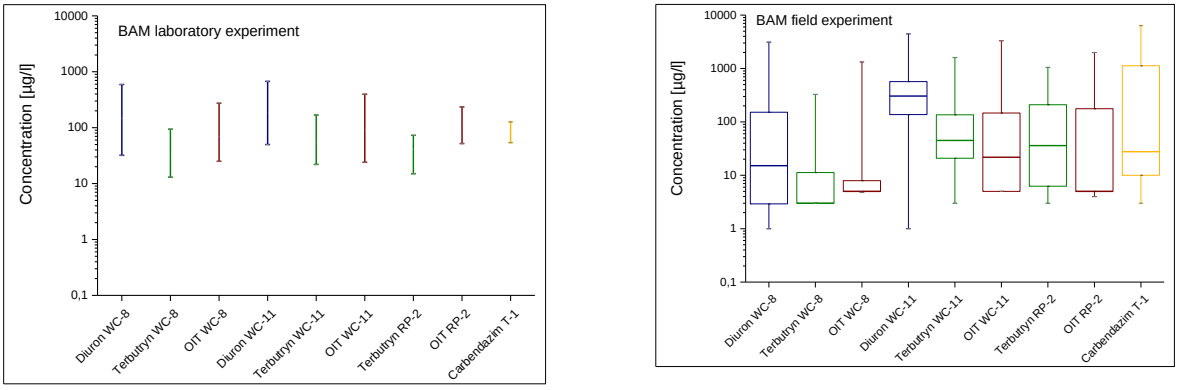
The informative value of field experiments depends on the number and frequency of analysis of runoff samples. Results for merged runoff samples provide only general information on the amount of leached substances during certain periods of the experiment. If the last data from field experiments were obtained during the summer it cannot certainly be concluded that no further increase of emissions will occur since this observation can be influenced by degradation processes and evaporation. Estimations on the range of concentrations of target substances in runoff and conclusions on the dependency of leaching on actual exposure conditions is only possible, if the number of analysed samples is increased.

4.3 Comparison of laboratory and field experiments

4.3.1 Concentration of active substances in eluates and runoff-samples

The observed ranges of concentrations of active substances were larger in runoff samples from field studies compared to eluates from laboratory experiments (see Figure 46). While the concentrations of the target substances decreased with the number of immersion cycles in the laboratory experiments, the results alternate considerable during the field study. There is a tendency of decreasing concentrations with the duration of exposure, but variation also depends on actual exposure conditions. The maximum concentrations determined in runoff samples were usually higher than maximum concentrations in eluates. However, very low concentrations of the target substances have to be determined in a number of runoff samples as well, i.e. field studies require more sensitive analytical methods than laboratory experiments. It can be necessary to pretest the concentration of target substances in runoff samples before validated analytical methods can be applied.

Figure 46: Concentration of active substances in eluates and runoff samples



Concentration ranges of active substances in eluates from laboratory experiments (left side) and in runoff samples from BAM field studies (right side). The boxes for the field data represent median values, 25th and 75th percentiles, the whiskers indicate minimum and maximum values. Data for the MPA field studies are demonstrated in Chapter 4.2, Fig. 24 and 25.

4.3.2 Cumulative emissions of active substances in laboratory and field experiments

Data are mainly available to compare results from laboratory experiments and field studies on vertically exposed test specimens that were coated with different paints (wood coatings and roof paints). For all investigated paints and active substances the emissions were considerably higher during nine immersion cycles in laboratory tests than during field experiments, even after more than two years of exposure (see Table 10). This is caused by more intensive water contact in laboratory tests, i.e. the large amount of water related to the surface area on the one hand and the long duration of water contact on the other hand.

Gaps in mass balances between the initial amounts of the active substances and amounts detected in runoff samples and eluates were higher for test specimens from field experiments than from laboratory experiments. This indicates that additional processes cause degradation or loss (e.g. evaporation) of active substances under outdoor conditions. The ratio between gaps in mass balances is especially high for WC-8 compared to WC-11. It is assumed that longer availability of water on the surfaces of WC-8 (see Chapter 4.1.7) promotes degradation of the active substances in the water film.

Only one test specimen coated with the roof paint RP-2 was exposed horizontally in a field experiment. The emissions of terbutryn and OIT within eighteen months of outdoor exposure were in similar ranges as the results from the laboratory tests. The lower ratio between emissions in field and laboratory tests that were observed for OIT compared to terbutryn can be caused by its lower stability. Again, the gap in the mass balances is higher for the test specimen from the field experiment than for the test specimens from the laboratory experiment.

Different results were obtained for the impregnated textile. The emissions of carbendazim were higher during the field experiment, even for vertically exposed test specimens within fifteen months of exposure. It is assumed that degradation of the impregnation promotes emission of carbendazim under outdoor conditions. In fact, UV radiation of the textile increased leaching of carbendazim under laboratory conditions (see Chapter 4.1.4). The ratio between emissions under laboratory and field conditions can be different for zinc pyrithione since this substance is sensitive to UV radiation whereas carbendazim was stable under the test conditions. However, zinc pyrithione could not be analysed in runoff samples due to its instability. Gaps in mass balances of carbendazim were small for test specimens from laboratory and field experiments, indicating that degradation and/or evaporation are less important. See also Annex IV, Figures A IV-1 to A IV-9 for comparison of cumulative emissions, and Tables 6 (Chapter 4.1.3) and 9 (Chapter 4.2.4) for mass balance data.

Table 10: Emissions and mass balances in laboratory and field experiments

Treated article	AS	Laboratory test			Field experiment					Field/Laboratory	
		n	E_{cum}	Gap	Duration	Exp.	n	E_{cum}	Gap	E_{cum}	Gap
Code			%	%	Months			%	%	Ratio	Ratio
WC-8	D	4	27	14	25	v	1	2.6	73	0.10	5.1
	T		5.2	-7				0.3	92	0.06	
	O		21	15				1.7	79	0.08	5.2
WC-9	T	2	2.0		8	v	1	0.1		0.06	
	O		41					1.2		0.03	
WC-11	D	4	21	26	19 - 25	v	4	4.4	55	0.21	2.1
	T		6.0	45				1.3	71	0.22	1.6
	O		18	33				4.7	70	0.26	2.1
WC-12	T	2	4.8		8	v	1	0.5		0.10	
	O		26					3.9		0.15	
	C		7.9					0.6		0.08	
RP-2	T	3	3.1	34	18	h	1	4.2	85	1.36	2.5
	O		14	67				8.2	92	0.58	1.4
	T	3	3.1		15	v	1	1.1		0.37	
	O		14					2.9		0.20	
RP-5	T	2	3.0		15	v	1	0.4		0.15	
	O		21					1.9		0.09	
T-1	C	4	4.9	20	15	v	4	9	16	1.84	0.8
						h	1	46	14	9.39	0.7

Explanations: AS: active substance, n: number of experiments, Exp.: exposure, v: vertically exposed, h: horizontally exposed (grey background); E_{cum}: cumulative emission; gap: difference in mass balances between initial amount of active substance, amounts in either eluates or runoff samples and residues in test specimens; WC-8 to WC-12: test specimens of pine wood in the laboratory tests and birch plywood in the field experiments, RP-2 and RP-5: test specimens from fibre cement in both types of experiments;
D: diuron, T: terbutryn, O: OIT, C: carbendazim

It has to be taken into account that the exposure to driving rain is higher for relatively small test specimens in field experiments compared to facades of buildings (see Chapter 4.2.1) if data from vertically exposed test specimens are applied for risk assessments. That means that the ratios between cumulative emissions under real service conditions and laboratory results are probably lower than the values given in Table 10.

4.3.3 Comparison of active substances and treated articles

Relative emissions of active substances were in the same order for all investigated treated articles: OIT ~ diuron > carbendazim ~ terbutryn in laboratory and field experiments (see E_{cum} in Table 10). Be aware that percent data should be taken with caution, since these data do not represent actual amounts of substances that are emitted into the environment. Leaching data should be reported as actual emissions related to the emitting surface area as given in Table 11.

Table 11: Comparison of emissions of active substances from treated articles

Treated article	AS	Initial amount	Laboratory test		Field experiment					
					MPA			BAM		
Code		mg/m²	n	E_{cum} mg/m²	n	Duration Months	E_{cum} mg/m²	n	Duration Months	E_{cum} mg/m²
WC-8	D	250	4	65	1	25	6.31	1	15	6.14
	T	130		13.3			0.78			0.61
	O	250		30.7			2.52			2.29
WC-11	D	390	2	81.4	2	25	18.0	1	15	18.2
	T	200		24.6			4.33			5.01
	O	390		40.3			17.4			10.3
Ratio [%] WC-8/ WC-11	**D**			**80**			**35**			**34**
	T			**54**			**18**			**12**
	O			**76**			**15**			**22**
WC-9	T	100	2	2.0				1	8	0.13
	O	60		24.5						0.75
WC-12	T	280	2	13.5				1	8	1.41
	O	100		25.6						3.92
	C	320		25.3						1.94
Ratio [%] WC-9/ WC-12	**T**			**15**						**9**
	O			**96**						**19**
RP-2	T	560	3	16.1				1	15	5.89
	O	300		43.6						8.60
RP-5	T	420	2	12.7				1	15	1.85
	O	210		43.9						3.93
Ratio [%] RP-2/RP-5	**T**			**127**						**318**
	O			**99**						**219**

Explanations: AS: active substance, E_{cum}: cumulative emission; WC-8 to WC-12: test specimens of pine wood in the laboratory tests and birch plywood in the field experiments, RP-2 and RP-5: test specimens from fibre cement in both types of experiments; comparison of products is given as ratio [%]
D: diuron, T: terbutryn, O: OIT, C: carbendazim

In a few cases, treated articles of the same type were investigated in parallel during field studies, i.e. (a) WC-8 and WC-11, (b) WC-9 and WC-12 and (c) RP-2 and RP-5 (see Table 11). WC-9 and WC-12 are commercial products that are composed like WC-8 and WC-11, respectively, but contain microencapsulated active substances.

Most data are available to compare WC-8 and WC-11. Cumulative emissions [mg/m²] were higher for diuron, terbutryn and OIT from WC-11 in laboratory experiments and the field studies both at MPA Eberswalde and BAM. The cumulative emissions and the ratios between the emissions of the target substances from both

products were similar for the field experiments at the two test sites. However, the difference between WC-8 and WC-11 is bigger in the field studies compared to the laboratory experiments, indicating that parameters that are not included in the laboratory experiments act on leaching processes under outdoor conditions (see the discussion on water film on WC-8 under 4.3.2).

Test specimens from WC-9 and WC-12 were installed at BAM only seven months later than the other experiments. However, these experiments confirm the laboratory results that emissions are lower from the commercial products containing microencapsulated active substances compared to the corresponding wood coatings that contain emulsified active substances. The emissions of terbutryn were lower from WC-9 compared to WC-12 both in laboratory and field experiments. Whereas the emissions of OIT were similar for both wood coatings in the laboratory tests, the OIT emissions were higher from WC-12 than from WC-9 in the field experiment.

Emissions of terbutryn and OIT from RP-2 and RP-5 were in similar ranges in laboratory tests whereas higher amounts of both substances were detected in runoff samples from RP-2. A possible explanation is that leaching is promoted by the black surface of RP-2 compared to the red surface of RP-5 (see the discussion on the effect of global radiation in Chapter 5.2). However, there are not sufficient experiences on the influence of different colours to confirm this assumption.

4.3.4 Leaching processes under laboratory and field conditions

Graphs including primary and secondary x-axes are used for joint presentations of leaching curves from laboratory and field experiments (see Figure 47 for an example). Cumulative emissions during the field experiments are related to cumulative runoff, and cumulative emissions during laboratory experiments are related to immersion cycles. One immersion cycle represents 50 l water in contact to 1 m² of emitting surfaces of the test specimens. Insofar, both x-axes represent a certain amount of water that was in contact with the surfaces of the test specimens. However, the duration of water contact was different in both types of experiments. Therefore, the chosen ratio is arbitrary, and does not represent a fixed relation between exposure during laboratory and field experiments. A complete set of graphs is included in Annex IV, Figures A IV-10 to A IV-16.

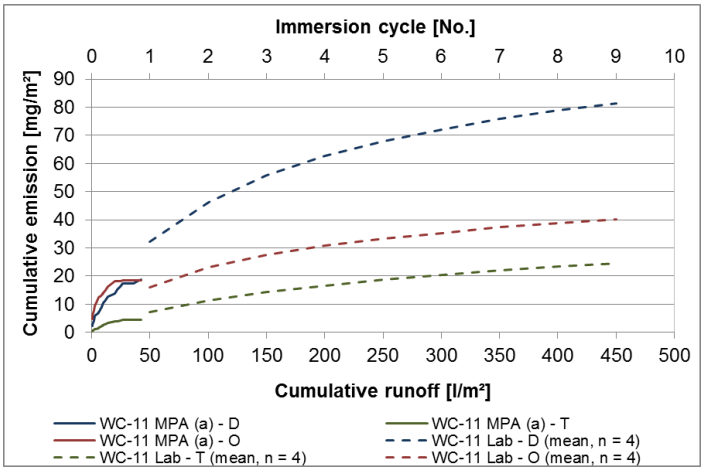
The graph in Figure 47 is representative for data obtained for paints on vertically installed test specimens. While cumulative emissions increase continuously during the laboratory experiments, the emissions stagnate during certain periods of the field experiments. It appears that the amount of emissions detected in the laboratory experiment will not be achieved under field conditions in many cases. The curves for terbutryn and OIT for the horizontally installed RP-2 test specimen run steeper than the leaching curves from the laboratory test at the beginning of outdoor exposure. During later periods these curves stagnate. The curves for carbendazim emissions from the impregnated textile under outdoor conditions run considerably steeper than laboratory data both for experiments on vertically and horizontally installed test specimens.

Another option to compare leaching processes is presentation as double logarithmic graphs. These graphs allow conclusions on the factors that control leaching processes (see Chapter 4.1.1). Examples for comparison of these presentations are given in Figures 48 and 49. A complete set of these graphs is included in Annex IV, Figures A IV-17 to A IV-19.

Leaching processes appear diffusion controlled under laboratory conditions in many cases. Depletion was observed in some cases during the late immersion cycles. Although leaching curves from field experiments cannot run as consistent as laboratory data, diffusion appears to be important also under field conditions. Stagnation of the leaching curves from the field experiments does not necessarily indicate depletion of active substances in the paints, but can also be caused by the actual weather conditions (see Figure 48). Leaching of carbendazim from the textile T-1 appears solution controlled at the beginning of the experiments and diffusion controlled during later periods under laboratory and outdoor conditions (see Figure 49).

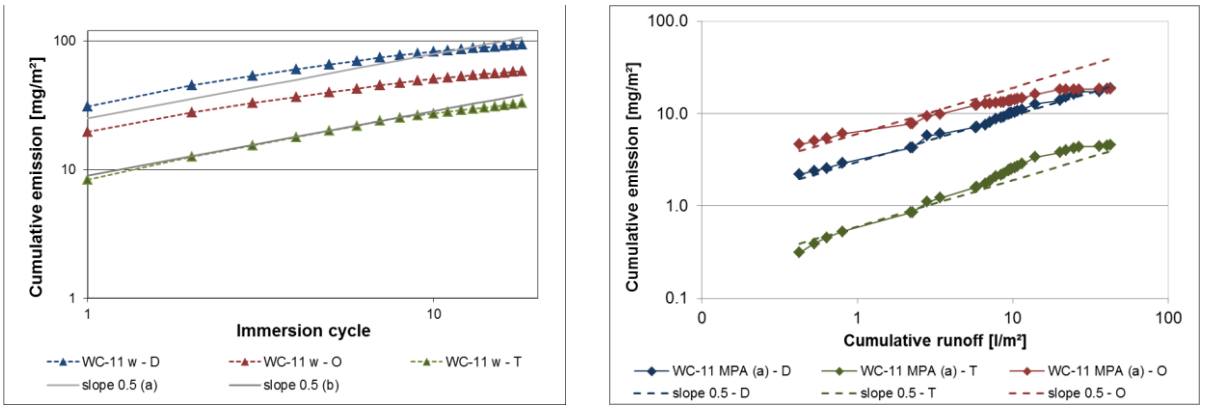
Relationship between laboratory and field data was also analysed by means of mathematical models (see Chapter 5.3).

