Danish Ministry of the Environment
Environmental Protection Agency

Water driven leaching of biocides from paints and renders

Methods for the improvement of emission scenarios concerning biocides in buildings

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Water driven leaching of biocides from paints and renders

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Preface

This study has been undertaken to determine to which extend biocides in paints and renders applied to buildings are washed out under Danish climate conditions. It should also demonstrate which compounds are dominant and which mechanisms are relevant for this leaching process. So all in all, experimentally determine parameters which determine concentrations in Danish storm water, urban lakes and the aquatic environment in general.
This is of great concern to the agency, regulating biocides registration and Danish water quality, as well as the public.
It was conducted taking the newly established biocide directive and the biocide regulation into account as well as the newly established environmental target concentrations of the water framework directive of several of the compounds currently used as biocides in buildings.
The authors acknowledge the input of Jørn Kierkegaard and Anne Munch Christensen from the Danish Environmental Protection Agency (EPA) for their input.
The authors also acknowledge the help from the help of various multiple waste water treatment plants. Camilla Tang (Technical University of Denmark, Copenhagen, Denmark) is especially acknowledged for her contributions to the waste water and combined sewer data as is Katarzyna Styszko (AGH University of Science and Technology, Krakow, Poland) in respect to sorption/leaching experiments.
Discussions with Michael Burkhardt (HSR University of Applied Sciences, Rapperswil, Switzerland) helped a lot to keep this study as close as possible to industrial practices. Timothy P. Wangler and Jan Carmeliet (ETH Zurich, Zurich, Switzerland) inspired us with ideas on material science and driving rain.

Sammenfatning

I løbet af projektet kunne det påvises, at biocidemissioner fra separat regnvand og fællessystemers afstrømning fører til betydelige koncentrationer af biocider i urbant overfladevand. Disse koncentrationer var meget afhængige af bygningskonstruktioner i oplandet samt vejrforhold. Jævnlig regnafstrømning førte til forhøjede koncentrationer i overfladevand, der var fundet at være stærkt biocidpåvirket.

Undersøgelse af biocidniveauet i afstrømmet regnvand fra et separatkloakeret parcelhusopland resulterede i fundet af høje biocidkoncentrationer, selvom der i oplandet primært var murede facader og kun en beskeden andel af pudsede eller malede overflader. Der blev ofte fundet høje niveauer af carbendazim og terbutryn, og koncentrationer af cybutryn og terbutryn oversteg ofte kvalitetskriteriet for ferskvand.

Markedsundersøgelse: En undersøgelse af det danske marked (som også må anses at være typisk for det europæiske marked) har vist, at octylisothiazolinone, iodocarb, terbutryn, zink pyrithion og diuron i dag benyttes i byggematerialer som film præservativer, mens benzalkoniumchloride bruges til udendørs rengøring. Anvendelse som konserveringsmidler for at øge holdbarhed før åbning af formulerede produkter (in-can konserveringsmidler) blev ikke vurderet i produkt screeningen. Nogle af forbindelserne blev detekteret i feltundersøgelser udført i dette projekt, særlig methyl-isothiazolinon (MIT) og benzyl-isothiazolinen (BIT) blev detekteret.

Tilstedeværelse i afstrømmet regnvand: Nogle biocider (især cybutryn , terbutryn og mecoprop) blev fundet i regnvand i niveauer, der sommetider overstiger vandkvalitetskriterier fastsat i forordninger som vandrammedirektivet eller overfladevanddirektivet. Andre biocider såsom carbendazim, isothiazolinoner (anvendt som in-can konserveringsmidler), azol-fungicider, mecoprop, som anvendes i forbindelse med beskyttelse af byggematerialer, blev også fundet i afstrømmet regnvand i høje koncentrationer. Udledningen var oftest kontinuerlig og opførte sig derfor ikke som partikulært bundet forurening så som PAH'er, der oftest kommer med højest koncentration i starten af en afstrømningshændelse (first flush).

Tilstedeværelse i spildevand: Det viste sig, at de fleste biocider, der anvendes til beskyttelse af bygningsmaterialer, er til stede i spildevand fra fælleskloakerede afløbssystemer under både tørvejr og regnvejr. Biocidernes tilstedevær i tørvejrsafstrømning skyldes sandsynligvis en kombination af vask af værktøjer og bortskaffelse af materialerester så som maling. I nogle prøver var koncentrationerne (af især propiconazol) dog så høje, at de næppe kan begrundes i biocider fra byggematerialer, men snarere må skyldes professionelt urbant gartneri. Mens anvendelse i landbruget er begrænset, er anvendelse i danske væksthuse lovlig.

Frigivelse/partitionering: Med hensyn til materialeegenskaber blev det konstateret, at sorption (og udvaskning) er meget pH-afhængig for alle biocider. Det skal her tages i betragtning, at pH i porevandet af de testede pudsmaterialer er mellem 9 og 10, mens regnvandet har en pH omkring 5, hvilket gør forudsigelse vanskelig på nuværende tidspunkt.

For nogle af biociderne er sorptionen afhængig af polymermængden i pudset, mens det kun sjældent er af betydning hvilken polymer (acrylat eller silikone) der anvendes.

Ved undersøgelse af samspillet mellem vejr og udvaskning af biocider fra virkelige vægge viste det sig, at en række parametre såsom solbestrålingsintensitet, varighed af den forudgående tørvejrsperiode, regnintensitet osv. ikke havde en påviselig indflydelse på udvaskningen. Kun vandmængden, der som følge af slagregn faktisk nåede muren, havde en effekt på udvaskningen af biocider fra byggematerialerne. Det viste sig, at for nogle biocider er transformation på vægflader relevant, og omdannelsesprodukter bør indgå i fremtidige studier. Der blev ikke konstateret forskel mellem silikone- og acrylatbaseret puds med hensyn til udvaskning af biocider.

Der blev udviklet en model, der beskriver udvaskning og afstrømning af biocider i separatkloakerede oplande. Modellen kan forudsige biocidkoncentrationer i andre oplande, men kræver dog detaljeret data i form af antal, areal og art af behandlede overflader, tilslutningsgrad af regnvand til kloak, osv.

Summary

During the project it could be shown, that the biocide emissions from storm water and combined sewers lead to considerable concentrations of biocides in urbanized surface waters. These concentrations were highly dependent on the building structures in the catchment as well as on the weather. Regularly rainfall led to elevated concentrations in those waters that are heavily influenced by biocides.
An assessment of a best case for storm water contamination (separated sewers in a rural catchment with mostly brick surfaces) resulted in still high concentrations of biocides in water. High values for carbendazim and terbutryn where often detected. Cybutryn and terbutryn often exceeded the environmental target levels due to their high toxicity.

Market survey: A study of the Danish market (as being also typical for the European market), showed that octylisothiazolinone, iodocarb, terbutryn, zinc pyrithion, and diuron are used in current building materials as film preservatives while benzalkoniumchloride is used for outside cleaning. The use as in-can preservatives (compounds to increase shelf life of formulated products) was not assessed in marked surveys. Some of these compounds were assessed in the environmental studies of this project. Especially Methyl-isothiazolinone and Benzyl-isothiazolinone originating from use as in-can preservatives were detected.
Presence in storm water: Some compounds (especially cybutryn, terbutryn and mecoprop) are present in storm water in levels sometimes exceeding receiving water quality standards set in regulations such as the water framework directive or the surface water directive. Other compounds such as carbendazim, isothiazolinones (used as in-can preservatives), azole fungicides, mecoprop, that are used in connection with building protection were found in the storm water studies with high concentrations as well. The discharge mostly occurs continuous thus there is no option of treating just the first flush as for other parameters (particulate matter or PAH).
Presence in wastewater: It turned out that most of the biocides used in building protection are present in current dry weather wastewater as well as in rain weather combined sewer. It is assumed that a combination of washing tools and disposing residues of materials such as paints is mostly responsible for the findings at dry weather. However in some samples the concentrations (especially of propiconazole) were so high, that rather professional urban gardening (flower and greenhouses) than handling of biocides from construction materials seem to be able to explain the findings. While the use in agriculture is restricted, the use in greenhouses is currently considered legal in Denmark.
Leaching/partitioning: Considering material properties, it was found out that, for all of the compounds the sorption (and leaching) is highly pH-dependent. It must be take into account that the pH in the porewater of the tested render materials is between 9 and 10 while the rainwater is around 5, thus making prediction difficult at this stage.
For some of the compounds the sorption is dependent on the amount of polymer in the render, while it is only rarely of importance which polymer is used.
Considering the interaction of weather with the leaching of biocides from real walls it turned out that a lot of parameters such as irradiation intensity, length of dry period, rain intensity etc. did not have a detectable influence on the leaching. Only the water amount that due to driving rain indeed reached the wall had an effect to the leaching of biocides from building materials. It turned out that for some compounds transformation is relevant on the wall surfaces, and transformation products should be included in future studies. Again a difference between silicone and acrylate based renders in concern of leaching of biocides was not detectable.

Modelling biocide emissions: The developed model allows predictions on concentrations of biocides in other catchments. However, it craves essential input parameters such as treated surfaces areas, connection rate to storm water system etc.

Introduction

To increase the energy efficiency of heating, new as well as old houses are currently equipped with enhanced thermal insulation. This consists of an insulation layer added on top of the old outer shell of the building. This insulation layer is then protected against weather by a new layer of render[1]. As this new top layer is usually a polymeric based render, it is protected by biocides against algal, fungal and bactericidal attack. From discussions with construction industries it is known that triazines (terbutryn, cybutryn) and phenyl ureas (diuron, isoproturon) are used as algicides, carbamates such as carbendazim and iodocarb are used as fungicides, while isothiazolinones such as benzisothiazolinone, octylisothiazolinone, and dichlorooctylisothiazolinone are used as bactericides (film preservatives). The bactericides are also used to increase shelf life of the formulated products (in-can preservatives). Both renders and paints are being equipped with such biocides.

In recent projects is was demonstrated that these biocides can be washed of construction material surfaces (paints and renders) in idealized laboratory experiments, which were conducted with testing materials that were constantly soaked with water but also under forced rain in combination with drying periods (Schoknecht *et al.* 2003; Burkhardt *et al.* 2009; Schoknecht *et al.* 2009; Burkhardt *et al.* 2011). This results in unnecessary emissions as well as in unreliable materials. It is thus the intention of this project to systematically explore the mechanism of delivery, which has been found out to be far too fast to rely on diffusion, (Simmler 2008; Zuleeg 2008) thus active water transport such as well-known in soils (Glotfelty *et al.* 1989) is probably involved.

In a very small but well characterized catchment area (9 buildings), high concentrations (i.e. several $\mu g\ L^{-1}$) have been found in the runoff waters. Some initial efforts have been undertaken to model the concentrations of toxic compounds in storm water, but up to now the data input was too low, to trigger good models for leaching of biocides from buildings (Wittmer *et al.* 2011)**.** Thus there is a substantial risk, that urban waters become contaminated with concentrations exceeding the Lowest Observable Effect Level (LOEL) of these biocides by orders of magnitude. Successively, the target of good ecological status of the WFD is not reached. Gerecke *et al.* (2002) suggested that indeed a significant proportion of pesticides found in urbanized surface waters in Switzerland rather stem from buildings protection than from agriculture. Thus the theory was formed, that biocides from buildings can be introduced with storm or rainwater into surface waters to an extent that effects are probable. There are hints for these biocides being present in the larger rivers as about 0.003-2.53 $\mu g\ L^{-1}$ terbutryn were found in German surface waters (Quednow & Puettmann 2007, 2009). However, the effective concentrations, e.g. of algaecides, such as cybutryn are often very low to aquatic organisms (Mohr *et al.* 2008).

Thus effects in surface waters due to usage of biocides in building materials seem to be probable but currently neither the delivery mechanism nor means to control this process is clear, nor the amount of biocides leached to the surface waters is described in a manner that general assessments are possible.

[1] *Render or plaster*: the English literature uses both wordings in a synonymous way; in the following this document sticks to the word *render*.

1.1 Specific research aims and approaches

1. The mobility of biocides in render material and the wash-off shall be predicted by physico-chemical properties of the compounds in combination with physico-chemical properties of the compounds as well as the materials:
   a. Render parameters: Organic matter content, pH of the pore water, and eventually detergent concentrations are influencing the mobility.
   b. Compound parameters: lipophilicity (K_{OW}) and acid constant (K_a) are influencing the mobility of the compounds in the render.

   In order to determine different parameters several laboratory experiments were performed to study the mechanism of the leaching (paragraph 5.1). These were based on equilibrium sampling but also some kinetic studies.

2. It is assumed that the leaching is controlled by weather; relevant parameters might be: rain amount, rain intensity, length of drying period, radiation during dry period, amount of driving rain. This was determined with the help of semi-field experiments: The leaching from artificial walls under natural weather was analyzed and compared to weather parameters (paragraph 0)

3. If biocides are emitted via storm water run-off into surface waters they should be detectable in separated sewer systems as well as combined sewer systems during rainy weather. During dry weather periods, no biocides should be detectable. Hence, the discharge in separated sewer systems (paragraph □) as well as combined sewer systems (paragraph 5.4) was studied.

4. Biocides from buildings will be present in surface waters. The concentrations might be relevant and exceeding quality targets of the water framework directive. In order to determine the occurrence of biocides in Danish cities urban surface waters were analyzed (paragraph 5.5).

5. In order to provide a model to estimate the leaching of biocides a qualitative model based on the monitoring studies was establish (paragraph 5.6).

2. Biocides in building materials

2.1 Utility of biocides

Biocides are regulated in the European Union (EU) and defined in the European biocidal product directive (BPD) (European Parliament and Council 1998a, 2012) as substances designed *"to destroy, deter, render harmless, prevent action of, or otherwise exert a controlling effect on any harmful organism by chemical or biological means."*
Due to rain, but more important, dew building façades get wet and offer a good environment for microorganisms to grow. Especially polymeric based renders and paints are known to be very susceptible to algae and fungi growth, due to their specific physical-chemical properties (Reichel *et al.* 2004).
Hence, in recent years more and more façade materials are equipped with biocides in order to prevent microbial growth on the building façades. The increasing mounting of thermal insulation systems (Figure 1), which requires the usage of polymer based renders and paints, accounts for an increase in biocide containing materials.

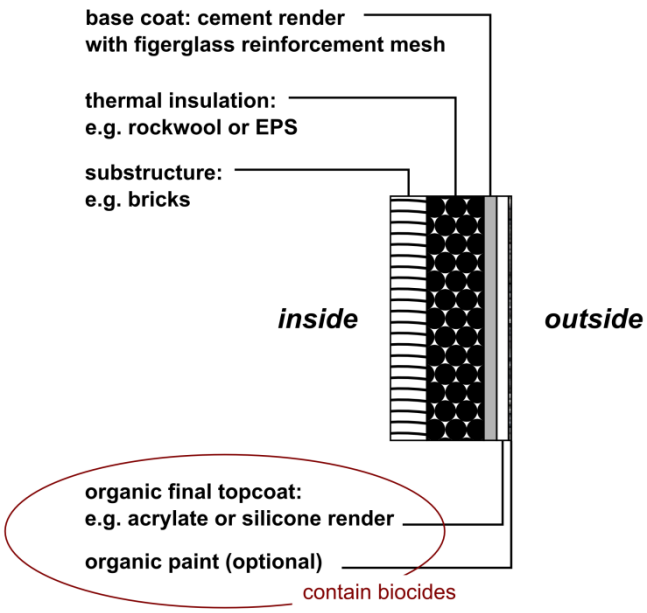


FIGURE 1. PRINCIPAL CONSTRUCTION OF A BIOCIDE-CONTAINING EXTERNAL THERMAL INSULATION COMPOSITE SYSTEM (ETICS) - THE TOP-PAINT-LAYER IS OPTIONAL. EITHER THE ORGANIC RENDER OR THE PAINT OR BOTH LAYERS MAY CONTAIN BIOCIDES.

Both renders and exterior paints can be equipped with film preserving compounds. It is known that triazines and phenylureas are used as algicides and carbamates as fungicides, while isothiazolinones are used as bactericides for such purposes (Paulus 2005). Besides the use as film preservatives some of the biocides, are only added to the products to increase shelf life of the formulated products until they are used (in-can preservatives) (European Commission 2011). The concentration per

single biocide is about 0.1 – 2 g kg^{-1} in render, which corresponds to 0.3 – 4 g m^{-2} wall area (Burkhardt *et al.* 2011). In-can and film preservatives consist of mixtures of about one to eight different biocides, leading to a total content of biocides in render and exterior paints from 0.5 % to 1 % (Burkhardt *et al.* 2011). Besides the previous named biocides, triazoles are used for the preservation of wood, as they are very effective fungicides (Schultz *et al.* 2007).
The setup is different to the one used for testing wood protection agents (Nordic Innovation Centre 2005; OECD 2007; European Committee for Standardization 2008; OECD 2009; European Committee for Standardization 2012)., In contrast to the wood protection agents which form a water tight film, the material of the renders is to some extent porous. Also a higher data density was required for a research project. Additionally there was already upcoming data, suggesting, that driving rain would influence the leaching of the biocides from building materials, which is not taken into account in the older wood protection tests.

2.2 Compounds covered within this project

The selection of the compounds covered by this study was based on three criteria (Appendix 1:):
Criteria 1 Compounds with relevance for the Danish market (Appendix 2:). Considering the market survey the following compounds were chosen for the project: octylisothiazolinone, iodocarb, terbutryn, and diuron. Zinc pyrithion and benzalkoniumchloride were not chosen, as they demand another analytical procedure.
Criteria 2 Compounds that has been studied before and allow comparisons with the situations in other countries. Compounds included due to criteria 2 are cybutryn (Irgarol 1051), isoproturon, dichlorooctylisothiazolinone, benzisothiazolinone, and carbendazim.
Criteria 3 Compounds with relevance for regulatory purposes of the Danish EPA. They had a need for data concerning diuron, iodocarb, tebuconazole, and propiconazole. Hence, they were added to the compound list though tebuconazole and propiconazole are more used in wood preservation than in renders.

Thus, the following biocides were analyzed for this project (Table 1): cybutryn (Irgarol 1051), terbutryn, diuron, isoproturon, benzisothiazolinone, octylisothiazolinone, dichlorooctyliso-thiazolinone, carbendazim, tebuconazole and propiconazole. Other compounds (mecoprop and methylisothiazolinone) were added, because it was possible without more effort to spend.

TABLE 1: BIOCIDES COVERED WITHIN THIS STUDY: NAME, ACRONYM, CAS-NUMBER, PHYSICAL-CHEMICAL PROPERTIES(OCTANOL-WATER PARTITION COEFFICIENT (LOG K_{OW})[1], WATER SOLUBILITY (WS)[1], HENRY´S CONSTANT (K_H)[1], VAPOR PRESSURE (P_{VAP})[1], AND PREDICTED-NO-EFFECT-CONCENTRATION (PNEC)[2]), ACTIVITY AND PRODUCT TYPES REGISTERED UNDER THE BIOCIDAL PRODUCT DIRECTIVEV CODED PT[3] AND COSMETIC DIRECTIVE[4] IN THE EUROPEAN UNION. COMPOUNDS MARKED (A) ARE USED AS PESTICIDE IN DANISH AGRICULTURE (IN 2010)[5], (B) ARE USED AS PLANT PROTECTION PRODUCTS IN DANISH PRIVATE GARDENING (IN 2010)[6], (C) CAN BE FOUND AS PESTICIDES ON FRUITS AND VEGETABLES SOLD, BUT NOT PRODUCED IN DENMARK[7].

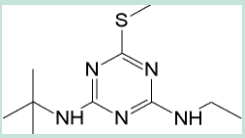
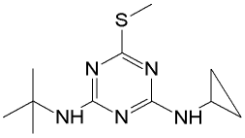
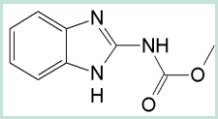
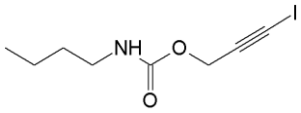
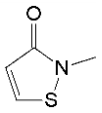
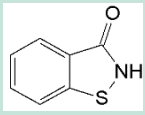
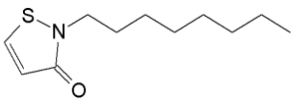
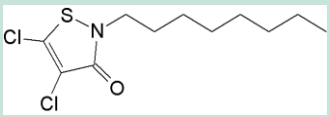
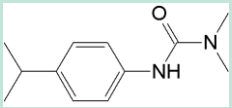
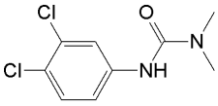
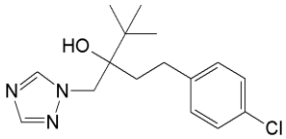
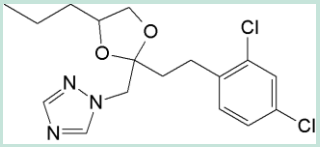
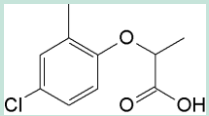
Group Compound (Abbreviation) CAS-No.	Formula	Physical-chemical properties	Activity, Product types (BPD) Pesticide in DK
Triazines			
Terbutryn **(TB)** **886-50-0**		Log K_{OW}: 3.77 WS: 42 mg L^{-1} k_H: 9.1*10^{-9} atm m^3 $mole^{-1}$ p_{vap}: 2.4*10^{-5} mmHg PNEC: 34 ng L^{-1}	Algaecide Biocide: PT 7, 9, 10 Pesticide: -
Cybutryn, Irgarol 1051 **(IRG)** **28159-98-0**		Log K_{OW}: 4.07 WS: 20 mg L^{-1} k_H: 5.3*10^{-9} atm m^3 $mole^{-1}$ p_{vap}: 3.7*10^{-6} mmHg PNEC: 1 ng L^{-1}	Algaecide Biocide: PT 21 Pesticide: -

TABLE 1. CONTINUE.

Group Compound (Abbreviation) CAS-No.	Formula	Physical-chemical properties	Activity, Product types (BPD) Pesticide in DK
Carbamates			
Carbendazim **(CD)** **10605-21-7**		Log K_{OW}: 1.55 WS: 3112 mg L^{-1} k_H: 1.5*10^{-12} atm m^3 $mole^{-1}$ p_{vap}: 5.4*10^{-9} mmHg PNEC: 34 ng L^{-1}	Fungicide Biocide: PT 7, 9, 10 Pesticide: c
Iodocarb **(IPBC)** **55406-53-6**		Log K_{OW}: 2.45 WS: 436 mg L^{-1} k_H: 6.9*10^{-9} atm m^3 $mole^{-1}$ p_{vap}: 4.6*10^{-4} mmHg PNEC: 26 ng L^{-1}	Fungicide Biocide. PT 6, 7, 8, 9, 10, 13 Cosmetics Pesticide: a
Isothiazolinones			
Methylisothiazolinone **(MI)** **2682-20-4**		Log K_{OW}: < 0 WS: 9.6*10^5 mg L^{-1} k_H: 5.0*10^{-8} atm m^3 $mole^{-1}$ p_{vap}: 0.031 mmHg	Bactericide/ Fungicide Biocide: PT 6, 11, 12, 13 Cosmetics Pesticide: -
Benzisothiazolinone **(BIT)** **2634-33-5**		Log K_{OW}: 0.64 WS: 22204 mg L^{-1} k_H: 6.9*10^{-9} atm m^3 $mole^{-1}$ p_{vap}: 2.6*10^{-5} mmHg	Bactericide/ Fungicide Biocide: PT 2, 6, 9, 11, 12, 13 Pesticide: -
Octylisothiazolinone **(OIT)** **26530-20-1**		Log K_{OW}: 2.61 WS: 309 mg L^{-1} k_H: 3.6*10^{-7} atm m^3 $mole^{-1}$ p_{vap}: 2.0*10^{-4} mmHg PNEC: 13 ng L^{-1}	Bactericide/ Fungicide Biocide: PT 6, 7, 9, 10, 13 Pesticide: -
Dichlorooctylisothiazolinone **(DCOIT)** **64359-81-5**		Log K_{OW}: 3.59 WS: 27 mg L^{-1} k_H: 1.9*10^{-7} atm m^3 $mole^{-1}$ p_{vap}: 2.3*10^{-6} mmHg PNEC: 8 ng L^{-1}	Bactericide/ Fungicide Biocide: PT 7, 8, 9, 10, 11, 21 Pesticide: -
Phenylureas			
Isoproturon **(IP)** **34123-59-6**		Log K_{OW}: 2.84 WS: 92 mg L^{-1} k_H: 1.9*10^{-9} atm m^3 $mole^{-1}$ p_{vap}: 7.9*10^{-6} mmHg	Algaecide Biocide: PT 7, 10 Pesticide: -
Diuron **(DR)** **330-54-1**		Log K_{OW}: 2.67 WS: 102 mg L^{-1} k_H: 5.3*10^{-10} atm m^3 $mole^{-1}$ p_{vap}: 4.7*10^{-6} mmHg PNEC: 20 ng L^{-1}	Algaecide Biocide: PT 7, 10 Pesticide: -
Triazoles			
Tebuconazole **(TBU)** **107534-96-3**		Log K_{OW}: 3.89 WS: 97 mg L^{-1} k_H: 5.1*10^{-10} atm m^3 $mole^{-1}$ p_{vap}: 4.6*10^{-6} mmHg	Fungicide Biocide: PT 7, 8, 9, 10 Pesticide: a/b/c
Propiconazole **(PPZ)** **60207-90-1**		Log K_{OW}: 4.13 WS: 11 mg L^{-1} k_H: 14*10^{-9} atm m^3 $mole^{-1}$ p_{vap}: 3.6*10^{-6} mmHg	Fungicide Biocide: PT 7, 8, 9 Pesticide: a
Miscellaneous			
Mecoprop **(MCPP)** **93-65-2**		Log K_{OW}: 2.94 WS: 471 mg L^{-1} k_H: 1.8*10^{-8} atm m^3 $mole^{-1}$ p_{vap}: 4.6*10^{-4} mmHg	Algaecide Roof protection (not registered under BPD, since higher plants)

Pesticide: -

1. **Calculated with EPI Suite™ v4.10 of the US EPA: http://www.epa.gov/oppt/exposure/pubs/episuitedl.htm.**
2. **(Burkhardt *et al.* 2009)**
3. **(European Commission 2013b, a); Biocide product types (European Parliament and Council 2012): 6 In-can preservatives, 7 Film preservatives, 8 Wood preservatives, 9 Fibre, leather, rubber, and polymerised material, 10 Masonry preservation, 11 Preservatives for liquid-cooling and processing systems, 12 Slimicides, 13 Metalworking-fluid preservatives, 21 Antifouling products.**
4. (European Parliament and Council 2009b)
5. (Danish Environmental Protection Agency 2011a)
6. (Danish Environmental Protection Agency 2011b)
7. (Danish Veterinary and Food Administration 2011)

2.3 Biocide leaching

2.3.1 Laboratory studies

Schoknecht et al. (Schoknecht *et al.* 2003; Schoknecht *et al.* 2009) demonstrated that triazine, phenylurea and isothiazolinone biocides can be washed of construction material surfaces (paints and renders) in idealized laboratory experiments, when the testing materials is constantly soaked with water. Further experiments were conducted by the EAWAG (Swiss federal research institute for water research) Rainwater group in cooperation with EMPA (Swiss federal research institute for material science) building technologies and the applicant). They showed that these biocides can be leached in significant fractions from the respective materials (paints and renders) under forced rain in combination with drying periods (Burkhardt *et al.* 2009; Burkhardt *et al.* 2011).
In recent projects it has been found out, that the delivery of the biocides through the materials is very different, even though the used renders were very similar. In the following discussions it was agreed that issues as not considered before (such as detailed water transport, micro-structure of the material etc.) are important and are most probably dominating the transport in the materials, leading in some cases to complete loss of active biocidal ingredient from the materials within a year (Burkhardt 2008). This results in unnecessary emissions as well as in unreliable materials.
So far, the mechanism of delivery is not finally described, since it has been found out to be far too fast to rely only on diffusion (Simmler 2008; Zuleeg 2008), and, hence, active water transport such as well-known in soils (Glotfelty *et al.* 1989) is probably involved. Also the extent of the influences of different material and compound parameters as the affinity of the organic substance to matrix, the organic carbon content, the surface structure or porosity of the matrix are known (Schoknecht *et al.* 2009).

2.3.2 Assessment of used test systems:

Schoknecht et al. (Schoknecht *et al.* 2003; Schoknecht *et al.* 2009) used a test derived from established testing wood protection agents. This test has been normalized to be used in registration (CEN/TS15119-1 and CEN/TS15119-2). In this test, a normalized body of treated render material is put into a normalized water volume; neither the render body, nor the water body is moved. After a given time, the biocide concentration in the water is analysed. While this test is easy to normalize and comparable results can be achieved, its relevance for assessing emissions under realistic conditions is somewhat limited. While in this test a relative huge amount of water is contacted with the material in a stagnant way, in reality relative little amounts of water run down the treated surfaces. In this laboratory test, the transport of biocides through the water will have an important role, which they would not in reality. Additionally no weathering is mirrored in this test. It is very difficult to assess whether the laboratory test rather over or under estimates the leaching.
Additionally outside weathering tests are used by industry but also in the Nordtest (NT Build Method 509). In this test, areas of treated material are exposed to the weather, runoff is collected and analysed for assessing leaching. 4 samples are used over a one year period. The emissions are calculated using rain amount data. As the data density and the background weather data in this test are limited, the results are though useful for regulative purposes not considered suitable for a research project. From discussion with industries it was already known, that if the wind situation is

not fully under control, similar exposure of the same material on the same site results in tremendously different results.
The third test used in the literature (Burkhardt *et al.* 2009, 2011) was forced weathering where 1 m^2 walls were exposed to forced rain under laboratory conditions. In these experiments the rainfall of more than a year was directly applied on the treated surfaces within a few days. These experiment were helpful to establish

i) that leaching is occurring and also
ii) what might be the dimensions of the leaching,
iii) whether temperature and light have an effect

but it was never intended to produce a scenario, that could be used for quantitative assessments.

2.3.3 Surface water concentrations

Previous studies showed that leaching from building materials is a major source of biocide pollution concerning urban waters (Burkhardt *et al.* 2007). Driven by rain, the biocides enter surface waters and soil, where they might undergo degradation processes. As rainwater runoff (storm water) is often collected in separated sewer systems and either directly discharged into surface waters or infiltrated into groundwater, the contamination of storm water is of special concern.
In a very small but well characterized catchment area (9 buildings), high concentrations (i.e. several µg L^{-1}) have been found in the runoff waters. Some initial efforts have been undertaken to model the concentrations of toxic compounds in storm water, but up to now the data input was too low, to trigger good models for leaching of biocides from buildings (Wittmer *et al.* 2011).
Bucheli et al. (Bucheli *et al.* 1998a; Bucheli *et al.* 1998b) have shown that herbicides from protecting flat roof bitumous sealings can be a major source for herbicides such as MCPP (mecoprop) in urban surface waters. Gerecke et al. (Gerecke *et al.* 2002) suggested that indeed a significant proportion of pesticides found in urbanized surface waters in Switzerland rather stem from buildings protection than from agriculture. Thus the theory was formed, that biocides from buildings can be introduced with storm or rainwater into surface waters to an extent that effects are probable. There are hints for these biocides being present in the larger rivers as up to 5.6 µg L^{-1} terbutryn were found in German surface waters (Quednow & Puettmann 2007, 2009) or 9 µg L^{-1} diuron in an urban river in France (Blanchoud *et al.* 2004). Biocides have also been detected in combined sewer systems (Singer *et al.* 2010) during rainy weather periods.