Figure 47: Leaching curves for active substances from W-11 from laboratory and field experiments



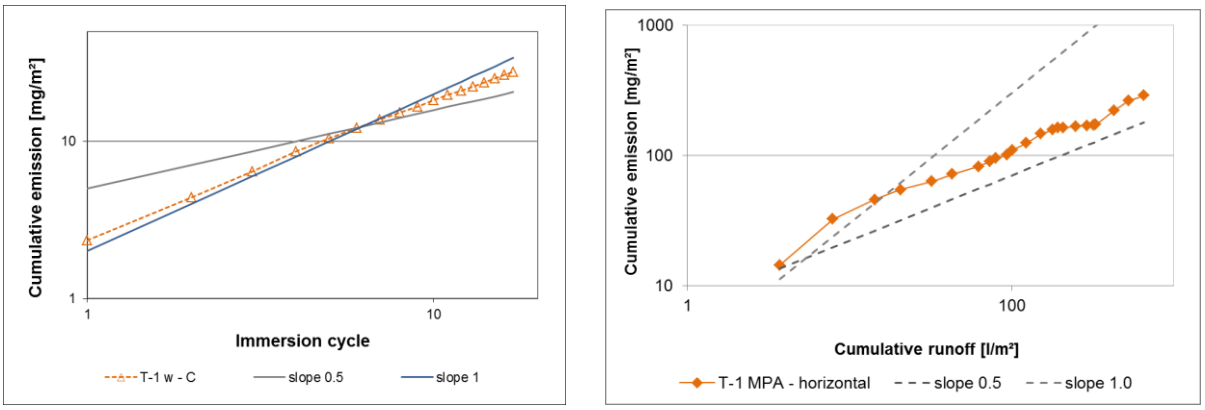
D: diuron, O: OIT, T: terbutryn

Figure 48: Leaching processes from W-11 in double logarithmic graphs



Laboratory (left) and field (right) experiments. Curves with a slope of 0.5 indicate diffusion controlled processes; D: diuron, O: OIT, T: terbutryn

Figure 49: Leaching processes of carbendazim from T-1 in double logarithmic graphs



Laboratory (left) and field (right) experiments. Curves with a slope of 0.5 indicate diffusion controlled processes, and curves with a slope of 1 indicate solution controlled processes. C: carbendazim

4.3.5 Observations on material properties under laboratory and field conditions

A few observations were made on material properties both under laboratory and field conditions:

Occurrence of a higher number and longer residence time of water drops were observed on the surfaces of the WC-8 test specimens compared to WC-11 specimens during MPA and BAM field experiments and also when test specimens were sprayed in the laboratory (see Chapter 4.1.7, Figure 20). However, this property cannot be observed during the laboratory leaching tests due to the design of these experiments. Water contact is forced during immersion events. Under these conditions, water uptake was slightly higher for test specimens coated with WC-8 compared to WC-11 (see Annex II, Table A II-4).

Certain properties were observed to change during laboratory as well as field experiments:

It was demonstrated that water repellency of the impregnated textile decreased under laboratory test conditions and outdoor exposure (see Figure 21 in Chapter 4.1.7). In addition, water vapour sorption differed for samples from test specimens depending on previous exposure to either immersion or weathering (see Annex II, Table A II-6). For instance, water vapour sorption was higher for T-1 samples that were exposed to either immersion in the laboratory experiment or weathering compared to the textile in its original state. Water vapour sorption of paints appears to decrease during laboratory and field experiments.

Emission of TOC can be associated with changes of chemical properties of materials. Changes of the chemical composition of treated articles during leaching experiments were indicated by infrared spectra of treated articles and residues of evaporated runoff samples. These investigations are still running and are not reported here.

4.3.6 Summary of comparative observations

Estimation of target substances in runoff samples from field experiments requires more sensitive analytical procedures than analysis of eluates from laboratory experiments, especially if it is intended to observe single rain events. Emissions tend to be higher in laboratory experiments compared to field studies on vertically installed test specimens. However, there is no constant ratio between results from both test procedures. Emissions from a horizontally installed test specimen were in the range of emissions during the laboratory tests for one example. Experiments with the impregnated textile indicate that emissions can be higher under field conditions if the material itself is not stable towards weathering.

There are no comparative data for emissions from treated articles for small-area applications like sealing masses and sealing tapes under outdoor conditions. However, it seems to be acceptable to use laboratory data for risk assessments, if actual small emitting surface areas are considered. Emissions per surface area are probably overestimated, especially if e.g. joints are not exposed to the total amount of rain.

Differences between emissions of active substances and emissions from treated articles are indicated consistently by laboratory experiments and field experiments. However, actual ratios between results for active substances and emissions from different treated articles can vary. Additional parameters that are neglected in the laboratory test probably cause these differences. The following parameters seem to be important: (a) hydrophilic properties of surfaces, (b) degradation of active substances under weathering conditions, and (c) evaporation of active substances from warmed-up surfaces. So far, there are experimental data that support assumptions on the influence of hydrophilic properties and degradation under UV radiation, but not on the relevance of increased evaporation. Obviously, changes of material properties that influence leaching processes, e.g. hydrophilic properties, water vapour sorption and the chemical composition of treated articles, occur under laboratory as well as outdoor conditions.

The amount of water that is in contact with the test specimens seems to be a suitable parameter to compare laboratory and field test data, although the duration of water contact is neglected. Leaching appears to be controlled by similar processes, i.e. diffusion and solution of target substances, under laboratory and field conditions. Therefore, it can be assumed that better understanding of the relevance of competing processes under outdoor conditions will improve the evaluation of laboratory leaching data for risk assessments.

5. Modelling

This chapter deals with the modelling of the laboratory test data and field test data. The chapter is divided into four sections. First, the results of modelling of the laboratory data are explained. After that the results of modelling of the field data are shown. Third, the relation between laboratory data and field data are examined and the results for the modelling of this relation are shown. And at last, courses of actions which are arised from the results of the modelling are pointed out.

5.1 Laboratory data

5.1.1 Introduction

Laboratory leaching data do not lend themselves to extrapolation and prediction on the basis of regression models. On the one hand, regression models do not take into account the physical and chemical processes which play a role in leaching. Moreover, the regression parameter estimates are not readily interpretable in terms which would then enable a description of the leaching processes. A further drawback is that the parameter estimates are highly dependent on the choice of regressors, e.g. whether time is quantified in terms of the number of cycles, the total time or the contact time, etc. Finally, the estimates are highly sensitive to irregularities in the experimental tests.

In order to overcome these shortcomings of regression models, a semi-analytical approach has been adopted. This approach is based on a model which was first published in Schoknecht et al. 2012. Since then, the model has been further enhanced by QuoData. This section describes the enhanced model as well as the results which were obtained.

5.1.2 Data basis

The modelling of the laboratory test data is based on the results of the in-house laboratory experiments of the BAM Berlin. In total, 74 experiments from 8 different active substances and 11 different treated articles have been taken into account. An overview of the modelled test series is listed in Table 12. For detailed information it is referred to Annex II.

Table 12: Data basis for the modelling of the laboratory test data

Treated article		Active substance [no. of experiments]							
Type	Code	Carben-dazim	Dichlo-fluanid	Diuron	IPBC	OIT	Terbu-tryn	Tolyl-fluanid	Zinc pyrithione
Wood coating	WC-2		3						
	WC-3							3	
	WC-5				2	2			
	WC-6				2				
	WC-8			6		6	6		
	WC-11			6		6	6		
Roof paint	RP-2					5	5		
Sealing mass	SM-2	2							
	SM-3	2							
Sealing tape	PVC-1					4			
Textile	T-1	4							4

5.1.3 Semi-analytical laboratory model

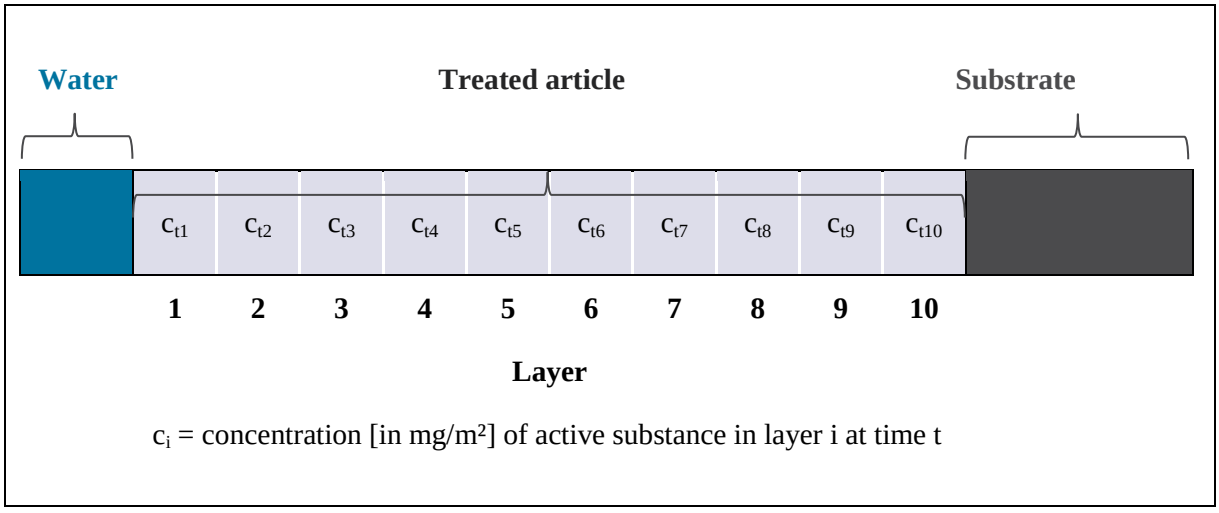
The model adopted here is a discrete transport model based on a simplified description of temporally and spatially dependent processes. It is a semi-analytical model as it attempts to construct analytical approximations of the underlying physical and chemical processes. This semi-analytical model is explained step by step in the following subsections.

5.1.3.1 Discretisation of space and time

In laboratory tests according to EN 16105 the amount of active substance leached from the treated article depends mainly on the transport processes of leaching and diffusion. Leaching refers to the transport of the active substance from the treated article into water when the test specimen is immersed. Diffusion refers to transport processes within the treated article, namely the transport of dissolved active substance in the wet treated article as a result of a concentration gradient (from a high to a low concentration). Both processes depend on the number of previous immersions and the length of time between immersions.

In order to describe these processes the treated article is subdivided into layers. For the sake of simplicity, in the model published in 2012 only 3 layers were considered. However, it is now clear that 10 layers result in a better fit. The following Figure 50 illustrates the subdivision of the treated article into layers. At any particular time point, a concentration of active substance is assigned to each layer of the treated article. As the emission is measured in mg/m², the amount of active substance in each layer is expressed in the same units.

Figure 50: 10-layer-model of the semi-analytical model – Cross section of the treated article



A further step of simplification consisted in time discretization, i.e. determining the concentration in each layer at regular intervals. For this purpose, hourly intervals proved expedient. The experimental period of 9 immersion cycles (also called 'immersion day' in this chapter) according to EN 16105 corresponds to 438 hours (18 days and 6 hours), in total. Accordingly, the experimental period is subdivided into 438 points in time.

5.1.3.2 Assumptions in the semi-analytical model

The model is based on the following assumptions:

- At any point in time, the distribution of the molecules of the active substance is homogeneous within each layer of the treated article, i.e. the concentration of the active substance is constant within each layer.
- The concentrations at time 0 h are identical in all 10 layers. The time 0 h means the time before the test specimen is immersed for the first time. It is assumed that the concentration at time 0 h corresponds to the known initial amount of the active substance in the treated article.
- The transport of active substance into the water (i.e. leaching) during the immersion of the test specimen only occurs between the boundary layer and the water, i.e. layer 1.
- There is no transport of active substance from the treated article to the substrate.

- There is no loss of active substances due to desorption or degradation processes, e.g. evaporation. Such processes are neglected since it is assumed that the experiments are carried out under controlled and constant laboratory conditions and no environmental factors affect the test specimens.
- The transport of active substances only occurs between adjacent layers, i.e. between the layers 1 and 2, 2 and 3, 3 and 4, …, 9 and 10.

5.1.3.3 Modelling of leaching and diffusion

In order to model both transport processes of leaching and diffusion, the two constant parameters p_L and p_D are used. It is assumed that a certain percentage p_L of the amount of the active substance in layer 1 (the boundary layer between treated article and water) is transported into water when the test specimen is immersed. Furthermore, it is assumed that, if there is a difference between the concentrations of active substance of two adjacent layers of the treated article, a certain percentage p_D of this difference is transported from the layer with the higher amount to the layer with the lower amount. It is assumed that the percentage p_D is identical for all layers.

The calculations of the modelled emission values are carried out on the basis of finite differences both in space and time. The two parameters p_L and p_D are used to determine the concentration of the active substance in each layer at a specific time t. For any particular layer, the concentration at time t hours is determined on the basis of the concentration at time (t – 1) hours.

The calculations are demonstrated with a numerical example. In this example let the initial concentration at time 0 h be 200 mg/m², let the percentage of leaching from the boundary layer into the water be 2 % and let the percentage of diffusion between adjacent layers be 5 %. The results for the first 3 hours are given in the following Table 13. This calculation is continued up to the time t = 438 h.

After the first immersion of the test specimen, 4 mg/m² = 0.02 ·200 mg/m² are leached. Therefore, the concentration of the active substance in layer 1 decreases to 196 mg/m² after 1 h and there is a concentration gradient between layer 1 (196 mg/m²) and layer 2 (200 mg/m²). This concentration gradient leads to diffusion of active substance and thus the concentration in layer 1 after 2 h is 196.2 = 196 + 0.05 ·(200-196).

Table 13: Numerical example for the calculation of the concentration of the active substance in each layer at a specific time t

Time	Im-mer-sion	Amount of active substance [in mg/m²] in layer no.									
		1	2	3	4	5	6	7	8	9	10
0 h	**no**	200	200	200	200	200	200	200	200	200	200
1 h	**yes**	196 = 200- **0.02** · 200	200	200	200	200	200	200	200	200	200
2 h	**no**	196.2 =196 + **0,05**· (200-196)	199.8 = 200 – **0.05**· (200 - 196)	200	200	200	200	200	200	200	200
3 h	**no**	196.38 =196.2 + **0.05**· (199.8-196.2)	199.63 = 199.8 – **0.05**· (199.8-196.2) + **0.05**· (200-199.8)	199.99 = 200 – **0.05** · (200-199.8)	200	200	200	200	200	200	200

Assumptions: The initial concentration at time 0 h is 200 mg/m², the leaching percentage is 2 % and the diffusion percentage is 5 %.

5.1.3.4 Calculation of the emitted quantity per immersion cycle

According to EN 16105 the test specimens are immersed twice on the 1st, 3rd, 5th, 8th, 10th, 12th, 15th, 17th and 19th experimental day. The eluates are merged and analysed after each of the 9 immersion cycles and thus a particular eluate is the result of two one-hour immersions. This implies that the modelled emitted quantity of active substance per immersion cycles results from the sum of the two amounts of active substance leached from layer 1 into the water during each of the two immersion events per immersion cycle. The concrete immersion scheme according to EN 16105 is summarized in Table 14.