TABLE 2: BIOCIDE CONCENTRATIONS IN SELECTED STUDIES IN DIRECT FACADE RUNOFF, STORM WATER, COMBINED SEWER AND SURFACE WATERS [NG L^{-1}].

Water type	CD	TB	DR	IP	MCPP	IRG	Ref.
New facade		100-800 µg/L					(Burkhardt *et al.* 2011)
Storm water	50-1100	20-1800	<LOD		100-10000		(Burkhardt *et al.* 2011)
Storm water	10-206	<20-50	50-310	50-5500	50-1750	<LOD	(Wittmer *et al.* 2010)
Combined sewer		5-183	28-2526	1-90			(Masiá *et al.* 2013)
Combined sewer	60-80	16-24	30-50	10-50	420-1600	4-6	(Singer *et al.* 2010)
River water		20-5600					(Quednow & Puettmann 2007, 2009)
River water (urban)			9000				(Blanchoud *et al.* 2004)
Surface water		4-15	10-68	3-9			(Masiá *et al.* 2013)

2.4 Possible sources

Besides the usage as in-can as well as film preservative in building material like render, paint or wood, biocides have a broad usage spectrum and it is known that most of the compounds used in façade coatings have other application forms as well. As shown in Table 1 they are used as preservatives for various types of material, e.g. leather or rubber, as well as industrial working fluids (European Commission 2013b, a). Methylisothiazolinone and iodocarb are also registered as preservatives in cosmetic products (European Parliament and Council 2009b), while cybutryn (irgarol 1051) is used as antifouling paints for ships (Thomas *et al.* 2002).

2.5 Environmental fate, effects and limit values (EU/National regulation)

The used biocides are toxic to aquatic organisms and may cause long-term adverse effects in the aquatic environment already at low concentrations. For example the effect concentration of cybutryn, which causes an effect in 10 % of the test organisms (EC_{10}), is 10 ng L^{-1} (Mohr *et al.* 2008). Additionally, the predicted no effect concentrations (PNEC) of biocides are in the low ng L^{-1} range, e.g. terbutryn and carbendazim 34 ng L^{-1}, octylisothiazolinone 13 ng L^{-1} (Burkhardt *et al.* 2009). About half of the biocides applied in façade material are persistent (Burkhardt *et al.* 2011). Beyond these are the triazines (cybutryn, terbutryn) and diuron (Thomas *et al.* 2002). Slow degradation from water was observed for the azole fungicides by Kahle *et al.* (2008). By contrast, dichlorooctylisothiazolinone and iodocarb are known to undergo hydrolysis and, hence, are not persistent in the aqueous phase (Juergensen *et al.* 2000; Thomas *et al.* 2002).

Burkhardt *et al.* (2007) expected that urban biocide emissions lead to concentrations exceeding the European drinking water quality standard for pesticides (100 ng L^{-1} for single pesticide and 500 ng L^{-1} for total pesticide concentration (European Parliament and Council 1998b)) up to ten fold in the first flush of storm water runoff. However, these values are only relevant for those biocides that are registered as pesticides as well, for all others no threshold value for drinking water

exists and, hence, also substances, forbidden in agricultural usage, are still used as biocides without any regulation in respect to drinking water. Nevertheless, the presence of biocides exceeding effect levels in surface water would be in conflict with the European water framework directive (WFD) (European Parliament and Council 2000). A new directive on priority substances under the WFD recommends annual average environmental quality standard (AA-EQS) for inland waters of 2.5 and 64 ng L^{-1} for cybutryn and terbutryn, and 200 and 300 ng L^{-1} for diuron and isoproturon, respectively (European Parliament and Council 2013). The other biocides are not regulated under the WFD.

In this project there are compounds regulated that are regulated solely via the EU-biocides regulation (European Parliament and Council 2012) while others have been regulated as biocides as well as as pesticides via the pesticides regulation (European Parliament and Council 2009a) for both compound groups secenarios are calculate based on the expected use- which would be quite different for the pesticides and the biocides respectively. For biocides used in film preservatives two standard scenarios are calculated one for a house in a city (with all waters being sent to waste water treatment) and one for a house in the countryside (with all water directly infiltrated into the soil). Several compounds used as biocides are or have been used as plant protection products (PPPs) in agriculture as well as private gardening (Danish Environmental Protection Agency 2011b, a), in order to *"protect plants or plant products against all harmful organisms"* and *"destroy undesired plants"* (European Parliament and Council 1991). Some of the compounds are typical wood protection agents (tebuconazole, propiconazole, iodocarb).

3. Objectives

Objective 1)

Find out whether biocides are relevant on the Danish market and if so, which ones.

Hypothesis 1) In Denmark the same biocides are relevant as in the rest of Northern Europe.

Objective 2)

Find out which parameters control the leaching of biocides on the materials side.

Hypothesis 2.1) It is assumed that the acrylate based renders perform differently to the silicone based ones.

Hyphothesis 2.2) The Organic matter fraction in the render will play a crucial role in controlling the release of biocides from the render.

Hypothesis 2.3) It is hypothesized that partitioning experiments give basic insight, but cannot really be used for predicting leaching from real walls.

Objective 3)

Find out what role weather plays in leaching the biocides from real walls.

Hypothesis 3) Radiation intensity, rain amount, rain strength, wind, and temperature play crucial roles in leaching from real systems.

Objective 4)

Find out which role biocides from building materials play in the Danish environment.

Hypothesis 4.1) Biocide concentrations in Denmark are less, as in Denmark the materials are used less than in Switzerland or Germany.

Hypothesis 4.2) Biocide concentrations in Danish storm water catchments will behave similar as in other countries if the building structure is similar. First flush events will dominate the emissions as they do for PAHs and heavy metals.

Hypothesis 4.3) Biocides will be present in combined sewage during rainfall, but not during dry weather.

Hypothesis 4.4) The concentrations in well-kept urban waters will be below the quality targets.

Objective 5)

Establish quantitative models to predict concentrations and loads.

Hypothesis 5) Quantitative modelling will predict loads for diverse catchments as well as extreme weather scenarios.

4. Experimental section

4.1 Materials

4.1.1 Biocides

This study covered 12 biocides used in building material (Table 1): cybutryn (Irgarol 1051), terbutryn, diuron, isoproturon, methylisothiazolinone, benzisothiazolinone, octylisothiazolinone, dichlorooctylisothiazolinone, carbendazim, tebuconazole, propiconazole and mecoprop. The selection process is described in paragraph 2.2.

4.1.2 Render material

In paragraph 5.1 on leaching mechanisms and paragraph 0 on leaching from artificial walls two commercial façade renders were used:

a) One render based on acrylate (KHK, Quick-Mix, Osnabrück, Germany). This is a product from the German marked, with parallel products are used on the Danish marked) and
b) One render based on silicone resin binder (HECK SHP KC1, BASF Wall Systems, Marktredwitz, Germany), which is regularly used on the Danish marked.

The exact kind of polymer has been requested from the producers, but has not yet been made available, due to trade secret issues.
The particle size and, hence, the application thickness is 2 mm for the acrylate render and 1 mm for the silicone render. The binder content was determined by measuring the losses during combustion at 550 °C. This temperature releases carbon from organic matter but no carbon from calcium carbonate. The initial organic content was 10 % in the dry acrylate render, while it was 15 % in the silicone render. The acrylate render contained commercial amounts of octylisothiazolinone but none of the other studied biocides, while the silicone render contained methyl- and benzisothiazolinone. The dried acrylate render had a BET surface of 1.12 $m^2\ g^{-1}$, a density of 1.79 g mL^{-1} and a calcium carbonate content of 66 %. The dried silicone render had a BET surface of 0.63 $m^2\ g^{-1}$, a density of 1.53 g mL^{-1} and a calcium carbonate content of 25 % The initial water content of the renders were 10 %. Consequential, the pore volume was estimated as 10 %.

4.2 Methods used for determination of biocides from various matrices

Two different methods with and without extractions were established and used to check for correctness of field data. One direct injection method for a quick screening with relative high detection limits. The other one includes the direct method but relies on a solid phase extraction for pre-concentration and final extracts are in organic solvents and not in water, thus better limits of quantification and sample preservation are reached.

4.2.1 Direct injection with internal standard quantification

1 mL of water sample is spiked with 50 µL of internal standard (1 µg mL^{-1} in methanol (gradient grade *lichrosolv*, *Merck*, Darmstadt, Germany): isoproturon-D6, terbutryn-D5, cybutryn-D9, tebuconazole-D6, carbendazim-D4) and directly injected into the HPLC-MS/MS. The quantification was performed with and without use of the internal standards in comparison.

4.2.2 Solid phase extraction with internal standard quantification

The solid phase extraction (SPE) was performed following Bester and Lamani (2010) with minor modifications. A flow diagram can be seen in Figure 2. In a volumetric flask a 100 mL sample was spiked with 50 µL of a surrogate standard solution, containing a mix of deuterated biocides (1 µg mL^{-1} in methanol (gradient grade *lichrosolv*, *Merck*, Darmstadt, Germany): isoproturon-D6, terbutryn-D5, cybutryn-D9, tebuconazole-D6, carbendazim-D4). In addition 3 mL of a 0.2M phosphate buffer was added to adjust to pH = 7. A Bakerbond SDB-2 (6 mL, 200 mg) SPE-cartridge (*Mallinckrodt Baker*, Deventer, The Netherlands) was conditioned with 12 mL acetonitrile (gradient grade *lichrosolv*, *Merck*, Darmstadt, Germany) and 12 mL Millipore-water successively. After extracting the 100 mL sample (using a velocity of ~ 2 mL min^{-1}) the cartridge was washed with 12 mL Millipore-water and slightly dried with vacuum. The combined eluates of 12 mL acetonitrile and 12 mL methanol were condensed to 1 mL in a BÜCHI Syncore® multiport condenser (*Büchi*, Flawil, Switzerland) at 50 °C, 280 rpm, and 100 mbar for about 90 min. The extracts were transferred to 1.5 mL autosampler vials.

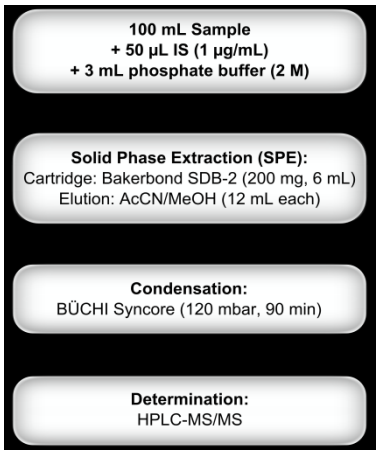


FIGURE 2. FLOW DIAGRAM OF THE EXTRACTION METHOD.

For the analysis of water from combined sewer a centrifuge step (5 min, 4000 rpm) was added prior to the solid phase extraction in order to remove particles.

4.2.3 Instrumental analysis

The analysis was performed by high performance liquid chromatography with tandem mass spectrometry (HPLC-MS/MS) using electrospray ionization in positive mode (ESI(+)) on an Ultimate 3000 dual gradient low pressure mixing HPLC-system (*Dionex,* Sunnyvale, CA, USA) coupled to an API 4000 triple-quadrupole-MS (*AB Sciex*, Framingham, MA, USA). The separation was performed at 5 °C using a Synergy Polar-RP column (L=150 mm, ID=2 mm, particles=4 µm, *Phenomenex*, Torrance, CA, USA). Contrary to Bester and Lamani (2010) a neutral multi-step gradient of water (A) and methanol (B) was optimized and used: 0-3 min 0 % B, 3-5 min 0 to 50 % B, 5-15 min 50 to 80 % B, 15-15.5 min 80 to 100 % B, 15.5-19 min 100 % B, 19-20 min 100 to 0 % B, 20-25 min 0 % B. Post column prior to introduction to the ion source of the mass spectrometer the eluent was changed to acidic conditions by adding a flow of 0.03 mL min^{-1} of 0.2 % formic acid in water in order to support the ionization process and, likewise, avoiding low retention in the HPLC-column.

4.2.4 Quality assurance

The direct injection method (paragraph 4.2.1) does not include any sample treatment steps thus it is treated as having 100 % recovery. Recoveries of the solid phase extraction method (paragraph 4.2.2) ranged between 74 and 105 % (except iodocarb (26 %), methylisothiazolinone (47 %), and octylisothiazolinone (49 %) and dichlorooctylisothiazolinone (15 %)) (Table 3). The recovery rates were not used to correct the presented results. The limits of detections (LODs) of the solid phase extraction method were below 1 ng L^{-1} for all substances, except methylisothiazolinone (6.9 ng L^{-1})

and mecoprop (1.1 ng L^{-1}). Every set of 24 samples was extracted together with a blank, in order to exclude contamination during sample preparation.
A test was performed with real world samples from paragraph ☐ in order to compare the two sample preparation methods (Paragraph 4.2.1 & 4.2.2). Except a single outlier both methods give comparable results and no matrix effects (ion suppression or ion enhancement etc.) could be detected. Hence, the methods are not only repeatable but also correct in the storm water samples.

TABLE 3. RECOVERY RATES (IN %), INSTRUMENT LIMIT OF DETECTION (IN NG L-1, CALCULATED FOR SPE-EXTRACT OF 100 ML SAMPLE, DIRECT INJECTION METHOD HAS 10X HIGHER LODS), AND INSTRUMENT LIMIT OF QUANTIFICATION (IN NG L-1, CALCULATED FOR SPE-EXTRACT OF 100 ML SAMPLE).

Substance (Acronym)	Internal standard used for quantification	Recovery rate ± std. dev. [%] (Internal cal.)	Limit of detection [a] [ng L^{-1}]	Limit of quantification [b] [ng L^{-1}]
Terbutryn (TB)	TB-D5	104 ± 23	0.07	0.2
Cybutryn, Irgarol 1051 (IRG)	IRG-D9	99 ± 22	0.07	0.2
Carbendazim (CD)	CD-D4	92 ± 18	0.3	1.0
Iodocarb (IPBC)	IP-D6	26 ± 19	0.3	0.8
Isoproturon (IP)	IP-D6	76 ± 22	0.7	2.3
Diuron (DR)	IP-D6	77 ± 21	0.08	0.3
Methylisothiazolinone (MI)	CD-D4	45 ± 13	6.9	22.8
Benzisothiazolinone (BIT)	CD-D4	74 ± 37	0.8	2.7
Octylisothiazolinone (OIT)	CD-D4	49 ± 29	0.2	0.8
Dichlorooctyl-isothiazolinone (DCOIT)	CD-D4	15 ± 10	0.7	2.3
Tebuconazole (TBU)	TBU-D6	105 ± 24	0.1	0.4
Propiconazole (PPZ)	TBU-D6	78 ± 17	0.1	0.5
Mecoprop (MCPP)	CD-D4	81 ± 20	1.1	3.7

a) 3*c/(Signal/Noise) b) 10*c/(Signal/Noise)

4.3 Methods to study the mobility of biocides in the material

4.3.1 Desorption equilibrium experiments

Render materials were spiked with six different concentrations of biocides (0.03-10 µg g^{-1}) to obtain a good database to calculate distribution coefficients (K_d). The experiments were conducted for each concentration in duplicate. Each experiment was conducted for a silicone and an acrylate render system. The experiments were conducted at three different pH values. (5.6, 9.5 and for control reasons 7.0). As both the different parts of the render system and the compounds undergo protonation/deprotonation reactions the number of experiments was limited to those pH values that are important to the system (rain water pH 5.6 and pore water pH 9.5). The acrylate system was run with 4 different acrylate concentrations.

In detail:
The well mixed systems were air dried within two days, thus resulting in realistic hardened renders following normal industry practice. The thus dried and spiked materials were homogenized in a mortar on the successive day. The experiments were performed by monitoring the equilibrium concentrations of the biocides between 200 mg spiked render and 10 mL deionised water. After 24 h contact time (equilibrium status verified) about 2 mL of the liquid phase was separated from the render by centrifugation. Successively, exactly 1 mL of the supernatant was transferred to 2 mL autosampler vial, spiked with 50 µL surrogate standard solution (1 µg mL^{-1} in methanol (gradient grade *lichrosolv*, *Merck*, Darmstadt, Germany): isoproturon-D6, terbutryn-D5, cybutryn-D9, tebuconazole-D6, carbendazim-D4) for analysis by means of HPLC/MS-MS (paragraph 4.2.3).
All desorption equilibrium experiments were performed in duplicate on two different pH-levels: 5.6 and 9.5. The higher one results from contact of renders with water and, thus, is considered as pore water pH. Hence, this one is relevant for transports within the render. The pH = 5.6 was considered to be the rainwater controlled surface water film pH and, hence, relevant for the final desorption of the biocides from the material. The respective pH values were generated by using phosphate buffers (Na_2HPO_4/NaH_2PO_4), at concentrations 0.01/0.5 mol L^{-1}. By changing the pH, the respective biocide can be affected through protonation and deprotonation processes. At the same time the render materials are affected by similar reactions e.g. carbonates can be protonated and deprotonated.

4.3.2 Kinetic mobility studied by 2-dimensional liquid chromatography

As, additionally to water/render sorption equilibria, also the water flowing through the render material is relevant, a 2-dimensional liquid chromatography set up was chosen. Render might get wetted either through heavy rain, drew falling or even water vapor that enters the render during daytime, while it condenses over night when the temperature drops several centigrade. The liquid water might then evaporate from the outer surface of the render thus creating a hydraulic flow of water from the deeper layers to the top. With this waterflow certainly biocides would be transported to the surface. Thus an “active transport” might be relevant. This would best be studied by chromatographic approaches.
As shown in Figure 3 this approach was based on two parallel running liquid chromatography systems connected via a 6-port valve which served as loading valve for the second system. A process glass column (LC Tech, GPC 10010, 500 x 40 x 25 mm) was filled with 84 g (dry weight) commercial acrylate render and quartz sand (Table 4) and connected to an Agilent 1100 system with a constant flow (0.15 mL min-1) of 100 % Millipore-water.
The second (analytical) pump system (Dionex Ultimate 3000), working at 300 µL min^{-1}, run the following multistep gradient (A: water, B: methanol) on the analytical column (Phenomenex, Synergy 4u Polar-RP 80A, 150 x 2 mm): 3 min B = 0 %, increased to B = 50 % within 5 min, increased to B = 80 % within 10 min, increased to B = 100 % within 0.5 min, held for 2.5 min, decreased to B = 0 % within 1 min, held for 5 min. The column oven was set to 5°C. The UV detector ran constantly at 235 nm.
A mix of biocides (0.04 mg mL^{-1} in 20 % MeOH in H_20) was once injected to the process column. Every 25 min 100 µL of the eluate was injected to the analytical column. Parallel to the online analysis by HPLC-UV the eluate from the process column was collected in one-day fractions and analyzed by HPLC-MS/MS (paragraph 4.2.3).
Due to time limitations the column system A (10% acrylate) was tested in triplicate, while column B (20% acrylate) was analyzed only once.

TABLE 4. COMPOSITION OF THE TWO TESTED COLUMNS (WET MATERIAL).

Column	Quartz sand [g]	Acrylate render [a] [g]	Acrylate suspension [b] [g]
A: 10 % acrylate	187	93	-
B: 20 % acrylate	177	70	13

a) water content: 10 % b) water content: 50 %

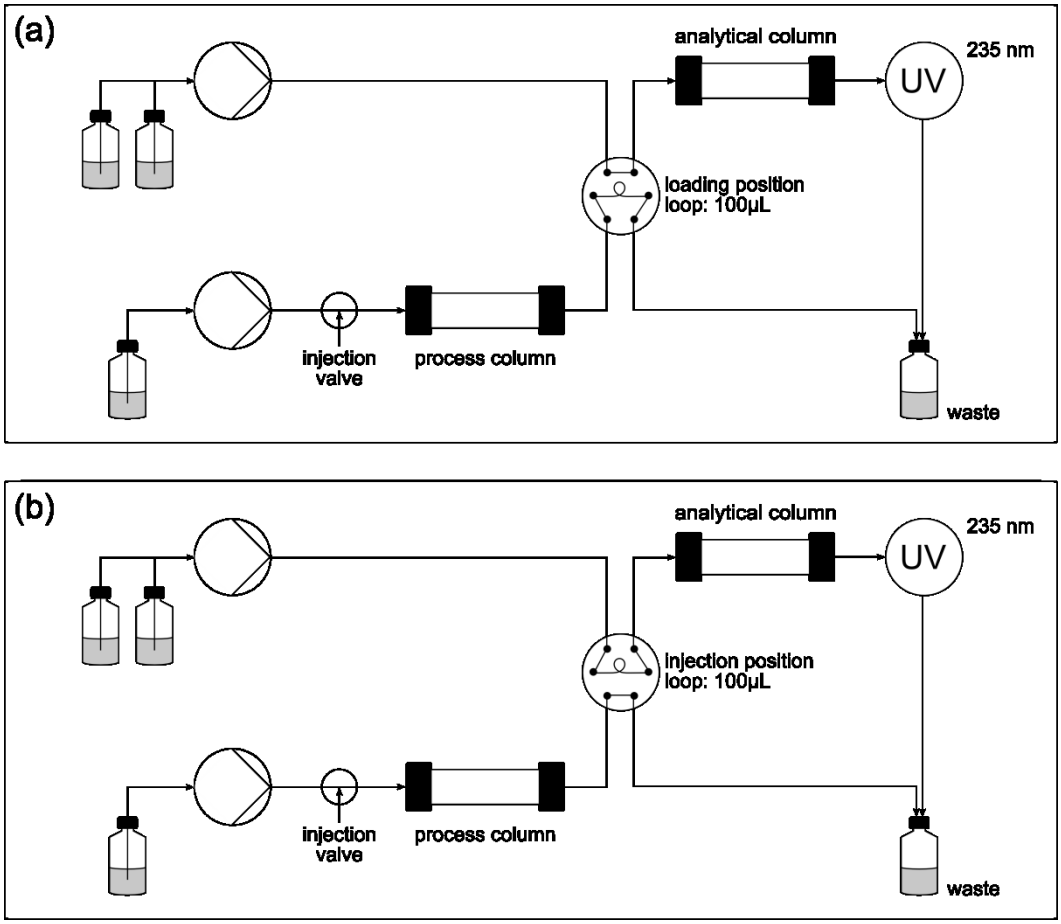


FIGURE 3. 2D-LC APPLICATION TO STUDY THE LEACHING OF BIOCIDES FROM RENDER: (A) LOADING OF THE 100 µL LOOP (LEACHING PROCESS), (B) INJECTION TO ANALYTICAL COLUMN (EVERY 25 MIN FOR 3 MIN).

4.4 Emission from artificial walls (test panels)

4.4.1 Construction of panels

Six panels (Figure 4) were constructed according to usual construction practice. A 1x1 m² polystyrene plate was attached on a wooden plate in a metal frame 1 m above the ground as substructure. Afterwards a base coat with fiberglass reinforcement mesh was applied which was then coated with acrylate (3 panels) and silicone (3) final top render, respectively, according to industrial practice.

Prior to the application the organic final topcoat was spiked with biocides following this procedure: to an aqueous biocide-suspension, render was added bit by bit while stirring thoroughly. The final concentrations of the biocides ranged between 1.0 and 2.3 mg g^{-1}, which equals to 2.7 to 6.2 mg and

1.8 and 4.1 mg per panel for acrylate rendered and silicone rendered panels, respectively (Table 5). The concentrations are normal for industrial products, while in industrial products usually only 1-6 different active ingredients are being used.

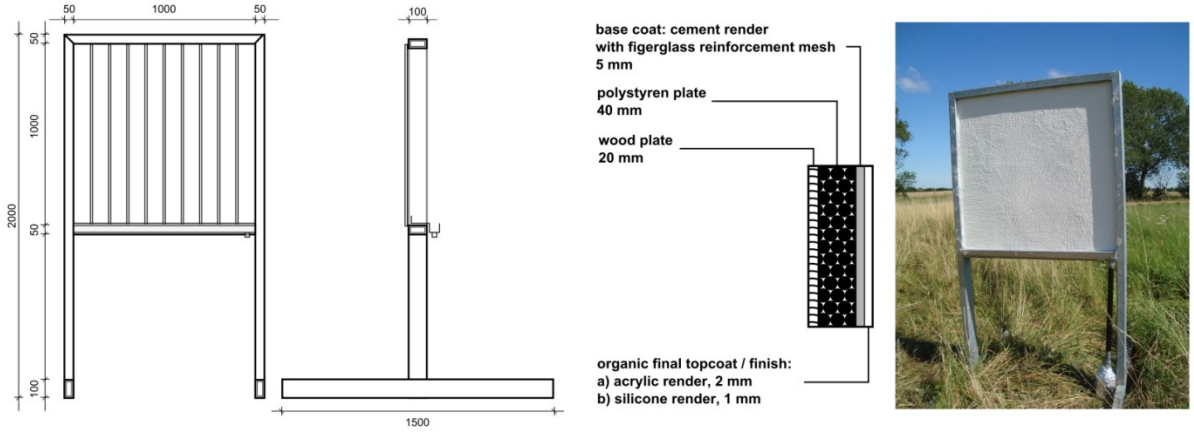


FIGURE 4. PANELS (1X1 M²) INSTALLED IN ROSKILDE, DENMARK. THE PANELS FACE DIRECTION SOUTWEST- AS THIS IS THE PREDOMINATING WIND DIRECTION.

TABLE 5. A) BIOCIDE CONCENTRATIONS IN THE RENDER AND B) TOTAL AMOUNT OF APPLIED BIOCIDES PER M² (MASS PER PANEL). THE CONCENTRATIONS OF THE BIOCIDES ARE IN THE CONCNETRATIONS USUALY USED IN INDUSTRIAL PRODUCTS.

A) Start-Concentration										
[µg g⁻¹ dry material]	MI	BIT	CD	IP	DR	IPBC	TB	OIT	TBU	DCOIT
Acrylate render	1526	1469	1420	1101	2152	2304	1741	1979	1034	1983
Silicone render	1856	1637	1537	1094	2192	2310	1210	1404	1016	1884

B) Mass per panel										
[mg panel⁻¹]	MI	BIT	CD	IP	DR	IPBC	TB	OIT	TBU	DCOIT
Acrylate render	4120	3966	3834	2972	5809	6220	4700	5343	2792	5355
Silicone render	3341	2947	2767	1968	3946	4158	2178	2526	1829	3390

4.4.2 Sampling and analysis of panel samples

Panels were exposed to natural weather during the period August 2012 – June 2013. Water samples were collected in aluminum wrapped glass bottles, which were exchanged after every rain event. In total, façade run off from 38 rain events, equally to about 35 L run-off volume, were collected.
The samples were diluted with methanol (event 1-14: 1:100, event 15-38: 1:10). To 1 mL of diluted sample 50 µL surrogate standard (1µg mL⁻¹ in methanol (gradient grade (lichrosolv), *Merck*, Darmstadt, Germany): isoproturon-D6, terbutryn-D5, cybutryn-D9, tebuconazole-D6, carbendazim-D4) was added and analyzed according to paragraph 4.2.3.

4.5 Emissions into separated sewers

4.5.1 Selection of catchment

In order to find a most appropriate catchment for the monitoring of biocide discharges into separated sewer a screening of different catchments in Denmark was performed. The screening consisted of collecting samples from 13 catchments from Aalborg, Silkeborg, Aarhus, Odense, Lemming, and Roskilde with different characteristics. The samples were collected as grab samples from storm water ponds. In such ponds, storm water typically has a residence time of some weeks, thereby representing an averaged concentration over several events. The target compounds will to some degree have been degraded while the storm runoff resided in the ponds. The concentration levels can therefore only be taken as indications towards the presence of the identified compounds, not as a measure of the average compound concentration in the storm water that originally ran off the urban surfaces. The screened catchments are shortly described in 0. Some catchments were sampled several times. The samples were analyzed directly according to paragraph 4.2.1 & 4.2.3. Selected results for the screening of biocides in storm water ponds are shown in

Table 6. Based on the screening results, the Silkeborg North catchment was selected for detailed studies. The catchment had previously been hydraulically analyzed in detail as it was constructed in connection with an EU LIFE project (Silkeborg Municipality 2009). Hence, all following results are based on the more detailed study on the storm water monitoring in Silkeborg North.

4.5.2 Characterization of the Silkeborg catchment and sampling procedure

The storm water runoff was collected in a catchment in Silkeborg (Denmark), which is a typical example of a northern European suburban area. The catchment is residential and covers in total 21.5 ha with 140 single family houses. The buildings in the catchment were surveyed and it was found that single family houses, garages, etc. are well-kept and often newly painted. In order to estimate the total façade area and the biocide treated surfaces a survey of the catchment was conducted by walking through the streets and inspecting the surfaces visually. The total façade area accounts for about 20000 m^2. About 5 % of the facades are equipped with renders and paints, 20 % covered with painted wood, and 75 % are brick facades.

Within the sampling period between October 2011 and June 2012, a total of 8929 m^3 storm water runoff entered the storm water pond of which representatives of 2880 m^3 where sampled and analyzed (191 samples, 12 events entirely sampled). An automatic water sampler (ISCO 6712, Teledyne ISCO, Lincoln, NE, USA) was triggered by a flow-meter, allowing flow proportional storm water sampling. The automatic sampler held 24 glass bottles, hereby allowing up to 360 m^3 of water to be sampled with a sampling resolution of 15 m^3.
The samples were extracted and analyzed according to the previously described methods (paragraph 4.2.2 & 4.2.3).

TABLE 6. RESULTS OF THE SCREENING EXPERIMENTS.

Sample Code	Sample	Carbendazim	Isoproturon	Diuron	Terbutryn	Tebuconazole*
		[µg L^{-1}]	[µg L^{-1}]	[µg L^{-1}]	[µg L^{-1}]	[µg L^{-1}]
BIO_001	Silkeborg, 24.3.2011, Storm water tank In	nd	nd	nd	0.04	na
BIO_002	Lemming 24.3.2011 Storm water tank In	nd	nd	nd	nd	na
BIO_003	Aarhus Vandprøve 1	nd	nd	nd	nd	na
BIO_006	Aarhus, Vandprøve 2	nd	nd	nd	nd	na
BIO_004	Aarhus, Vandprøve 3	nd	nd	0.03	nd	na
BIO_007	Aarhus, Vandprøve 4	nd	nd	nd	nd	na
BIO_005	Aarhus, Vandprøve 5	nd	nd	nd	nd	na
BIO_008	Lemming, 2010-8410	nd	0.1	nd	nd	na
BIO_009	Odense, 2010-8411	nd	nd	nd	nd	na
BIO_010	Silkeborg, 2010-8412	nd	0.03	nd	0.11	na
BIO_011	Aarhus, 2010-8413	nd	nd	0.02	0.02	na
BIO_017	Roskilde B, Trekroner Alle	0.33	nd	nd	nd	0.04
BIO_018	Roskilde C, RUC	0.13	nd	nd	nd	0.05
BIO_019	Roskilde E, Nordens Parkvej	nd	nd	nd	nd	0.02
BIO_020	Roskilde A, Knolden	nd	nd	nd	nd	0.03
BIO_021	Roskilde F, Drosselvej	nd	nd	nd	nd	0.03
BIO_022	Roskilde D, Metalvej	nd	nd	0.04	nd	0.13
BIO_024	Silkeborg 1	nd	nd	0.01	0.11	0.03
BIO_023	Silkeborg 2	nd	nd	0.03	0.10	0.04
BIO_026	Silkeborg 3	nd	nd	nd	nd	0.02
BIO_025	Århus, Gellerupparken	nd	nd	nd	nd	0.03

* Blank for Tebuconazole in this screening experiment: 0.045 and 0.095 µg/L

nd: not detected;

na: not analysed

4.6 Emissions into combined sewers

4.6.1 Overview over the waste water treatment plants sampled

Samples were taken from different wastewater treatment plants (Table 7) in Denmark and Sweden. Both influent and effluent samples were taken. Sampling was performed as grab sampling, 24 h-composite samples, and 2 h-composite samples over 24 h. In addition, different weather conditions

have been sampled. A detailed overview on the sampling can be found in the 0. Afterwards the samples were analyzed according to paragraph 4.2.2 and 4.2.3.

TABLE 7. OVERVIEW OF THE SAMPLED WASTE WATER TREATMENT PLANTS.

Waste water treatment plant	PE	Description
Roskilde Bjergmarken	125 000	Conventional WWTP
Copenhagen Lynetten	750 000	Conventional WWTP
Copenhagen Mølleåværket	135 000	Conventional WWTP
Copenhagen Avedøre	275 000	Conventional WWTP
WWTP South Sweden	200 000	Conventional WWTP with experimental set ups in side stream

4.7 Biocides in urban surface waters

4.7.1 Sampling locations and procedure

Samples were taken on 13 sampling locations in the Greater Copenhagen area (Table 8, Figure 5). The samples were taken once on May 7th 2013 after a long period with only little rain (March/April 2013) and secondly on May 27th 2013 after some heavy rainfalls.
Grab samples were taken with 1 L glass bottles, transported in cooling boxes back to the institute and stored in the fridge (4 °C) until extraction (about a week). Samples were extracted and analyzed according to the paragraphs 4.2.2 & 4.2.3.

FIGURE 5. SAMPLING LOCATIONS IN THE GREATER COPENHAGEN AREA FOR SCREENING OF URBAN SURFACE WATERS.

TABLE 8. SAMPLING LOCATIONS IN THE GREATER COPENHAGEN AREA FOR SCREENING OF URBAN SURFACE WATERS.

Sampling station	Coordinates		Comments
Roskilde Marina	55° 39.060'N	12° 4.602'E	Marina
Ørestad North	55° 38.466'N	12° 35.005'E	New city quarter (build 2001-today)
Ørestad Channels	55° 38.024'N	12° 34.890'E	New city quarter (build 2001-today)
Ørestad Lakes	55° 36.946'N	12° 34.184'E	New city quarter (build 2001-today)
Sortedams Sø	55° 41.483'N	12° 34.328'E	Down town Copenhagen
Peblinge Sø	55° 41.198'N	12° 33.725'E	Down town Copenhagen
St Jørgens sø	55° 40.503'N	12° 33.347'E	Down town Copenhagen
Furesø North	55° 48.419'N	12° 23.324'E	
Furesø South	55° 47.384'N	12° 26.671'E	
Utterslev mose	55° 42.949'N	12° 30.413'E	Large wetland and park
Damhus sø	55° 40.857'N	12° 28.412'E	
Damhusåen	55° 38.942'N	12° 29.351'E	Receives most of Copenhagens combined sewer overflow ($0.26*10^3$ m^3) (Københavns kommune 2008)
Sydhavn KBH	55° 38.572'N	12° 32.496'E	Fishing harbor, Slipway

4.8 Quantitative modelling

The occurrence of biocides in storm water runoff depends on hydrological characteristics of the catchment, on conveyance system layout, on weather factors such as rain and wind, and on the characteristics of the surfaces that release the biocides. Some of these parameters vary from site to site, while others vary from rain event to rain event. The occurrence of biocides in storm water can hence be expected to vary between sites as well as between events. Ideally this variability should be investigated based on measurements in the field. Governing parameters and border conditions should be identified in both space and time for a wide range of catchments, and the biocide content of runoff measured on long time series.

Doing so is in principle possible, it would, however, be very costly and time consuming. An alternative approach is to build a model that includes mathematical descriptions of the system and the most relevant processes. Such model will always be a simplification of reality, but it does, on the other hand, allow investigating the studied phenomena at a much lower investment of time and resources. How well such model reflects reality depends on how well the involved system and processes are described and on how well the border conditions are defined. In practice such model needs to be calibrated up against measurements in order to yield trustworthy results and conclusions.

To extend the conclusions from the field measurements on emissions from separated sewers to other, related, catchment types, a quantitative model of the studied catchment is developed and calibrated. The model is then implemented on related catchment types and longer time series in order extend the conclusions to a more general case.

4.8.1 Basis of the model

4.8.1.1 Precipitation

The runoff is driven by the precipitation in the catchment. The precipitation used for runoff simulation is measured by the Danish grid of rain gauges operated by the Wastewater Committee of the Danish Society of Engineers (SVK, Spildevandskomitéens regnmålersystem) (SVK 2013) . These gauges measure precipitation with a time resolution of 1 minute and a precipitation resolution of 0.2 mm. Historical rain series of approximately 30 years are used to assess the runoff quality from the modeled catchments.

4.8.1.2 Surfaces contributing to the storm water runoff

The storm water is rooted from the urban surfaces to the receiving waters by means of a semi-dynamic runoff model applying the well-established time-area approach (Winther *et al.* 2006). The time resolution of the runoff model is one minute and hence corresponding to the time resolution of the precipitation data.

The model applies the fraction of the total catchment surfaces (A_{tot}) that is impervious or semi-impervious (A_{imp}), i.e. covered by hard materials such as pavements, macadam, and roofs. It is denoted α, and hence $A_{imp} = \alpha A_{tot}$.

Even though a surface is covered by a hard material, it is still to some degree permeable. Furthermore, some of the water that falls on such surface will drain to pervious surfaces such as lawns and gardens. This is taken into account by a hydrological reduction factor, φ. The model further takes into account that not all impermeable surfaces are connected to the sewer network. Some such surfaces drain to permeable surfaces like lawns, flower beds, and swales where the storm water infiltrates into the subsoil (see examples of such surfaces in Figure 6 and Figure 7). The degree of connectedness, τ, must therefore be introduced when identifying the surface contributing to runoff. The reduced area contributing to runoff hence becomes $A_{runoff} = \tau \alpha \varphi A_{tot}$.

The build surfaces are further divided into horizontal surfaces such as roofs, streets and parking lots, A_h, and vertical surfaces such as façades, A_v. In the traditional approach for storm water runoff modeling, the contribution from the horizontal surfaces and the vertical surfaces are lumped. The vertical surfaces are therefore seen as a subset of the total impervious surfaces, i.e. $A_{imp} = A_{imp,h} + A_{imp,v}$.

While the majority of the impermeable horizontal surfaces typically are connected to the storm sewer system, the same cannot be said for the vertical surfaces. The degree of connection can span from 0% connected to 100% connected, depending on the layout of the catchment. An example of a façade that is 100% connected is seen in Figure 7, while a façade that is mainly disconnected is seen in Figure 6. In practice it can often be difficult to determine if a surface is connected or not without detailed inspection of the catchment in question.

FIGURE 6. A SINGLE FAMILY HOME IN THE CATCHMENT STUDIED IN SILKEBORG. THE BUILDING FAÇADE DRAINS TO A PAWED AREA WHICH THEN AGAIN DRAINS TO A LAWN AND A FLOWER BED. THE CARPORT DRAINS TO A PAWED AREA THAT PARTLY DRAINS TO THE STORM SEWER IN THE ROAD.

In the model, the vertical and horizontal surfaces connected to the storm sewer are accounted for by each their degree of connectedness, namely τ_v for vertical surfaces and τ_h for horizontal surfaces. In other words, for the whole catchment, the surfaces contributing to the runoff are found as:

$$\begin{aligned} A_{runoff,h} &= \tau_h \alpha_h \varphi_h A_{tot,h} \\ A_{runoff,v} &= \tau_v \alpha_v \varphi_v A_{tot,v} \\ A_{runoff} &= A_{runoff,h} + A_{runoff,v} \end{aligned} \quad (1)$$

FIGURE 7. AN INDUSTRIAL BUILDING IN AARHUS. ALL OF THE FAÇADE DRAINS TO A PAWED AREA WHICH DRAINS TO THE STORM SEWER IN THE PARKING LOT SEEN IN FRONT OF THE PICTURE.

4.8.1.3 Precipitation running off vertical surfaces

The amount of precipitation that runs of a building façade or other vertical surfaces has been studied by numerous researchers. It has been studied not so much to determine the amount of water running off a façade, but to assess the moisture accumulation in the materials the façades consist off. The reason being that moisture in a façade can lead to water penetration, discoloration, salt migration, and structural cracking of the façade material (Blocken *et al.* 2013). Numerical models have been developed that for specific façades and specific conditions can predict the façade runoff (Blocken & Carmeliet 2012).

When the structural details of the façades are not known, and when detailed climate data are not available, a simplified model for the runoff is, however, called for. Such has been applied by Burkhardt *et al.* (2012), based on work presented by Blocken and Carmeliet (2004). This model is semi-empirical and relates the specific façade runoff intensity, also termed the wind driven runoff, i_{wdr} [m³ m⁻² s⁻¹], to the horizontal rain intensity, i_{rain} [m³ m⁻² s⁻¹], such as measured by a rain gauge as shown in Figure 8. Note that Equation 2 is an empirical equation and the unit of i_{rain} must be L m⁻² h⁻¹ (and not m³ m⁻² s⁻¹) to get the correct magnitude of i_{wdr}, also in the unit of L m⁻² h⁻¹. Here after units must be converted back to standard SI units (m³ m⁻² s⁻¹). The relation is defined as:

$$i_{wdr} = \frac{2}{9} C_R C_T O W \cdot i_{rain}^{0.88} \cdot u \cdot \cos\theta \qquad (2)$$

where

C_R	is a roughness coefficient [-], varying from 0.95 (open field) to 0.45 (dense urban area with tall buildings)
C_T	is a topography coefficient [-], varying from 1.0 to 1.6
O	is an obstruction factor [-], varying from 0.2 (obstruction a some 4-8 m from the façade) to 1.0 (obstruction over 120 m from the façade)
W	is a wall factor [-], varying from 0.2 for tall buildings to 0.4 for low buildings
u	is the wind speed 10 m above ground [m s⁻¹]
θ	is the angle the wind makes to the plane of the façade

4.8.1.4 Biocide wash-off from vertical surfaces

The wash-off of pollutants from urban surfaces has been studied in detail by a number of researchers. Their focus has, however, been the wash-off of pollutants from horizontal surfaces rather than vertical surfaces and has not integrated leaching processes. The general approach valid for horizontal surfaces is, though, also reasonable for vertical surfaces such as façades. It is appropriate to distinguish between two different principles for the release of pollutants during a storm event, namely:

Dry weather accumulation of a pollutant on a surface, followed by wash-off during a storm event

Rain-driven release of a pollutant bound to or stored in a surface

An example of the prior mechanism is the dry weather accumulation of dust and associated pollutants on a road surface, followed by the wash-off of the dust during a storm event. An example of the latter is the release of copper from a copper roof while the material is wetted. To some degree, the latter can, though, also contain an aspect of dry weather accumulation. In the example of the copper roof, this would be the formation of an oxidized layer on the cupper surface, which might be more readily released during rain. A general pollutant wash-off model must therefore contain both aspects of release during a storm event. The mechanisms and equations presented below are mainly based on work by Chen and Adams (2006) , Shaw *et al.* (2010), Soonthornnonda *et al.* (2008), and Van Dijk *et al.* (2002).

To cover the situation a), the model must both describe the buildup of the pollutant during dry weather and the wash-off during storms. Such model can be formulated as in Equation 3 where the first term describes the buildup and the second term describes the wash-off.

$$\frac{dm_a}{dt} = k_a \cdot \left(1 - \frac{m_a}{m_{a0}}\right) - \kappa_a \cdot m_a \cdot i_{rain} \qquad (3)$$

Where

m_a is the mass of compound M (kg) per unit area (kg m^{-2}) that alternating builds up and is washed off the surface (i.e. M_a)

t is the time (s)

k_a is a rate coefficient for buildup (kg m^{-2} s^{-1})

m_{ao} is a limit mass per unit area above which no further buildup on the surface takes place (kg m^{-2})

i_{rain} is the specific rain intensity (m^3 m^{-2} s^{-1})

κ_a is a coefficient for wash-off (m^2 m^{-3})

The model presented in Equation 3 does, however, not cover the case where a rapid wash-off in the beginning of a storm event is followed by a slower and prolonged wash-off later in the event. This issue can be managed by introducing a second fraction of compound M which is slowly released from the surface. This approach would also cover the release mechanism b) described above.

$$\frac{dm_b}{dt} = -\kappa_b \cdot f\left(m_b\right) \cdot i_{rain} \tag{4}$$

Where

m_b is the mass off compound M (kg) per unit area (kg m^{-2}) that is continuously released from the surface (kg m^{-2})

$f(m_b)$ is a function describing how the mass of compound M, which can be continuously released from the surface (i.e. M_b), affects its release (kg m^{-2})

κ_b is a coefficient for wash-off (m^2 m^{-3})

As a first assumption, $f(m_b)$ can be set equal to m_b, i.e. assuming that the release of compound M_b is a first order processes in M_b. Furthermore is:

$$M = M_a + M_b \tag{5}$$

In the Equations 3 and 4 it is implicitly stated that the release rate of compound M is proportional to the rain intensity that generates the runoff q (q is calculated as the product of the rain intensity, i_{rain}, and the impervious surface area, A_{imp}). This is not necessarily true as this assumption does not take into account the physical and chemical mechanisms generating the release of the compound when rain hits the surface and runs off it. Situations where the release of compounds depends on the actual rain in terms of e.g. drop size and drop velocities can easily be envisioned. For the mechanism described in Equation 3 it is reasonable to assume that such release depends on the kinetic energy of the rain drops, and the process is often described by a power function in the rain intensity, i.e. $g(i) = i^n$. No simple dependency between wash-off rate and rain intensity is known for the mechanism described in Equation 4. As a first approximation it is assumed that $h(i) = i$. If a further distinguishing is made between horizontal and vertical surfaces, this leads to the following four equations governing the buildup and wash-off of compound M on urban surfaces:

$$\frac{dm_{a,h}}{dt} = k_h \cdot \left(1 - \frac{m_{a,h}}{m_{a0,h}}\right) - \kappa_{a,h} \cdot m_{a,h} \cdot g\left(i_{rain,h}\right) \tag{6}$$

$$\frac{dm_{b,h}}{dt} = -\kappa_{b,h} \cdot f\left(m_{b,h}\right) \cdot h\left(i_{rain,h}\right) \tag{7}$$

$$\frac{dm_{a,v}}{dt} = k_v \cdot \left(1 - \frac{m_{a,v}}{m_{a0,v}}\right) - \kappa_{a,v} \cdot m_{a,v} \cdot g\left(i_{wdr}\right) \tag{8}$$

$$\frac{dm_{b,v}}{dt} = -\kappa_{b,v} \cdot f\left(m_{b,v}\right) \cdot h\left(i_{wdr}\right) \quad (9)$$

Where the index *h* relates to horizontal surfaces and the index *v* relates to vertical surfaces and where the rain has been split into its horizontal component, $i_{rain,h}$, and its vertical component, i_{wdr}. The materials of the various surfaces in the catchment differ, and hence not all surfaces contain the compound *M*. This issue is addressed by introducing a parameter, ε, accounting for the fraction of the area *A* that contains the compound *M*. I.e. the total mass of *M* in the catchment becomes $M = \varepsilon A m$. It should furthermore be noted that two otherwise similar surfaces could contain different concentrations of *M*, for example because they have been treated (e.g. painted) at different times in the past. A catchment surface should hence be subdivided into elements of same properties with respect to the content of *M*. Further introducing the simplifying assumptions presented previously, the model used for describing release of compound *M* from a specific façade or horizontal surface element becomes:

$$\frac{dm_{a,h}}{dt} = k_h \cdot \left(1 - \frac{m_{a,h}}{m_{a0,h}}\right) - \kappa_{a,h} \cdot m_{a,h} \cdot i_{rain,h}^n \quad (10)$$

$$\frac{dm_{b,h}}{dt} = -\kappa_{b,h} \cdot m_{b,h} \cdot i_{rain,h} \quad (11)$$

$$\frac{dm_{a,v}}{dt} = k_v \cdot \left(1 - \frac{m_{a,v}}{m_{a0,v}}\right) - \kappa_{a,v} \cdot m_{a,v} \cdot i_{wdr}^n \quad (12)$$

$$\frac{dm_{b,v}}{dt} = -\kappa_{b,v} \cdot m_{b,v} \cdot i_{wdr} \quad (13)$$

4.8.1.5 Boundary conditions for model calibration

The model is calibrated to the whole duration of the sampling campaign, i.e. the period from October 2011 and June 2012. In this period a total of 8,929 m³ of storm water runoff was measured. Hereof samples were collected from 2,880 m³ (191 samples, covering 12 entire events).

Precipitation

For calibration of the model to data from the studied catchment in Silkeborg, the rain gauge 22419 placed at Tietgensvej 3, 8600 Silkeborg, is used (Figure 8). The distance from the gauge to the center of the intensively monitored catchment is 2000 m and the gauge therefore deemed to give a good representation of the actual precipitation experienced.

FIGURE 8. THE RAIN GAUGE USED TO CALIBRATE THE RUNOFF MODEL.

Catchment area

The impervious surface area contributing to the runoff, A_{imp}, is from a previous study known to be 7.1 ha with a hydrological reduction factor, φ, of 0.80 (Silkeborg Municipality 2009) . These data were found by calibrating a hydrodynamic model to measured runoff and assuming a degree of connectedness, τ, of one. Recalibrating the data to runoff measured in the present campaign did though yield a somewhat lower hydrological reduction factor, namely 0.50.

The total vertical area (façades), $A_{tot,v}$, are found from aerial photos of the catchment (Table 9). The ratio of impervious area to total area, α_v, is assumed unity as all façades are assumed impervious. The degree of connectedness, τ_v, is estimated from aerial photos as the façades that drain to pawed surfaces that again potentially could drain to the storm sewer. A fraction of the potentially connected surfaces ($\alpha_v \tau_v A_{tot,v}$) will instead drain to lawns, flower beds, and other permeable surfaces. Pawed surfaces are, furthermore, not all completely impermeable and some rain will infiltrate through the pawed surface. In other words, the hydrological reduction factor, φ_v, must be found for these areas. This hydrological reduction factor is given the index 'v' as it determines the fate of the runoff from the façades, even though it strictly speaking does not refer to a vertical surface. The exact determination of this parameter is problematic as it would demand a complex and detailed survey of all surfaces in the catchment. The φ_v was therefore estimated based on literature and experience. So did for example Thorndahl *et al.* (2006) for a similar catchment find that only a small fraction of driveways, terraces, and etcetera were in reality contributing to the runoff. Based here on, the φ_v was set at 0.10, i.e. one fifth of the global hydraulic reduction factor.

TABLE 9. THE TOTAL VERTICAL AREA (FAÇADES), ATOT,V, IS FOUND ASSUMING AN AVERAGE HEIGHT OF A FAÇADE OF 2.4 M. SEE ALSO (EQ 1).

$A_{tot,v}$ [m²]	τ_v [-]	$A_{imp,v}$ [m²]	α_v [-]	φ_v [-]	$A_{runoff,v}$ [m²]
23,910	0.215	5,141	1	0.10	514

Biocide contribution from vertical surfaces

The pollutants addressed in the present study are assumed to originate solely from façades and other vertical surfaces. The contribution from horizontal surfaces is hence assumed nil, i.e. $M_{a,h}$ and $M_{b,h}$ are set to zero, resulting in the processes described in equations 10 and 11 to not being expressed. The amount of a biocide compound in a façade varies but is for a newly treated surface assumed at 1 g m^{-2} (Burkhardt *et al.* 2011; Burkhardt *et al.* 2012). When simulating the facades, an initial distribution of biocides in the façades had to be assumed. This was done by randomly

assigning an initial time of treatment prior to start of simulations. Based on the time of application, the compound concentration at start of the simulations was calculated using an exponential decay function. This method was calibrated so that the average compound mass in the façades at the start of simulations was equal to the final compound concentration after about 3 decades of model simulation.
Based on the photo survey of the catchment, it was found that about 5 % of the facades are equipped with renders and paints, 20 % are covered with painted wood, and 75 % are brick facades. I.e. 25 % of the facades have received a surface treatment that can give off biocides. The rest is made of brick or similar material that has not received surface treatment, that is the fraction ε_v of the area A_v that can contain a compound M is 0.25. However, not all compounds are present in all façades so ε_v will in practice be between 0 and 0.25. Accordingly, the fraction of façades treated with paint or render containing compound M is found between 0 and 0.25 $A_{runoff,v}$. This façade area is (somewhat arbitrary) divided into individual elements with a treated area of 1 m², taking into account that some elements may only be partial façades like doors or windows. I.e. the vertical areas (Table 9) are divided into 514 m² *0.25 / 1 m² = 129 façade elements. Each façade element is given an orientation of either 0° (North), 90° (East), 180° (South) or 270° (West). The elements are equally distributed to the 4 directions. Each of the façade elements is assumed treated (e.g. painted) on average every 3 ±2 years, but never more often than once a year. The treatment frequency is assumed normal distributed around the average. All façade treatment is assumed to occur from April 1 to October 31. Based on this a stochastic model of façade treatment is build, describing the frequency of treatment of each façade element.
Each façade element is then subject to wash-out of compound M applying the rain series from the rain gauge at Tietgensvej 3 in Silkeborg. For each hour of the measuring period, the predominant wind direction and wind speed is picked from a corresponding DMI data file on climatic data. The data file is from the Isenvad monitoring station, being the monitoring station closest to the catchment (23 km).
For each façade the wind driven rain is then found by applying Equation 2 with the time resolution of the precipitation measurement, i.e. 1 minute. Depending on the wind direction and hereby the angle the wind has to the plane of the façade, this means that between ¼ and ½ of the façade elements at any given point in time can contribute to the runoff.
The other parameters of Equations 12 and 13 are subsequently found by model calibration. For part of the calibration, long time-series of precipitation and wind was required. Due to the length of rain gauge 22419 being rather short, long time series for precipitation were obtained from other rain gauges, namely another in Silkeborg, one in Odense, one in Sønderborg, and one in Holbæk. The wind data series for these long time series had to be produced from agglomerating and repeating wind data from several DMI stations, namely Isenvad, Aarhus-syd, and Aarslev, each covering 1/1/2008-4/24/2009.

Boundary conditions for scenario simulation

The calibrated model is used for simulating selected urban scenarios and to determine median pollution loads and extreme concentration statistics. One of the catchments is based on the one used for calibration, and represents a typical Danish suburban catchment of single family houses. The second catchment is medium dense and build with 2- story terrace houses with their own gardens and green areas between the houses (Danish: tæt-lav-bebyggelse). The third catchment is dense and contains buildings having 3-5 stories, equivalent to typical Danish city centers. The forth catchment is an industrial catchment. For all the catchments the impervious area was set to 10 ha and the hydrological reduction factor was set to 0.7.

5. Results and Interpretations

5.1 Mobility of biocides in materials including partitioning

In order to study the mechanisms of the leaching process a 2-dimensional liquid chromatography system was established in order to simulate a leaching process only dependent on the material and the biocide properties but independent from weather conditions (see paragraph 4.3.2). In addition equilibrium desorption constants for biocides from organic render to water were determined (see paragraph 4.3.1).

Both experiments were performed with acrylate render with different acrylate content for the assessment of the effect of acrylate contribution on leaching biocides. For this purpose the commercial acrylic render with 10 % of acrylate was topped with acrylate (Plextol D498, Synthomer Deutschland, Marl, Germany) to give 15 %, 20 % and 30 % of acrylate in the final product.

5.1.1 Desorption equilibrium experiments

5.1.1.1 Desorption constants

The desorption constants were obtained by plotting the concentration in the render (c_S) against the concentrations in the water (c_W) at equilibrium time (for experimental procedure see paragraph 4.3.1). The resulting desorption constants (K_d) are calculated using:

$$K_d = \frac{c_S}{c_W} \tag{14}$$

The resulting desorption constants for both pore water (pH 9.5) and surface water (pH 5.6) are listed in

Table 10 as well as the desorption constant normalized to the organic matter content (f_{OM}):

$$K_{OM} = \frac{K_d}{f_{OM}} \quad (15)$$

For porewater (pH 9.5) on the acrylate system K_d's ranged from 8.1 (isoproturon) to 9634 (IPBC). For the silicone render the values are similar: Isoproturon showing the lowest K_d (K_d=9.8) and DCOIT the highest (K_d=5761). As both the render material and the biocides can be protonated and deprotonated the values for surface rain water (pH 5.6) differ to those for pore water.
Based on these data, compounds with low desorption constants as isoproturon and carbendazim would be assumed to desorb much faster than compounds with high desorption constants (e.g. cybutryn or DCOIT).

TABLE 10. DESORPTION CONSTANTS (K_D) IN L KG^{-1} OF BIOCIDES BETWEEN RENDER (MODIFIED BY ACRYLATE AND SILICONES) AND WATER AT PH=5.6 AND 9.6. IN ADDITION THE LINEAR REGRESSION COEFFICIENTS (R^2) AND THE DESORPTION CONSTANT NORMALIZED TO THE ORGANIC MATTER CONTENT (LOG K_{OM}) (N=2).

		Acrylate modified render		Silicone modified render	
	pH	**5.6**	**9.5**	**5.6**	**9.5**
Carbendazim (CD)	K_d	4.0 ± 0.8	33.8 ± 1.0	1.8 ± 0.1	310.8 ± 4.4
	R^2	0.9330	0.9965	0.9770	0.9990
	log K_{OM}	1.6	2.5	1.3	3.5
Isoproturon (IP)	K_d	20.5 ± 1.4	8.1 ± 0.6	19.6 ± 0.6	9.8 ± 0.2
	R^2	0.9820	0.9807	0.9962	0.9979
	log K_{OM}	2.3	1.9	2.3	2.0
Diuron (DR)	K_d	63.5 ± 4.7	17.9 ± 1.5	78.1 ± 1.0	21.4 ± 0.7
	R^2	0.9835	0.9862	0.9991	0.9956
	log K_{OM}	2.8	2.3	2.9	2.3
Cybutryn (IRG)	K_d	213.6 ± 3.6	26.0 ± 0.3	682.1 ± 4.7	121.4 ± 1.0
	R^2	0.9986	0.9995	0.9998	0.9996
	log K_{OM}	3.3	2.4	3.8	2.9
Tebuconazole (TBU)	K_d	130.3 ± 1.2	65.8 ± 1.4	307.5 ± 3.0	700.6 ± 7.7
	R^2	0.9996	0.9977	0.9995	0.9994
	log K_{OM}	3.1	2.8	3.5	3.8
Iodocarb (IPBC)	K_d	114.8 ± 4.9	9634 ± 1611	302.6 ± 8.9	70.8 ± 2.8
	R^2	0.9909	0.9471	0.9957	0.9925
	log K_{OM}	3.1	5.0	3.5	2.9
Dichlorooctyl-isothiazolinone (DCOIT)	K_d	-	3750 ± 416	-	5761 ± 1075
	R^2	-	0.9759	-	0.9349
	log K_{OM}	-	4.6	-	4.8

5.1.1.2 Enhanced polymer experiments

The experiments were performed with renders with different acrylate contribution for assessment of the effects of the acrylate fraction on leaching biocides (for experimental procedure see paragraph 4.3.1).

In addition to different pH-values the desorption of biocides from acrylate with varying binder content was tested. Figure 9 shows a clear correlation between desorption constant and the fraction of acrylate in the render system for iodocarb, DCOIT, tebuconazole, cybutryn, and carbendazim, while the two phenylureas diuron and isoproturon are hardly interacting with the acrylate at all.

Hence, the release of some compounds can at least to some extent be controlled by the organic fraction in the render system.

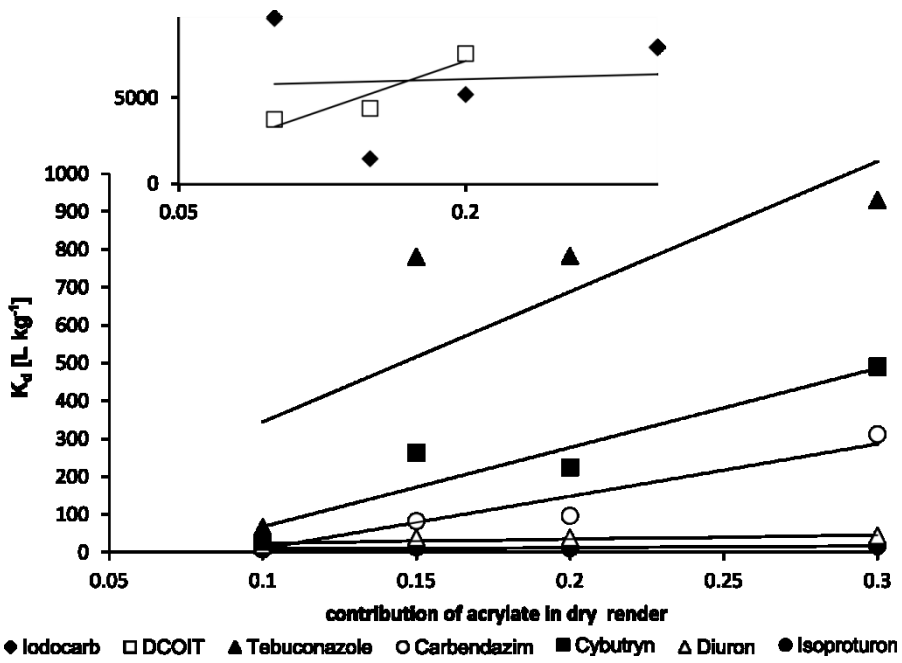


FIGURE 9. EFFECTS OF VARYING ACRYLATE CONCENTRATIONS ON DESORPTION CONSTANTS.

5.1.2 Kinetic mobility experiments (2-dimensional liquid chromatography)

This setup allowed the observation of the biocide leaching by studying the retention volume from the render column (leachate volume column 1, Figure 10). By transferring it into a 2-dimensional graph (Figure 11) the retention volume (50 % leachate volume) could easily be defined by the infection point.

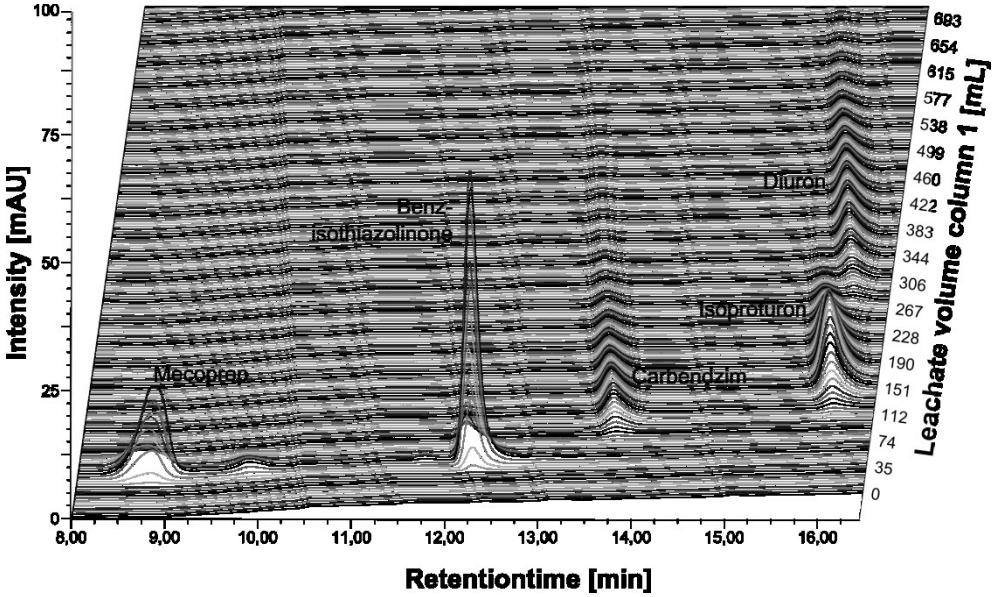


FIGURE 10. 3-DIMENSIONAL CHROMATOGRAM OF STUDYING THE LEACHING OF BIOCIDES FROM A RENDER FILLED COLUMN (COLUMN A. 10 % ACRYLATE).