Table 14: Immersion scheme according to EN 16105

Immersion cycle	Experimental Day	Hour of Immersion
1	1	1 and 6
2	3	49 and 54
3	5	97 and 102
4	8	169 and 174
5	10	217 and 222
6	12	265 and 270
7	15	337 and 342
8	17	385 and 390
9	19	433 and 438

It must be noted that the model adopted here is not limited on the immersion scheme according to EN 16105. Indeed, this model can be applied with any immersion scheme as long as the same laboratory conditions as defined in EN 16105 are observed. The time discretization allows great flexibility. For instance, it would be possible to consider one-minute immersion events by introducing a finer time discretization, e.g. values by minute instead of by hour. Furthermore, the model allows the consideration of temporal changes in the experiments, e.g. on the 4th immersion cycle the test specimen was immersed 2 hours by mistake or the immersion of the test specimen had to be postponed from the 12th to the 13th experimental day.

5.1.3.5 Estimation of the parameters

Based on the 9 measured emission values – one for each immersion cycle - the two parameters:

(1) percentage of leaching from the boundary layer and

(2) the percentage of diffusion between adjacent layers

are estimated by means of the statistical method of weighted least squares in order to achieve the best approximation between modelled and measured emissions.

The weights are based on the measurement uncertainty of the analytical method. The higher the measurement uncertainty, the lower the weight. The weights are computed as the inverse of the squared measurement uncertainty, where it is assumed that the relative measurement uncertainty is constant at 5 %. In other words, the higher the measured value, the higher the measurement uncertainty and the lower the weight.

Exemplary calculation: Weighting of measurement uncertaincy

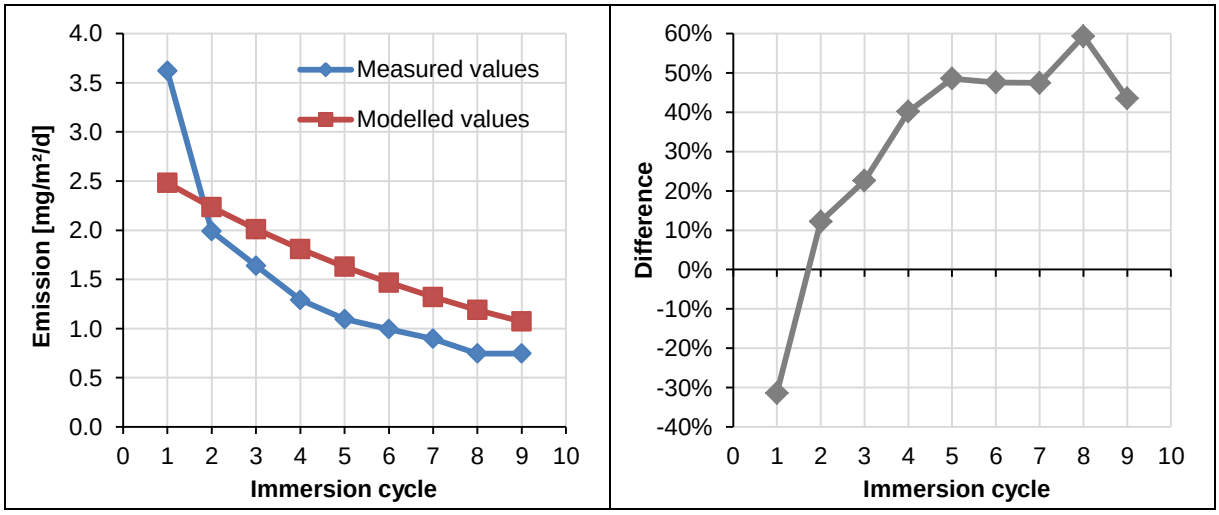
The measurement uncertainty of the analytical method is assumed to be 5 %. Assuming a measured test result of 10 mg/m²/d, the absolute measurement uncertainty would be 0.05·10 mg/m²/d = 0.5 mg/m²/d. Thus, the squared difference between the observed value of 10 mg/m²/d and the modelled value would be weighted by a factor of 1/0.5 = 2. In the case the measured test result is 1 mg/m²/d, the weighting factor would be 20.

The numerical implementation of the semi-analytical approach and the parameter estimation are realised by means of the software package GAUSS. GAUSS is a matrix programming language for mathematics and statistics, developed and marketed by Aptech Systems.

5.1.3.6 Model improvement

If only the leaching and the diffusion parameters are estimated, the fit is insufficient as can be seen in the following example for the active substance terbutryn from the treated article wood coating WC-8 on pine sapwood. The actual shape of the curve joining the measured values is not reflected and a maximum difference between measurement and fitted values of 60 % is obtained.

Figure 51: Fit of the emitted quantity of terbutryn from WC-8 on pine sapwood by means of the semi-analytical model taking into account only the leaching percentage and the diffusion percentage



Left side: Measured emission and modelled emission per immersion cycle. Right side: Percentage difference between measured emission and modelled emission per immersion cycle

In order to improve the quality of the fit, several plausible model adjustments were performed. Here there is a short summary of these adjustments:

- The number of layers of the treated article has been varied from 3 to 20.
- It has been assumed that leaching, i.e. transport of active substance into the water occurs from lower layers as well. It has been assumed that the percentage of the amount of active substance which is leached from layer i (i=1,…,10) follows a Poisson distribution, i.e. the closer the layer to the substrate of the treated article the lower the percentage of leaching.

- It has been assumed that the concentrations of the active substance at time 0 h differ from layer to layer. It has been assumed that the concentration at time 0 h in layer i follows an exponential distribution, i.e. the closer the layer to the substrate the lower the initial concentration.
- It has been assumed that the active substance is transported into the substrate, i.e. a certain percentage p_T of the amount of active substance diffuses into the substrate and cannot be leached.
- A third transport process has been taken into account. It has been assumed that active substance is lost due to evaporation. It has been assumed that in periods without water contact a certain percentage p_E of the amount of active substance evaporates from layer no. 1.
- Instead of evaporation, the degradation process has been taken into account. It has been assumed that a certain percentage p_a of the amount of active substance in each layer decays and thus cannot be leached.

Whereas these different approaches led to better fits, their quality still was not satisfactory. The difference between measured and modelled emissions was considerably greater than twice the relative measurement uncertainty (i.e. greater than 10 %).

However, good quality fits are obtained when a time-dependent transport probability is introduced.

5.1.3.7 Time-dependent transport probability

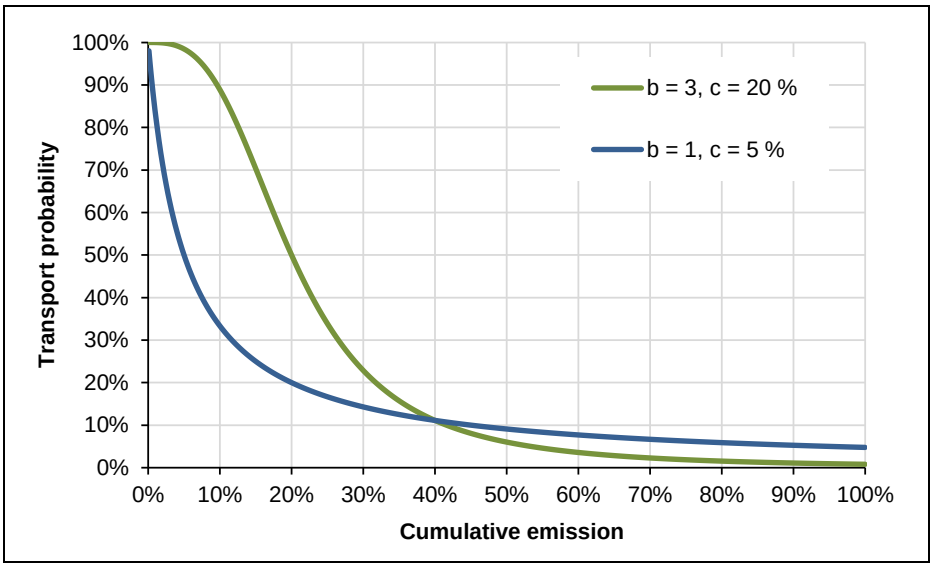
This model enhancement is based on the assumption that the transport probability for the molecules of the active substance is time dependent. For any time t the probability that a molecule is transported must be determined. It is assumed that this transport probability decreases with each further immersion. Over time and due to the contact with water, both the desorption capability of the active substance and the water absorption of the treated article change. The more molecules have already been leached, the lower the transport probability of the remaining molecules. This assumption reflects the fact that the higher the number of previous immersions and the longer the time without water contact the lower the availability of molecules to diffuse and to leach.

It is assumed that the transport probability can be described by the following sigmoid curve, the transport probability at time t only depending on the total amount of active substance which has been leached up to time t:

$$p(t) = 1 - \frac{1}{1 + \left(\frac{x(t)}{c}\right)^{-b}}$$

where p(t) denotes the transport probability at time t, x(t) denotes the percentage cumulative emission at time t, and where b and c are the curve parameters. The period of drying and the number of immersion cycles are implicitly taken into account in the cumulative emission. The influence of both parameters is illustrated by the following Figure 52.

Figure 52: Transport probability curve



The chart shows that the transport probability is around 90 % for the green curve and 33 % for the blue curve if the cumulative emission is 10 %, i.e. 10 % of the initial amount of the active substance has been leached. The parameter c represents the cumulative emission leading to a transport probability of 50 % (20 % for the green curve and 5 % for the blue curve). The parameter b controls the slope of the curve. The lower b, the steeper the curve at a transport probability of 50 %.

The introduction of the transport probability ensures to model the leaching parameter p_L and the diffusion parameter p_D as time dependent parameters. The larger the cumulative emission the lower both percentages. Multiplying the leaching and diffusion parameters by the transport probability at time t, we obtain the corresponding percentages of active substance which are leached and diffused between the layers at time t, i.e. $p_L(t) = p_L \cdot p(t)$ and $p_D(t) = p_D \cdot p(t)$.

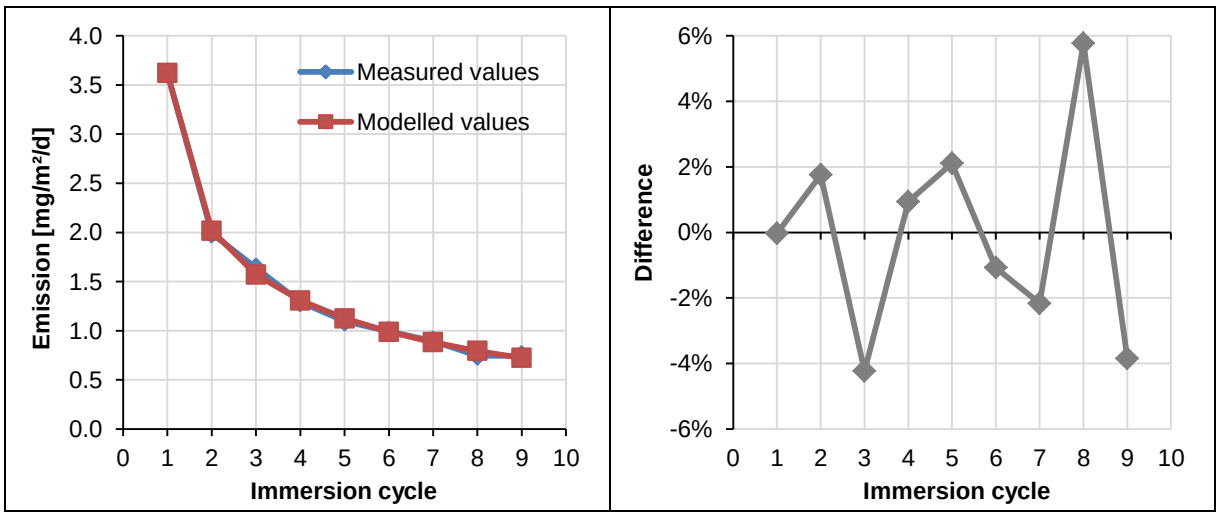
5.1.3.8 Final semi-analytical model

As a result, the final semi-analytical model now includes four parameters to be estimated:

1) Diffusion parameter p_D (parameter describing the transport within the treated article)
2) Leaching parameter p_L (parameter describing the leaching from the boundary layer between treated article and water)
3) Parameter b of the time-depending transport probability curve p(t) and
4) Parameter c of the time-depending transport probability curve p(t).

The good quality of the fit of laboratory leaching data by means of this semi-analytical model is demonstrated by the example mentioned above (terbutryn from WC-8 on pine sapwood). The differences between measured and modelled values lie in the range -4.2 % to 5.8 %.

Figure 53: Fit of the emitted quantity of terbutryn from WC-8 on pine sapwood by means of the final semi-analytical model



Left side: Measured emission and modelled emission per immersion cycle. Right side: Percentage difference between measured value and modelled value per immersion cycle

5.1.3.9 Extrapolation of the semi-analytical model

For the purpose of extrapolation the immersion scheme is continued. The model parameters are calculated from the immersion cycles 1 to 9, and the real experiment is continued artificially by continuing the timeline and the transport processes. Thus, it is possible to determine the emission at a later specific time, e.g. the emission after 25 immersion cycles or an experimental time of one year.

5.1.4 Results of the modelling by means of the semi-analytical model

The semi-analytical model provides good fits of the laboratory test data for different treated articles (roof paint RP-2, wood coatings WC-8, WC-11, textile T-1, sealing tape PVC-1 and the sealing materials SM-2 and SM-3), different substrates (fibre cement, pine sapwood, birch plywood, glass) and different active substances (OIT, terbutryn, diuron, carbendazim, zinc pyrithione). The following figures illustrate how well the model describes the measured data for quite different experiments. The model is best suited for roof paints, wood coatings WC-5, WC-8 and WC-11 and sealing material. Often the differences between the modelled and measured values are in the range of the roughly estimated measurement uncertainty of ± 10 %. The peak of IPBC from WC-5 on immersion cycle 7 is due to increased temperature and decreased air humidity between the immersion cycles 6 and 7. The greater differences between the modelled and measured values for WC-2 and WC-3 are due to the fast transformation of dichlofluanid and tolylfluanid. The complete set of modelling results is given in Annex V.