The different shapes of the curves for carbendazim and isoproturon show that these two compounds are undergoing quite different interactions with the render material i.e. one might interact through

hydrogen bonds and another one might interact through van der Waals interactions and cannot be detected that easily by equilibrium experiments.

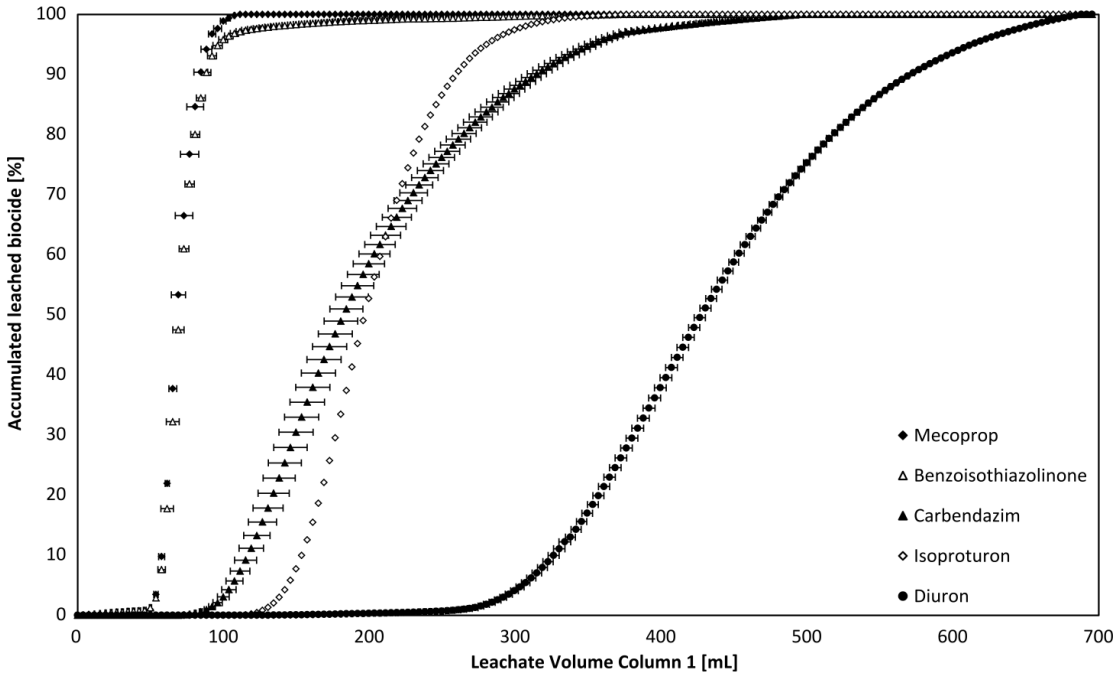


FIGURE 11. ACCUMULATED LEACHED BIOCIDE FRACTION IN RELATION TO THE LEACHATE VOLUME: COMMERCIAL ACRYLATE RENDER (10% ACRYLATE) MIXED WITH QUARTZ SAND (COLUMN A, DEAD VOLUME 57 ML, PH ~8).

TABLE 11. COMPARISON OF THE EFFECTIVE LEACHATE VOLUME [ML] FOR COMMERCIAL ACRYLATE RENDER (10%, COLUMN A, N = 3) AND RENDER WITH ENHANCED ACRYLATE CONTENT (20%, COLUMN B, N = 1) AS WELL AS THE RELATIVE STANDARD DEVIATION (RSD) OF THE TRIPLICATE MEASUREMENT ONF THE TRIPLICATE ANALYSIS OF COLUMN A (10% ACRYLATE).

Compound	effective leachate volume [mL]		RSD [%]
	10 % Acrylate	**20 % Acrylate**	**10 % Acrylate**
Mecoprop	11	2	0.9
Benzisothiazolinone	13	7	1.5
Carbendazim	125	nd	11.4
Isoproturon	140	451	1.5
Diuron	371	1767	2.6
Iodocarb[a]	624	na	
Cybutryn[a]	3622	na	

(a) measured by HPLC-MS/MS; n=1; (nd) not detected; (na) not analysed

Table 11 shows the effective leachate volumes (V_{eff}) of different studied biocides, calculated as the difference of retention volume (V_{ret}) and void volume (V_{void}) (equation 16). The void volume equals the pore volume for the render columns.

$$V_{eff} = V_{ret} - V_{void} \quad (16)$$

Benzisothiazolinone and mecoprop leached out very fast, needing only a few milliliters more than void volume (57 mL). In contrast carbendazim, diuron, isoproturon, iodocarb, and cybutryn needed several column volumes to leach, indicating towards strong interactions with the render material. Following this, cybutryn sorbs ten times stronger to the render than diuron does.
The leaching of the biocides was studied on a column with commercial acrylate render (10 % acrylate) as well as the same render with an increased amount of acrylate (20 %). Hence, by comparing the relative leachate volumes the influence of the organic binder content can be studied. It can be seen that the different biocides were affected differently by the increasing polymer content. While benzisothiazolinone and mecoprop were leaching faster from the column, the phenylureas isoproturon and diuron leached four times slower.
Linking the effective volume V_{eff} to the void volume V_{void} and the mass of render in the system (m_{render}) gives a constant ($K_{transport}$) that indicates the strength of the interaction between render and biocidal compound (equation 17).

$$\left(\frac{V_{eff}}{V_{void}}\right)/m_{render} = K_{transport} \quad (17)$$

This constant indicates the strength of the sorption: the higher the constant, the stronger the sorption of the biocide towards the render. With the data from the 2-dimensional experiment all data can be gained to calculate $K_{transport}$ (Table 12, with V_{eff} see Table 11, V_{void} = 57 mL, m_{render} = 84 g).

TABLE 12. CHROMATOGRAPHICALLY GAINED CONSTANTS FOR COMPARING RENDER COLUMNS TO REAL RENDER SYSTEMS; THE PARAMETER V_{EFF}/V_{VOID} IS ASKING ON HOW OFTEN THE PORE VOLUME NEEDED TO BE FILLED WITH WATER AND EMPTIED AGAIN UNTIL HALF OF THE AMOUNT OF A RESPECTIVE BIOCIDE IS LEACHED.

	column A (10 % acrylate)		1 m² render system	
void volume [mL]	57		300	
render [g]	84		3000	
	V_{eff} [mL] (Data from Table 11)	$K_{transport}$ (see eq. 17)	V_{eff} [mL]	V_{eff}/V_{void}
Mecoprop	11	0.002297	2067	6.89
Benz-isothiazolinone	13	0.00272	2443	8.15
Carbendazim	125	0.0261	23496	78.3
Isoproturon	140	0.0292	26315	87.7
Diuron	371	0.0775	69736	232
Iodocarb	624	0.130	117293	391
Cybutryn	3622	0.756	680827	2269

With the constants gained a prediction on the effective volume on real render systems with different geometry can be calculated. In Table 12 this is performed for a 1 m² render system with 3 mm thickness (thus containing 3000 g render and having 300 mL pore volume). The parameter V_{eff}/V_{void} is asking on how often the pore volume needed to be filled with water and emptied again until half of the amount of a respective biocide is leached.
The result based on V_{eff}/V_{void} in respect to benzisothiazolinone results in about 8 times a total fill of the pore volume of the render system would be sufficient to remove half of the biocide. In respect to cybutryn, the system needed about 2200 filling/emptying of the pore volume to leach half of the compound. The water could be delivered by heavy rains or via dew cycles. During dew cycles the

water would enter the system as vapor, condense during the night and evaporate from the surface e.g. the next morning or in case of heavy dew the material could be soaked completely.

5.1.3 Comparison of the partitioning results from the chromatographic and the equilibrium approach

The two experimental setups were conducted to support each other in the determination of the leaching mechanism. In this paragraph the octanol water partitioning coefficient is sued to calibrate the column experiments. Table 13 compares the observed leaching in the 2-dimensional setup with leaching volumes predicted based on the desorption constants derived from the equilibrium experiments (paragraph 5.1.1) or the octanol water partition coefficients.

TABLE 13. COMPARISON OF RETENTION VOLUMES FOR COMMERCIAL ACRYLATE RENDER DERIVED FROM THE KINETIC MOBILIY EXPERIMENTS IN COMPARISON TO PREDICTED ONES BASED ON DESORPTION CONSTANT (K_D) DERIVED FROM DESORPTION EQUILIBRIUM EXPERIMENTS AS WELL AS OCTANOL-WATER-PARTITION-COEFFICIENT (LOG K_{OW}).

Compound	Observed leachate volume (paragraph 5.1.2) [mL]	Expected leachate volume based on K_d (see eq. 19, paragraph 5.1.1) [mL]		Expected leachate volume based on log K_{OW} (BIT as reference, see eq. 18) [mL]
pH	6-7	5.6	9.5	7
Mecoprop	11	-	-	245
Benzisothiazolinone	13	-	-	13
Carbendazim	125	325	2748	62
Isoproturon	140	1669	663	207
Diuron	371	5168	1457	158
Iodocarb	624	9342	784269	117
Cybutryn	3622	17375	2120	2672

The observed leachate volume of an arbitrary compound was calculated using the data of benzisothiazolinone for the prediction based on the octanol-water partitioning coefficient ($V_{logK_{OW}}$) using equation 18. This approach assumes that the ratio of the octanol-water partitioning coefficient equals the ratio of the leachate volumes. Hence, with octanol-water partitioning coefficients and the experimental determined leachate volume for benzisothiazolinone, the leachate volume for a second compound can be predicted.

$$V_{logK_{OW}} = \frac{logK_{OW}}{logK_{OW(BIT)}} V(BIT) \qquad (18)$$

Based on the desorption constant K_d the equilibrium amount of water was calculated in relation to the total mass of render in the column (m_{render}):

$$V_{K_d} = m_{render} \cdot K_d \qquad (19)$$

The obvious numerical differences from the two methods maybe explained by

a) one experiment (desorption equilibrium) is a true equilibrium experiment, while the other (kinetic mobility experiment) has a transport factor included and diffusion processes play an important role and
b) the equilibrium experiment was conducted with the material as is (including all formulation agents, soluble ions etc.) while the chromatographic experiment was conducted under

conditions excluding all these. The column system is intrinsically washed during the experiment, while the equilibrium system is not.

Different pH-values might also be a reason for this. While the octanol-water partition coefficient is predicted for the uncharged compound, the leachate of the column is slightly basic (pH ~8) and the desorption constants are calculated for pH 9.5 and 5.6.

5.1.4 Interpretations "Laboratory studies of the mobility of biocides in material"

Both approaches to study the mechanisms of the leaching process showed:

- The leaching is influenced by the organic binder content with higher render content giving less leaching and can at least to some extent be controlled by the organic fraction in the render. However, the different biocides are affected to various extents. While IPBC, Diuron, Isoproturon and Tebuconazole do not seem to be strongly influenced by the fraction organic material in the render, the desorption of DCOIT, Cybutryn, are heavily influenced by that. This is indicating towards two different dominating sorption mechanisms: while DCOIT and Cybytryn probably rather underlie a partitioning equilibrium towards the polymeric fraction of the render, the other compounds, probably rather undergo electrostatic interactions with the mineral phase (Carbonates) of the render. However this finding should at this moment rather be considered as a hypothesis.
- Assessing the desorption just on basis of K_{OW} (at neutral conditions) leads to the assumption that an order like MI>BIT>Carbendazim>IPBC>OIT>Diuron>Isoproturon>DCOIT>Terbutryn>Tebuconazole>Cybutryn>Propiconazole would be expected (Table 1).
- Changes in the pH leads to different desorption behavior. Considering the leaching of a complete system, it needs to be determined which process is the predominant (diffusion in the pores or desorption from the surface) in order to define the most suitable parameters to decrease the leaching.
- Considering the porewater pH (9.5) a ranking on desorption equilibrium was obtained: Isoproturon>Diuron>Cybutryn>Carbendazim>Tebuconazole>DCOIT>IPBC was obtained for acrylate render, while the ranking changed slightly to Isoproturon>Diuron>IPBC>Cybutryn>Carbendazim>Tebuconazole>DCOIT for the silicone render. With the exceptions of IPBC, both render systems give the same order, indicating towards that generally speaking it does not matter that much whether the binder is silicone based or acrylate based, if a similar TOC is reached. An assessment based on Kow would lead to considerably wrong results.
- Considering surface pH (5.6), the ranking on desorption equilibrium was different to the one at porewater pH: Carbendazim>Isoproturon>Diuron>IPBC>Tebuconazole>Cybutryn for the acrylate render and Carbendazim>Isoproturon>Diuron> IPBC=Tebuconazole>Cybutryn. It thus seems like the acid constants of the active ingredients are dominating over the protonation behavior of the render system concerning the desorption/leaching at equilibrium.
- The kinetic mobility experiments (conducted with pH 7 which was controlled by the porewater itself) on an acrylate render resulted with a ranking of Carbendazime>Isoproturon>Diuron>IPBC>Cybutryn. It is thus rather similar to the surface water pH experiment of the equilibrium experiment.
- Wet/dry (or pore fill/empty) cycles might contribute to the leaching of the materials, no further details are available from this project, but this might be an issue of future projects.
- The laboratory results will be compared with real leaching data in paragraph in paragraph 0 in order to test the usability to predict the leaching of biocides from façade renders in test set ups.

5.2 Wash-off from artificial walls

In order to estimate the influence of several weather parameters as e.g. rain amount, rain intensity or length of the drying period on the leaching of biocides artificial walls has been build and exposed to natural Danish weather.

5.2.1 Concentrations in run-off from artificial walls

Average concentrations range from 0.2 mg L^{-1} (DCOIT) to 30 mg L^{-1} (Methylisothiazolinone) for acrylate render and from 0.3 mg L^{-1} (DCOIT) to 14 mg L^{-1} (Methylisothiazolinone) for silicone render, respectively. However, the relative standard deviations of the concentrations in the samples is high, demonstrating the power of different variables (weather) for the leaching (Table 14

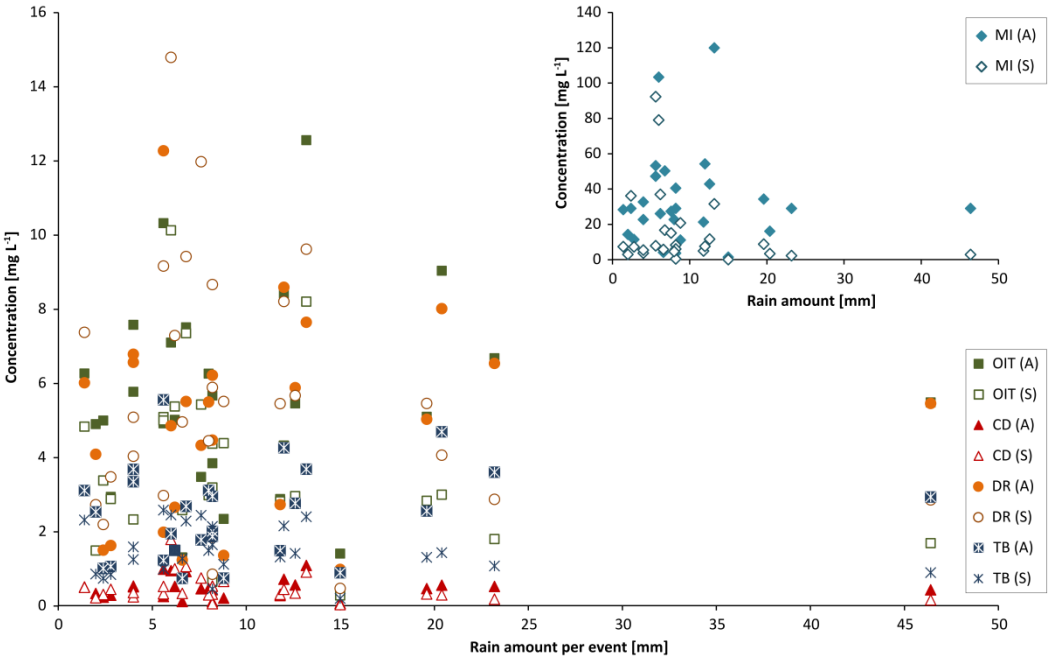


FIGURE 13. CONCENTRATIONS IN RUN-OFF WATER FROM ARTIFICIAL WALLS EQUIPPED WITH ACRYLATE (A) AND SILICONE (S) TOP RENDER (AVERAGE VALUES FROM 3 PANELS EACH) DURING 6 MONTHS EXPOSURE TO NATURAL WEATHER (AUGUST 2012 – FEBRUARY 2013; TOTAL RAIN AMOUNT WITHIN THIS PERIOD: 415 MM) PLOTTED AGAINS THE RAIN AMOUNT DURING THE SPECIFIC EVENT. ABBR.: MI - METHYLISOTHIAZOLINONE, OIT - OCTYLISOTHIAZOLINONE, CD - CARBENDAZIM, DR - DIURON, TB - TERBUTRYN.

Table 14) (compare chapter 5.2.3). Overall the concentrations do not show any significant trend for most of the compounds within the first four months of exposure to natural weather. Only the concentrations of the in-can preservative methylisothiazolinone decrease, for silicone render more obvious than for acrylate render (Figure 12).

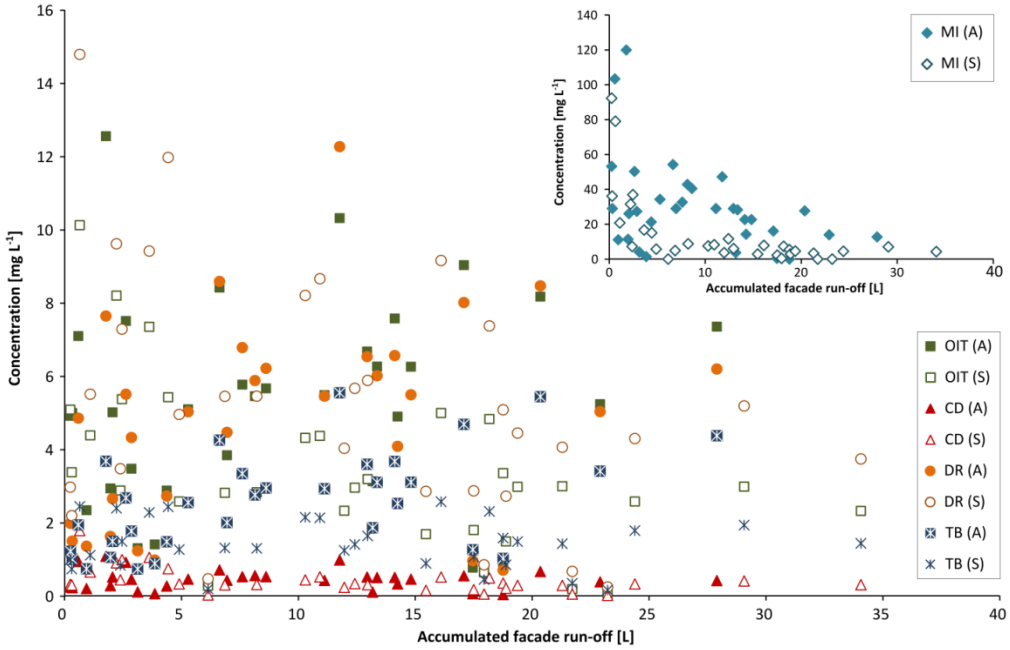


FIGURE 12. CHANGES OF THE CONCENTRATIONS IN RUN-OFF WATER FROM ARTIFICIAL WALLS EQUIPPED WITH ACRYLATE (A) AND SILICONE (S) TOP RENDER (AVERAGE VALUES FROM 3 PANELS EACH) DURING 6 MONTHS EXPOSURE TO NATURAL WEATHER (AUGUST 2012 – FEBRUARY 2013; TOTAL RAIN AMOUNT WITHIN THIS PERIOD: 415 MM). ABBR.: MI - METHYLISOTHIAZOLINONE, OIT - OCTYLISOTHIAZOLINONE, CD - CARBENDAZIM, DR - DIURON, TB - TERBUTRYN.

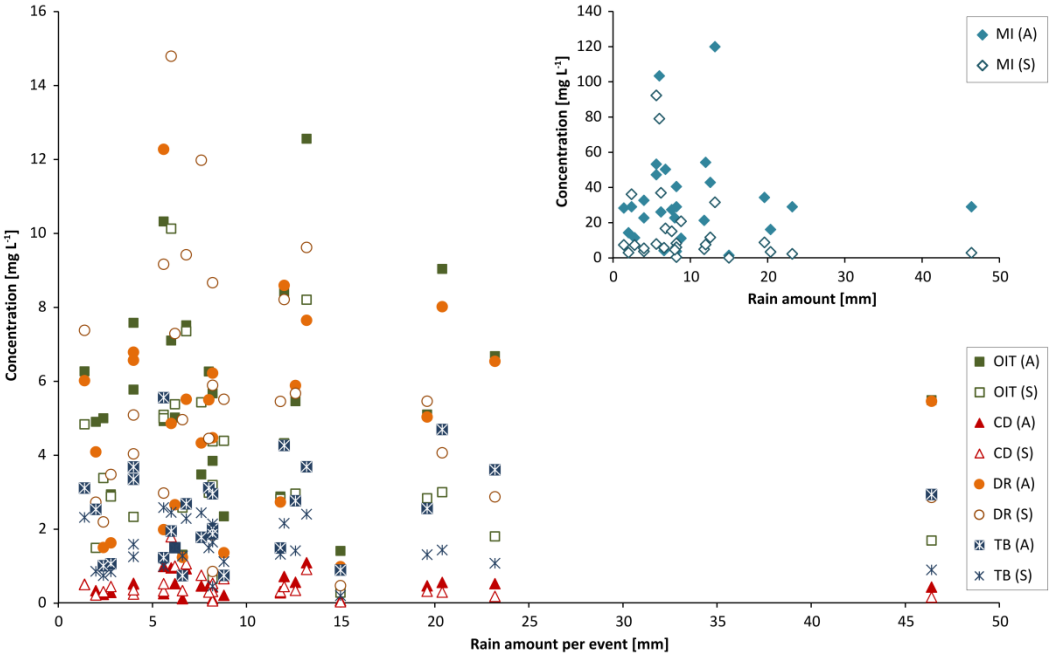


FIGURE 13. CONCENTRATIONS IN RUN-OFF WATER FROM ARTIFICIAL WALLS EQUIPPED WITH ACRYLATE (A) AND SILICONE (S) TOP RENDER (AVERAGE VALUES FROM 3 PANELS EACH) DURING 6 MONTHS EXPOSURE TO NATURAL WEATHER (AUGUST 2012 – FEBRUARY 2013; TOTAL RAIN AMOUNT WITHIN THIS PERIOD: 415 MM) PLOTTED AGAINS THE RAIN AMOUNT DURING THE SPECIFIC EVENT. ABBR.: MI - METHYLISOTHIAZOLINONE, OIT - OCTYLISOTHIAZOLINONE, CD - CARBENDAZIM, DR - DIURON, TB - TERBUTRYN.

TABLE 14. AVERAGE CONCENTRATIONS (CONC) AND RELATIVE STANDARD DEVIATIONS (RSD, BASED ON ALL SAMPLES FROM THE SAME RENDER INDIVIDUALLY: N = 96) IN RUN-OFF WATER FROM THE FIRST 38 EVENTS.

		MI	BIT	CD	IP	DR	IPBC	TB	OIT	TBU	DCOIT
Acrylate render	Conc. [mg L^{-1}]	30.0	1.5	0.5	8.0	4.7	8.6	2.6	5.4	2.5	0.2
	RSD [%]	96	157	69	71	69	77	63	59	63	76
Silicone render	Conc. [mg L^{-1}]	13.9	0.4	0.4	5.9	5.3	4.2	1.4	3.4	0.8	0.3
	RSD [%]	190	244	88	79	66	60	51	69	46	73

5.2.2 Mass flow from artificial walls

Based on previous studies a decrease in the release with exposure time is expected and, hence, after a sharp increase the accumulated mass load curve would remain static. As shown in Figure 14 only in the case of methylisothiazolinone the accumulated leached fraction tended to trail of, though not becoming fully static, since the release declined rapidly after about 5 L of run-off volume from silicone based renders and 20 L for acrylate based renders, respectively. For all other biocides, the ones shown in Figure 14 as well as the non-shown ones, no reduction in the release rate can be seen in the curves and the accumulated mass still increasing with further rain events. This presumes that the concentration in the render is not (yet) the limiting factor for release.
All data including the rain amount data is available in o and o.

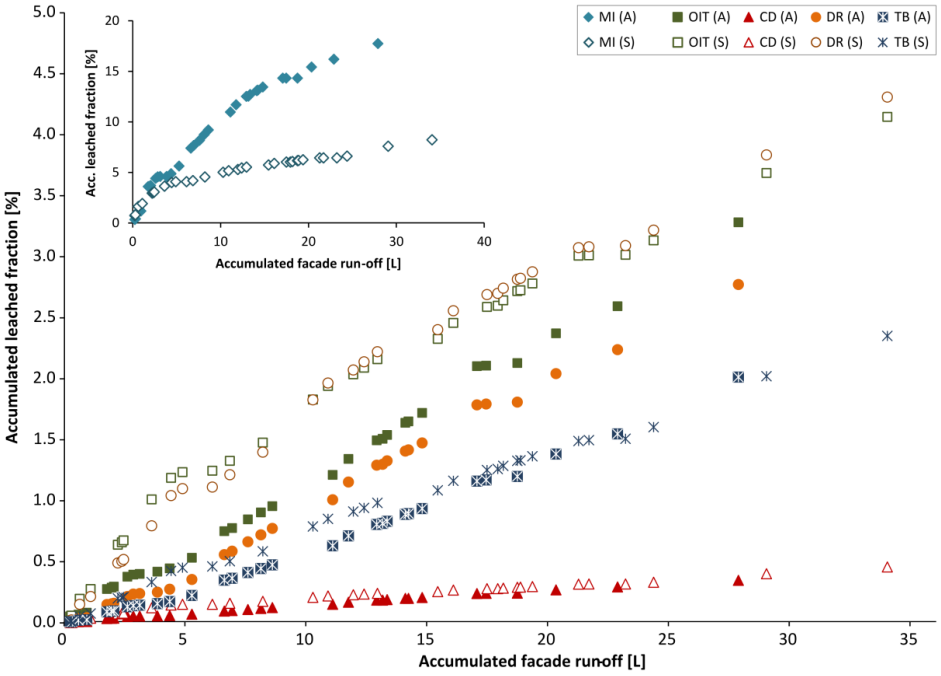


FIGURE 14. ACCUMULATED EMITTED FRACTION FROM ARTIFICIAL WALLS EQUIPPED WITH ACRYLATE (A, FILLED BULLETS) AND SILICONE (S, OPEN BULLETS) TOP RENDER (AVERAGE VALUES FROM 3 PANELS EACH) WITHIN THE FIRST 6 MONTHS OF EXPOSURE TO NATURAL WEATHER (AUGUST 2012 – FEBRUARY 2013; TOTAL RAIN AMOUNT WITHIN THIS PERIOD: 415 MM). ABBR.: MI - METHYLISO-THIAZOLINONE, OIT - OCTYLISOTHIAZOLINONE, CD - CARBENDAZIM, DR - DIURON, TB - TERBUTRYN. (COMPARE o, o)

Between 0.1 and 9.3% of the initial contents are leached within the first 6 months of exposure for these biocides (Figure 15). Considering the uncertainty of the measurements, no trends are observable yet, a solid assessment of the duration of the leaching is not yet possible. To gain tentative insight, a decrease of the concentration over a postulated lifetime of 10 years was estimated. Considering this, the concentrations should be between 77% and 98% of the original, if photodegradation and biodegradation on the walls could be excluded, which is improbable. However, although the leaching of methylisothiazolinone seems to be stopped only 18 % of the biocides contained in the acrylate render and 8 % of the biocides contained in the silicone render of the initial MI-content are leached, respectively. Hence, the question rises what happened to the remaining 80-90%. A main reason for decreasing amount of leaching, while only less than 20 % had leached, might be evaporation and, more important, degradation processes.
All in all, the differences between the leached fraction from acrylate render and from silicone render are not pronounced for most of the compounds. Only for tebuconazole, methylisothiazolinone and benzisothiazolinone a significant (WELCH-test) higher fraction leached from the acrylate than from the silicone render. A significant (STUDENT´S T-test) higher fraction of diuron leached from the silicone render than from acrylate render.

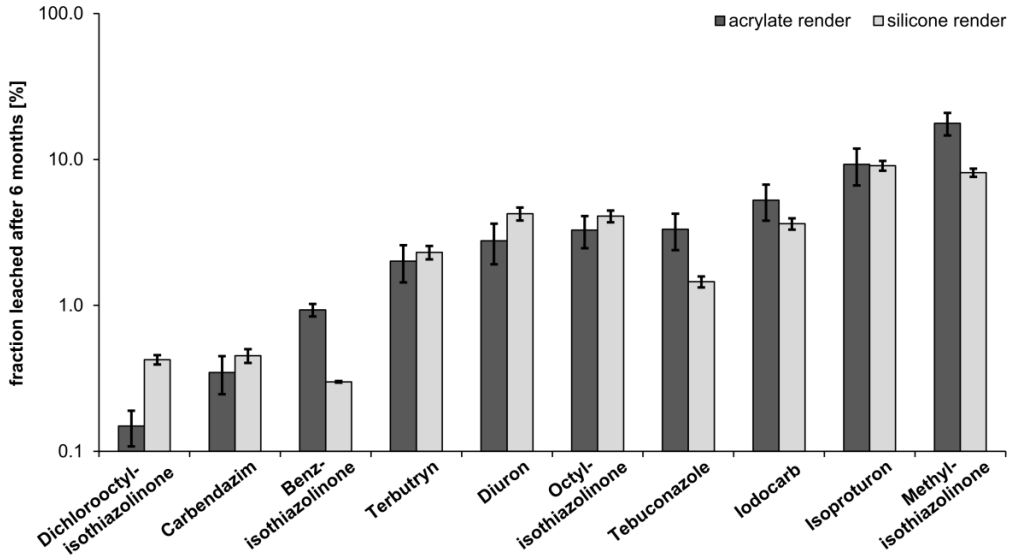


FIGURE 15. LEACHED FRACTION FROM ARTIFICIAL WALLS (AVERAGE FROM 3 PANELS, 1X1 M²) AFTER THE FIRST 6 MONTHS OF EXPOSURE TO NAURAL WEATHER (AUGUST 2012 – FEBRUARY 2013; TOTAL RAIN AMOUNT WITHIN THIS PERIOD: 415 MM).

5.2.3 Factors controlling the emissions form the walls

A comparison of the leached fraction with the octanol-water partition coefficients as well as the water solubilities shows that most likely the one with higher water solubility leached from the facades. However, not all compounds follow this trend. Carbendazim and benzisothiazolinone are among the most soluble ones of the studied compounds, whereas they are among the compounds with the lowest leached fractions. Contrary, the behavior of isoproturon, which has a relatively low water solubility while the leached fraction is rather high in comparison with the other biocides. Figure 16 shows the comparison of the detected concentrations from the artificial walls with predicted concentrations based on the desorption constants from the equilibrium experiments (paragraph 5.1). The concentrations were predicted using equation 14 for partitioning eqilibria. It is obvious that the predictions of biocide leaching based on desorption coefficients (K_d) would lead to slightly higher concentrations, since the contact time on the wall is much lower than desorption equilibrium time.

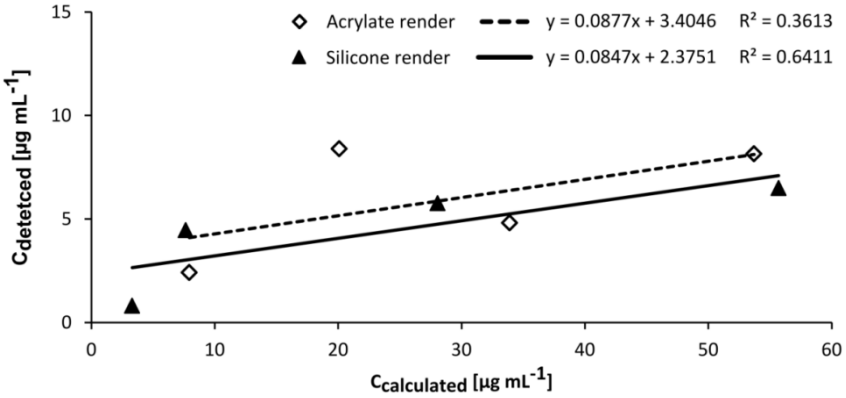


FIGURE 16. COMPARISON OF PREDICTED LEACHING CONCENTRATIONS USING DESORPTION CONSTANTS (PARAGRAPH 5.1) WITH REAL CONCENTRATIONS FROM ARTIFICIAL WALLS.

Obviously, besides water solubility and the partition from the render into the water other processes and material/ compound properties are influencing the leaching of the different biocides as well, as expected. Hence, in order to predict the biocide leaching further experiments, e.g. with shorter contact time needs to be performed and tested.

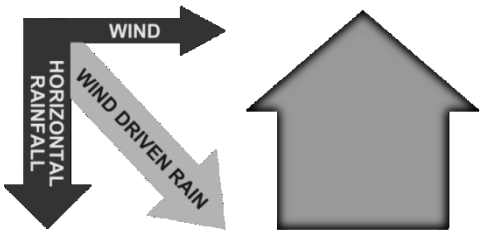


FIGURE 17. THE WIND DRIVEN RAIN (WDR) IS A VECTOR PRODUCT OF THE HORIZONTAL RAIN FALL INTENSITY AND THE WIND SPEED; A MORE DETAILED DESCRIPTION CAN BE FOUND IN PARAGRAPH 5.6.

Besides the compound specific and the material properties also the weather is influencing the leaching. Burkhardt *et al.* (2012) suggested the wind driven rain, hence, that part of the horizontal rain that actually hits the façade due to wind disturbance (Figure 17), as the main factor for biocide leaching. A clear correlation between the mass load per event and the run-off volume per event can be seen (Figure 18), which experimentally supports the findings from Burkhardt *et al.* (2012). The correlation coefficients R^2 are > 0.7 (except MI and BIT) for the acrylate render system and > 0.6 (except MI and BIT) for the silicone render system. However, the variability of the concentrations is higher than expected from analysis variability and, hence, another not yet known factor is supposed to influence the leaching.

It could not be demonstrated by simple correlation studies on (i) the dry period, (ii) relative humidity, (iii) radiation, (iv) temperature and (v) sunshine length prior to the event and vi) the rain intensity as well as vii) the rain amount during the event had any effect on the leaching of biocides from walls.

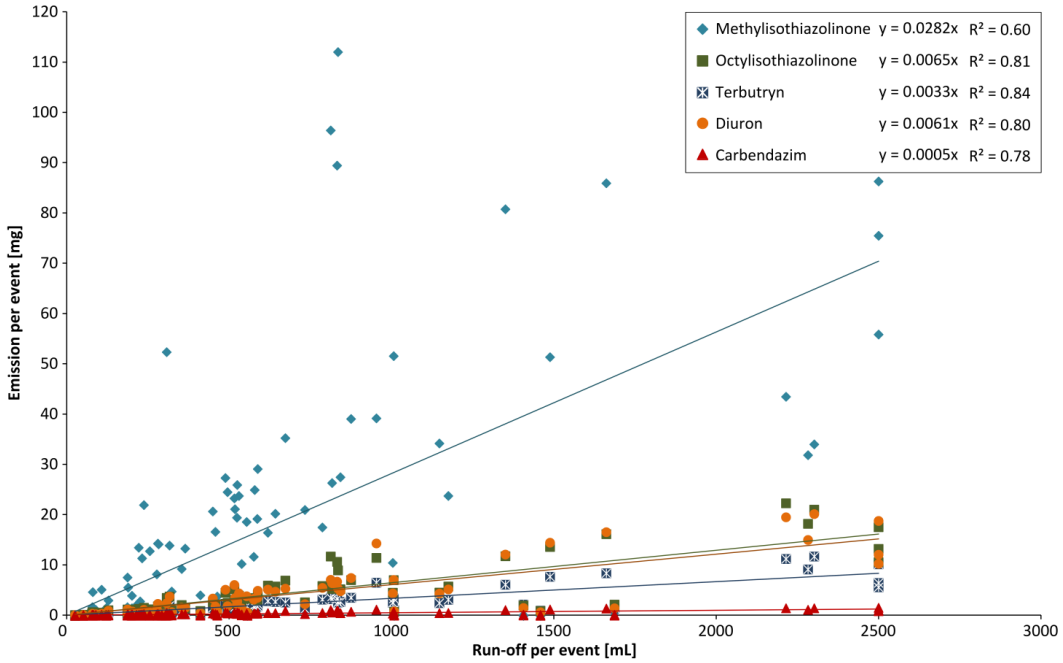


FIGURE 18. BIOCIDE EMISSIONS PER EVENT CORRELATED TO WIND DRIVEN RAIN, EXPRESSED AS THE RUN-OFF PER EVENT (ACRYLATE RENDER).

5.2.4 Interpretations "Emissions from test panels"

The study of the biocide leaching from artificial walls has been performed from August 2012 to February 2013. Since the emissions do not show a decreasing trend yet it is not possible to estimate a lifetime by now, thus longer experiments are needed for that.

- However, a row can be constructed considering leaching under weathering conditions for acrylate render: Methylisothiazolinon(MI)>Isoproturon>Iodocarb> Tebuconazole =octylisothiazolinon(OIT) =Diuron>Terbutryn>Benzisothiazolinon(BIT)>Carbendazim> Dichloro-n-Octylisothiazolinon(DCOIT). This is significantly different to the order predicted by the Kow, and it is also different to the order found by partitioning experiments. However, the results from the partitioning experiment can be used to some extent to predict results from the test walls if uncertainties of a factor up to 10 are taken into account (Figure 16). The main set-back is that the uncertainty is substance specific.
  The differences in the order/row may be due to
  i) transport phenomena in the material dominate on the longer run over the surface equilibrium partitioning or
  ii) photodegradation on the surface of the materials effect in compounds, reaching the surface from the deeper layers are faster photodegraded than leached.
- The comparison of the results with **compound and material properties** as well as the weather parameters showed:
  i) Material/ Compound properties: Water solubility and partitioning constants can explain some of the leaching behavior of the different biocides.
  ii) However, in order to predict the leaching based on laboratory experiments further studies need to be performed.
  iii) Generally the biocides leached very similar from the silicone and the acrylate. However, there were strong differences (67%) between the silicone and the acrylate renders in the test walls in respect of the leaching of the in-can preservative Methylisothiazolinone. All other compounds showed less pronounced differences (OIT, Diuron, and Carbendazim 32, 40 and 17% respectively, while other compound such as Terbutryn were leached quantitatively similar in both systems.
- **Weather:** Wind driven rain is the most important but not the only weather factor influencing the leaching of biocides from walls.

- In comparison to the experiments currently used for the regulation of for wood protection agents it turns out that the documentation on driving rain (not the rainfall) is essentially needed for understanding (and regulating) the leaching of biocides from building materials.

5.3 Discharges into separated sewer systems

Biocides from building material are supposed to enter surface waters via storm water run-off. Hence, biocides are supposed to be present in the separated sewer system. High resolution flow controlled sampling enables studying the emission dynamic throughout storm water events such as first flush phenomena.

5.3.1 Concentrations in separated storm water sewers

The median and average concentrations of the analyzed biocides for all 191 analyzed storm water samples from Silkeborg are shown in Figure 19. The box plot shows concentrations for all biocides, focusing around a median, with some outliers which usually originate from a few events with concentrations, one or more orders of magnitudes higher than the median (peak events). A more detailed discussion about frequency and possible causes for occurrence of these peak events is given in the paragraph about the mass loads (paragraph 5.3.3).

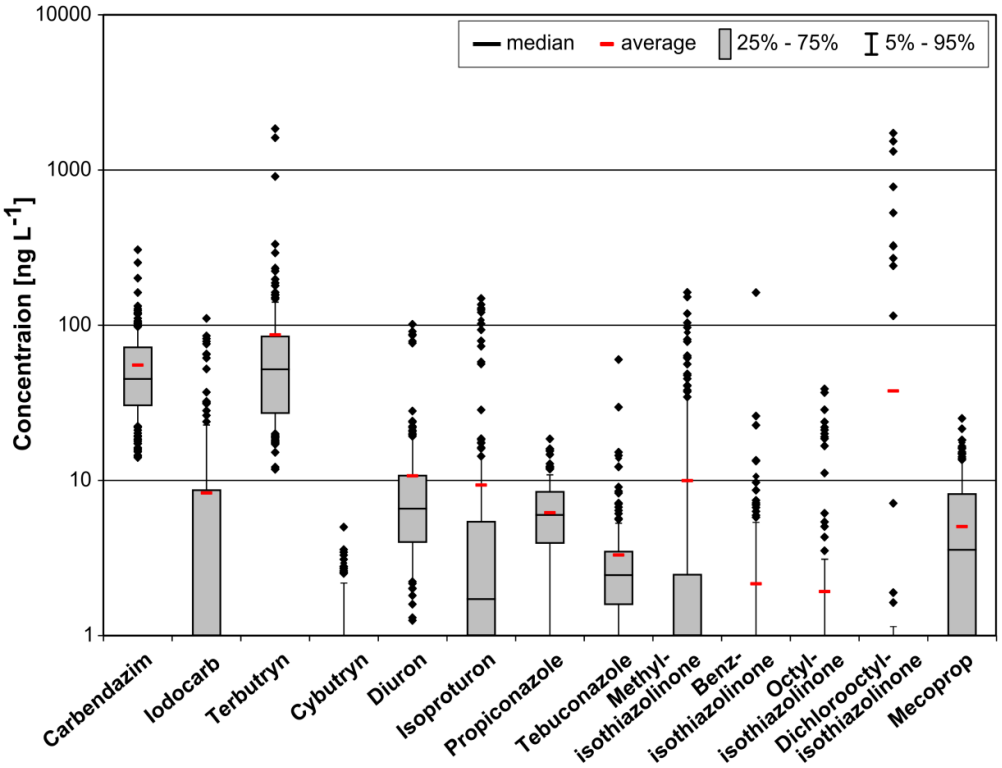


FIGURE 19. CONCENTRATIONS OF DIFFERENT BIOCIDES IN THE SILKEBORG CATCHMENT FROM OCT. 2011 TO JUNE 2012. CONCENTRATIONS SMALLER THAN THE LOD WHERE SET TO ZERO, IN ORDER TO ENABLE THE CALCULATIONS OF THE AVERAGE.

Compounds found in all analyzed samples with high median concentrations were carbendazim and terbutryn (45 and 52 ng L^{-1}), while they occurred with up to 306 and 1840 ng L^{-1} in peak events, respectively. Diuron, isoproturon, propiconazole, and iodocarb as well as mecoprop were detected with median concentrations between 2 and 7 ng L^{-1}. However, these substances where not detected in all samples. Some biocides, e.g. methylisothiazolinone, benzisothiazolinone and dichlorooctyl-isothiazolinone, were only detected in a few events, but in these cases with very high concentrations (up to 1,720 ng L^{-1}), possibly indicating transport in polymer paint particles.

The concentrations of the triazines and phenylureas are in the same range as experienced by Burkhardt *et al.* (2012), and Wittmer *et al.* (2010) for surface waters, but lower as found for terbutryn (Quednow & Puettmann 2007, 2009) in German surface waters (50-5,000 ng L^{-1}) as well as the diuron in French river water (9,000 ng L^{-1} (Blanchoud *et al.* 2004)). They are considerably lower than in the direct material leachate (10-1,000 µg L^{-1}) from a freshly treated building complex (Burkhardt *et al.* 2011). On the other hand, the results obtained for terbutryn from Swiss surface water (median < 10 ng L^{-1} (Wittmer *et al.* 2010)) agree well to those found in the present study. The concentration of carbendazim is comparable toBurkhardt *et al.* (2012). No comparison data is available for the iodocarb and the isothiazolinones. The differences in the substance pattern between the German, French and Swiss studies and the present study may originate from the different building structures in the respective areas and, hence, different materials in use.
The comparison with the ecotoxicological data (Burkhardt *et al.* 2009) shows that the median concentrations of carbendazim and terbutryn are in the same range as the PNEC-values. However, in some events also other biocides exceeded the PNEC values by far. The median concentration of terbutryn is similar to the AA-EQS of 65 ng L^{-1} proposed in the European water framework directive (European Commission 2012), while cybutryn exceeds the AA-EQS level of 2.5 ng L^{-1} in some storm water samples.

5.3.2 Concentration dynamics of biocides during storm events

The high-resolution flow-proportional sampling enables new findings about the dynamics of the biocide emissions during the rain events. The main issue to test was, whether the release of the biocides is constant during the rain event or a fast release of biocides occurs in the beginning of the event and decelerating later on. Doing so, conclusions can be drawn about, whether biocides accumulate during dry weather on surfaces, where they are loosely attached and are released via first flushes, or are leached out of the materials during the rain event.
An often used term with regard to describing the dynamics of pollutants in storm water runoff is the first flush phenomenon. Bertrand-Krajewski *et al.* (1998) defined the first flush phenomenon when 80 % of the pollutant load is emitted during the first 30 % of discharge volume.
Considering compound specific dynamics, neither first nor post flushes could be detected for any compound in 5 out of 12 events. Independent from the actual flow the concentrations were already in the first 15 m^3 of runoff water on a certain concentration level, well corresponding with the overall median concentrations from all samples (Figure 19), and dropped down with the tail of the hydrograph. An example for these commonly detected events is shown in (Figure 20a).
A first flush would occur if the biocides release is very fast in the beginning, due to an accumulation of biocides on the surface of the façade or in dust, and slowing down as soon as this is washed off. A simple graphical test for the first flush behavior is the relation between the emitted mass and the accumulated (hydraulic) flow, which would result in an upwards curved (convex) line in case of first flush. Contrary to the expectations of a first flush, as suggested from Coutu *et al.* (2012), a linear relation was commonly observed during the events (Figure 20b) which indicates continuous emission of the biocides from the facades. This was also observed by Burkhardt *et al.* (2011), who analyzed storm water runoff from a small urban catchment in Switzerland. Continuous emissions also agree well to the models based on laboratory experiments developed by Wangler *et al.* (2012) and Schoknecht *et al.* (2009) who discuss a diffusion based process as the controlling mechanism for the release of biocides from render.

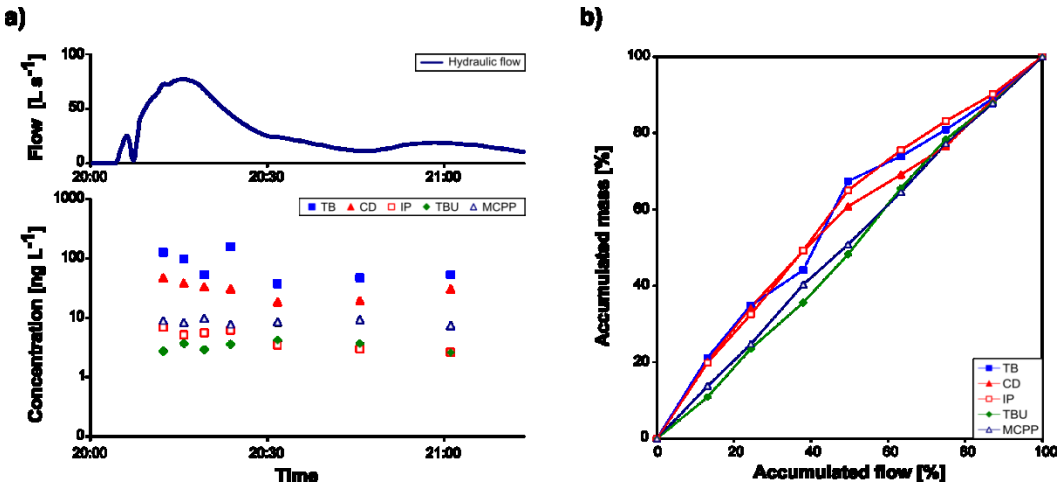


FIGURE 20. COMMON BIOCIDE CONCENTRATION DYNAMICS DURING A RAIN EVENT (A) AND EVALUATION OF FIRST FLUSH DYNAMICS IN A COMMON RAIN EVENT (B). ABBREVIATIONS: TB: TERBUTRYN, CD: CARBENDAZIM, IP: ISOPROTURON, TBU: TEBUCONAZOLE, MCPP: MECOPROP. SAMPLING DATE: 25.11.2011, 20:00-21:30.

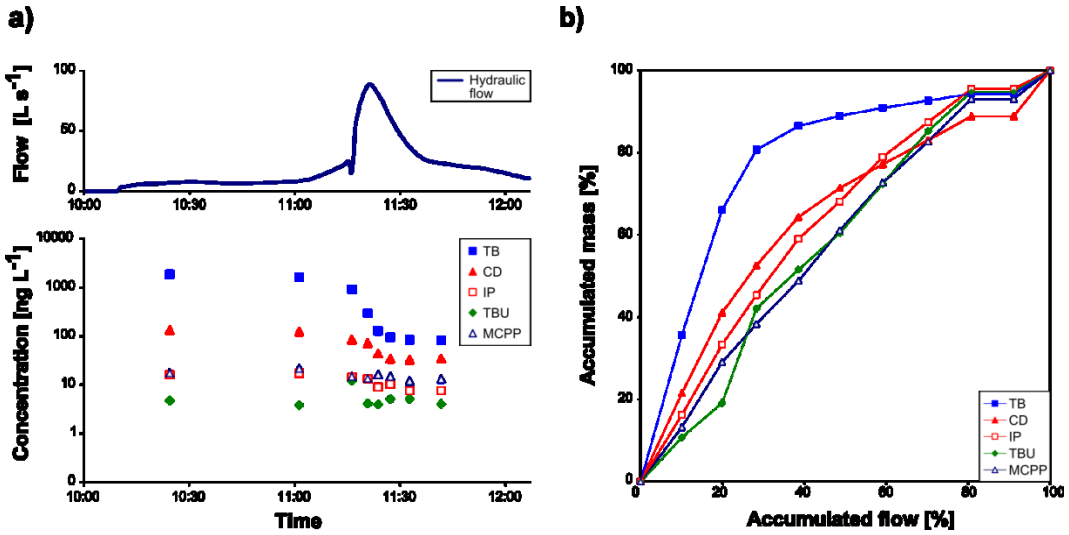


FIGURE 21. BIOCIDE CONCENTRATION DYNAMICS (A) AND EVALUATION OF FIRST FLUSH DYNAMICS IN THE RAIN EVENT ON NOVEMBER 25TH, 2011 (B): OCCASIONALLY OCCURRING FIRST FLUSH FOR TERBUTRYN AFTER A LONG DRY PERIOD. ABBREVIATIONS: TB: TERBUTRYN, CD: CARBENDAZIM, IP: ISOPROTURON, TBU: TEBUCONAZOLE, MCPP: MECOPROP. SAMPLING DATE: 25.11.2011, 10:00-12:00.

However, during three out of the 12 events first flush behavior was detected for terbutryn, methylisothiazolinone, cybutryn and diuron as demonstrated in Figure 21 for terbutryn. This event showed a notable first flush for terbutryn. In the beginning of the event remarkable high concentrations for terbutryn were detected (up to 1,840 ng L^{-1}, qualifying this first flush event also as a peak event), which decreased very fast to a level of below 100 ng L^{-1}. Also for carbendazim slightly higher concentrations in the beginning and a decrease afterwards were observed during this event. However, the other biocides had rather constant concentrations during the entire rain event, the long dry weather period prior the event is presumably not the only main reason for this behavior.

Additionally, for iodocarb and cybutryn, also post flush behavior was detected in two separated events, meaning, more was emitted at the end than during the event.

Treatment of only the first flush is thus not an option to minimize these compounds in receiving waters.

5.3.3 Mass loads in separated storm water sewers

In addition to the concentrations, the mass loads for the twelve events analyzed were determined individually. In this normal distributed data set (DAVID test) some outlier events were identified by GRUBB outlier test as well (Danzer 2007). For the calculation of the average mass loads per event these outlier events were excluded and shown separately in Table 15. However, it has to be mentioned that the outlier identification was based on average values of the events and conducted separately for each substance, since the occurrence of peak events were compound specific: while an event was a peak event for one compound, it was usually quite regular for other compounds.
On average about 8 mg terbutryn were emitted in the Silkeborg catchment during each rain event; within the outlier event even more than 70 mg. Except carbendazim (7 mg) and methylisothiazolinone (1.6 mg), the average mass load was below 1 mg per event for all other biocides. Nevertheless, in some outlier events the mass loads were also very high for those substances with low mass flows in average events. It is interesting to note that events with peak loads contributed about as much to the total biocide loads of the catchment as the standard events, since only every 10th event was a peak event with about ten times higher mass load.

TABLE 15. MASS LOADS PER EVENT OF DIFFERENT BIOCIDES IN THE SILKEBORG CATCHMENT (OCT. 2011 – JUNE 2012, 12 RAIN EVENTS). UP TO TWO OUTLIER EVENTS (PEAK EVENTS) WERE IDENTIFIED BY GRUBB-OUTLIER TEST. THE RESULTS ARE CALCULATED FOR 140 HOUSES IN THE CATCHMENT.

Biocide	Mass load [1] ± standard deviation [mg event^{-1}] without peak events	Mass load of the highest peak event [mg event^{-1}] (number of peak events)	Emissions per average house per event [µg event^{-1} house^{-1}]
Carbendazim (CD)	7.0 ± 6.0	No peak event identified	62±38
Iodocarb (IPBC)	0.5 ± 0.7	11.2 (2)	3.7±4.7
Terbutryn (TB)	8.3 ± 5.6	77 (1)	68±30
Cybutryn (IRG)	0.02 ± 0.03	0.2 (1)	0.2±0.4
Diuron (DR)	0.8 ± 0.6	10.1 (1)	7.8±5.2
Isoproturon (IP)	0.4 ± 0.3	15.3 (2)	3.2±3.1
Propiconazole (PPZ)	0.6 ± 0.4	2.3 (1)	5.3±3.3
Tebuconazole (TBU)	0.4 ± 0.3	No peak event identified	3.2±1.7
Methylisothiazolinone (MI)	1.6 ± 3.5	No peak event identified	12±25
Benzisothiazolinone (BIT)	0.1 ± 0.2	2.6 (2)	0.7±1.6
Octylisothiazolinone (OIT)	0.03 ± 0.05	3.7 (2)	0.2±0.4
Dichlorooctylisothiazolinone (DCOIT)	0.01 ± 0.02	108 (2)	0.1±0.2
Mecoprop (MCPP)	0.8 ± 0.7	No peak event identified	6.1±4.8

1) in order to enable the calculation of the average values mass loads < LOD where set to zero.

Possibly, these peak events are due to compound specific mobilization caused by special weather conditions (though these could not be identified). Moreover, fresh applications might lead to peak loads. November 2011 was extremely mild with friendly weather and temperature up to 15 °C thus new paintings etc. cannot be excluded. Peak events may also have been observed by Coutu *et al.*

(2012) as in some cases the model predictions in that paper, which were not including first flush assessments were quite accurate while in other ones the measured data exceeded the modeled ones considerably.
The Silkeborg catchment covers about 140 single family homes. Only a few of them are to some extend equipped with render. The rest of the houses are mainly covered by painted wood or masonry. A comparison with emission rates from artificial walls (Burkhardt *et al.* 2012) shows that observed emissions (normal as well as peak) agree to the hydraulic characterization of the present catchment. Assuming that the Silkeborg catchment is representative for other suburban residential catchments, emissions per standard house were calculated (Table 15), in order to provide a comparable number for the emissions from a random suburban catchment with single family houses, for which the actually biocide-equipped façade area or the amount of façades directly connected to the sewer system is unknown. The average emissions of a single family house turned out to be 68 and 62 µg event^{-1} house^{-1} terbutryn and carbendazim, respectively. Emissions for the other biocides ranged from 0.1 to 12 µg event^{-1} house^{-1} (Table 15). This catchment based assessment results in considerably lower emissions than those assessed by Wangler et al. based on pure fresh render processes ignoring the ratio of transfer of water from the walls into either the soil or the storm water sewers (Wangler *et al.* 2012). For emissions into surface water this shows, that this transfer rate is essential. The difference between our emission data and the older work is probably the fraction that is emitted into the soil. However, in the assessments for the European biocidal product directive (European Parliament and Council 1998a, 2012) it is considered that the mass flow into the soil is the dominating or only one for suburban regions, while obviously also the runoff into surface waters is relevant. It was tested, on whether the mass load per event was dependent on length of dry period preceding the event, hydraulic flow per event or length of rainfall on a catchment scale. Only tebuconazole was (linearly) dependent on the accumulated flow with a correlation of $R^2 = 0.64$, while all other tests gave $R^2 < 0.1$.

5.3.4 Driving rain affects mass flows of biocides in separated sewers

Driving rain i_{wdr}, i.e. the rain that actually hits the façade surfaces, (Blocken & Carmeliet 2012; Burkhardt *et al.* 2012; Blocken *et al.* 2013) is usually calculated as

$$i_{wdr} = \frac{2}{9} C_R C_T O W \cdot i_{rain}^{0.88} \cdot u \cdot \cos\theta \qquad (20)$$

with C_R= roughness coefficient; C_T= Topography coefficient, O= obstruction factor, W= wall factor, u= wind speed, i_{rain}= rain intensity, θ= angle of the wind. In a given catchment driving rain is linearly dependent on wind speed and rain intensity, considering that effects from wind direction will level out in a catchment of reasonable size (equation 21):

$$i_{wdr} = C_C \cdot i_{rain} \cdot u \qquad (21)$$

Assuming that the cumulative mass of released biocide is proportional to the accumulated runoff from a façade – as for example reported by Burkhardt *et al.* (2012) and also found in the present study – the mass flow of compound M during the respective rain event becomes:

$$M_{wdr} = C_C C_S \cdot i_{rain} \cdot u \qquad (22)$$

with C_C being a catchment specific factor including $\frac{2}{9} C_R C_T O W$ and C_S a substance specific constant including e.g. the façade area containing the compound, different usage pattern or release mechanisms. The product $C_C C_S$ can be found by plotting mass loads versus the product of rain intensity and wind speed. In our approach we took i_{rain} equaling the total hydraulic flow at the outlet of the catchment of the respective event divided by the area of the catchment. The average wind speed was gained from a weather station during the respective event.
On the other hand, the mass loads in the storm water sewer of carbendazim, terbutryn, methylisothiazolinone, iodocarb, propiconazole and tebuconazole were linearly dependent on driving rain on a catchment basis (Figure 22). As the product $C_C C_S$ is the same for terbutryn and carbendazim (0.40 and 0.44, respectively) it can be concluded that these compounds are emitted

and used in a very similar way in this catchment. However, $C_C C_S$ for propiconazole and tebuconazole (0.06 and 0.02, respectively) differ widely from those for the other compounds. As tebuconazole and propiconazole are predominantly used in wood protection while terbutryn and carbendazim are used in paints and renders this difference might indicate different usage or release mechanisms. Hence, methylisothiazolinone seems to have similar usage as terbutryn and carbendazim, as its product $C_C C_S$ is similar to the one of those two compounds, while iodocarb is most likely predominantly used in wood protection as it is similar to propiconazole and tebuconazole.
However, despite the similar usage of terbutryn, carbendazim, and methylisothiazolinone, the release factors for these three compounds were expected to be quite different as their lipophilicity (K_{ow}) is quite different.

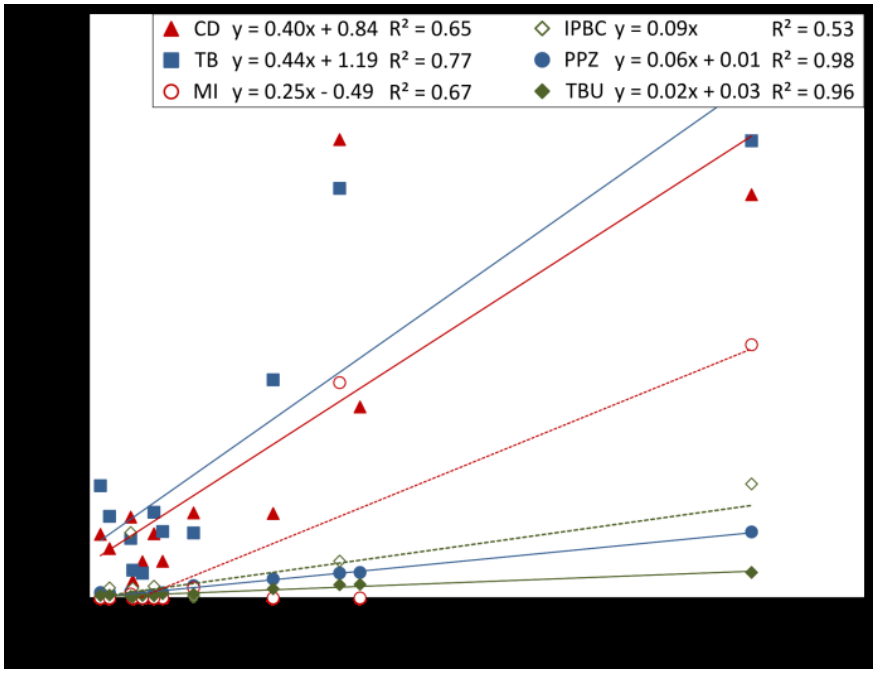


FIGURE 22. MASS FLOW OF BIOCIDES (M_{WDR}) IN RELATION TO RAIN INTENSITY (I_{RAIN}) TIMES WIND SPEED (U) IN THE SILKEBORG STORM WATER CATCHMENT (SHOWN ARE ALL COMPOUNDS WITH R^2 > 0.5; ABBREVIATIONS: CD: CARBENDAZIM, TB: TERBUTRYN, MI: METHYLISOTHIAZOLINONE, PPZ: PROPICONAZOLE, TBU: TEBUCONAZOLE; ONE PEAK EVENT FOR TERBUTRYN IS EXCLUDED).

5.3.5 Different usage and properties triggers different emissions

The different concentration profiles in the storm water runoff events can be ascribed to different emission pathways and application forms of the biocides. First of all, the constantly occurring biocides as terbutryn, carbendazim, isoproturon, diuron, tebuconazole, propiconazole, and mecoprop were detected in most of the samples. These compounds are used as film preservatives and slowly released to the environment (Burkhardt *et al.* 2012; Wangler *et al.* 2012). In contrast to these, benzisothiazolinone, iodocarb, and methylisothiazolinone were only detected in a few selected samples during some rain events. This indicates that these compounds are heavily driven by one-time emissions possibly via abrasion of polymer particles and eventually due to fresh applications which goes along with the usage as in-can preservatives and their high water solubility and low K_{OW} values (Table 1).