Figure 54: Fit of the emission quantities by means of the semi-analytical model

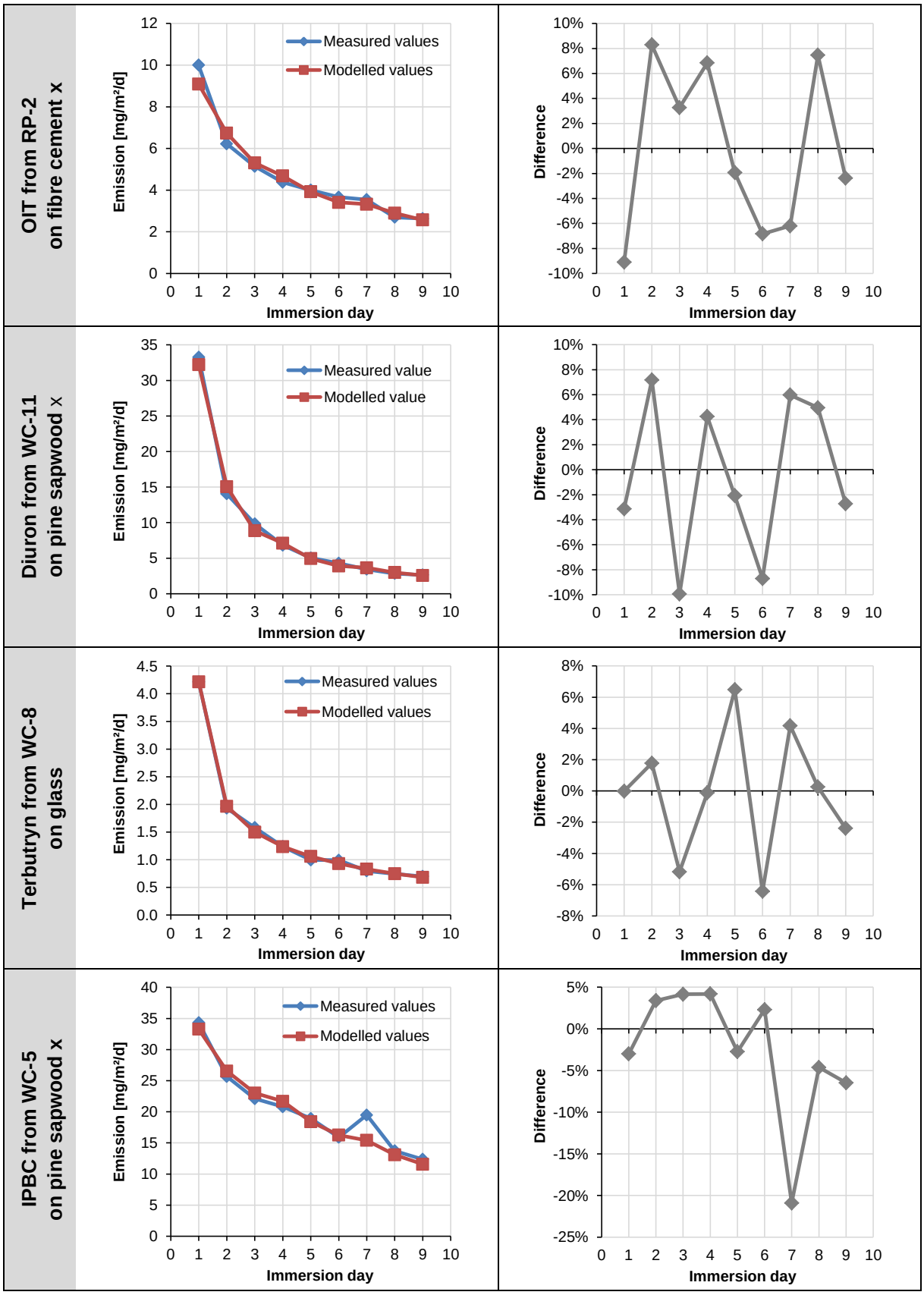


Figure 55: Fit of the emission quantities by means of the semi-analytical model

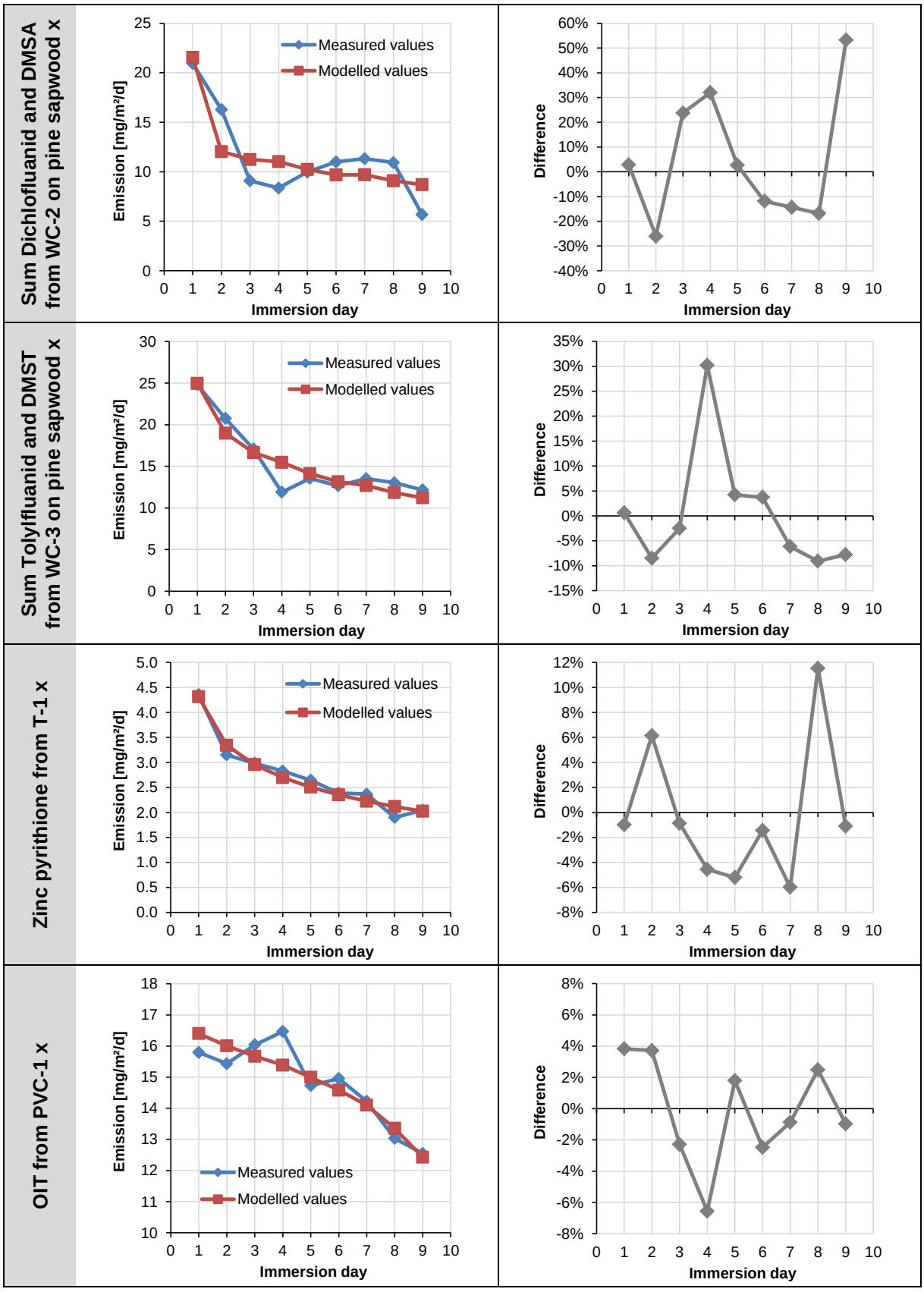
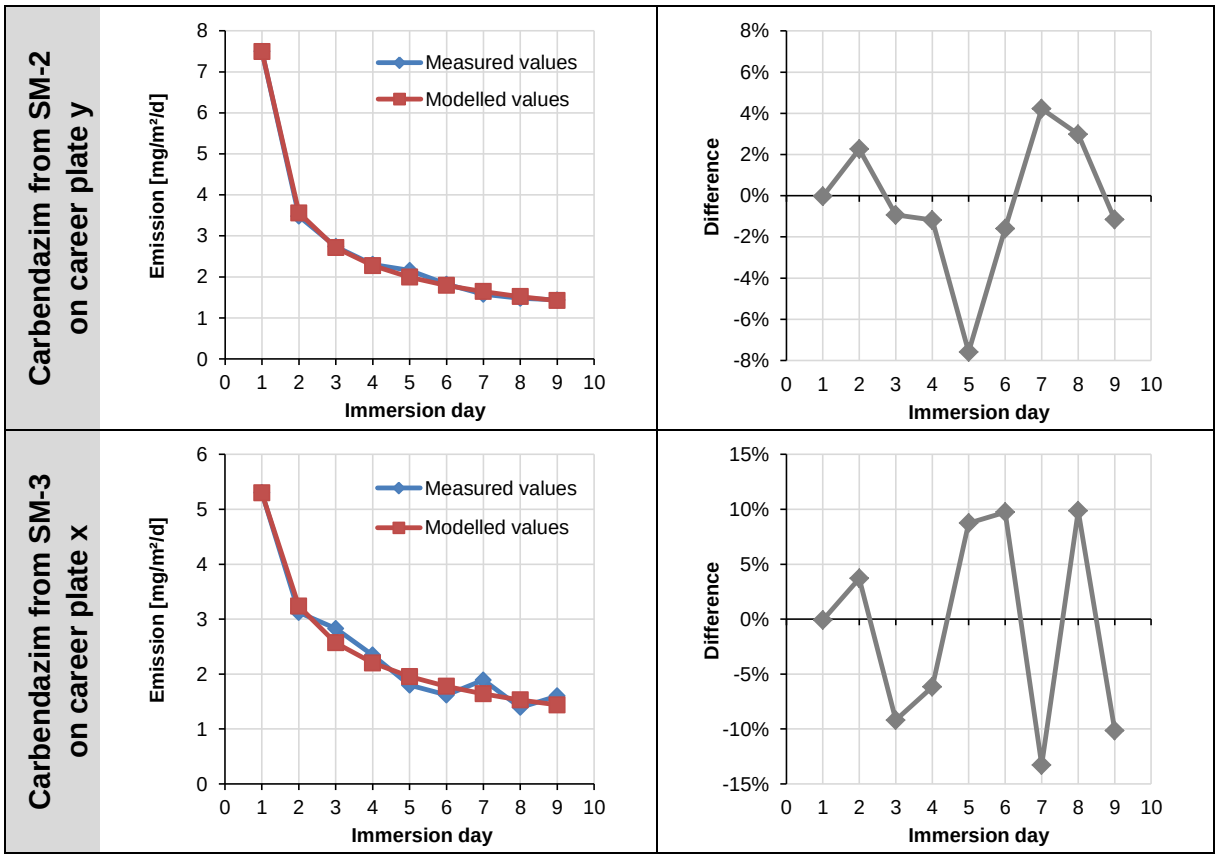


Figure 56: Fit of the emission quantities by means of the semi-analytical model

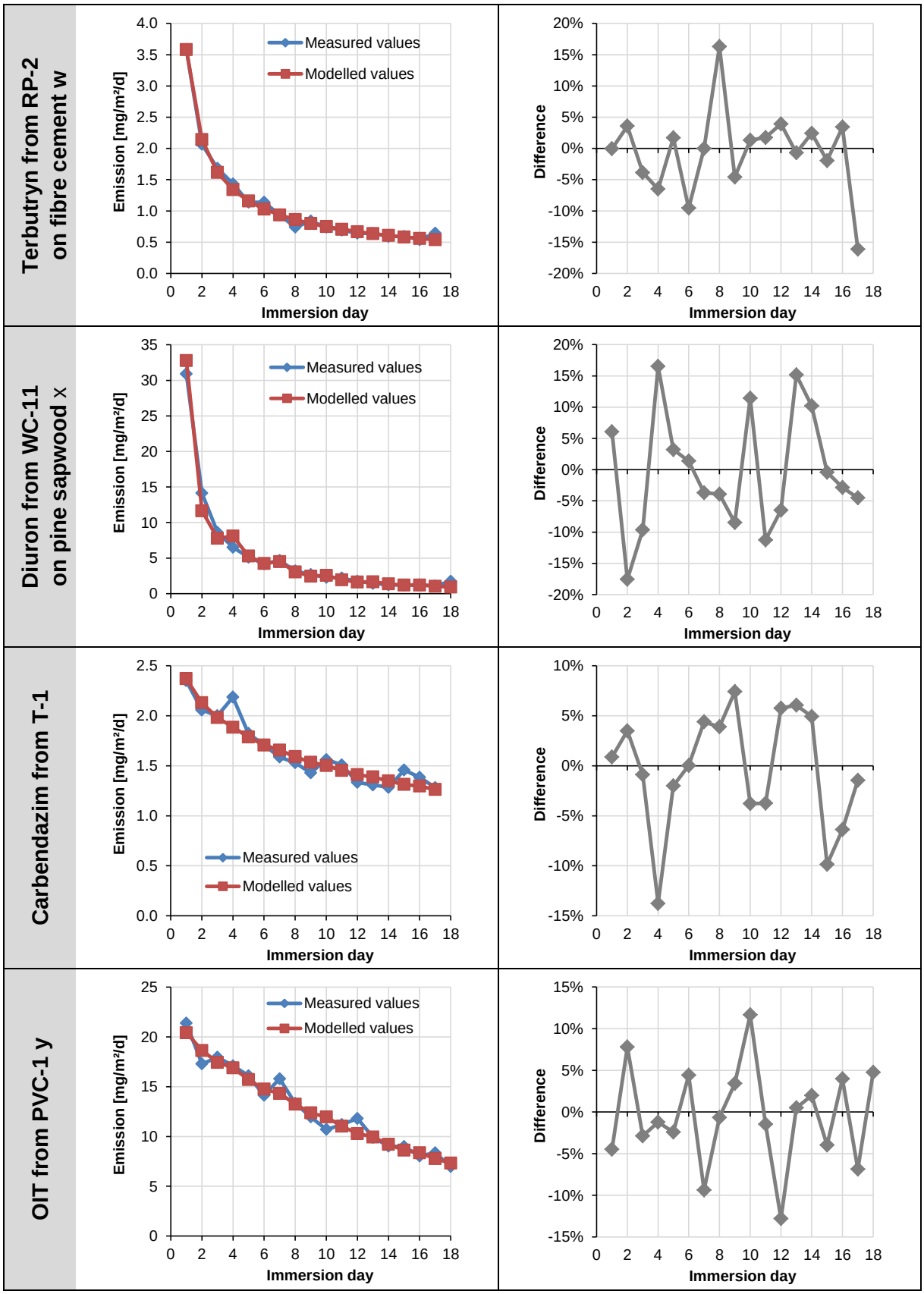


5.1.5 Fitting of long-term data

Extended experiments with 17 - 18 immersion cycles have been conducted for WC-8 on pine sapwood, WC-11 on pine sapwood, RP-2 on fibre cement, PVC-1 and T-1. The data obtained from these experiments were used to demonstrate that the semi-analytical model is suitable for the purpose of prediction. The semi-analytical model reflects the measured values for all 17 and 18 measurement values if the estimation is based on the first 9 immersion cycles only. Some of the results are illustrated in Figure 57.

Modelled values within the range of twofold the measurement uncertainty, i.e. 2· 5 %, do not differ from the measured value. Occasional differences could be caused by random effects, i.e. occasionally a higher or lower amount of active substance is dissolved than expected. There was no trend towards higher or lower results from the model compared to the measured values, which would indicate systematic errors.

Figure 57: Fit by means of the semi-analytical model for extended experiments



5.1.6 Summary of the modelling of laboratory data

The semi-analytical model (1) provides good fits of laboratory leaching data, (2) enables the extrapolation of emissions in laboratory tests and (3) describes the transport processes arising in laboratory tests according to EN 16105.

In contrast to regression models, the semi-analytical model attempts to take into account the changing properties of the treated article (changing water absorption and changing chemical composition) as well as resulting changes in the desorption capability of the active substance.

The semi-analytical model fits the specific emission curves obtained in laboratory experiments for almost all active substances and treated articles well (see Annex V).

Based on 9 immersion cycles the semi-analytical model predicts the emission curves for extended test series (up to 18 immersion cycles) very well.

The semi-analytical model is well-suited to extrapolation. It can be used for the determination of emissions after any number of immersion cycles or experimental days. It can also be used for the determination of emissions after shorter immersion events, e.g. after an immersion time of 10 minutes.

The modelling is based on the results of the in-house laboratory experiments of the BAM Berlin. It was not possible to check the reproducibility of the parameters, i.e. the extent of differences between the parameters corresponding to the fitted curves computed on the basis of data from several laboratories which perform the same immersion experiments for the same active substances and the same treated articles.

The model does not directly take into account degradation and evaporation of the active substances.

Should the testing procedure according to EN 16105 be changed (UV-treatment, temperature changes), the model will need to be adapted.

5.2 Field data

5.2.1 Introduction

In contrast to laboratory tests, in field tests the environmental influences are not controlled. In field tests the test specimens are exposed to random natural weathering conditions, i.e. varying precipitation, varying air humidity, varying temperature, varying UV radiation, varying wind and varying air quality etc..

Considering the emissions [mg/m²] during significant rain events for one treated article – active substance – combination, the variation between directly adjacent test specimens can exceed 50 % and the variation between nearby test specimens can exceed even 100 %. Individual emissions thus differ significantly despite identical or very similar weather conditions. Without knowledge of the impact of the meteorological factors on the leaching properties of the active substance and the treated article, it is not possible to use the semi-analytical model to predict the leaching behavior from field tests.