5.3.6 Interpretations “Discharge into separated sewer”

In general, the study of the separated sewer showed that:

- Biocide emissions are not only important in certain city centers, but also in Northern European suburbs, though the thermal insulation systems with polymeric top render is less common in these regions (Quednow & Puettmann 2007, 2009; Wittmer *et al.* 2010; Burkhardt *et al.* 2011).

- Comparable concentrations were detected as experienced for Swiss surface waters (Wittmer *et al.* 2010; Burkhardt *et al.* 2011), but lower as found in German surface (terbutryn) (Quednow & Puettmann 2007, 2009) and French river water (diuron) (Blanchoud *et al.* 2004).
- The constantly high emissions in suburban regions raise the question whether the risk assessments for these compounds – saying in suburban areas 100 % will be infiltrated into the ground – need to be refined, particularly with regard to surface waters.
- It could be demonstrated that it is not efficient to focus on first flushes when assessing treatment options of storm water.
- Even though the application of the different biocides in construction materials is very similar, the emission behavior on the catchment scale in respect of first flush etc. is very different.

5.4 Discharge of biocides into combined sewer systems

Assuming all biocides in urban waters derive from building material, biocides would only be present in combined sewer during rainy days (being washed of and leached in those periods). In order to confirm this hypothesis, sampling of combined sewage during dry and rainy weather periods were performed.

5.4.1 Concentrations and mass loads in combined sewer

The concentrations of biocides in wastewater during rainy weather ranged from not detected to several hundred ng L^{-1} (Table 16). It turned out to the authors' surprise that the dry weather concentration were generally not lower than the rain weather concentrations, efforts were thus taken to make sure this was not an artifact from one treatment plant.

TABLE 16. INFLUENT CONCENTRATIONS [NG L^{-1}] IN SEVERAL WASTE WATER TREATMENT PLANTS (SAMPLING: 24H – 24H COMPOSITE, 12X2H – 12X 2H COMPOSITE; IN BRACKETS: BLANK VALUES[A]).

WWTP	Roskilde Bjerg-marken	Roskilde Bjerg-marken	Roskilde Bjerg-marken	Copen-hagen Avedøre	Copen-hagen Lynetten	Copen-hagen Mølleå-værket	WWTP in South Sweden
Weather (Sampling)	**dry (24h)**	**rain (12x2h)**	**dry (12x2h)**	**dry (24h)**	**dry (24h)**	**dry (24h)**	**dry (grab)**
MCPP	nd	9 - 115 (12)	nd	nd	nd	nd	33 - 34
DCOIT	nd	nd	nd - 27 (69)	11 (135)	230 (135)	56 (135)	12 - 13 (9)
OIT	nd	nd -34 (7)	nd	nd	nd	nd	nd
BIT	nd	nd	nd	nd	nd	nd	nd
MI	nd	nd - 191 (45)	nd - 23	nd	nd	nd	nd
IP	nd	15 - 58 (45)	nd	8	nd	43	3-4
DR	8	8 - 37 (36)	4 - 39	8	3	7	5-8
IPBC	nd	nd -12 (9)	nd - 7 (3)	3 (5)	nd	7 (5)	1-2 (2)
CD	78	38 - 63 (17)	14 - 62 (2)	58 (1)	20 (1)	29 (1)	16 - 55 (1)
IRG	nd	1 - 3 (1)	nd - 8	nd	nd	nd	nd
TB	62	8 - 23 (16)	6 - 55 (1)	18	14	21	5-7
TBU	10	27 - 41 (23)	18 - 78 (7)	9 (16)	4 (16)	5 (16)	nd - 1 (2)
PPZ	39	nd	125 - 4540 (3)	17	17	15	4 - 5

a) Due to contamination during extraction; concentrations have to read with care in these cases.
nd) not detected; < LOD.

The study of biocide occurrence during a rainy day in WWTP Roskilde Bjergmarken (Figure 23) shows that mecoprop occurred in the storm water containing samples (sampling interval 08:00-

02:00) with mass loads up to 350 ng L^{-1} following the intensity of the hydraulic flow. However, with the end of the rain and the decrease in hydraulic flow (sampling interval 04:00-08:00) other biocides appeared in the combined sewer, that were not detected in the beginning of the day during the rain. This means, that some biocides enter the combined sewer by storm water while others are only detectable if the dilution of the combined sewer with storm water is low.
Contrary to the expectations several biocides could be detected in the dry weather samples as well (Table 16). The concentration levels during dry weather are similar to the rainy weather samples with up to several hundred ng L^{-1}. Only for propiconazole remarkable high concentrations were detected in WWTP Roskilde Bjergmarken with up to 4.5 µg L^{-1}.
Thus, when comparing biocide concentrations and mass loads during rainy days with those on dry days it is obvious that building material as such is not the only source for biocides in waste water.

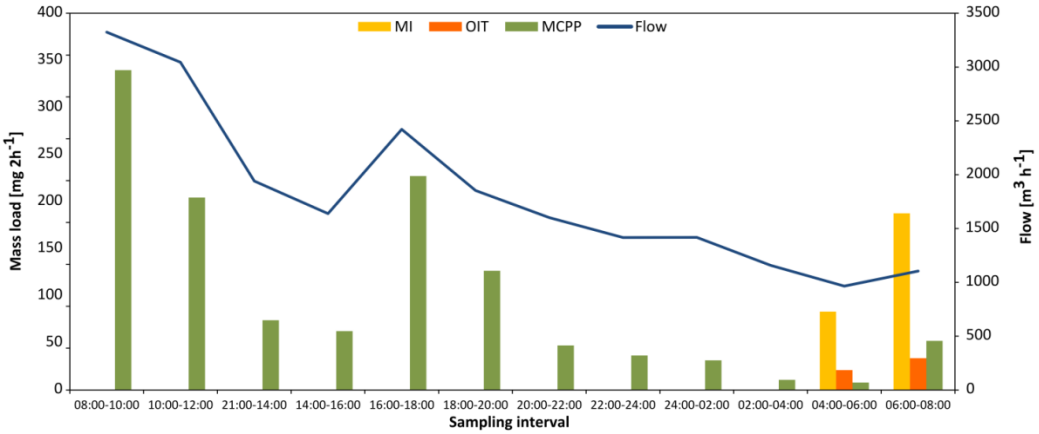


FIGURE 23. INFLUENT MASS LOADS OF SELECTED BIOCIDES AND HYDRAULIC FLOW DURING A RAINY DAY (25./26.4.2012) IN WWTP ROSKILDE BJERGMARKEN (MI: METHYLISOTHIAZOLINONE, OIT: OCTYL-ISOTHIAZOLINONE, MCPP: MECOPROP).

5.4.2 Possible dry weather sources

In order to gain information about possible dry weather sources a diurnal cycle was studied using 2 hour-composite samples within a period of 24 hours from WWTP Roskilde Bjergmarken (Figure 24, Figure 25). For most of the compounds the emissions were higher in the day/evening hours than during the night. This indicates that the biocide emissions during dry weather depend on human activity, since they were not emitted constantly into the sewer. Thus it is improbable that contious sources like larger residues of paints and renders in the sewer system themselves are the controlling sources for dry weather concentrations.
Propiconazole showed a very sharp peak in the evening (sampling interval 19:30-21:30) which was decreasing slowly afterwards (Figure 25). Following Roskilde forsyning, a 1- 3 hours runtime in the sewer system from the residential areas to the treatment plant should be taken into account. The whole would indicate rather one point source than several diffusive sources.
The reasonability of several possible dry weather sources where evaluated. Most probable for all biocides is the inappropriate disposal of paints and renders into the sewer for example when washing used paint brushes and other equipment. Methylisothiazolinone is used in personal care products as for example in shampoos which could most likely lead to the detected concentrations. The only explanation for the very high propiconazole concentrations would be inappropriate disposal of pesticide formulations. The total amount disposed leading to the daily load detected would be about 70 mL of pure formulation. Some bathroom paints are equipped with the analyzed biocides as well and might contribute to dry weather occurrence. The washing-off from fruits and vegetables can only partly explain the detected loads.

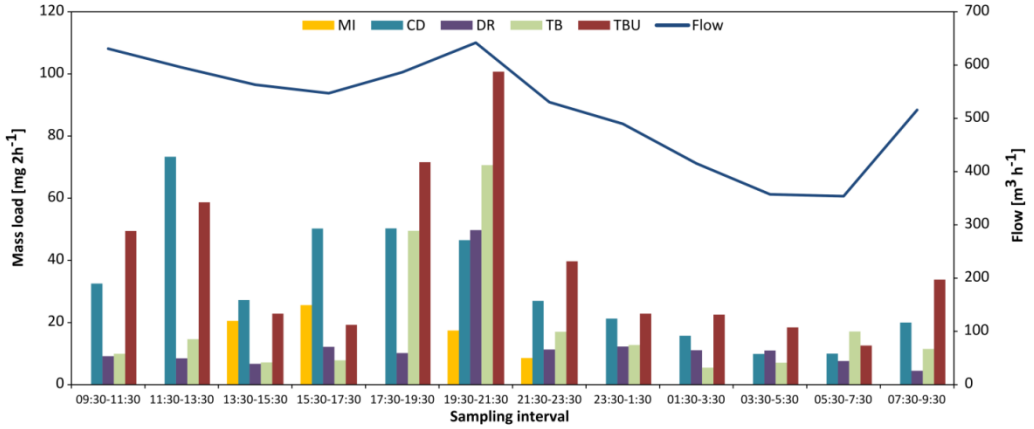


FIGURE 24. INFLUENT MASS LOADS OF SELECTED BIOCIDES AND HYDRAULIC FLOW DURING A DRY WEATHER DAY (4./5.6.2013) IN WWTP ROSKILDE BJERGMARKEN (MI: METHYLISOTHIAZOLINONE, CD: CARBENDAZIM, DR: DIURON, TB: TERBUTRYN, TBU: TEBUCONAZOLE).

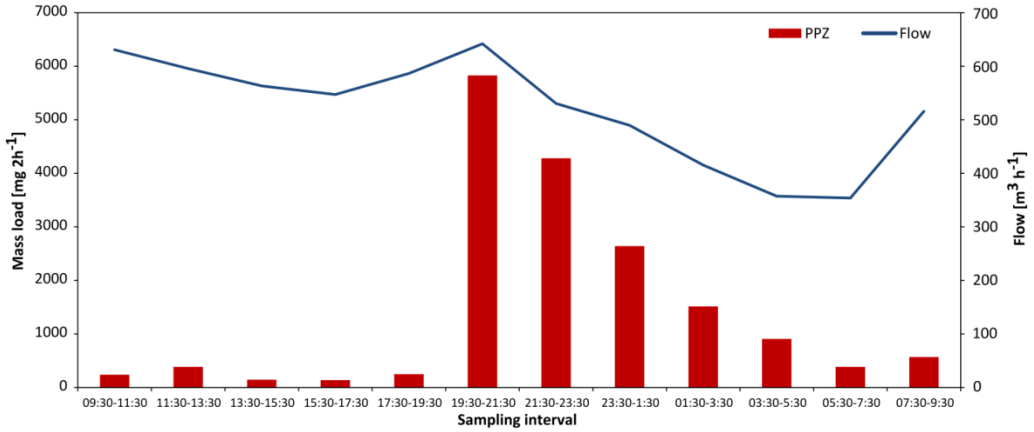


FIGURE 25. PROPICONAZOLE MASS LOAD (PPZ) AND HYDRAULIC FLOW IN THE INFLUENT OF WWTP ROSKILDE BJERGMARKEN DURING A DRY WEATHER DAY (4./5.6.2013).

5.4.3 Interpretations "Discharge into combined sewer"

Contrary to the expectations biocides can not only be detected in combined sewer during rainy periods. Some compounds (e.g. mecoprop) follow the storm water input into the combined sewer, while others (carbendazim, terbutryn, tebuconazole, propiconazole) have higher or are solely detectable concentrations during dry weather periods.
It is probable that mainly inappropriate disposal of pesticide formulation (propiconazole, tebuconazole) or of paint and render into the sewer might lead to biocide occurrence in the wastewater during dry weather. Only for a few compounds the usage as preservatives in personal care products (methylisothiazolinone), and washing off from painted bathroom-walls (octylisothiazolinone) might contribute as dry weather sources.

5.5 Biocides in surface waters

If biocides from building material are leached by rain into storm water they will be present in urban surface waters as these are the recipients of the storm water. Hence, two monitoring campaigns were performed in the Greater Copenhagen area.

5.5.1 Biocide concentrations in urban surface water

The concentrations are in the lower ng L^{-1} range (Figure 26). All biocides were detectable at least in a few sampling locations. Only carbendazim, diuron, iodocarb, tebuconazole, propiconazole, and dichlorooctylisothiazolinone are detected frequently. For most of the compounds no connection

between concentrations and storm water input can be seen, since the concentrations are rather similar for both sampling campaigns.
Damhusåen is supposed to receive a large amount of combined sewer overflow (Københavns kommune 2008). The huge increase in carbendazim, tebuconazole, and propiconazole concentrations after the rain supports this (Figure 26). Tebuconazole and propiconazole showed a reasonable storm water footprint in *Sortedams sø* and *Sydhavn* as well, which indicates that these sampling locations received storm water polluted with azole compounds.
The three lakes *Preblinge sø*, *St. Jørgens sø*, and *Sortedams sø* in Copenhagen center were thought to behave similar. According to Københavns Spildevands plan (Københavns kommune 2008) they do not receive any separated sewer or combined sewer overflow, but direct storm water from the surrounding city quarter. The increased concentrations in tebuconazole and propiconazole in *Sortedams sø* might derive from the metro construction site which is surrounded by green painted wooden hoarding and located in one quarter of *Sortedams sø* (Metroselskabet I/S).
The concentrations of mecoprop and diuron were highest in *Ørestad* which can be explained with the rather new buildings in this city quarter. Most of the building have flat roofs which might be equipped with mecoprop (Bucheli *et al.* 1998b). A remarkable lower water level (~ 40 cm) was noticed for the *Ørestad channels* during the second sampling campaign compared to the first, which might be caused by an active water management meaning the water was pumped out during or after rain events and might explain the lower concentration of mecoprop on May 27th 2013 after heavy rainfalls. However, mecoprop exceeded the single pesticide level of 0.1 µg L^{-1} which is stated in the European water frame work directive (European Parliament and Council 2000).
Terbutryn and cybutryn could only be detected in *Sydhavn*. Hence, they are not shown in Figure 26. Terbutryn was detected with concentrations of 1 ng L^{-1} in both sampling campaigns, while cybutryn was only detected in the second. Nevertheless, cybutryn exceeded the AA-EQS of 2.5 ng L^{-1} in *Sydhavn* with a concentration of 3 ng L^{-1} on May 27th 2013. However, the source for cybutryn is most probably residues of antifouling paints for ships, although only allowed for ships > 25 m any longer in Denmark (Miljøministeriet 2011), and not building material. Terbutryn and cybutryn have previously been studied in Danish marine and fresh waters (Vorkamp *et al.* 2012), among these also *Damhus sø*, *Utterslev Mose* and *Sydhavn* in a separate project of the Department of Environmental Science of Aarhus university. The recent concentrations are slightly lower at the respective sampling locations that those determined in September 2012.

5.5.2 Interpretations "Biocides in urban surface water"

Concentrations of biocides in urban surface waters are in the lower ng L^{-1} range (Figure 26). Only carbendazim, diuron, iodocarb, tebuconazole, and propiconazole are detected frequently in the greater Copenhagen area.
Different regions in greater Copenhagen were attributed to different patterns, e.g. mecoprop occurring in regions with flat roofs (*Ørestad*).
Only triazole compounds showed pronounced storm water footprint (i.e., a strong difference between before and after rainfall) in certain surface waters. This parameter is of course only relevant for surface water systems that predominantly contain groundwater and only receive storm water occasionally. The Ørestad surface waters are so predominantly driven by storm water runoff, that there is no doubt that the high concentrations in this system are due to leaching from the surrounding buildings.

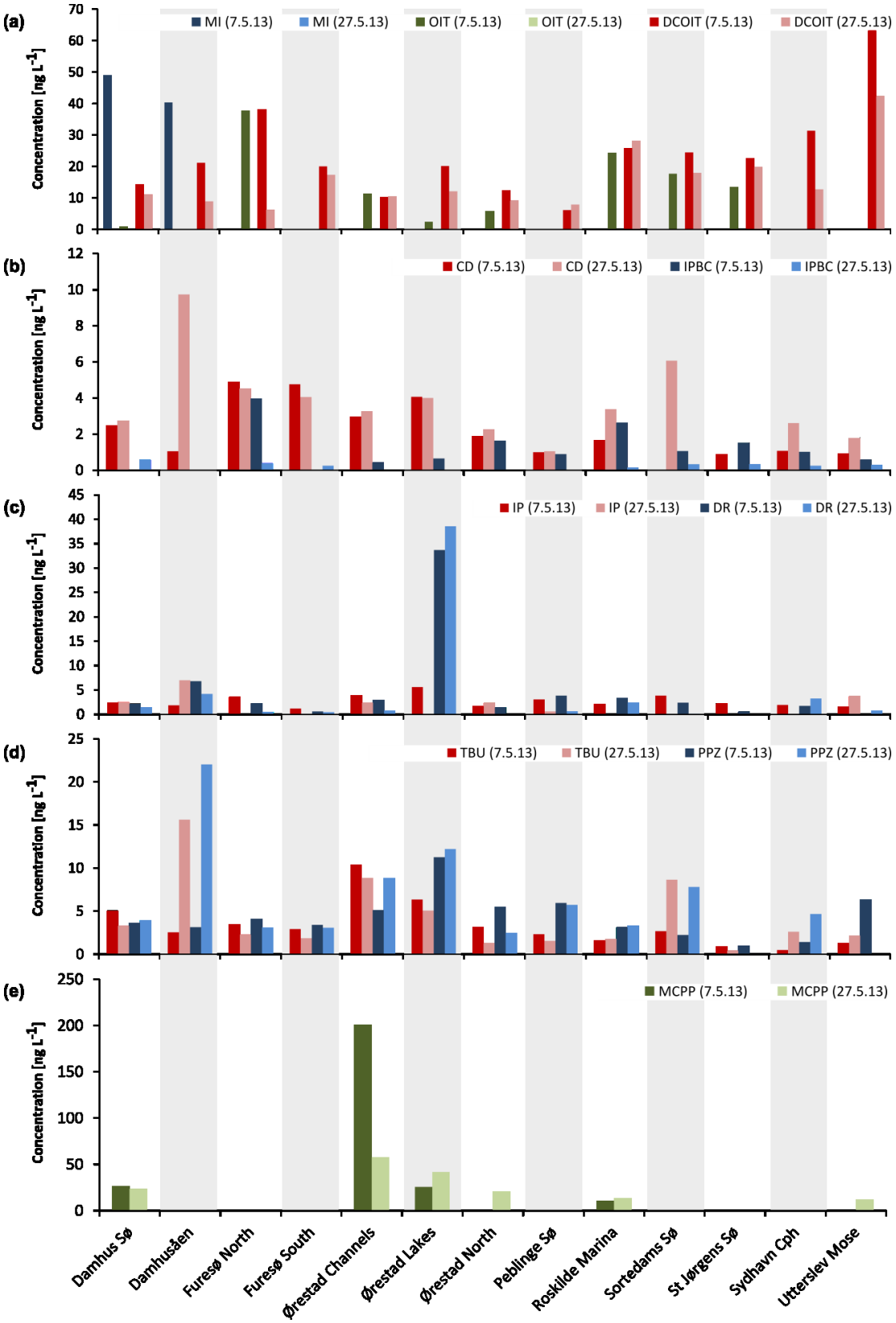


FIGURE 26. CONCENTRATIONS IN URBAN SURFACE WATERS: (A) ISOTHIAZOLINONES: METHYLISOTHIAZOLINONE (MI, BLANK: 47 NG L^{-1}), BENZISOTHIAZOLINONE (BIT), OCTYLISOTHIAZOLINONE (OIT, BLANK: 5 NG L^{-1}), DICHLOROOCTYLISOTHIAZOLINONE (DCOIT, BLANK: 34 NG L^{-1}), (B) CARBAMATES: CARBENDAZIM (CD, BLANK: 5 NG L^{-1}), IODOCARB (IPBC, BLANK: 2 NG L^{-1}), (C) PHENYLUREAS: DIURON (DR, BLANK: 1 NG L^{-1}), ISOPROTURON (IP), (D) TRIAZOLES: TEBUCONAZOLE (TBU), PROPICONAZOLE (PPZ), (E) MECOPROP (MCPP).

5.6 Quantitative modelling

To be able to synthesize the data and make eventually predictions, a model for biocides in runoff was developed and calibrated to data from the Silkeborg catchment that was intensively monitored in 2011 and 2012 (paragraph 4.5). The calibrated model was then applied on a number of hypotized standard catchments which are meant to represent a range of typical Danish separate sewer catchments. The outcome of the modeling was used to determine median pollution loads and extreme concentration statistics.
The model for simulating biocides in urban runoff contains a number of different elements which in the following are discussed in some detail.

5.6.1 Model calibration

The measurements of biocide concentrations in the runoff of the Silkeborg catchment showed that there in most events was no clear first flush. Instead the concentration in the runoff was more or less constant during an event or varied somewhat arbitrary. This indicates that the release mechanism is not following the concept formulated in Equation 12, i.e. a build-up during dry weather followed by a wash-off during storm events. The release mechanism is better described by the concept formulated in Equation 13, i.e. a certain mass of pollutant initially present in a surface becomes washed out proportional to the runoff from that surface. Even though the latter behavior does not per se give a first flush, it can give varying concentrations in the runoff and hereby also a concentration profile which on a first glance looks like a first flush or a post flush. This phenomenon is illustrated in Figure 27 where the concentration of a compound *M* is simulated based on measured precipitation and measured wind.
Equation 13 contains 3 parameters, the wash-out coefficient κ_{bv}, the mass of compound *M* in the façade, m_{bv}, and the intensity of the wind driven rain, i_{wdr}. Of these parameters, i_{wdr} is determined by Equation 2, m_{bv}, is assumed at a value of 1 g m^{-2} immediately upon application, but the wash-out coefficient κ_{bv} is only poorly known. It would not only depend on the compound in question but also on the application of which it is part. In other words, different paints and renders would release the same compound with different rates.

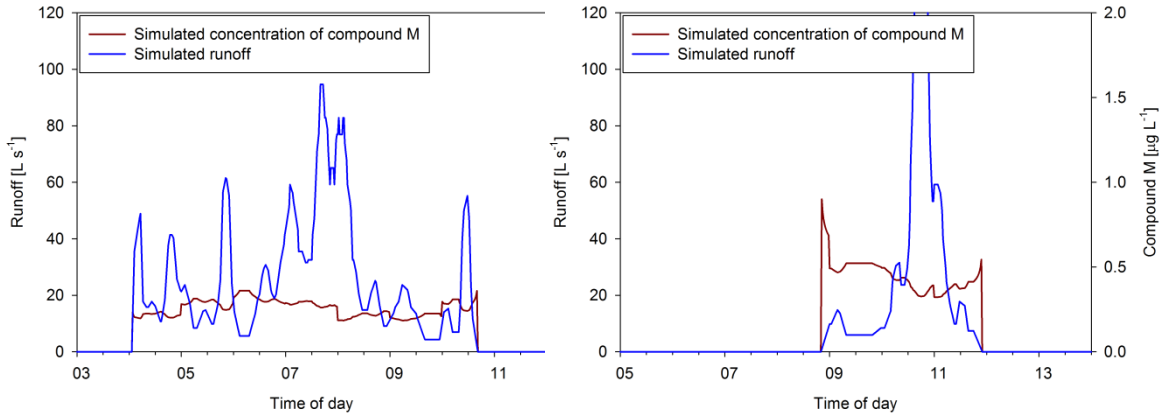


FIGURE 27. TWO EXAMPLES OF SIMULATED RUNOFF AND SIMULATED COMPOUND CONCENTRATION APPLYING EQUATION 13. THE FIRST EXAMPLE SHOWS A MORE OR LESS CONSTANT CONCENTRATION DURING THE EVENT, WHILE THE SECOND SHOWS DATA WHICH LOOK LIKE A FIRST FLUSH EVENT, BUT IN REALITY IS A RESULT OF THE RAIN AND WIND PATTERN IN THE CATCHMENT DURING THE EVENT

Burkhardt *et al.* (2012) measured the release of various biocides from paints and renders applied on panels on a model house in Switzerland. They found that some compounds were slower released than others. After one year approximately the following percentages of the original contents were

still present in the façades: diuron: 44 %; isoproturon: 39 %; terbutryn: 67 %; cybutryn: 68 %; iodocarb: 27 %; octylisothiazolinone: 25 %; dichlorooctylisothiazolinone: 21 %. To cover the range of biocide release, it was in the present study chosen to work with 3 different wash-out coefficients: κ_{bv1} corresponding to approximately 33 % being washed out within one year; κ_{bv2} corresponding to approximately 60 % being washed out within one year; and κ_{bv3} corresponding to approximately 80 % being washed out within one year.

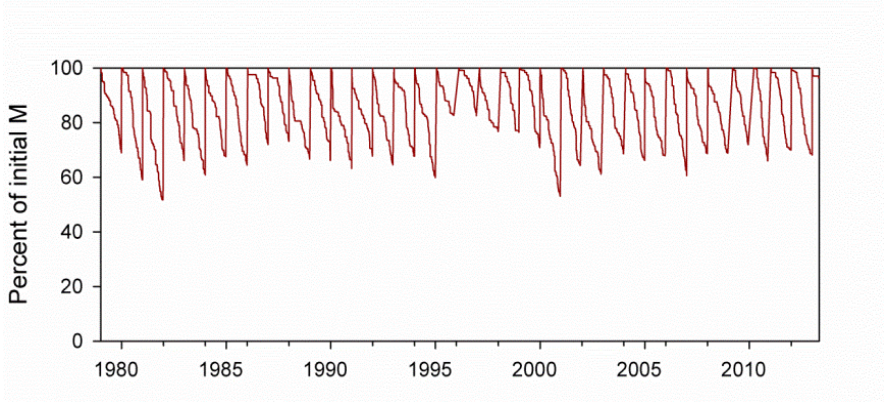


FIGURE 28. DETERMINATION OF KBV BY MEANS OF MODEL SIMULATION, CF TEXT

Figure 28 shows a simulation of washout in the artificial situation where all façades in the catchment are freshly treated on January 1st each year for 34 years. As washed-out masses vary with the weather, this approach allows estimation of κ_{bv} as the parameter value which on average yields the release of a certain percentage of the biocides after one year. In the case of Figure 28, 33 % of the biocide mass was on average released after 1 year. Applying this method, the κ_{bv} values were found to: κ_{bv1}: 17.5; κ_{bv1}: 44; κ_{bv3}: 90 $m^2\ m^{-3}$.

Applying the so-found model parameters, the model was calibrated to the measured biocide concentrations in terms of 10-minutes average concentrations during runoff events. In the following, all mentioned medians and percentiles refer to values averaged over 10-minutes of runoff. First the model was run with the 129 façade elements of 1 m^2 each. Applying wash-off constant κ_{bv1}, this yielded a median concentration of compound *M* of 1750 ng L^{-1}. Comparing this to the measured median of around 50 ng L^{-1} for carbendazim and terbutryn (Figure 19), this overshoots the observed median by about a factor 35. The assumption that all treated façade elements contained these compounds is hence probably not valid. An alternative explanation is that the estimation of connected façade area is significantly over-estimated. The number of façade elements that contained these compounds was hence reduced to 4 elements of 1 m^2 each. This reduced the simulated median concentration to 50 ng L^{-1} with 5 and 95 percentiles of 7 and 161 ng L^{-1}, respectively. The 99.9 percentile was 226 ng L^{-1}. This brings the simulation in good agreement with measured carbendazim (Figure 19). However, the extreme values observed for terbutryn were not as well simulated. The higher extreme values could, though, be simulated using the faster wash-off constants κ_{bv2} and κ_{bv3}. The relative variability of the concentrations increased with increasing wash-off rate to a level where the observations could be reproduced well. Figure 29 shows the results of these simulations. In the figure, the terms refer to $\kappa_{bv\#}$ and the number of connected façade elements, i.e. k1-4 refers to a simulation applying κ_{bv1} together with 4 façade elements.

Applying still fewer façade elements, the observations that some compounds were only present in some events could also be simulated well (Figure 29). So did for example a wash-off constant κ_{bv1} or κ_{bv2} together with 1 to 2 façade elements simulate compounds like iodocarb or mecoprop rather well. In general the overall statistical behavior of the observed biocides was well represented by the model.

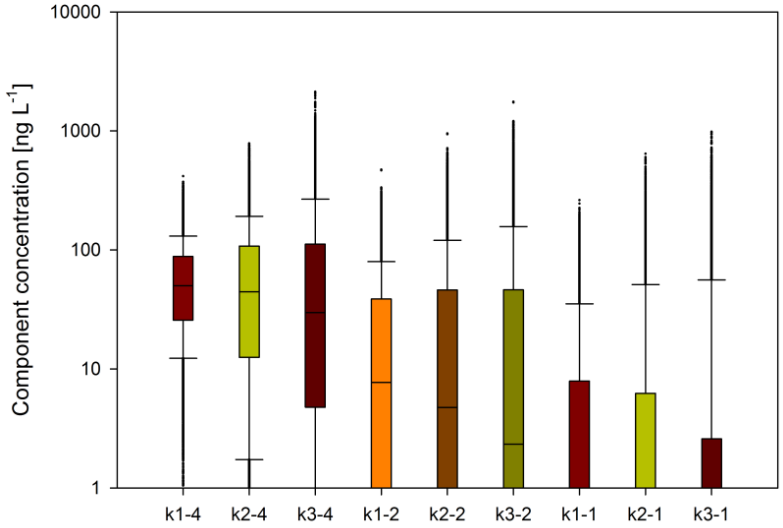


FIGURE 29. SIMULATION OF DISTRIBUTION OF A COMPOUND *M* IN RUNOFF APPLYING THE THREE WASH-OFF COEFFICIENTS (K_{BV1}, K_{BV2}, K_{BV3}) TOGETHER WITH 4, 2 AND 1 FAÇADE ELEMENTS OF 1 M² EACH.

5.6.2 Scenario predictions

For each of the 4 scenarios, the 3 wash-off coefficients as well as 3 different façade numbers were simulated. For the typical suburban catchment of single family houses, the number of façade elements where chosen to 8, 4 and 2 because the impervious area times the hydrological reduction factor of the scenario catchments are twice as large compared to the studied Silkeborg catchment. The number of façade elements for the other building categories was estimated, as was the areas of façade elements and the return period of treatment. Hereby an overview over expected concentration statistics is achieved, whereas the absolute discharged concentrations must stay a guesstimate only. Simulation results for the catchment types presented in

Table 17 are given in the following figures and tables.