It is thus necessary to analyse the impact of the meteorological factors in order to identify correlations between the amount of active substance leached and the weather conditions.

5.2.2 Data basis

In total, the following 36 measured emission curves were analysed. Detailed information about the field experiments and the measured values can be found in Annex III.

Table 15: Data basis for the modelling of the field test data

Experiment no.	Treated article		Active substance [no. of emission curves]			
	Type	Code	Diuron	OIT	Terbutryn	Carbendazim
1 – 2	Wood coating	WC-8	2	2	2	
4 – 9		WC-11	6	6	6	
11 – 12	Roof paint	RP-2		2	2	
13		RP-5		1	1	
14 – 19	Textile	T-1				6

The analyses of the emission curves were limited to the time period from June 2012 to April 2014. The number of measured emissions varies between 18 (experiment no. 8) and 42 (experiments no. 2, 9, 12 and 13).

5.2.3 Precision of field data

First of all, the reliability of the data needs to be checked, in order to ensure the validity and precision of the statistical analyses. It was determined that the reliability of the data should be checked by comparing the relative cumulative emissions (relative to the initial amount) after 10 l/m² runoff across the different experiments. Since the cumulative emission highly depends on the cumulative runoff, it makes sense to consider the relative cumulative emission after a fixed runoff value. The value of 10 l/m² is suitable as this amount is exceeded in all experiments on vertically exposed tests specimens.

For each active substance, each treated article and each experiment the cumulative emission after 10 l/m² runoff was calculated by means of linear interpolation on the basis of the values of the cumulative emission at the next lower and next higher cumulative runoffs of 10 l/m². A small numerical example should illustrate the calculation.

Exemplary calculation: Relative cumulative emission at 10 l/m² cumulative runoff

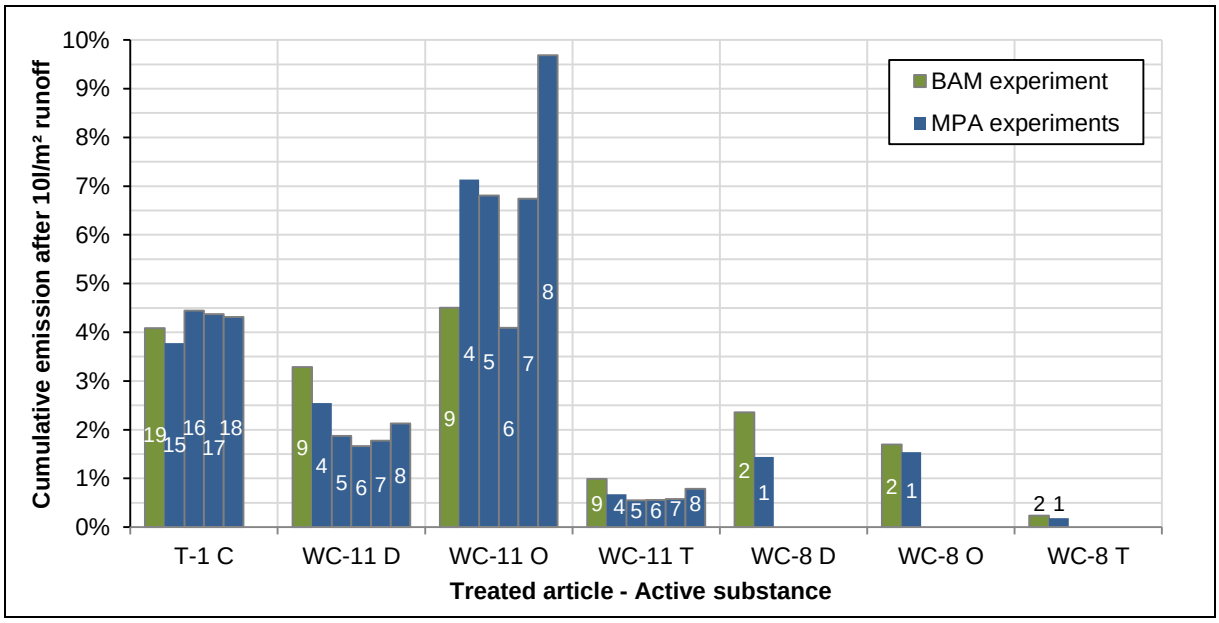
According to Table A III-16 in the field experiment no. 18 for carbendazim on T-1 the cumulative emissions for a cumulative runoff of 8.64 l/m² and 10.5 l/m² are 27.2 mg/m² and 31.2 mg/m², respectively. Then the cumulative emission at 10 l/m² cumulative runoff can be calculated by 10 l/m² times slope + offset = 30.1 mg/m², where

$$\text{slope} = \frac{31.2\ \text{mg/m}^2 - 27.2\ \text{mg/m}^2}{10.5\ \text{l/m}^2 - 8.64\ \text{l/m}^2} \quad \text{and} \quad \text{offset} = 27.2\ \text{mg/m}^2 - 8.64\ \text{l/m}^2 \cdot \text{slope}.$$

As the initial amount according to the recipe is 700 mg/m² the relative cumulative emission at 10 l/m² cumulative runoff is 4.32 %.

The calculated relative cumulative emissions after 10 l/m² runoff for the field experiments on vertically exposed tests specimens are illustrated in Figure 58.

Figure 58: Relative cumulative emission after 10 l/m² runoff for T-1, WC-11 and WC-8 from the BAM and MPA experiments.



The experiment no. according to Table A III-1 is labelled on or above the bar. C: carbendazim, D: diuron, O: OIT, T: terbutryn

The variability of these values will now be determined on the basis of the standard deviation of the logarithmized values as a measure of precision and reliability. It has to be noted that the statistical certainty of the precision data is low as the calculated standard deviations depend on only three locations (BAM, MPA Möllerstraße and MPA Drachenkopf) and only on three treated articles (T-1, WC-11 and WC-8). Nevertheless, the obtained standard deviation provides some information as to what differences can be expected. It must be noted, however, that the impact of meteorological factors has not been taken into consideration at this point. Indeed, the results are based on very specific weather conditions (06/2012 – 01/2014 in Eberswalde as well as 08/2013 – 04/2014 in Berlin).

5.2.3.1 Precision of parallel field tests at the same location

This precision is derived from the MPA experiments for T-1 and WC-11.

Table 16: Relative cumulative emission after 10 l/m² runoff for MPA-experiments no. 4, 5 and 15-18

Treated article	Experiment no.	Carbendazim	Terbutryn	OIT	Diuron
T-1	15	3.78 %			
T-1	16	4.45 %			
T-1	17	4.37 %			
T-1	18	4.32 %			
WC-11	4		0.68 %	7.14 %	2.54 %
WC-11	5		0.55 %	6.81 %	1.87 %
Standard deviation		**7.5 %**	**14.8 %**	**3.3 %**	**21.8 %**

The four experiments for the textile specimens were exposed to different directions, whereas the two experiments 4 and 5 for WC-11 were exposed to the same direction and can be considered as "repeated measurements". Across the three active substances terbutryn, OIT and diuron the average "repeatability" standard deviation is 15.3 %, i.e. it is realistic that for a given active substance and a given treated article the cumulative emissions after 10 l/m² runoff of two test specimens which are located directly adjacent to one another differ by more than 30 % (=1.96 times 15.3 %. The value of 1.96 is based on the fact that 95 % of the area of a normal distribution is within 1.96 standard deviations of the mean).

5.2.3.2 Precision of parallel field tests at nearby locations of the same site

This precision is derived from the test specimens which were installed at the MPA test sites 'Möllerstrasse' and 'Drachenkopf'.

Table 17: Relative cumulative emission after 10 l/m² runoff for MPA-experiments no. 4 and 6

Treated article	Experiment no.	Terbutryn	OIT	Diuron
WC-11	4	0.68 %	7.14 %	2.54 %
WC-11	6	0.56 %	4.09 %	1.66 %
Standard deviation		**13.7 %**	**39.3 %**	**30.0 %**

Across the three active substances the average standard deviation is 29.6 %. If test specimens are exposed to the same direction and they are only 1 km away from each other the differences of the cumulative emission after 10 l/m² runoff for one active substance and one treated article can exceed 60 % (=1.96 times 29.6 %).

5.2.3.3 Precision of subsequent field tests at the same location of the same site

This precision is derived from test specimens which were installed at the MPA test site 'Möllerstrasse' but started at three different times.

Table 18: Relative cumulative emission after 10 l/m² runoff for MPA-experiments no. 4, 7 and 8

Treated article	Experiment no.	Terbutryn	OIT	Diuron
WC-11	4	0.68 %	7.14 %	2.54 %
WC-11	7 (time lag of 3 months)	0.57 %	6.74 %	1.78 %
WC-11	8 (time lag of 6 months)	0.79 %	9.69 %	2.13 %
Standard deviation		**15.6 %**	**19.5 %**	**17.9 %**

Across the three active substances the average standard deviation is 17.8 %. It can be noted that there is no significant impact of the variability between subsequent field tests as this average value is not significantly higher than the repeatability standard deviation with a value of 15.3 %.

5.2.3.4 Precision of subsequent field tests at different locations and different sites

This precision is derived from the tests which were performed at the MPA test site 'Möllerstrasse' (exposed to SE) and the BAM (exposed to SSW). The distance between both test sites is approx. 60 km.

Table 19: Relative cumulative emission after 10 l/m² runoff for BAM- and MPA- experiments no. 1, 2, 4, 9, 18 and 19

Test site	T-1		WC-8				WC-11			
	Exp.	C	Exp.	T	O	D	Exp.	T	O	D
BAM	19	4.08 %	2	0.24 %	1.69 %	2.36 %	9	0.99 %	4.50 %	3.29 %
MPA	18	4.32 %	1	0.18 %	1.54 %	1.44 %	4	0.68 %	7.14 %	2.54 %
Standard deviation		**3.9 %**		**19.3 %**	**6.9 %**	**34.8 %**		**26.8 %**	**32.6 %**	**18.1 %**

The average standard deviation is 23.2 % across the 7 analysed treated article – active substance – combinations. There is no significant effect between the subsequent field tests performed in Eberswalde and Berlin. For one treated article – active substance – combination the standard deviation is below 40 %. Thus, the precision of field test data can be deemed satisfactory considering that the precision is comparable to the precision of "simple" chemical analyses.

5.2.4 Analysis of individual emission curves

5.2.4.1 Regression model and influence factors

After checking the reliability of the data, it is necessary to determine the most relevant influence factors by considering the individual, i.e. the time-specific, location-specific, treated article-specific and active substance-specific emission curves. The aim is to explain the observed (logarithmized) concentration [mg/l] of the active substance in the runoff-samples by means of weighted linear regression models by taking into account the following 9 meteorological factors:

- Amount of collected runoff
- Cumulative runoff
- Precipitation (amount of rain)
- Amount of driving rain
- Temperature
- Relative humidity
- Wind velocity
- Wind direction
- Global radiation

These factors were taken into account because, on the one hand, information related to these factors was available (apart from a few exceptions) and it is known that these factors have a potential influence on the amount of emission. In order to determine the dependency of the concentration on the time and the runoff, 4 additional parameters were taken into account:

- Day of the experiment
- Number of days from the previous sampling
- Concentration of the previous sampling
- Reciprocal value of the amount of collected runoff

The reciprocal value of the runoff is used to examine whether the impact of the runoff is very strong for lower values of the runoff. The original value of the runoff is used to determine the percentage change in concentration resulting from a 1 l/m² increase in runoff.

5.2.4.2 Statistical processing of the data

The day of the experiment as well as the number of days from the previous sampling follow from the experimental design. The concentration of the previous sampling and the reciprocal value of the runoff are known. The amount of water in the samples collected which reflects the runoff and the amount of rain have been quantified directly both in Berlin and Eberswalde. The amount of driving rain was directly measured at the Eberswalde test sites only. Data for the amount of driving rain at the BAM test site were not available.

The meteorological factors temperature, relative humidity, wind velocity, wind direction and global radiation were taken from recorded data of the MeteoGroup weather station in Eberswalde and a DWD weather station directly adjacent to the BAM test site in Berlin-Lichterfelde. Data for the global radiation for the Berlin test sites

were taken from a weather station which is supported by Freie Universität Berlin in the Botanical Garden (2.5 km away). The available recorded data are continuous values at 10-minute-intervals.

However, there are no data available for the relative humidity in Eberswalde. Moreover, there are no records of temperature from the weather station in Eberswalde from 49 days, in total (during the periods 17 - 20 August 2012, 05 - 06 January 2013, 14 - 24 June 2013, 09 July 2013, 21 – 26 August 2013 and 05 – 29 January 2014).

For the temperature, the relative humidity, the wind velocity, the wind direction and the global radiation, the averaged values of the 10-minute-intervals between the time of sampling and the previous sampling were included in the regression model. In order to normalize the data, the relative humidity and the wind direction were transformed beforehand. All 10-minute-values of the relative humidity (H) were Logit-transformed, i.e. the logarithm of the ratio between H and 1-H, and the averaged Logit-values were included in the regression model. The 10-minute values of the wind direction were averaged as follows: The sine and the cosine were calculated for each direction. The results of all sines are summed and the results of all cosines are summed. The averages are calculated for both the sines and the cosines. The sines average is then divided by the cosine average and the resulting number is transformed back in the average direction using the arctangent function. In order to quantify the wind effect more precisely the four periodic functions sin(W), sin(2·W), cos(W) and cos(2·W) of the average wind direction (W) were included in the regression model.

5.2.4.3 Interaction effects

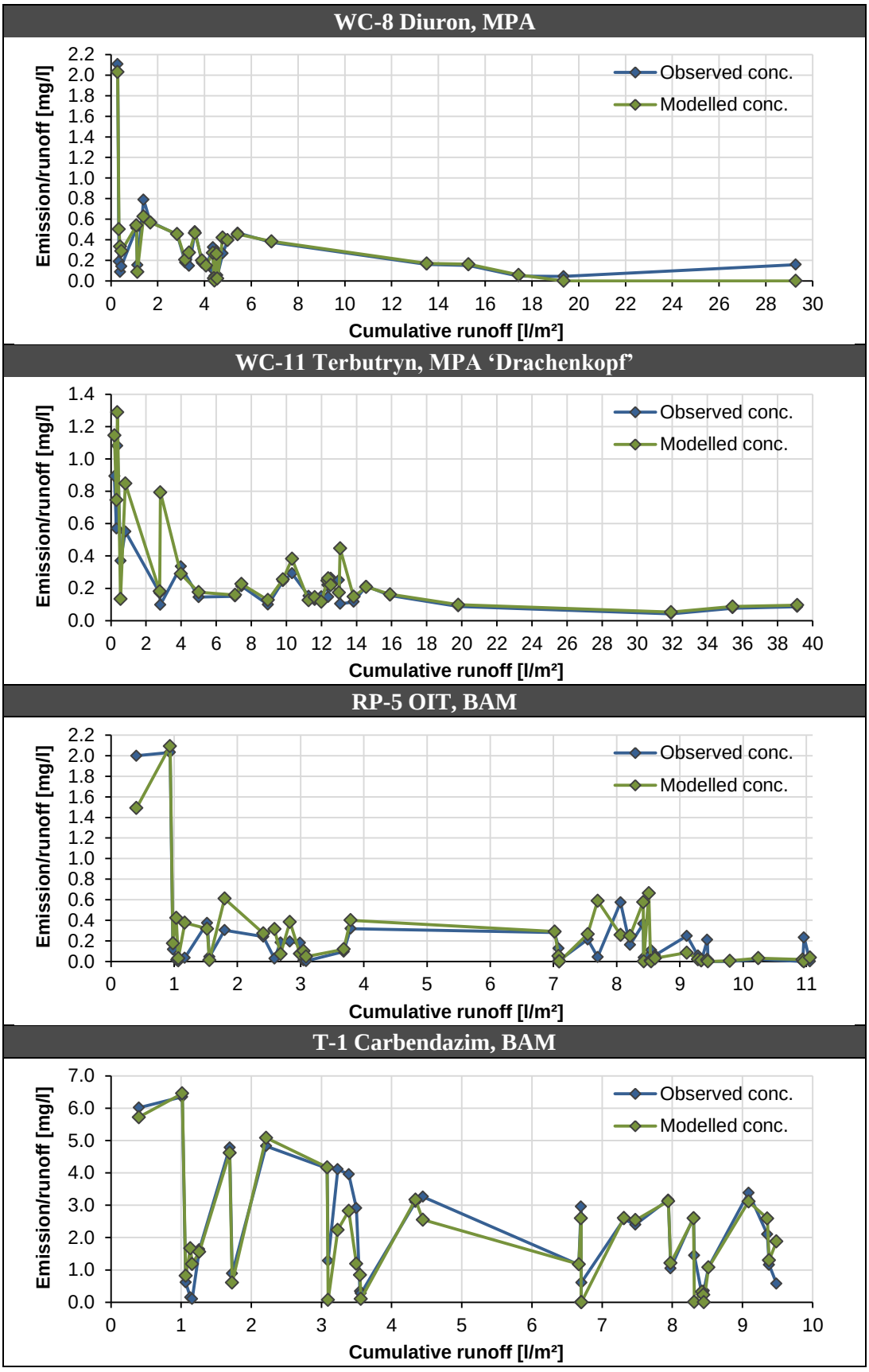
One difficulty in considering the influence factors results from the fact that each factor not only has a separate impact on the emission, but also interacts with the other factors. If the pairwise interactions of the 9 meteorological factors were included in the regression model, 36 (= 9·8/2) interaction effects would have to be added to the model. However, there are only 18 – 42 observations (depending on the experiment) and there are missing values within the recorded meteorological data. Taking into account the interactions would lead to an overparameterised model. Thus, only the 9 meteorological factors as well as the 4 additional parameters mentioned in section 5.2.4.1 were included in the regression model.