TABLE 17. OVERVIEW OVER CATCHMENTS SIMULATED FOR EXTREME STATISTICS

Catchment type	No of façades connected	Area of façade element	Return period of treatment	Comment
Typical and rather well-kept suburban catchment of single family houses with large gardens	8, 4, 2	1 m²	3 ±2 years	Few façades connected to the storm sewer. Façades are treated (painted) often
Medium dense and build with 2- story terrace houses, rather well-kept, having their own garden	12, 6, 3	1 m²	4 ±3 years	More façades connected to the storm sewer. Façades are treated (painted) regularly
Dense urban center and contains buildings of 3-5 stories, no gardens	12, 6, 3	4 m²	8 ±4 years	Larger façades connected to the storm sewer, less often treated
Dense industrial catchment with large facades, few green areas	20, 10, 5	5 m²	12 ±4 years	Larger façades connected to the storm sewer, seldom treated

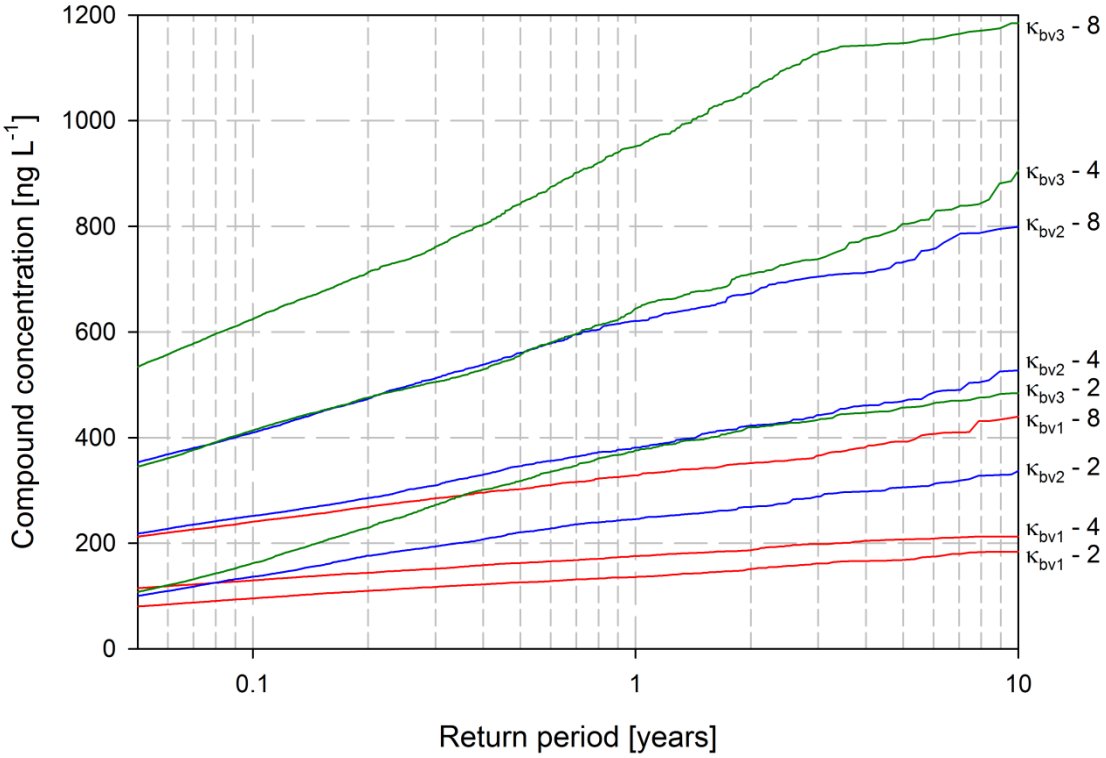


FIGURE 30. EXTREME STATISTICS FOR A CATCHMENT CONSISTING OF TYPICAL AND RATHER WELL-KEPT SUBURBAN CATCHMENT OF SINGLE FAMILY HOUSES WITH LARGE GARDENS, CF. (

TABLE 17). GREEN LINES INDICATE RESULTS APPLYING WASH-OFF COEFFICIENT K_{BV3}, BLUE INDICATES RESULTS WITH K_{BV2}, AND RED INDICATES RESULTS WITH K_{BV1}

TABLE 18. MEDIAN AND AVERAGE CONCENTRATIONS OF COMPOUNDS CORRESPONDING TO FIGURE 30

	Façade elements					
	8		4		2	
	Median	Average	Median	Average	Median	Average
κ_{bv1}	57.9	69.4	28.0	34.6	4.0	13.9
κ_{bv2}	69.6	93.8	32.2	49.6	0.0	7.4
κ_{bv3}	59.6	106.1	19.9	53.7	0.0	6.3

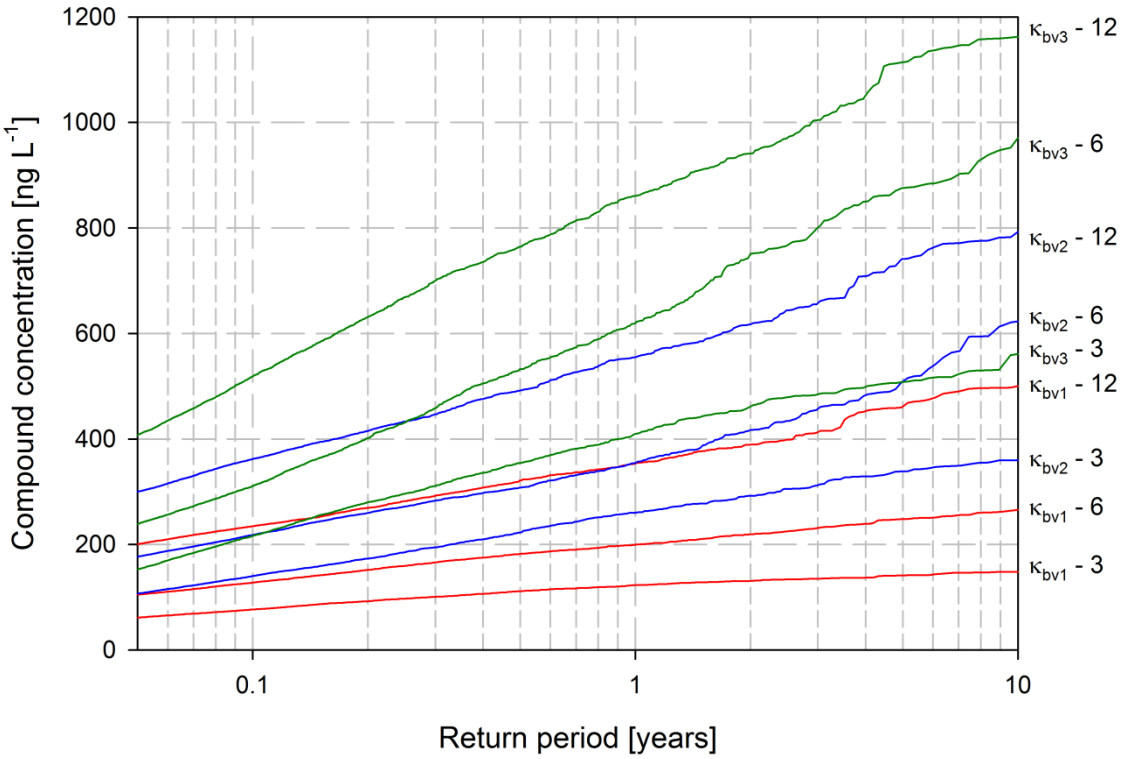


FIGURE 31. EXTREME STATISTICS FOR A CATCHMENT CONSISTING OF MEDIUM DENSE AND BUILD WITH 2- STORY TERRACE HOUSES, RATHER WELL-KEPT, HAVING THEIR OWN GARDEN, CF.

TABLE 17). GREEN LINES INDICATE RESULTS APPLYING WASH-OFF COEFFICIENT K_{BV3}, BLUE INDICATES RESULTS WITH K_{BV2}, AND RED INDICATES RESULTS WITH K_{BV1}

TABLE 19. MEDIAN AND AVERAGE CONCENTRATIONS OF COMPOUNDS CORRESPONDING TO FIGURE 31

	Façade elements					
	12		6		3	
	Median	Average	Median	Average	Median	Average
κ_{bv1}	4.7	29.6	1.9	14.1	0.4	6.9
κ_{bv2}	5.2	39.5	0.1	17.5	0.0	8.9
κ_{bv3}	0.4	43.0	0.0	17.7	0.0	9.8

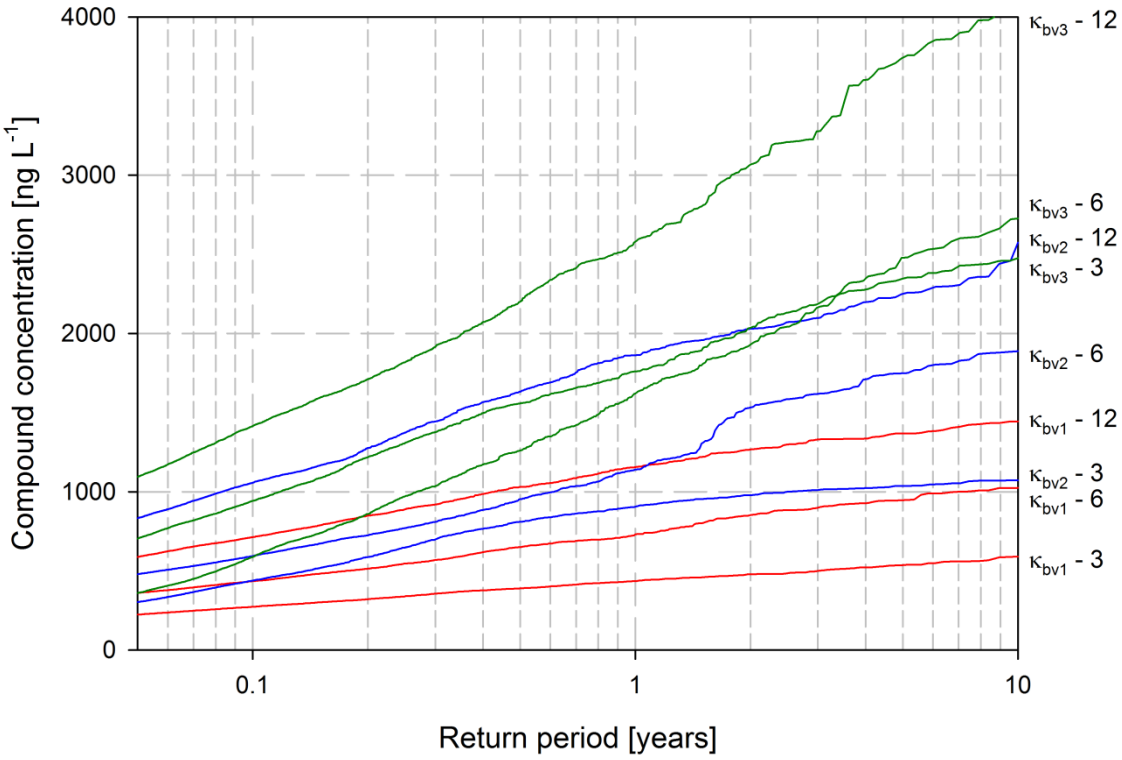


FIGURE 32. EXTREME STATISTICS FOR A CATCHMENT CONSISTING OF DENSE URBAN CENTER THAT CONTAINS BUILDINGS OF 3-5 STORIES, NO GARDENS, CF. (

TABLE 17). GREEN LINES INDICATE RESULTS APPLYING WASH-OFF COEFFICIENT K_{BV3}, BLUE INDICATES RESULTS WITH K_{BV2}, AND RED INDICATES RESULTS WITH K_{BV1}

TABLE 20. MEDIAN AND AVERAGE CONCENTRATIONS OF COMPOUNDS CORRESPONDING TO FIGURE 32

	Façade elements					
	12		6		3	
	Median	Average	Median	Average	Median	Average
K_{bv1}	23.9	92.1	3.6	44.4	2.2	23.6
K_{bv2}	1.5	83.7	0.2	40.8	0.0	21.2
K_{bv3}	0.2	95.4	0.0	50.1	0.0	21.1

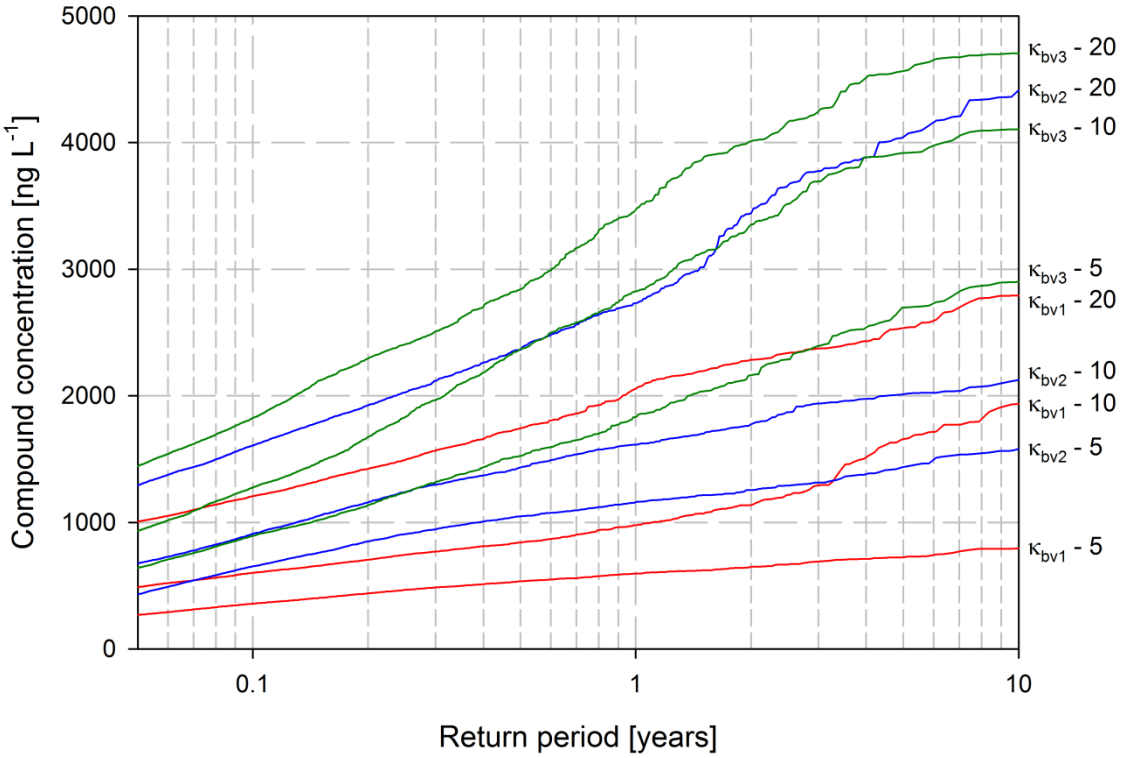


FIGURE 33. EXTREME STATISTICS FOR A CATCHMENT CONSISTING OF DENSE URBAN CENTER THAT CONTAINS BUILDINGS OF 3-5 STORIES, NO GARDENS, CF.

TABLE 17). GREEN LINES INDICATE RESULTS APPLYING WASH-OFF COEFFICIENT K_{BV3}, BLUE INDICATES RESULTS WITH K_{BV2}, AND RED INDICATES RESULTS WITH K_{BV1}

TABLE 21. MEDIAN AND AVERAGE CONCENTRATIONS OF COMPOUNDS CORRESPONDING TO FIGURE 33

	Façade elements					
	20		10		5	
	Median	Average	Median	Average	Median	Average
K_{bv1}	21.8	137.3	6.8	60.2	3.1	29.6
K_{bv2}	6.4	143.0	0.1	58.5	0.0	30.8
K_{bv3}	0.2	121.9	0.0	62.7	0.0	36.4

In general the simulations show that the more rapid the release rate, the higher do extreme concentration become – however, without necessarily affecting the average concentrations much. For combinations of few façade elements and faster wash-off rates, a large portion of the storm water contained no biocides. However, the extreme concentrations could still be rather high. The median and also the mean values for the 4 scenarios were not that different, taking varying façade areas and number of façade elements into account. However, the extreme values did vary significantly more.

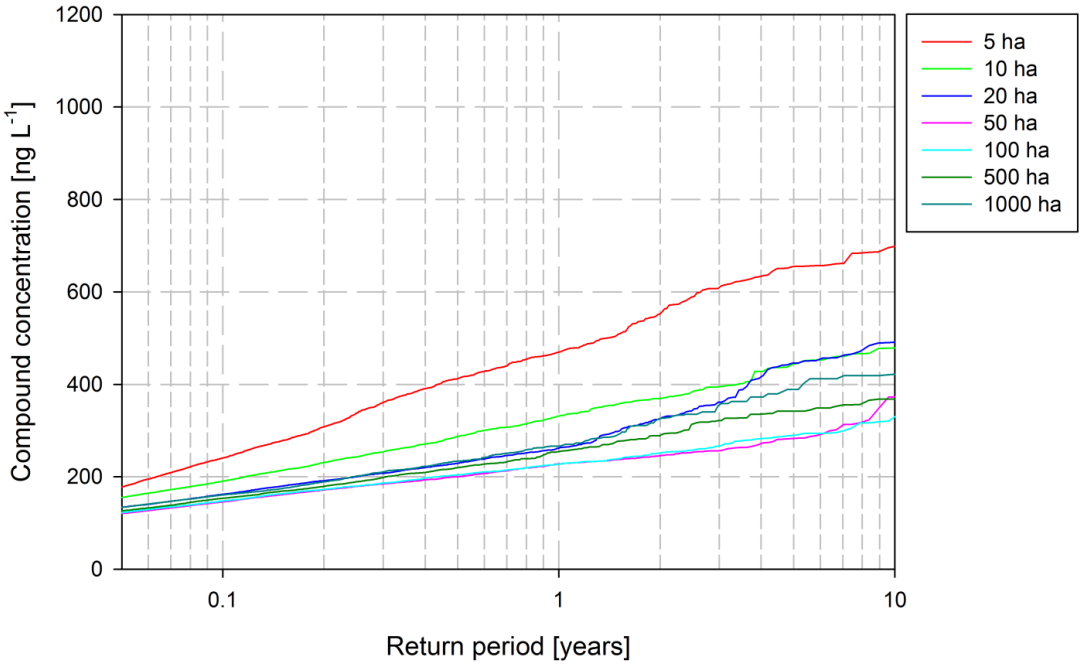


FIGURE 34. AN EXAMPLE OF EXTREME STATISTICS FOR VARYING CATCHMENT SIZES. THE WASH-OF COEFFICIENT OF K_{BV2} WAS USED TOGETHER WITH 4 FAÇADE ELEMENTS PER 10 HA, CF. SECTION 4.8.1.5

To test the impact of the catchment size on the extreme statistics, the typical suburban catchment was scaled to 5 ha, 10 ha to 20 ha, 50 ha, 100 ha, 500 ha, and 1000 ha. The simulations are presented in Figure 34 and show that small catchments produce significantly higher extreme concentrations compared to large catchments. However, the larger catchments still show significant extreme concentrations compared to median values (Table 18). The reason here for must be sought in the fact that the number of contributing façades is comparatively small and that the stochastic

behavior related to which façade contributes how much during which event tends to overshadow a possible effect of equaling out peak concentrations due to catchment sizes. The average compound concentrations from the different catchment sizes were nearly identical.

5.6.3 Interpretations “Quantitative modelling”

The quantitative modelling shows how the conclusions from the field measurements on biocide emission from separate sewers can be broadened to related catchment types and longer time series. The approach allows for example gaining understanding of extreme concentrations in runoff, comparing different catchment types, and comparing large and small catchments. Main interpretations are:

- In the experimental catchment, the area of façades contributing to the biocide in the storm water was small compared to the total façade area
- A low number of façade elements can cause significant extreme concentrations even though the median concentration in the runoff is low or even zero
- A fast biocide release rate results in correspondingly higher extreme concentrations
- Runoff from small catchments is prone to higher extreme concentrations of biocide than runoff from larger catchments.

While the model simulations give information on statistical trends and orders of magnitude, they do not allow a general quantification of the biocide load from urban runoff on receiving water systems. To achieve such knowledge, more catchments and of different characteristics need to be investigated and the mass load from the runoff compared to these characteristics.

6. Discussion

At the current state of knowledge we assume that leaching, though a simple word consists of different processes (Wittmer *et al.*, 2011) which have in this project been identified as: A) The delivery from the deeper layers of the render material to the surface. B) the partitioning of the biocides between render and water on the surface of the render system, C) the transport of the water away from the render (running off/down) (Burkhardt et al., 2011, 2012), D) Photolysis especially on the surface layer of the render (Burkhardt, et al., 2009). Leaching is thus quantitatively a complex process. Very little literature relates to these processes in real renders and the detailed chemical and physical mechanisms leading to leaching are only poorly understood.

6.1 Presence of compounds on the market

Hypothesis 1): In Denmark the same biocides are relevant as in the rest of Northern Europe.

This study showed that terbutryn, diuron, octylisothiazolinone, iodocarb, benzoylchloride and Zn-pyrithion are relevant as film preservatives or similar in masonry products (renders or paints) on the Danish Market. The spectrum is thus a bit moved from the ones known in Germany and Switzerland in earlier studies (Burkhardt et al., 2009). Whether this is a geographic effect, or a temporal one is difficult to resolve and has not been subject of this project. It was rather assumed that at least cybutryn, isoproturon and dichloro-N-octylisothiazolinone would still play a role. They seem to do so in the catchments, but no current products were identified. Due to the biocide regulation (European Parliament and Council, 2012) and the ongoing registration during the project, there is some indications that some products and active ingredients were not registered and thus phased out during the project Europe wide. The hypothesis thus probably holds true to some extent: The Danish marked is similar to the European one.

6.2 Which parameters control the leaching of biocides on the materials side?

Hypothesis 2.1) It is assumed that the acrylate based renders perform differently to the silicone based ones.

Except in some outliers, both materials proved to behave pretty similar. Only for selected compounds a changed order in elution from one material to the other could be detected. As there is few data available in the white literature this cannot be compared to findings of other research groups (Styszko et al., 2014). Hypothesis 2.1 is thus rejected.

Hypothesis 2.2) The organic matter fraction in the render will play a crucial role in controlling the release of biocides from the render.

The experiments with enhanced acrylate content in renders showed that several compounds partitioned less into the water when the acrylate and, thus, the TOC value was enhanced in the material. Hence, it can be assumed the release for these compounds is controlled by the TOC. This was not relevant for diuron and isoproturon. It is well known that these compounds occasionally are precipitated on carbonate particles already during the formulation process. Hypothesis 2.2 can be

considered as acceptable except for diuron and isoproturon. Comparison of the K_{ow} (from the literature) and the K_{oc} (partitioning against organic matter content) gave reasonable results, but not excellent ones. Anyway the results seemed generally speaking better than those ones discussed based on water solubility as used by primary assessments (Schoknecht & Burkhardt, 2008).
It turned out that the partitioning is also heavily influenced by the pH value of the leaching water. It is assumed that the surface water pH is slightly acidic, while the porewater pH value is certainly controlled by the carbonates included and is thus rather alkaline. In this project the surface water pH was considered to dominate the partitioning, while the porewater pH will rather influence the transport within the material. To which extent this is really true, cannot be decided at the moment. However the partitioning experiments at pH 5.6 seem to better agree with the results from the walls exposed to rain, than those obtained at pH 9.5. It is thus obvious that the dissociation constant K_a of the biocide in question is also important when assessing the leaching potential.
The transport within the material might also be controlled by diffusion either in the porewater or in the polymer.

Hypothesis 2.3) It is hypothesized that partitioning experiments give basic insight, but cannot really be used for predicting leaching from real walls.

Similar orders were found to be relevant for the wall experiments as found for the partitioning experiments. For the partitioning experiments: Methylisothiazolinon > Benzisothiazolinon > Carbendazime > IPBC > Octylisothiazolinon(OIT) > Diuron > Isoproturon > Dichloro Octylisothiazolinon(DCOIT) >Terbutryn > Tebuconazole > Cybutryn > propiconazole, while for the walls the order Methylisothiazolinon > Isoproturon > IPBC > Tebuconazole > Octylisothiazolinon(OIT) > Diuron > Terbutryn > Benzisothiazolinon > Carbendazime > Dichloro Octylisothiazolinon(DCOIT) were found.
Indeed quantitative predictions were not possible as several parameters were unclear or uncertain. No literature is available on this issue except those published based on chapter 4.1. . From literature it is known, that the phenylureas diuron and isoproturon leach faster than the triazines terbutryn and cybutryn (Burkhardt et al., 2012). Significant differences were, however detected for renders on the one hand and paints on the other hand, as well as between the different formulations. Additionally Schoknecht et al. (2009) found a similar order as in this project in her partitioning experiments that were derived from the normalized wood testing.

6.3 To what extent influences weather the leaching the biocides from real walls?

Hypothesis 3) Radiation intensity, rain amount, rain intensity, wind and temperature play crucial roles in leaching from real systems.

In the experiments on the artificial walls, it turned out that driving rain, i.e. the product of rainfall and wind speed had a significant influence on the leached amounts. Basically that means the more water reaches the surfaces the more biocides are leached. None of the other parameters had an effect that could be detected in the extensive dataset. This issue had been mentioned before by Burkhardt *et al.* (2012) but never been proven that clearly. Interestingly enough, the same was also detected on the catchment scale. Coutu *et al.* (2012) argue with wetted surfaces but did not really link to driving rain. On the other hand of course, the driving rain is different for the different parts of the building. Anyway, it should thus be considered to relate all leaching experiments primarily to driving rain and not to any other parameters.

6.4 Which role does biocides from building materials play in the Danish environment?

Hypothesis 4.1) Biocide concentrations in Denmark are less, as in Denmark the materials are used less than in Switzerland or Germany.

The Silkeborg catchment was chosen because of its good infrastructure and it could be demonstrated it is a suitable one. It proved to provide water with low to relatively high concentrations (ie. ng L 1 - µg L 1) it is not too surprising that those catchments in Switzerland that have been used to study highest possible and hotspots often deliver higher concentrations (Burkhardt et al., 2007,2008, 2009). Background concentrations in urban stormwater in Switzerland are similar to those found in Silkeborg (Wittmer et al., 2010). However, some of the samples from urban surface waters have biocide concentrations in the same range or even higher as those in Switzerland. Terbutryn concentrations in a Rhine tributary in Hesse/Germany (Quednow & Püttmann, 2007, 2009) proved to be considerably higher than those found in the Danish samples, but then they were also considerably higher than those found in surface waters in Switzerland (Wittmer et al.,, 2010). Terbutryn concentrations determined by Kai Bester (unpublished data) in the Rhine-Ruhr area were usually several 10 ng L 1 and thus similar to samples from this project.

Hypothesis 4.2) Biocide concentrations in Danish storm water catchments will behave similar as in other countries if the building structure is similar. First flush events will dominate the emissions as they do for PAHs and heavy metals.

As discussed above, the building structure in the respective catchment and the rainwater management affects the biocide concentrations in stormwater considerably. In city quarters, where new buildings are heavily equipped, the concentrations are found to be high; where other building structures predominate, the concentrations are less. This thought that has not been depicted in the literature yet. The models and approaches used by Coutu et al. (2012) assume that all buildings in one city are equally equipped, which can obviously not be true, though the big picture might be displayed correctly. The concentrations found in the Silkeborg catchment with few buildings that are equipped are thus somewhat lower than the hot spots studied in Switzerland where the studies were conducted on building complexes which were 100% equipped (Burkhardt et al., 2011).

Hypothesis 4.3) Biocides will be present in combined sewage during rainfall, but not during dry weather.

All biocides were present in combined sewer during rainfall. However several of them were also present during dry weather, leading to new assumptions of unaccounted sources as disposal of water used for washing tools (brushes, clothes) used in construction and decoration work on buildings. If looking carefully through literature it is possible to determine hints towards other authors had similar data, but did not really trust them (Burkhardt et al., 2007). However, there were reports at the SETAC Europe 2013 confirming these findings also for Germany. Hypothesis 4.3 can thus be accepted to be verified in respect of the rainy weather; however it needs modification concerning the dry weather.

Hypothesis 4.4) The concentrations in well-kept urban waters will be below the quality targets.

Though in most samples biocides were determined, the majority were indeed below the environmental quality targets in urban waters, On the other hand the concentrations in storm water ponds were higher. However, mecoprop was detected with over 200 ng L^{-1} (well above the limits set by the older surface water directive) in one sample in *Ørestad*. This is indicating towards problems with the water quality that thus needs to be improved. The concentrations were often somewhat lower than those reported for German, Swiss or French water (Bucheli *et al.* 1998a; Blanchoud *et al.* 2004; Quednow & Puettmann 2007; Wittmer *et al.* 2010), but still significant and in some cases exceeding effect levels (Mohr *et al.* 2008; Burkhardt *et al.* 2009).

6.5 Quantitative models to predict concentrations and loads

Hypothesis 5) Quantitative modelling will predict loads for diverse catchments as well as extreme weather scenarios.
It turned out that quantitative modelling was helpful to understand the mechanisms relevant for the processes in a stormwater catchment. It was also helpful in making predictions on the return period for repeat of extreme emissions. However, a large number of parameters are needed to calibrate the model to a concrete catchment, here among the fraction of façades hydraulically connected to the storm sewer, the number of façade elements equipped, wind accessibility of the buildings, and preferred materials used when using biocidal products. These parameters could be obtained or deducted for the studied catchment in Silkeborg, albeit significant effort was required to do so. Addressing other catchments without such effort, i.e. using an un-calibrated model, it must be kept in mind that results may only be viewed as indicative. Other modelling approaches in literature focus on explaining processes on the materials only empirically, with little understanding of the materials (Wittmer et al., 2011) or considered catchments based on the assumptions that all houses are equal (Coutu et al., 2012).

6.6 Overall discussion

Biocides originating from building materials are relevant for the Danish environment. However, their presence is not ubiquitous, but it is related to areas were buildings actually have an outer shell which is equipped. If this part of the building is exposed to water, usually driving rain, the concentrations in the stormwater and stormwater-receiving surface waters will be high and effects might be expected. This project has shown that driving rain is the main factor in leaching these compounds from the materials. However, also material and compound properties work together in steering the leaching.

7. Conclusions

This project provided new insight in respect to the presence of materials that are equipped with biocides, the leaching behavior of biocides from building materials as well as their relevance for the Danish environment be it stormwater catchments, wastewater or surface waters in urban areas.

Presence of building products that are equipped with biocides on the Danish market.

- Biocides from construction materials are relevant in the Danish environment (stormwater, urbanized surface waters, wastewater).
- On the Danish market terbutryn, diuron, octylisothiazolinone, and zink-pyrithion were the main compounds used as film preservatives in render/paint systems in 2010/11. Other compounds (not subject to the market survey in this project) were used for wood protection, protecting bitumous sealings of roofs (mecoprop), and roof cleaning (quarternery ammonium salts).

Leaching of biocides from render materials (laboratory tests)

- The mobility or leaching of the biocides in polymeric renders is dependent on the relative compound and the water contact (wind driven rain) of the material. Additionally, dependencies on pH and organic matter content of the render on the mobility of the biocide have been demonstrated. While equilibrium data give a principal overview, kinetic data is essential for better assessment. Generally speaking a trend like carbendazim > isoproturon > diuron > IPBC > tebuconazole > cybutryn with carbendazim leaching the fastest can be assumed based on surface equilibrium considerations. This row follows to some extent, but not strictly the K_{OW} at pH 7 carbendazim < IPBC < diuron = isoproturon < DCOIT <tebuconazole < cybutryn with carbendazim having the lowest K_{OW}.
- The kinetic column experiments resulted in an order carbendazim > isoproturon >diuron> IPBC > cyburyn with carbendazim eluting the fastest. The two experiments thus show qualitatively similar results. Increase of polymer content in the kinetic column experiments also had drastic effects on isoproturon and diuron.
- Though the kinetic column experiments qualitatively agree to those from the equilibrium partitioning, the numerical data did not agree to the desorption equilibrium experiments in quantitative measurements, indicating towards processes that are not understood yet.
- The lower the pH, the higher the desorption of compounds from the render material, however, different compounds are affected differently as their K_a values differ.
- The higher the polymer content, the lower the desorption/leaching for carbendazim, cybutryn, DCOIT, while the polymer content hardly affected the desorption of diuron and isoproturon, while tebuconazole and IPBC are affected to a small extent.
- Polymeric renders with silicones and acrylates as binders resulted in very similar partitioning rates for all compounds as long as the binder concentration was similar and the pH was similar, except for IPBC, which showed drastic differences between acrylate and silicone renders. The pH made a bigger difference than which polymer was used.