5.2.4.4 Fit by means of the regression model

The regression models have been calculated using the open source statistical software R. It was possible to improve the fits of the individual emission curves by weighting the observed concentrations with the squared runoff, i.e. concentrations which are based on a higher amount of collected runoff were given a stronger weighting.

The models enable a satisfactory fit of the observed concentrations. The adjusted coefficient of determination R^2_{adj} indicating how well the data is fitted lies between 76 % and 99 %. The residual standard error representing the variation between observed and modelled concentration is 22 % average across all 36 combinations (18 % across the 33 vertically exposed combinations and 46 % across the 3 horizontally exposed combinations). The goodness of fit is illustrated by Figure 59 by means of four selected examples. The figures compare the observed concentration with the concentration according to the regression model.

Figure 59: Fit of the observed concentration by means of the regression model



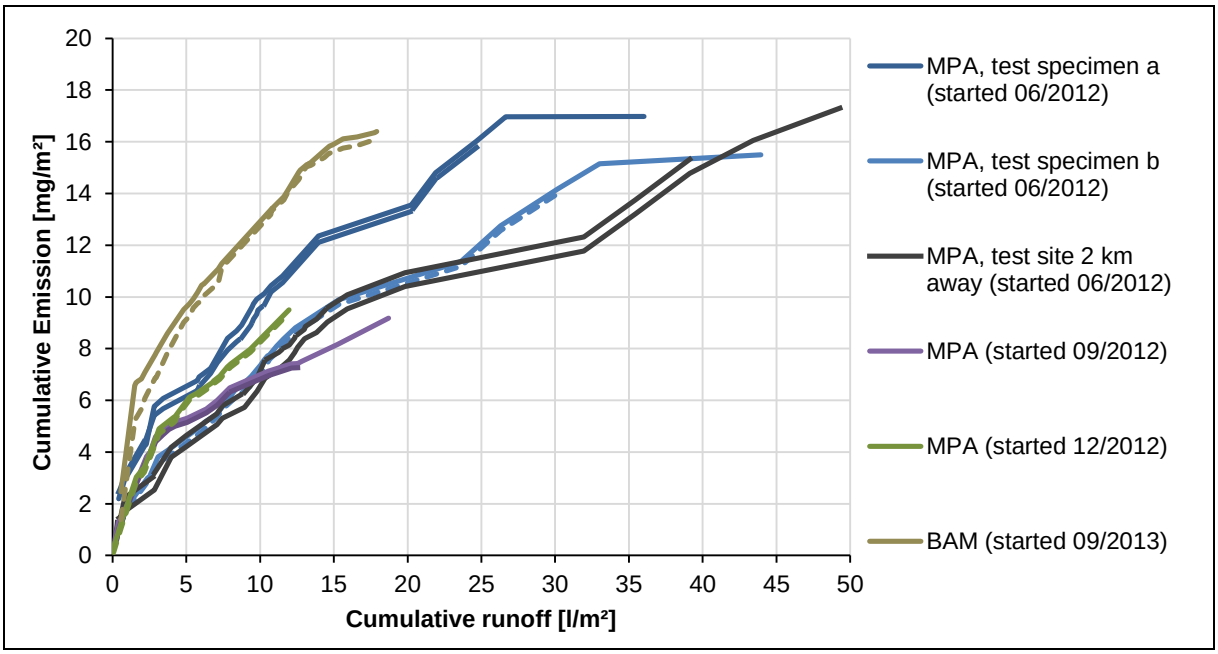
The examples, in particular terbutryn from WC-11 at MPA 'Drachenkopf', show two limits of the regression models:

(i) The fit of the concentration of the first two sampling points is not very good. At the beginning of the experiment the leaching is not primarily driven by meteorological factors. The high leaching rate at the beginning can be attributed to a high percentage of active substance that is not firmly bound in the matrix and is thus available for leaching.

(ii) For a very few sampling points there are larger differences between observed and modelled concentrations. A reason for this could be that the averaging of the meteorological factors slightly distorts the true weather conditions that prevailed between the 2 sampling points.

Besides the comparison of the observed and modelled concentrations a more important aspect is the comparison between the observed cumulative emission and the cumulative emission obtained from the model. The differences are relatively small as can be seen in the following figure which displays the results for diuron from WC-11. Due to missing values within the meteorological records the modelled curves (dashed line) are shorter than the observed curves (solid line) for some test specimens. If considering the last sampling point from which a concentration can be predicted by means of the regression model, for each of the 36 combinations the cumulative emission according to the model differs from the observed cumulative emission only by -8 % (OIT from RP-2 at the MPA) minimum and 9 % (terbutryn from RP-2 at the BAM Berlin) maximum.

Figure 60: Observed cumulative emission curve (solid lines) and cumulative emission curve obtained from the regression model (dashed lines) for diuron from WC-11 and for all test specimens



5.2.4.5 Interpretation of the results of the regression model

The interpretation of the estimated regression coefficients of the different variables is rather difficult (the estimated regression coefficients for each treated article – active substance – test specimen combination are listed in Annex V). It is more helpful to consider the factorial effects instead of the coefficients. The determined factorial effects are listed for each treated article – active substance – test specimen – combination in Table 22 and Table 21. As multiplicative relationships between the different factors and the concentration are assumed due to the taking of the logarithm of the concentration, each factor effect represents the change in concentration if the corresponding variable is increased by one unit. For example, the effect of the amount of rain of diuron from WC-11 at the BAM test site is 3.3 %, i.e. the concentration would be more than 3 % higher if the amount of rain was 1 l/m² higher, with all other variables held constant.

There is a good agreement of the factorial effects across the different active substances for one test specimen, although the levels are very different. This means the meteorological effects are surprisingly similar for one test specimen, e.g. OIT, diuron and terbutryn from WC-11 at the BAM test site. However, for each factor the effects vary considerably from one combination to another and from location to another as well. For example, the day of the experiment has a significant negative effect with a value of -3.2 % for OIT from WC-11 at the BAM test site and on the other hand the day of the experiment has a significant positive effect with a value of 4.3 % for the test specimen b at the MPA test site, i.e. under the assumption that there is no change of the other variables a further day of experiment would lead to a reduction of the concentration by almost 3 % in Berlin, whereas the concentration would be 3 % higher in Eberswalde. However, it has to be noted that the BAM started 15 months later. The interpretation of the effects is further complicated by the fact that data for the relative humidity, the amount of driving rain and the temperature were not available for all field experiments.

A semi-automated process of variable selection did not lead to a satisfactory result. Variables were removed successively by means of an iterative statistical method until the model contains only statistically significant factors. As the "best" subset of factors differs considerably between the 36 emission curves analysed, it was decided to revert to the model described above. A closer inspection of the effects, however, indicates possible relationships.

It is conspicuous that the relative air humidity shows a positive effect in all of the 11 BAM experiments. The amount of driving rain shows a negative effect in all 22 out of one MPA experiments. The global radiation shows a positive effect in 80 % of the cases. Additionally, it is conspicuous that in more than 50 % of the cases the temperature, the runoff, the cumulative runoff and the day of the experiment show a significant effect. However it has to be noted that there is a mutual dependency between the day of the experiment and the cumulative runoff. The longer the duration of the experiments, the higher the cumulative emission and vice versa. The concrete number and percentage of negative and positive effects for each factor are listed in Table 20. A negative or positive effect of the corresponding factor means, that an increase of this factor induces a lower or higher concentration of the active substance in the runoff-sample, respectively.

In addition to the tables given it has to be noted that the wind direction has a significant effect on the concentration in 6 out of 36 cases only.

Table 20: Number and percentage of negative and positive effects for each factor based on the regression model across all treated article – active substance – test specimen combinations.

Factor	Negative effect		Positive effect	
	Irrespective of significance	Significant at 5% level	Irrespective of significance	Significant at 5% level
Day of experiment [d]	18 (50 %)	14 (39 %)	18 (50 %)	6 (17 %)
No of days to previous sampling [d]	21 (58 %)	9 (25 %)	15 (42 %)	9 (25 %)
Conc. of previous sampling [mg/l]	17 (47 %)	8 (22 %)	19 (53 %)	3 (8 %)
Runoff [l/m²]	22 (61 %)	17 (47 %)	14 (39 %)	6 (17 %)
Cumulative runoff [l/m²]	21 (58 %)	12 (33 %)	15 (42 %)	12 (33 %)
Amount of rain [l/m²]	13 (36 %)	2 (6 %)	23 (64 %)	8 (22 %)
Amount of driving rain [l/m²]	21 (95 %)	7 (32 %)	1 (5 %)	0 (0 %)
Temperature [°C]	14 (56 %)	11 (44 %)	11 (44 %)	5 (20 %)
Global radiation [W/m²]	8 (22 %)	1 (3 %)	28 (78 %)	9 (25 %)
Relative humidity [%]			11 (100 %)	6 (55 %)
Wind velocity [m/s]	26 (72 %)	8 (22 %)	10 (28 %)	8 (22 %)

There are possible explanations for the effects which have been identified. The positive effect of the global radiation and the negative effect of the temperature could be explained by the fact, that the diffusion and the transport to the surface area are promoted by the heating of the surface area, but in contrast the degradation rate is increased with increasing temperature and UV radiation. Depending on the treated article, the active substance and the duration of the experiment one impact dominates. The negative effect of the driving rain could be due to dilution effects as the amount of runoff is also increased with increasing amount of driving rain, and thus the concentration in the runoff is decreased despite increasing emissions. The significant effect of the air humidity could be caused by the increase in the water availability in the treated article leading to an increase in the transfer of active substance into the aqueous phase.

Finally, the attempt was made to reproduce the emission curves across the different active substances, across the different treated articles and across the different test locations by an overall model with random and fixed effects. A satisfying model fit was not possible. The large number of factorial interactions and missing values of meteorological records made it difficult to find a good model. However, the following findings could be confirmed by the models obtained:

- The higher the cumulative runoff the lower the concentration in the runoff samples.
- The higher the temperature the higher the concentration in the runoff samples.

On the other hand, the unsatisfactory overall model fits demonstrate that the effects of the different meteorological factors depend on the properties of the treated articles and the active substances and depending on the weather conditions the properties change.

Table 21: Factorial effects for the test specimens WC-11

Treated article	Active substance	Test site	Exposure	Day [d]	No. of days to previous sampling [d]	Conc. of previous sampling [mg/l]	Runoff* [l/m²]	Cumulative runoff [l/m²]	Amount of rain [l/m²]	Amount of driving rain [l/m²]	Temperature [°]	Global radiation [W/m²]	Relative humidity [%]	Wind velocity [m/s]	Residual standard error	Adjusted R²
WC-11	D	BAM	v	-2.8%	13.2%	10.2%	-57.4%	32.8%	3.3%		13.4%	0.1%	94.3%	234.5%	20.2%	85.4%
		MPA, a	v	0.5%	-2.6%	-43.9%	-32.5%	-7.7%	1.3%	-12.6%	-17.5%	1.5%		-14.1%	18.1%	96.1%
		MPA, b	v	1.0%	-1.6%	-39.0%	-17.2%	-10.3%	0.5%	-5.2%	-12.2%	1.1%		-27.3%	15.4%	97.3%
		MPA, 1 km away	v	-0.1%	-7.1%	-48.9%	-19.3%	-2.8%	5.2%	-30.0%	-23.2%	2.2%		-56.7%	18.4%	98.4%
		MPA, + 3 months	v	-5.3%	-4.0%	10.8%	4.5%	99.2%	-3.7%	-14.2%		0.4%		-10.8%	10.5%	96.3%
		MPA, + 6 months	v	-2.3%	0.7%	-22.4%	22.9%	61.2%	-0.1%			0.5%		-45.9%	7.2%	96.9%
	O	BAM	v	-2.7%	11.2%	72.6%	-54.3%	31.9%	2.2%		14.5%	0.1%	105.0%	229.4%	19.6%	86.0%
		MPA, a	v	0.1%	-2.8%	-76.0%	-33.0%	-4.6%	2.5%	-5.4%	-9.9%	0.8%		-22.9%	12.9%	97.1%
		MPA, b	v	0.5%	-1.3%	-83.4%	-10.6%	-8.3%	1.0%	-5.4%	-11.3%	0.7%		-22.0%	13.5%	96.7%
		MPA, 1 km away	v	-0.1%	-6.9%	-83.7%	-17.5%	-3.7%	4.9%	-25.8%	-20.9%	1.7%		-53.3%	15.8%	97.9%
		MPA, + 3 months	v	-6.4%	-2.5%	7.9%	-1.8%	157.7%	-1.9%	-12.8%		1.0%		-1.9%	9.2%	96.4%
		MPA, + 6 months	v	-1.6%	0.4%	-49.0%	-9.1%	32.8%	0.2%			0.0%		-6.4%	7.6%	97.9%
	T	BAM	v	-3.2%	12.8%	-5.1%	-58.3%	27.3%	4.9%		10.6%	0.2%	113.7%	287.5%	24.3%	88.5%
		MPA, a	v	2.8%	1.9%	-18.2%	38.9%	-49.1%	-2.2%	2.9%	-19.8%	1.0%		-80.4%	24.3%	98.5%
		MPA, b	v	4.3%	-6.5%	-19.3%	59.3%	-44.7%	2.5%	-9.2%	-33.6%	3.3%		-55.7%	28.9%	98.8%
		MPA, 1 km away	v	0.6%	-5.8%	-27.9%	2.4%	-21.1%	4.4%	-27.1%	-25.1%	1.6%		-54.0%	23.8%	98.9%
		MPA, + 3 months	v	-0.6%	-9.2%	25.7%	239.0%	-5.3%	-1.5%	-22.1%		0.5%		-42.0%	12.5%	96.4%
		MPA, + 6 months	v	1.9%	6.4%	-12.8%	43.5%	-73.5%	-1.5%			-1.6%		-50.1%	23.1%	98.4%

Significant effects are highlighted in red.