Leaching from render equipped walls (weathering tests)

- Direct leachate of treated walls contains concentrations up to 200 $\mu g\ L^{-1}$ (e,g, the in-can preservative methylisothiazolinone). The film preserving compounds were emitted slowly during the exposure to natural weather and did not change significantly. In-can preservatives such as methylisothiazolinone were completely washed off during a 6 month period. However,

only 10 % of the methylisothiazolinone was recovered in the run-off water, giving thus a strong indication towards either photodegradation or evaporation being the main path of this compound. It seems however clear that not only film preservatives but also in-can preservatives are relevant for emissions into the environment.

- There were strong differences (67%) between the silicone and the acrylate renders in the test walls in respect of the leaching of the in-can preservative methylisothiazolinone, all other compounds showed less pronounced differences (OIT, diuron, and carbendazim 32, 40 and 17%, respectively), while other compound such as terbutryn were leached very similar in both systems.
- The amount of water being in contact with the treated surfaces (driving rain) was the only weather parameter that influenced the emissions, others such as rain amount, rain intensity, length of drying period, radiation during dry period etc. had no detectable influence on the emissions of biocides from walls. The more driving rain the higher the leaching.
- Prediction of results for weathered walls (panels) with the partitioning equilibrium experiments resulted in differences up to factor 10. The differences were very much dependent on the specific substance. If predictions based on partitioning equilibrium experiments are planned in the future an uncertainty of factors of at least 10 should be taken into account.

Biocides in stormwater catchments

- Considering the Silkeborg catchment as one with rather low amounts of treated surfaces in comparison to modern city quarters with high insulation rates, it can be concluded, that contamination of stormwater catchments with biocides from building materials is considerable. The concentrations for which well-established toxicological data exist (e.g. cybutryn) suggest that effective concentrations (EC10) will be reached, causing potentially adverse effects to plants or algae in stormwater treatment systems and urban lakes that are heavily influenced by stormwater. Terbutryn might reach the environmental quality standard of the water framework directive (European Commission 2012) .
- First flushes, though occurring eventually, do not determine the emissions of biocides in stormwater; the emissions are rather continuous or erratic than clearly first flush driven. Potential treatment can thus not focus on first flushes.
- The concentrations found in the Danish stormwater catchment are similar to those in Swiss surface waters, but lower than German waters.
- The current risk assessment on rural sites underestimates the concentrations found in suburban surface waters.

Biocides in wastewater

- The concentrations of biocides typical for protecting buildings in dry weather wastewater are, though smaller than in stormwater, also substantial (10-100 ng L^{-1}). Sources might include handling of paints, renders and tools including brushes in home use with successive washing of materials in water that is afterwards disposed into the sink. However in one case it seemed like these usages can hardly explain the high and very discontinuous use of propiconazole which is also used as pesticide e.g. in green houses. For some compounds it is obvious that disposal routes of used materials are the source in wastewater (terbutryn, cybutryn) For other compounds treatment of bathroom-sealants or cosmetics might also be relevant (methylisothiazolinone, octylisothiazolinone).

Biocides in urban surface waters

- In surface waters influenced by urban stormwater concentrations of 1-100 ng L^{-1} were detected, especially mecoprop became relevant in areas were flat roofs are used. Different regions in Greater Copenhagen were attributed to different patterns with mecoprop, and azoles (propiconazole and tebuconazole) being the most relevant compounds during the monitoring implemented in this project. Hotspots were the Ørestad channels and -lakes (mecoprop: 200 ng

L^{-1}, diuron: 40 ng L^{-1}), but also Damhusåen (propiconazole: 20 ng L^{-1}) and Utterslev mose (DCOIT 60 ng L^{-1}) had elevated concentrations.

Source identification

- There is an overlap of uses which in some cases make source allocation difficult. Some compounds are solely or predominantly used as biocides in building protection for renders and paints for renders (masonry related products): terbutryn, cybutryn. Some compounds are used only as biocides but with different usages: masonry, wood protection, cosmetics drilling fluids etc. methylisothiazolione (MI) and benzisothiazolinone (BIT), Iodocarb (IPBC) and octylisothiazolinone (OIT). Some compounds are used as biocides as well as pesticides in agriculture diuron, isoproturon, tebuconazole, propiconazole, carbendazim, and mecoprop. For these compounds a case by case decision based on expert knowledge or verifying experiments is needed to decide which source might be the relevant one in the respective catchment.

Modelling/Predictions

- Quantitative modelling gave better insight into the behavior of biocides in smaller stormwater catchments: the experimental data showed huge variations. The quantitative modelling demonstrated: in catchments relative small hot-spots (in relations to large areas which are not treated with biocides) are relevant for the emissions. These hot-spot are so small that they are exposed to weather differently.
- Quantitative modelling based on the experimental data of the Silkeborg catchment showed: a low number of façade elements thus cause extreme concentrations, if in contact with driving rain.
- Quantitative modelling based on the experimental data of the Silkeborg catchment showed: a fast release results in higher concentrations during extreme events.
- Quantitative modelling based on the experimental data of the Silkeborg catchment showed: runoff from smaller catchments is more prone to higher extreme concentrations of biocides than runoff from larger catchments (dilution into un-polluted runoff water).

8. Perspectives

8.1 Research perspectives

In this project it has been shown, that driving rain (i.e. water contact), partitioning of the biocide between render and water phase as well as transport from the deeper layers of the renders to the surface together control the leaching and emissions of biocides from render material. Some parameters that are important have been clarified in this project, while others still need principal or quantitative understanding:

- As it could be demonstrated that the emissions of biocides are considerable, and it is well known that the respective run-off waters are often directly infiltrated into the soil, usage of biocides on buildings poses a serious risk to clean ground water. It is thus essential to study the introduction of biocides from buildings into soil and urban groundwater. Studies on the mass flows, fates and transformation of biocides in urbanized soils are utterly needed.
- It could be in some cases demonstrated that the major fraction of the used biocides is not recovered in the effluent water and bio- and photo-transformation on the materials surfaces cannot be ignored it is thus essential to research on transformation products, and transformation rates, to be included into assessments. Other projects also have demonstrated on the importance of transformation products of terbutryn and diuron. While photo-transformation products to be expected from compounds with a pesticide background are probably not completely unknown, the photo-degradation pathways for the compounds used solely as biocides need to be explored.
  Considering photo-degradation kinetics, it needs to be taken into account, that the render surfaces contribute most probably to the photolysis reactions, either by reflecting/sorbing light or by quenching the incoming photons and thus making photons available for reactions that otherwise would not hit the organic molecule. It should be considered that the different organic binders would influence the photolysis rates as well as the mineral (pigment) constituents of the binder.
  Toxicity of photo-degradation products needs to be assessed, if not already done.
- How much biocides can be mobilized through wet/dry cycles is currently still unclear, even though this project demonstrated through the column approaches that they are relevant. It must be assumed that the overall leaching is affected by surface equilibria, active transports through the porous material, and diffusion processes through the polymer or through the pore water.
- As in rural areas most compounds will be introduced into the soil rather than into the surface waters it is crucial to describe mass flows, transport and transformation of biocidal compounds in urbanized soils.

8.2 Administrative perspectives

Within the project it was demonstrated that biocides originating from buildings and other sources are present in dry weather wastewater. It was concluded, that this can only be due to improper disposal though probably neither users, authorities nor manufacturers are really aware of this issue. Additionally concentrations of biocides were found in stormwater that are high enough to cause adverse effects. There are thus two obvious issues that can be initialized by the environmental administration:

- Reduce emissions into wastewater by enhancing disposing of materials (including water-based paints) at the recycling station instead of washing/spilling.

- Consider stormwater treatment as an option to reduce concentrations of biocides in surfaces waters – this could be performed with some regional focuses.

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Appendix 1: Overview on usage of compounds as well as selection of compounds for this project.

Compound	Abbr.	Identified in DK products (Appendix 2:)	Used in previous projects	Identified in pond screening	Used in products in the EU	Regulated by MST (for the EU)	Different chemical method	Suggested list
Cybutryn (Irgarol 1051)	IRG		X		(X)			X
Terbutryn	TB	X	X	X	X			X
Diuron	DR	X	X		X	X		X
Isoproturon	IP		X	X	(X)			X
Octylisothiazolinone	OIT	X	X		X			X
Dichlorooctylisothiazolinone	DCOIT		X					X
Benzisothiazolinone	BIT		X					X
Carbendazim	CD		X		(X)			X
Tebuconazole	TBU				X	X		X
Propiconazole	PPZ					X		X
Iodocarb	IPBC	X	X			X		X
Benzoylchloride	BAC	X					X	no
Zn-Pyrithion	ZnP	X			X		X	no

X yes
(X) may be

Appendix 2: Danish market survey "Biocides in paints and render".

By internet research a multitude of building materials (paints and renders) has been identified on the Danish market, which do contain biocides. The combinations *biocide AND puds AND .dk* as well as the combination *biocide AND maling AND .dk* were used. Additionally the respective compound names and the known players in the building sector were searched upon. By intensive telephone questioning it could be verified which active ingredients were contained indeed. Often the answers were only found in the international headquaters of the companies. However, it should be noted, that this kind of study is not really able to identify all products on the market. The results are documented below.
The following active ingredients were thus identified: Paint: octylisothiazolinone, iodocarb, terbutryn, zinc pyrithion, diuron. Wall cleaning: benzalkoniumchloride. Render: zinc pyrithion.

Product	*Active ingredient*	*supplier*	*Kind of product*	*Contact*
Weber.ton 411	OIT + algicide	Saint-Gobain Weber A/S	Puds	Saint-Gobain Weber A/S Silovej 3 Karlstrup DK 2690 Karlslunde T: +45/56 18 18 56
Silikoneharpikspuds KC Silikoneharpikspuds R	Silikoneharzpuds indeholder fungicid, til beskyttelse mod alger og svampe BASF: "Zinkomadine" Zink-Pyrithion	HEFA	Puds	HEFA Facadeisolering GmbH Skibbyvej 23 DK-8220 Brabrand T: +45 70201982 F: +45 70201983 www.hefa-facade.dk
Heck SHP Silikonepuds KC R	Heck SHP er allerede fra fabrikens side forsynet med biocide stoffer mod alger og svampe angreb Zink-Pyrithion	BASF	Puds	BASF Hallandsvej 1 DK 6230 Rødekro 73663030
Isover Egaliseringsfarve	god modstandsdygtighed overfor svampe, alger og mos Anvend biocider på en sikker måde.	Isover	Maling/ farver	Saint-Gobain Isover a/s | Østermarksvej 4 | 6580 Vamdrup | Telefon +45 72 17 17 17 | Telefax +45 72 17 19 19 | isover@isover.dk
Rajasil fungicide	Benzalkonium-chloride	BASF/ HECK/HEFA	Cleaning/ painting	HEFA Facadeisolering GmbH Skibbyvej 23 DK-8220 Brabrand T: +45 70201982 F: +45 70201983 www.hefa-facade.dk

Product	*Active ingredient*	*supplier*	*Kind of product*	*contact*
Antialgin	Benzalkonium-chloride	Nordsjö/Besma	Cleaning	Akzo Nobel Deco A/S (Nordsjö Farver) Holmbladsgade 70, 2300 København S, Danmark Tlf: +45 3269 8000 www.Nordsjo-guide.dk
777-xxx Acryl Plastmaling	3-iod-2-propynylbutylcarb amat (iodocarb) Terbutryn	Beck & Jørgensen A/S	Maling/ farver	Beck & Jørgensen A/S Hovedkontor Administration Beck & Jørgensen A/S Rosenkæret 25-29 2860 Søborg Tlf. 39 53 03 11 Fax 39 53 03 40
Murtex VNanotec facademaling	Zink pyrithion	Nordsjö	Maling/ farver	Akzo Nobel Deco A/S (Nordsjö Farver) Holmbladsgade 70, 2300 København S, Danmark Tlf: +45 3269 8000 www.Nordsjo-guide.dk
Murtex V Fin f academaling	Diuron, Iodocarb	Nordsjö	Maling/ farver	Akzo Nobel Deco A/S (Nordsjö Farver) Holmbladsgade 70, 2300 København S, Danmark Tlf: +45 3269 8000 www.Nordsjo-guide.dk
Murtex V olieemulsiom	Diuron, Iodocarb	Nordsjö	Maling/ farver	Akzo Nobel Deco A/S (Nordsjö Farver) Holmbladsgade 70, 2300 København S, Danmark Tlf: +45 3269 8000 www.Nordsjo-guide.dk
Sadolin Facade Extra - Nanotec	Zink pyrithion	Sadolin	Maling/ farver	Akzo Nobel Deco A/S (Sadolin) Holmbladsgade 70, 2300 København S, Danmark Tlf: +45 3269 8000 www.Nordsjo-guide.dk

Appendix 3: Description of the storm water ponds screened for the monitoring campaign

Catchment	Coordinates of pond	Short description
Lemming	56.2398; 9.5438	The catchment is a small country side village consisting of residential housing and a little bit of light industry. It is located north of Silkeborg. Impervious catchment area is 4 ha
Silkeborg, North	56.1945; 9.5486	The catchment is urban, residential with single housings only. An urban ringway also contributes to the runoff. The catchment is located in the northern part of Silkeborg Impervious catchment area is 7 ha
Århus, Gellerup	56.1451; 10.1371	The catchment is urban, residential with blocks of flats only. A shopping center and associated parking areas also contribute to the runoff. The catchment is located north of Lake Brabrand in Århus Impervious catchment area is 19 ha
Århus, Skjoldhøj 2	56.1691; 10.0940	The catchment is mainly urban, residential with single housings. There is a small industrial contribution. The catchment is located in the west of Århus Impervious catchment area is 21 ha
Århus, Skjoldhøj 3	56.1719; 10.0954	The catchment is urban and purely industrial. It is located in the west of Århus Impervious catchment area is 43 ha
Århus, Skjoldhøj 4	56.1719; 10.1018	The catchment is urban and purely industrial. It is located in the west of Århus Impervious catchment area is 4 ha
Århus, Skjoldhøj 5	56.1718; 10.1060	The catchment is urban and purely industrial. It is located in the west of Århus Impervious catchment area is 47 ha
Odense, Hvidkjærvej	55.3600; 10.3328	The catchment is urban and purely industrial. It is located in the south-west of Odense Impervious catchment area is 12 ha
Roskilde, RUC	55.6516; 12.1335	The catchment is a mix of urban and residential. It is located in the east of Roskilde Impervious catchment area is approximately 20 ha
Roskilde, Drosselvej	55.6520,12.1035	A residential catchment. It is located in the east of Roskilde Impervious catchment area is approximately 30 ha. The pond is an offline dry detention pond with some permanent water from where the sample was taken.
Roskilde, Metalvej	55.6473,12.1314	An industrial catchment. It is located in the east of Roskilde Impervious catchment area is approximately 20 ha. The pond is a dry detention pond with some permanent water from where the sample was taken.
Roskilde, Knolden	55.6521; 12.1149	A natural urban lake in the east of Roskilde. The site was used as reference site for comparison with urban storm water ponds

Catchment	Coordinates of pond	Short description
Roskilde, TrekronerAlle	55.6516; 12.1335	A natural urban lake in the east of Roskilde. The site was used as reference site for comparison with urban storm water ponds
Roskilde, NordensParkvej	55.6578; 12.1296	An artificial urban lake in the east of Roskilde. The site was used as reference site for comparison with urban storm water ponds

Appendix 4: Overview of sampling of combined sewer

Sampling	WWTP	Sample type		Sampling date	Weather conditions
1	Roskilde Bjergmarken	24h composite	Influent	4.-5.3.12 8am-8am	Dry weather
2	Roskilde Bjergmarken	12* 2h composite	Influent	25.-26.4.12 8am-8am	Rain
3	STP in South Sweden	Grab samples	Influent, effluent, after ozonation and chloration	31.1.13 & 1.2.13	-
4	Roskilde Bjergmarken	12* 2h composite	Influent	4.-5.6.13 9:30am-9:30am	Dry weather
5	Cph Lynetten	24h composite	Influent & effluent	26.02.13	Dry weather
6	Cph Mølleåværket	24h composite	Influent & effluent	25.02.13	Dry weather
7	Cph Avedøre	24h composite	Influent & effluent	22.01.13	Dry weather

Appendix 5: Data on artificial walls, rain events and concentrations of biocides in run-off from acrylate render façades (average from three panels)

Event	Date sampling end	Vol./ Sample	Acc.Vol	Rain	Concentration [µg/mL]									
		[mL]	[L]	[mm]	MI	BIT	CD	IP	DR	IPBC	TB	OIT	TBU	DCOIT
Average		872	9		30	2	0	8	5	9	3	5	3	0
Start	04/08/12 12:00													
1	05/08/12 12:00	254	0.25	6	53.2	3.6	0.3	3.6	2.0	2.2	1.2	4.9	0.9	0.2
2	06/08/12 18:00	81	0.33	2	29.0	0.2	0.2	2.4	1.5	1.4	1.0	5.0	1.0	0.1
3	22/08/12 10:00	260	0.59	6	103.4	5.3	0.9	8.8	4.9	5.7	1.9	7.1	1.8	0.2
4	24/08/12 17:00	349	0.94	9	11.1	0.9	0.2	1.9	1.4	1.4	0.7	2.3	0.8	0.2
5	27/08/12 09:30	827	1.77	13	120.0	10.7	1.1	13.4	7.6	12.3	3.7	12.6	3.2	0.3
6	29/08/12 11:00	197	1.97	3	11.4	0.1	0.3	2.5	1.6	2.1	1.1	2.9	1.2	0.1
7	31/08/12 16:00	92	2.06	6	26.1	0.0	0.5	4.1	2.7	3.7	1.5	5.0	1.6	0.0
8	11/09/12 16:00	565	2.62	7	50.3	4.2	0.9	9.7	5.5	9.1	2.7	7.5	2.4	0.0
9	20/09/12 11:00	242	2.87	8	27.3	0.0	0.5	6.9	4.3	6.1	1.8	3.5	1.9	0.0
10	24/09/12 11:30	267	3.13	7	4.1	0.0	0.1	1.6	1.2	1.7	0.7	1.3	1.0	0.1
11	25/09/12 10:30	730	3.86	15	1.4	0.1	0.1	1.1	1.0	1.5	0.9	1.4	0.9	0.1
12	26/09/12 10:45	509	4.37	12	21.2	1.7	0.3	5.2	2.7	4.6	1.5	2.9	1.4	0.1
13	27/09/12 09:30	919	5.29	20	34.2	3.8	0.5	9.4	5.0	9.1	2.6	5.1	2.4	0.2
14	28/09/12 10:30	1340	6.63	12	54.2	4.7	0.7	15.3	8.6	17.3	4.3	8.4	3.8	0.2
15	02/10/12 15:00	318	6.95	8	29.0	0.1	0.4	7.4	4.5	6.7	2.0	3.8	2.0	0.1
16	04/10/12 10:30	653	7.60	4	32.7	2.6	0.5	10.5	6.8	11.1	3.3	5.8	3.0	0.2
17	07/10/12 09:00	542	8.15	13	42.8	0.8	0.6	10.7	5.9	9.4	2.8	5.5	2.6	0.2
18	10/10/12 13:00	471	8.62	8	40.5	0.4	0.5	10.8	6.2	11.0	3.0	5.7	2.6	0.1
19	18/10/12 11:00	2500	11.12	46	29.0	0.4	0.4	8.9	5.5	10.2	2.9	5.5	2.8	0.2
20	30/10/12 11:00	653	11.77	6	47.2	1.5	1.0	20.8	12.3	21.2	5.5	10.3	5.3	0.3
21	05/11/12 14:00	1169	12.94	23	29.0	0.8	0.5	11.1	6.5	12.3	3.6	6.7	3.5	0.3
22	06/11/12 09:00	242	13.18	8	3.7	0.1	0.1	2.2	1.9	4.5	1.9	3.1	1.7	0.2
23	07/11/12 09:30	185	13.37	1	28.2	1.8	0.5	11.5	6.0	12.0	3.1	6.3	2.9	0.2
24	08/11/12 13:30	756	14.12	4	22.7	1.2	0.5	10.8	6.6	14.0	3.7	7.6	3.6	0.3
25	09/11/12 15:30	124	14.25	2	14.2	0.3	0.3	6.8	4.1	8.6	2.5	4.9	2.7	0.2
26	12/11/12 09:00	573	14.82	8	22.7	0.8	0.5	9.5	5.5	10.9	3.1	6.3	3.3	0.3
27	26/11/12 17:00	2267	17.09	20	16.1	1.4	0.6	13.1	8.0	16.4	4.7	9.0	4.9	0.5
28	05/12/12 14:00	380	17.47	6	0.4	0.0	0.1	1.3	1.0	1.5	1.3	0.8	1.1	0.1
29	17/12/12 10:00	1291	18.76	2	0.0	0.0	0.0	0.8	0.7	0.5	1.0	0.8	1.0	0.0
30-32	31/12/12 00:00	1598	20.36	6	27.7	0.8	0.7	15.3	8.5	19.3	5.4	8.2	5.6	0.5
33-36	11/01/13 14:00	2549	22.90	9	13.9	0.3	0.4	9.0	5.0	12.0	3.4	5.2	3.5	0.3
37-38	05/02/13 14:00	5000	27.90	13	12.7	0.1	0.4	10.9	6.2	15.5	4.4	7.4	4.4	0.5

Appendix 6: Data on artificial walls, rain events and concentrations of biocides in run-off from silicone render façades (average from three panels).

Event	Date sampling end	Vol./ Sample	Acc.Vol	Rain	Concentration [µg/mL]									
		[mL]	[L]	[mm]	MI	BIT	CD	IP	DR	IPBC	TB	OIT	TBU	DCOIT
Average		1064	12		14	0	0	6	5	4	1	3	1	0
Start	04/08/12 12:00													
1	05/08/12 12:00	251	0.25	6	92.2	3.5	0.3	5.1	3.0	2.4	1.0	5.1	0.6	0.2
2	06/08/12 18:00	55	0.31	2	36.1	0.1	0.3	2.9	2.2	1.2	0.7	3.4	0.5	0.1
3	22/08/12 10:00	345	0.65	6	79.1	2.6	1.8	21.8	14.8	7.3	2.4	10.1	1.4	0.6
4	24/08/12 17:00	449	1.10	9	20.8	0.7	0.7	7.2	5.5	3.1	1.1	4.4	0.7	0.4
5	27/08/12 09:30	1123	2.22	13	31.5	1.9	0.9	11.5	9.6	7.9	2.4	8.2	1.1	0.5
6	29/08/12 11:00	165	2.39	3	7.3	0.0	0.4	4.0	3.5	2.1	0.8	2.9	0.6	0.1
7	31/08/12 16:00	74	2.46	6	37.0	0.1	1.0	9.5	7.3	4.6	1.5	5.4	0.9	0.0
8	11/09/12 16:00	1162	3.62	7	16.6	1.0	1.1	10.5	9.4	7.2	2.3	7.4	1.0	0.4
9	20/09/12 11:00	808	4.43	8	15.1	0.3	0.7	14.4	12.0	8.0	2.4	5.4	1.3	0.2
10	24/09/12 11:30	473	4.90	7	5.7	0.0	0.3	4.7	5.0	3.4	1.3	2.6	0.9	0.2
11	25/09/12 10:30	1236	6.14	15	0.1	0.0	0.0	0.3	0.5	0.3	0.2	0.3	0.2	0.0
12	26/09/12 10:45	723	6.86	12	4.9	0.2	0.3	6.1	5.5	4.2	1.3	2.8	0.7	0.2
13	27/09/12 09:30	1365	8.23	20	8.7	0.5	0.3	6.6	5.5	4.3	1.3	2.8	0.7	0.2
14	28/09/12 10:30	2067	10.29	12	7.6	0.5	0.4	8.6	8.2	7.8	2.2	4.3	1.0	0.4
15	02/10/12 15:00	628	10.92	8	8.2	0.0	0.5	9.0	8.7	6.7	2.1	4.4	1.1	0.3
16	04/10/12 10:30	1044	11.97	4	3.7	0.1	0.2	3.3	4.0	4.0	1.2	2.3	0.6	0.3
17	07/10/12 09:00	448	12.41	13	11.6	0.1	0.3	7.1	5.7	4.2	1.4	3.0	0.7	0.2
18	10/10/12 13:00	548	12.96	8	6.0	0.0	0.3	5.6	5.9	5.1	1.6	3.2	0.8	0.3
19	18/10/12 11:00	2500	15.46	46	2.8	0.0	0.2	2.3	2.9	2.8	0.9	1.7	0.5	0.2
20	30/10/12 11:00	647	16.11	6	7.8	0.1	0.5	9.7	9.2	7.2	2.6	5.0	1.3	0.4
21	05/11/12 14:00	1390	17.50	23	2.2	0.0	0.2	2.3	2.9	2.7	1.1	1.8	0.6	0.3
22	06/11/12 09:00	441	17.94	8	0.4	0.0	0.1	0.7	0.9	0.6	0.5	0.6	0.3	0.0
23	07/11/12 09:30	235	18.18	1	7.3	0.1	0.5	7.5	7.4	7.1	2.3	4.8	1.2	0.5
24	08/11/12 13:30	582	18.76	4	5.4	0.1	0.4	4.5	5.1	5.3	1.6	3.4	0.9	0.6
25	09/11/12 15:30	127	18.88	2	3.0	0.0	0.2	2.9	2.7	2.3	0.9	1.5	0.6	0.2
26	12/11/12 09:00	494	19.38	8	4.6	0.0	0.3	4.0	4.5	4.3	1.5	3.0	0.9	0.5
27	26/11/12 17:00	1909	21.29	20	3.4	0.1	0.3	3.2	4.1	4.3	1.4	3.0	0.8	0.7
28	05/12/12 14:00	432	21.72	6	0.0	0.0	0.1	0.4	0.7	0.1	0.3	0.2	0.3	0.0
29	17/12/12 10:00	1510	23.23	2	0.0	0.0	0.0	0.1	0.2	0.1	0.2	0.1	0.1	0.0
30-33	31/12/12 00:00	1167	24.40	6	4.5	0.0	0.3	4.0	4.3	4.8	1.8	2.6	0.9	0.7
34-36	11/01/13 14:00	4668	29.06	9	7.0	0.1	0.4	6.1	5.2	5.5	1.9	3.0	1.0	0.7
37-38	05/02/13 14:00	5000	34.06	13	4.2	0.0	0.3	3.7	3.7	4.2	1.4	2.3	0.8	0.7

Appendix 7: Concentrations of biocides in urban surface waters (sampling: May 7th 2013)

Sampling location	PPZ	DCOIT	TBU	OIT	IRG	TB	IPBC	DR	IP	CD	MCPP	BIT	MI
Damhus Sø	3.6	14.4	5.1	0.9	nd	nd	nd	2.2	2.4	2.5	26.7	nd	49.1
Damhusåen	3.1	21.2	2.6	nd	nd	nd	nd	6.8	1.9	1.1	nd	nd	40.4
Furesø North	4.1	38.1	3.5	37.7	nd	nd	4.0	2.2	3.6	4.9	nd	nd	nd
Furesø South	3.4	20.0	2.9	nd	nd	nd	nd	0.6	1.2	4.8	nd	nd	nd
Ørestad Channels	5.1	10.3	10.4	11.4	nd	nd	0.4	2.9	3.9	3.0	201.0	nd	nd
Ørestad Lakes	11.3	20.2	6.4	2.5	nd	nd	0.7	33.7	5.6	4.1	25.8	nd	nd
Ørestad North	5.5	12.3	3.2	5.9	nd	nd	1.6	1.4	1.6	1.9	nd	nd	nd
Peblinge Sø	6.0	6.1	2.3	nd	nd	nd	0.9	3.9	3.1	1.0	nd	nd	nd
Roskilde Marina	3.1	25.8	1.6	24.4	nd	nd	2.6	3.3	2.1	1.7	10.6	nd	nd
Sortedams Sø	2.2	24.5	2.7	17.7	nd	nd	1.1	2.4	3.8	nd	nd	nd	nd
St Jørgens Sø	1.0	22.7	0.9	13.4	nd	nd	1.5	0.5	2.2	0.9	nd	nd	nd
Sydhavn Cph	1.4	31.4	0.5	nd	nd	1.2	1.0	1.8	1.9	1.1	nd	nd	nd
Utterslev Mose	6.3	63.3	1.3	nd	nd	nd	0.6	nd	1.6	0.9	nd	nd	nd
Blank 1	nd	20.1	0.4	4.9	nd	nd	1.7	0.5	1.4	nd	nd	nd	nd
Blank 2	nd	33.8	0.4	nd	nd	nd	nd	nd	nd	nd	nd	nd	47.2

Appendix 8: Concentrations of biocides in urban surface waters (sampling: May 27th 2013)

Sampling location	PPZ	DCOIT	TBU	OIT	IRG	TB	IPBC	DR	IP	CD	MCPP	BIT	MI
Damhus Sø	3.9	11.0	3.3	nd	nd	nd	0.6	1.4	2.5	2.7	23.5	nd	nd
Damhusåen	22.1	9.0	15.6	nd	nd	nd	nd	4.2	7.0	9.7	nd	nd	nd
Furesø North	3.1	6.2	2.3	nd	nd	nd	0.4	0.5	nd	4.5	nd	nd	nd
Furesø South	3.1	17.4	1.9	nd	nd	nd	0.3	0.5	nd	4.1	nd	nd	nd
Ørestad Channels	8.8	10.5	8.9	nd	nd	nd	nd	0.8	2.4	3.3	57.5	nd	nd
Ørestad Lakes	12.2	12.1	5.1	nd	nd	nd	nd	38.6	nd	4.0	41.8	nd	nd
Ørestad North	2.5	9.1	1.3	nd	nd	nd	nd	nd	2.3	2.3	20.6	nd	nd
Peblinge Sø	5.7	7.9	1.5	nd	nd	nd	nd	0.7	0.6	1.1	nd	nd	nd
Roskilde Marina	3.3	28.2	1.8	nd	nd	nd	0.2	2.4	nd	3.4	13.3	nd	nd
Sortedams Sø	7.8	18.0	8.7	nd	nd	nd	0.3	0.2	nd	6.1	nd	nd	nd
St Jørgens Sø	nd	19.9	0.4	nd	nd	nd	0.3	nd	nd	nd	nd	nd	nd
Sydhavn Cph	4.7	12.8	2.6	nd	2.6	0.9	0.3	3.3	nd	2.6	nd	nd	nd
Utterslev Mose	nd	42.3	2.1	nd	nd	nd	0.3	0.8	3.8	1.8	12.1	nd	nd
Blank 1	nd	13.3	nd	nd	nd	nd	nd	nd	nd	5.2	nd	nd	6.0
Blank 2	nd	6.9	nd	nd	nd	nd	nd	nd	nd	2.5	nd	nd	nd

Water driven leaching of biocides from paints and renders

In this report, the leaching of biocides from renders in laboratory as well in outdoor experiments is described. Additionally the occurrence of these biocides in urban stormwater, in combined wastewater as well as in urban surface waters is described and brought into context with its sources.

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