*) The effect of the runoff contains the effect of both the original and reciprocal values of the amount of collected runoff.

Table 22: Factorial effects for the test specimens RP-2, RP-5, T-1 and WC-8

Treated article	Active substance	Test site	Exposure	Day [d]	No. of days to previous sampling [d]	Conc. of previous sampling [mg/l]	Runoff* [l/m²]	Cumulative runoff [l/m²]	Amount of rain [l/m²]	Amount of driving rain [l/m²]	Temperature [°]	Global radiation [W/m²]	Relative humidity [%]	Wind velocity [m/s]	Residual standard error	Adjusted R²
WC-8	D	BAM	v	-2.9%	17.5%	86.1%	-64.3%	53.0%	5.8%		7.8%	0.7%	207.2%	267.7%	17.8%	91.4%
		MPA	v	0.6%	-2.1%	-8.2%	17.5%	-26.9%	0.5%	-10.1%	-14.0%	0.6%		-59.5%	6.7%	98.9%
	O	BAM	v	-1.6%	7.6%	2830%	-42.6%	23.4%	4.1%		11.0%	0.6%	138.8%	146.1%	10.4%	93.8%
		MPA	v	0.2%	-2.3%	25.1%	35.6%	-24.5%	1.0%	-10.8%	-7.7%	0.5%		-42.6%	5.7%	99.1%
	T	BAM	v	-1.9%	3.1%	4.5%	-26.1%	12.3%	5.6%		7.6%	1.3%	191.0%	99.4%	17.7%	91.5%
		MPA	v	4.2%	-0.7%	-1.9%	259.0%	-74.6%	-1.6%	-19.2%	-6.5%	0.7%		-76.6%	11.1%	99.2%
RP-2	O	BAM	v	-1.5%	1.5%	574.5%	-42.3%	19.2%	0.4%		10.8%	-1.7%	12.3%	-8.0%	17.5%	85.2%
	T	BAM	v	-3.1%	12.8%	96.6%	-69.2%	34.0%	3.3%		12.2%	-1.1%	75.7%	299.8%	23.9%	90.4%
RP-2	O	MPA	h	1.4%	-1.1%	463.1%	-31.3%	-1.8%	1.1%	-8.7%	4.6%	0.1%		-14.2%	35.6%	91.2%
	T	MPA	h	5.6%	-2.8%	22.3%	-10.4%	-4.3%	-0.3%	-7.3%	-4.5%	0.7%		-32.4%	59.1%	89.4%
RP-5	O	BAM	v	-3.0%	14.6%	46.3%	-69.5%	69.7%	4.4%		9.9%	0.3%	105.5%	521.0%	12.7%	75.8%
	T	BAM	v	-5.5%	23.6%	54.6%	-85.2%	108.3%	5.9%		-10.0%	3.1%	215.2%	2556%	20.5%	83.2%
T-1	C	BAM	v	-1.0%	-2.4%	-5.2%	-8.7%	24.6%	0.7%		12.1%	0.0%	16.5%	-52.8%	6.3%	95.8%
		MPA, SW	v	7.7%	-4.0%	67.1%	3353%	-75.0%	-9.3%	-12.7%		2.2%		-86.8%	19.0%	94.7%
		MPA, NE	v	6.8%	-3.5%	12.5%	575.6%	-66.7%	-5.2%	-18.3%		-2.7%		-56.7%	13.6%	95.6%
		MPA, NW	v	15.1%	-4.2%	17.9%	2822%	-90.9%	-8.4%	-25.5%		-1.0%		-74.0%	12.4%	95.7%
		MPA, SE	v	3.7%	4.0%	14.5%	473.6%	-48.7%	-3.3%	-2.7%		-2.3%		-44.2%	38.4%	91.2%
		MPA, SSW	h	2.1%	-2.0%	-2.9%	-95.4%	-2.1%	-1.7%	-14.9%		-0.3%		-54.9%	41.1%	87.1%

Significant effects are highlighted in red.

*) The effect of the runoff contains the effect of both the original and reciprocal values of the amount of collected runoff.

5.2.4.6 Model without meteorological factors

The attempt was made to explain the observed concentration without meteorological factors, i.e. only the factors day of experiment, number of days between two sampling points, runoff, cumulative runoff and concentration of the previous sampling were taken into account. These factors can be determined without much effort. In addition, to a considerable extent, the runoff is influenced by the type of precipitation (liquid, freezing, frozen precipitation), the intensity and duration of rainfall, the direction of prevailing wind, the wind velocity, the temperature, relative humidity etc. Thus the runoff reflects all these influencing meteorological factors.

The average residual standard error is 40 %. Therefore, the model without meteorological factor enables only a rough prediction of the observed concentrations. On the other hand, these results indicate the importance of the runoff and the meteorological effects.

5.2.5 Summary of the modelling of field data

The field test data is precise and reliable from a statistical point of view as the standard deviation of the relative cumulative emission after 10 l/m² runoff between the MPA and BAM test sites lies between 20 % and 40 % for each treated article – active substance – combination. Although the same weather conditions prevail, the observed emission after one single rain event can vary considerably between different test specimens. The differences can exceed 200 %.

Emission curves can be fitted well by means of linear weighted regression models. The observed emission [mg/m²] per amount of runoff [l/m²] can be explained by meteorological factors. Weather conditions play a crucial role for emissions. According to model calculations, the emission may vary by a factor of 10 or more. The analyses concluded that the runoff is the dominating factor affecting the emission. The amount of driving rain, the global radiation, the temperature and the air humidity proved to be the most important additional influencing factors. The cumulative emission can be described satisfactorily by means of the regression model taking into account all available meteorological factors.

5.3 Relationship between laboratory and field data

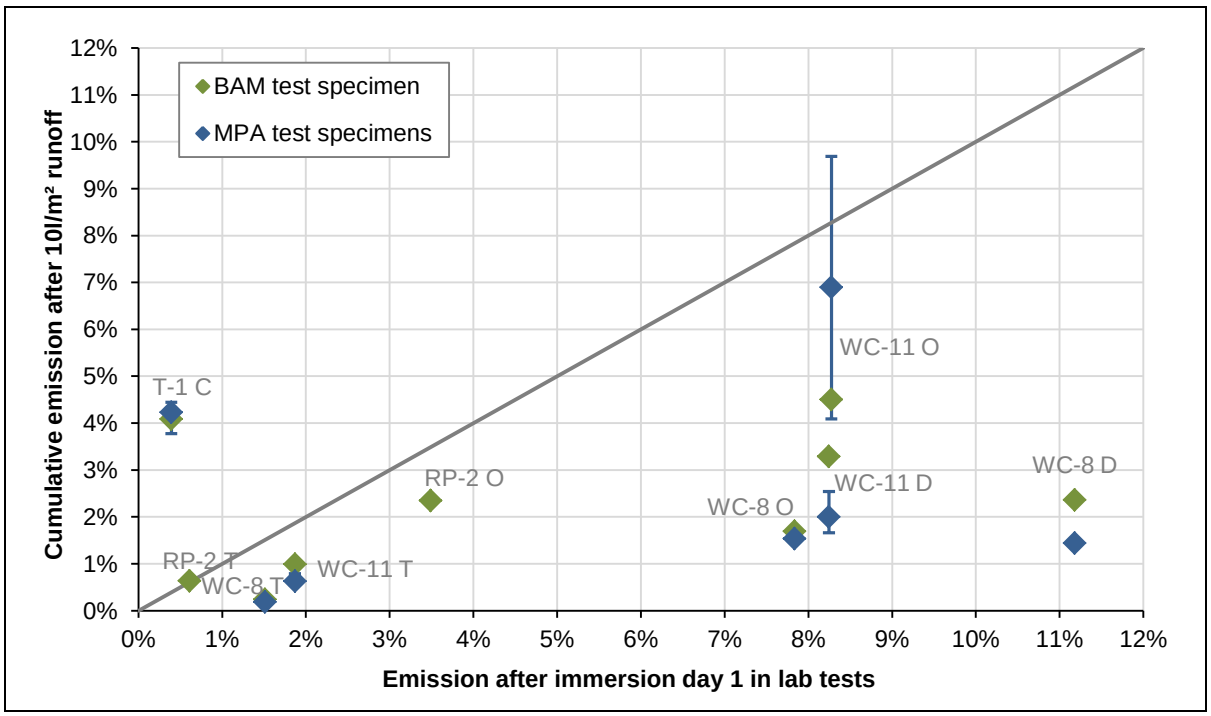
5.3.1 Introduction

Laboratory experiments overestimate vertically exposed field experiments considerably. Thus laboratory data represent a worst-case scenario. In order to clarify whether field tests can be derived from laboratory tests, the attempt was made to analyse the relationship between laboratory data and field data by means of mathematical models.

5.3.2 Laboratory data vs. field data

As can be seen in Figure 61, the cumulative emission from vertically exposed field tests after 10 l/m² runoff are much lower than the amount of emission measured on the first immersion cycle in the laboratory test. The only exception is carbendazim for the Textile T-1, where field experiments result in higher emissions than the laboratory test.

Figure 61: Emission after the first immersion cycle in the laboratory tests vs. cumulative emission after 10 l/m² runoff for the vertically exposed test specimens.



Data from test specimens in field experiments are compared to results of laboratory tests performed at BAM. The line represents equal data from both types of experiment. The vertical blue bars represent the different MPA test specimens.

An explanation for this difference between laboratory data and field data could be that in laboratory experiments degradation does not take place to the same extent. The analyses of field data showed that the temperature and the global radiation have a strong influence on the concentration. This suggests a modification of the structure of the treated article and a degradation of the active substance. These effects are highly dependent on the treated article and on the active substance. In the laboratory procedure these effects are not reflected.

5.3.3 Multivariate calibration based on laboratory data

In a first step, the attempt was made to explain the differences between laboratory data and field data by means of a statistical model with fixed and random effects. The (logarithmized) concentration was modelled across all treated articles, all active substances and all vertically exposed test specimens. The model took into account the relevant factors

which were identified in the analysis of the individual emission curves as well as the laboratory test data, e.g. the emission after the first immersion cycle and the cumulative emission after the ninth immersion cycle in the laboratory experiments. However, the imprecision of the model was too high, with the result that it was not possible to establish a calibration function between field data and laboratory data as the correlation between the two datasets was too low. Further modification is necessary before applying a multivariate calibration model.

In order to explore further the relationship between both datasets, a possible relationship between the immersion cycle in the laboratory tests and the runoff in the field tests was analysed.

5.3.4 Time adjustment

In a second step, a mathematical adjustment of the immersion cycle and the runoff was performed. It has to be mentioned that one immersion cycle in the laboratory test corresponds to a defined water volume per area of exposed surface. This water volume can be compared with the runoff in the field test.

It is assumed that there is a linear relationship between the immersion cycles in the laboratory tests and the cumulative runoff in the field tests. It is assumed that the immersion cycle t can be explained linearly by $t = a + b \cdot r$, where r is the cumulative runoff and the two parameters a and b represent the intercept and the slope, respectively. The intercept refers to the immersion cycle when the cumulative runoff is zero and the slope expresses the rate of change in the immersion cycles for a change of the cumulative runoff by 1 l/m². This means the corresponding cumulative runoff to a given immersion cycle t results from $r = \frac{t-a}{b}$. A simple example shall clarify this relationship. Assuming the parameter a is -2.0 and the parameter b is 0.25, the cumulative runoff r, which is assigned to the third immersion cycle, is 20 l/m² $= \frac{3-(-2)}{0.25}$.

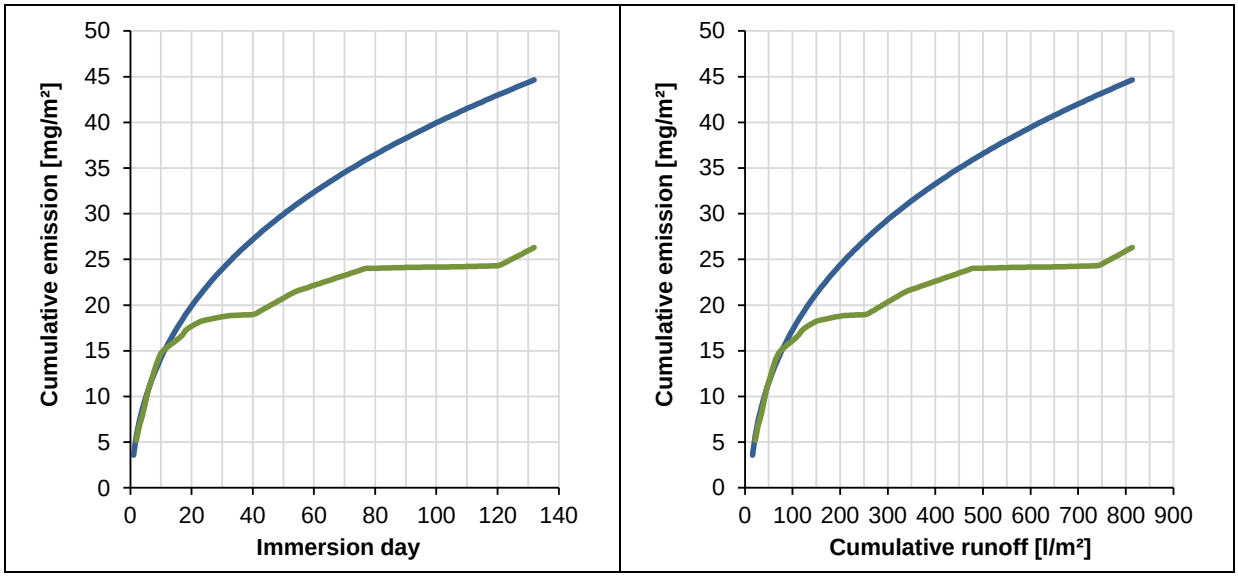
By means of the linear relationship $t = a + b \cdot r$, the cumulative emissions in the laboratory tests can thus be directly related to the cumulative emissions in the field tests. Applied to the example which has just been considered, the cumulative emissions in the field test corresponding to the runoff r = 20 l/m² would be compared to the cumulative emissions in the laboratory test corresponding to t = 3 immersion cycles. The exact cumulative emission at r = 20 l/m² will in all likelihood be unknown, since cumulative emissions are only given for a few discrete runoff values. However, it would be possible to compute any missing cumulative emission values by means of linear interpolation on the basis of the values at the next lower and next higher cumulative runoffs.

Furthermore, it is assumed that the emission measured on the first immersion cycle in the laboratory test is equal to the cumulative emission in the field test at the cumulative runoff which is assigned to the first immersion cycle. This assumption means that at the immersion cycle t = 1 and the cumulative runoff $r = \frac{1-a}{b}$, the emissions are equal and that, at least initially, the test specimens in the laboratory test and in the field test exhibit very similar (or identical) physicochemical properties.

For each treated article – active substance – test specimen combination the parameters a and b are calculated in such a way that there is an optimal adjustment between field test data and laboratory test data for cumulative runoffs less than 100 l/m² for horizontally exposed test specimens and for cumulative runoffs less than 3 l/m² for vertically exposed test specimens. This means that a and b are computed in such a way as to minimize initial differences with regard to the emission between laboratory experiments and field experiments. For the calculation, an extrapolation of the laboratory test data is required in order to obtain values for the entire necessary range of immersion cycles, e.g. for immersion cycles greater than 9 and immersion cycles lower than 1. This extrapolation is carried out by means of the semi-analytical model.

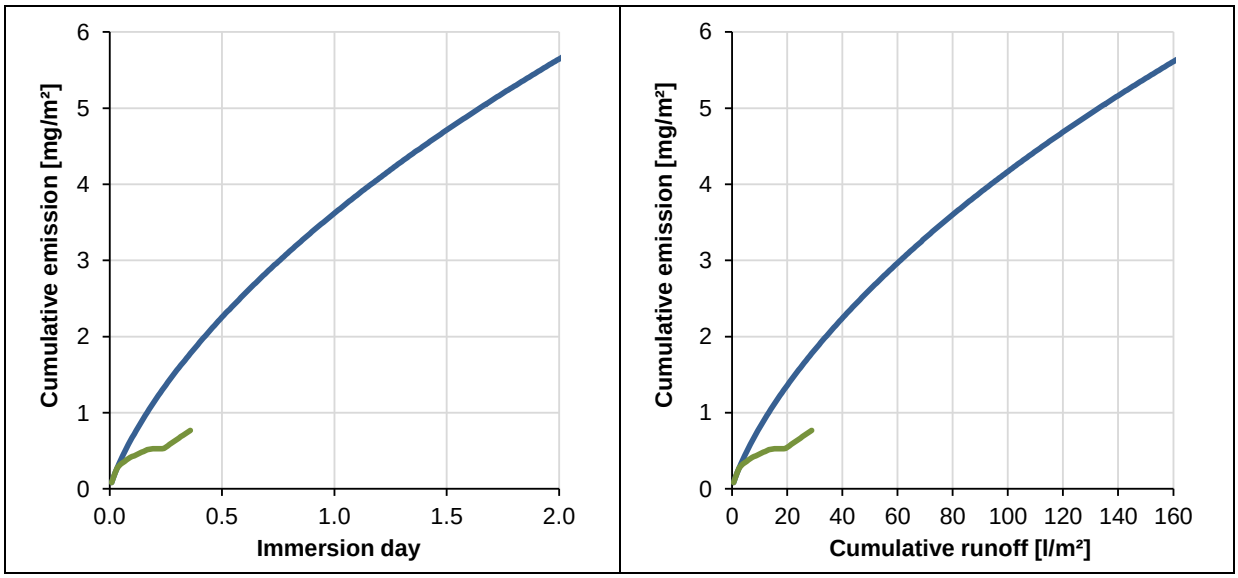
In Figure 62 and Figure 63 the time adjustments are illustrated with two typical examples for the horizontal and vertical exposure.

Figure 62: Time adjustment for the horizontal exposure, terbutryn from RP-2 at the MPA test site



The blue line and the green line represent the laboratory test data based on the semi-analytical model and the field test data, respectively. On the left side, both the laboratory data and the field data are shown depending on the immersion cycle, and on the right side, depending on the cumulative runoff.

Figure 63: Time adjustment for the vertical exposure, terbutryn from WC-8 at the BAM test site



The blue line and the green line represent the laboratory test data based on the semi-analytical model and the field test data, respectively. On the left side, both the laboratory data and the field data are shown depending on the immersion cycle, and on the right side, depending on the cumulative runoff.

For RP-2 terbutryn at the MPA test site the time adjustment is

immersion cycle = -1.56 + 0.16 · cumulative runoff.

For WC-8 diuron at the BAM test site the time adjustment is

immersion cycle = 0.001 + 0.012 · cumulative runoff.

The total emission of 0.78 mg/m² after a runoff of 29.3 l/m² is achieved in the laboratory after 44 min immersion in water (=0.361 immersion cycles = 0.361 · 2 immersion hours). It is noted that in the case of vertical exposure the shape of the curves is similar to the horizontal case.

Field data and lab data lie close to one another in the first couple of weeks of the field experiment, with an increasing difference after this period. This difference between field test and laboratory test could be caused by treated article-dependent and active substance-dependent long-term processes such as degradation (hydrolysis and photolysis) and evaporation in the field experiments. This difference is confirmed by the observed gaps in the mass balance (see Table 9, Chapter 4.2.4 and Table 10, Chapter 4.3.2). Thus, laboratory data represent a worst case scenario.

5.3.5 Attempted explanation of the gap between field tests and laboratory tests

If the assumption is correct that at the beginning of the field test there is a good agreement between laboratory test results and field test results and if it is true that the gap between the field data and the laboratory data can be explained by degradation factors, it can be concluded that under certain weather conditions the gap will diminish. This can be checked by extrapolation of the multivariate calibration model. This model may be applied not only to the weather conditions observed but also to hypothetical weather scenarios. It is thus possible to compare very extreme weather scenarios, e.g.

(i) high precipitations in the first 2 weeks with 1.5 l/m² runoff and after that low precipitations with 0.05 l/m² runoff vs.

(ii) low precipitations in the first half year with 0.05 l/m² runoff and after that one week with high precipitations with 1.5 l/m² runoff.

Theoretical calculations indicate that the cumulative emission at 25 l/m² is very much higher for weather scenario (i). Although the extrapolation of this model is not very reliable from a statistical point of view, it suggests that sensitivity with regard to the temporal incidence of precipitations is very high. Thus the multivariate model explains to some extent the gap between field and lab test results.

5.3.6 Discussion

For the prediction of total emissions in field tests, laboratory data cannot be used without further mathematical modelling and calibration. A direct comparison of field data and laboratory data reveals a significant overestimation based on laboratory data, especially in the case of vertical exposure. It is very likely that treated article- and active substance-dependent processes are important reasons for the low correlation observed between field data and laboratory data. Nevertheless, it was possible to establish a mathematical relationship between the cumulative runoff in the field tests and the number of immersion cycles in the laboratory tests.

Furthermore, it is expected that appropriate laboratory tests together with an extended multivariate calibration model with time adjustment might allow reasonable predictions for treated articles and substances that have not been investigated in field experiments.

5.4 Courses of action

Within the framework of the analyses of the laboratory data and field data, questions have arisen that could not be answered on the basis of the available information. This part of the report contains a proposal and a description of 6 possible courses of actions. The proposed courses of action can be broadly divided into two categories:

(1) fundamental investigations on the leaching behavior and

(2) support in the implementation of the procedure for evaluating biocidal products.

5.4.1 Fundamental investigations on the leaching behavior

5.4.1.1 Conduction of additional laboratory tests

The analyses of the field data reveal a strong impact of temperature and global radiation. The effects of the global radiation and the temperature are not taken into account in the laboratory tests according to EN 16015. In addition to the standard laboratory tests according to EN 16106, an additional laboratory test should be established. It is recommended that the temperature is changed and the test specimens are treated with ultraviolet light according to a specified experimental design.

To some extent, the gap between the field data and the laboratory data can be bridged by varying the temperature and the UV-treatment in laboratory tests. The variation of both factors requires the adjustment of the semi-analytical laboratory model.

5.4.1.2 Analysis of short-term weather scenarios

The conditions for the occurrence of high leaching rates in the field tests should be identified and the effects of the factors should be estimated by means of statistical models. In order to evaluate such short-term worst-case weather scenarios, records of all relevant factors must be available. The statistical models must also take into account the preparatory treatment of the product, the storage times of the test specimens and the adjusted global radiation (i.e. the global radiation linked with the position of the sun, the wind direction, the orientation of the test specimens and the color of the coating) etc.

5.4.1.3 Modelling of the effects of transformation processes and losses due to evaporation

In parallel to the leaching of the active substance, degradation and loss of the active substance take place. Considerable gaps in mass balances were detected - especially for field experiments (see Chapter 4.3.2, Table 10) - that cannot be assigned to definite processes so far. The models for the prediction of the emission curves in the field tests must be extended by taking into account the effects of transformation processes such as hydrolysis, and photolysis as well as losses due to evaporation to improve its reliability.

5.4.2 Support in the implementation of the procedure for evaluating biocidal products

5.4.2.1 Estimation of the variability of the total emission in field tests and in laboratory tests by means of interlaboratory studies

In order to be able to make statistically reliable statements about the reproducibility of emission data, it is recommended to conduct field experiments at several locations and an interlaboratory study for laboratory tests.

At least 6 laboratories should participate in an interlaboratory study for the laboratory tests according to EN 16105. The interlaboratory study is intended to determine firstly the precision of the measured emission data and secondly the reproducibility of the parameters of the semi-analytical laboratory model.

For the field tests at least 4 different locations are required for a coordinated interlaboratory study. Experimental data of test locations with very different weather conditions are required. It is recommended to conduct a factorial interlaboratory study taking into account the start time and end time, the orientation of the test specimens, the selection of the location and the treated article among other factors. This interlaboratory study is intended to quantify the precision of the obtained emission data from location to location. It is appropriate to conduct further tests with the wood coating WC-11 at other locations than the MPA Eberswalde and the BAM Berlin. Then the already available six data sets from this project could be used.

5.4.2.2 Inclusion of competitive processes in the assessment of biocidal products

Experiments revealed that other processes than leaching determine the fate of active substances considerably, i.e. gaps in mass balances can amount to about 90 % of the initial amount of active substances under field test conditions within two years. Reliable models on environmental impact of active substances require information on the expected relevance of these processes.

5.4.2.3 Provision of a software application for modelling of the laboratory test data

If it turns out that the semi-analytical laboratory model is suited to give a reproducible and reliable extrapolation of the emissions in laboratory tests, a software application could be provided. This tool would display the extrapolated cumulative emission value at a certain experimental time specified by the user, e.g. cumulative emission after 1 year. Thus, it would be possible to use this tool to make a reasonable prediction of unknown products by determining the prediction of a known product with similar characteristics. After importing the measured laboratory data, the software application would determine automatically the modelled emission curve. The estimated model parameters as well as graphical illustrations would be the output. If relevant, the software application would automatically carry out a calibration based on field data.

It is recommended that the software application should be able to store data sets. If different institutions upload their datasets, a large collection of different test series would be available.

5.4.2.4 Development of a database

The development of a systematic collection of leaching data, i.e. raw data, summary data about laboratory test data and field test data, would present many advantages:

- Data pool for scientific purposes,
- Data pool in support of the approval process,
- Data pool for the manufacturer of active substances,
- Comparison with similar products,
- Calibration of laboratory tests for field tests.

It is important that an independent, neutral institution is responsible for the maintenance of the database. In this context several other issues must be clearly defined such as the legal framework (is it allowed to share data), database users (who is allowed to use the database), data access (which data are allowed to be read), data validity (how is the validity of the data ensured), data approval (who is allowed to approve data) and so on.

6. Conclusions

Proposals for harmonised leaching test procedures, i.e. a laboratory leaching test method and a semi-field test method, were tested and its applicability proven for selected treated articles that include biocidal products of PT 7, PT 9 and PT 10. Guidance documents that describe these procedures were drafted and discussed with European experts representing competent authorities, institutes and producers, and are now provided on the ECHA website on Emission scenario documents to support provision of data for biocides risk assessments.

The laboratory test is based on an immersion scheme which was set arbitrarily taking into account commonly available analytical techniques, time and repeatability of test results. The main intention was to include drying phases to allow transport of water and target substances in treated articles and substrates. The laboratory procedure neglects some properties of target substances and treated articles that affect leaching, like stability of target substances and treated articles towards photolysis and hydrophilic properties of treated articles. In addition, the test procedure does not include temperature changes and is performed at rather constant relative humidity. Therefore, the test does not indicate variability of leaching processes. The proposed procedure is intended for treated articles that are exposed to occasional water contact. For treated articles that are in permanent contact to water, leaching tests according to CEN/TS 16637-2:2014, that was developed to assess the release of dangerous substances from construction products, should be an option.

The surface areas of the test specimens used for semi-field experiments are relatively small compared to large surface areas on real buildings, and the test specimens are oriented towards a direction that guarantees high exposure to driving rain at the test location. This results in rather high availability of driving rain for leaching processes on vertical surfaces and, consequently relatively high amounts of runoff per surface area. Field test results cannot be reproduced since leaching processes under outdoor conditions are affected by complex interactions of several variable meteorological parameters. However, presentation of emissions per surface area in relation to the amount of runoff proved to be suitable to compare results from different experiments. Some variation of the test results has to be accepted.

As a consequence, the informal value of both test procedures in relation to service conditions is limited. Nevertheless, both procedures indicate consistent general differences between active substances and treated articles that can be expected to occur also during service life. The leaching processes from the investigated treated articles were mainly controlled by diffusion under laboratory and outdoor conditions. Solution control was also observed in some cases, again in a similar way for both test approaches.

The laboratory leaching experiments performed during the project revealed considerably higher emissions than the corresponding semi-field experiments on vertically installed test specimens. One exception was observed, i.e. enhanced leaching of carbendazim from an impregnated textile that can be caused by changes of water repellency of the impregnation and leachability of carbendazim after UV radiation during outdoor exposure. However, the proposed laboratory procedure can be regarded as a leaching test under strong exposure conditions for materials under occasional water contact.

Differences between treated articles that appear at different ratios in laboratory and field tests are probably caused by certain properties of the treated articles. For instance, water drops remain on water repellent surfaces under outdoor conditions, and allow extended water contact for leaching, but also photolysis of substances. Different temperature on surfaces will affect diffusion within the material, but possibly also degradation of substances. It can be checked by supplementary laboratory tests whether these properties potentially impact either leaching of target substances or leachability of substances from treated articles. These tests can be rather simple, e.g. parallel leaching tests at different temperatures and UV exposure of test specimens either prior to or during leaching experiments. The ability of treated articles to take up water and possible changes of this property can be observed during the laboratory leaching test if mass data of the test specimens are recorded. Observation of water drops on surfaces sprayed with water can indicate water repellency and changes of this property due to water contact.

Mass balances including active substances in either eluates or runoff samples and residual amounts in test specimens compared to the initial amounts indicate that competing processes can occur under laboratory conditions, and to a higher extend under outdoor conditions. Degradation, e.g. due to photolysis, and evaporation are supposed to be important processes to explain the fate of active substances. These processes can exceed emissions due to leaching considerably. Results from the field experiments indicate that competing processes mainly occur during summer, and increased amounts of target substances can be observed in runoff samples during autumn again.

Further steps that are necessary to implement the proposed leaching test methods in the authorisation procedure for biocidal products have to be discussed and decided. It remains a challenging task to develop procedures to apply leaching test data for risk assessments. Preferably, this should be a joint activity including interested experts from several European countries.

A model has been developed which predicts the measured emission in laboratory tests according to EN 16105. This model can be used for extrapolation, as it takes into account the physicochemical processes which play a role in leaching.

The analyses of the field test data have shown that the runoff is the most crucial influence factor on the emission in field experiments. The analyses have also shown that the temperature and the global radiation have a crucial influence as well.

The analyses of the laboratory test data and the field test data provided two decisive results.

(1) There is a systematic difference between the laboratory test data and the vertically exposed field test data. The cumulative emission results as measured in the laboratory experiments are significantly higher than those measured in the vertically exposed field experiments. Accordingly, laboratory experiments can be seen as representing a worst case scenario. In the first couple of weeks of the field experiments there is good agreement between field data and laboratory data. After this period there is an increasing difference due to higher emissions in the laboratory tests. The difference could be caused by long-term processes such as degradation and evaporation.

(2) The total emission results in the field experiments are subject to considerable random variability. The total emission measured in a field experiment depends on the weather conditions that prevail during the experimental period. For this reason, even if two experiments take place at the same location, with the same orientation of the test specimen and for the same duration, it is not unrealistic that the corresponding total emission results will vary by a factor of 5 or more if the two experiments are run at different times, i.e. from one year to the next, different cumulative emissions could be observed.

In order to make reasonable predictions for unknown treated articles and unknown active substances it will be necessary

- to conduct additional laboratory tests which take into account the temperature and the UV radiation,
- to develop an extended multivariate calibration model that makes it possible to establish correlations between the test data obtained from laboratory and field experiments, and
- to examine the reproducibility of the total emission results obtained from field experiments. This means it will be necessary to compare emission results corresponding to different weather conditions. For this purpose it will be necessary to conduct further field experiments at different locations, for different orientations and for different durations.

Laboratory and field investigations that support further development of models for the prediction of emission curves in field tests, possibilities to provide a software application for modelling laboratory test data as well as development of a data base for leaching data are proposed.

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