Decreased bio-inhibition of building materials due to transport of biocides

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Bio-inhibition of buildings and structures is an important issue. In many cases building materials have biocides added to prevent growth of micro-organisms. Growth of micro-organisms on building materials has several negative effects; (1) Aesthetic damage, e.g. fungi, algae grow on the material, resulting in early replacement and high cleaning costs, (2) Material damage, and (3) Health problems. However, current legislation forces manufacturers to reduce the biocide load, which requires manufacturers to look for alternatives or other improvements. One way is to increase the efficacy of biocides. There are several factors which rule the efficacy of a biocide in a building material. In this paper we will give a short overview of the mechanisms that lead to a decrease in efficacy of biocides. One of the mechanisms, leaching into and from the materials is researched by using leaching experiments. This because leaching of biocides into and from building materials has not been researched to a great extent. In our experiments the leaching of Propiconazole (Wocosen 50TK) has been tested in gypsum layers applied on aerated concrete. The sample was then placed into an artificial rain setup which releases the biocides. The analyses of the samples show that the biocide leaches out of the gypsum layer and simultaneously into the aerated concrete. From the results it may be concluded that a biocide will leach from a plaster into an aerated concrete wall, which opens opportunities to improve the biocide efficacy by preventing this process from occurring.

Key words: Fungal growth, bio-inhibition, biocides, transport, moisture, building materials

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1 Introduction

1.1 General introduction

Bio-resistance of buildings and finishing materials usually requires addition of dedicated bioactive chemicals, so-called biocides. Two main reasons exist why biocides are added to materials for constructions. First of all, micro-organisms negatively affect the durability of material, i.e. induce biodegradation. Secondly, biocides are also used to prevent the growth of micro-organisms (algae, fungi and bacteria) that create unhealthy indoor environments or affect the esthetic value of the materials. Nowadays, several challenges exist with respect to adding biocides to materials; (1) Short bio-resistance of materials leads to early replacement and (2) environmental legislation restricts use of biocides and chemicals. These two challenges will be discussed, respectively.

Coatings in the built environment usually exhibit biocidal functionality between 0.5 and 2 years in extreme conditions, whereas the desired service life in building practice is at least 10 years. Application of an increased biocide concentration only results in a minor prolongation of the material service-life. Besides the environmental impact of early replacement of such functional coatings, an inherent disadvantage is the emission of a relatively large amount of biocide molecules into the environment. In addition, the limited bio-resistance of the material will allow the growth of micro-organisms, which negatively affect health, leading to hypersensitivity and allergic reactions such as rhinitis and asthma. This is a problem prevalent in homes and occupational buildings worldwide [1, 2]. A total of 11% of the entire global burden of disease has been attributed to unhealthy buildings. A recent pan-European housing survey by WHO clearly indicates a link between present-day housing conditions and human health and well-being. Therefore, the performance of biocide containing materials needs to be improved. Besides paints a similar discussion can be held for other materials, e.g. plasters.

The second challenge is the fact that the growing ecological demands and international environmental legislation increases even more the pressure on the materials' performance [3]. First, the application of active agents for materials' bio-resistance is regulated by the Biocidal Product Directive 98/08/EC, which sets strict conditions with respect to the use of bio-active agents [4]. On 12 June 2009, the European Commission adopted a proposal for a Regulation concerning the placing on the market and use of biocidal products (COM(2009)267). The proposed Regulation will repeal and replace the current Directive

98/8/EC concerning the placing of biocidal products on the market. The objective of the proposal for a Regulation concerning the placing on the market and use of biocidal products is to improve the functioning of the internal market in biocidal products while maintaining the high level of the environmental and human health protection. The proposed regulation is scheduled to enter into force on 1 January 2013. And second, the industrial trend towards eco-friendlier building products is often accompanied by an increase in the biodegradability, requiring even more biocides to compensate.

Consequently, new developments are required, in principle if the biocides can be made more effective, this would decrease the amount required.

The main question rises: *How can we make the biocides more effective?*

Figure 1. Fungal growth in a living room, a bathroom and algal growth on plaster

Traditionally, the action of biocides in materials, (e.g. coatings, plasters) is based on a passive and uncontrolled release principle, i.e. molecular dispersion of the active ingredients in the material matrix. As a consequence these bio-active agents have a high and inherent mobility in the matrix, which causes an initial boost in biocide activity and a steep decrease when time proceeds. Only when the biocides are present at the location, at which they are required to prevent the micro-organisms from growing, they are effective. To increase the effectiveness of the biocides one can think of solutions, for instance applying slow or smart release mechanisms. Currently, research is focussing at ways to implement these mechanisms inside materials. This is the work performed in the European project AXIOMA: "smart release of biocides in finishing materials for the sector of construction". In this paper we focus on determining how transport of biocides affects the efficacy. For that purpose, the main question to be answered is: What is the dominating factor that rules the efficacy of the biocide in a building material? Nowadays it is not clear whether active components of the material, such as biocides, lose efficacy by degradation or due to release from the material or into the construction itself (consequently the concentration at the surface diminishes). In this paper we address the following question: *Do we have leaching into the construction or material?*

2 Biocide efficacy

The efficacy of biocides depends on many factors, first of all the stability is of major importance. Secondly, the biocides should not be released (or leached) too easily from the materials. And thirdly, should not distribute throughout the construction or underlying materials. In this section we will discuss stability and leaching of biocides.

*2.1 **Stability***

The stability of biocides depends on their physico-chemical properties and the environmental conditions (including material matrix) to which they are exposed5. Biocides comprise a broad range of molecules with very different properties; consequently their stability properties and degradation mechanisms cannot be generalized. For example, studies on the most popular biocides in use such as Irgarol 1051 and diuron, persist in surface waters, while others, such as SeaNine 211, dichlorofluanid, zinc pyrithione, and chlorothalonil, disappear quickly [6].

Most of the research studies regarding degradation of biocides focus on determining the life time of specific biocides under particular environmental conditions, mainly in soil and water. However, the mechanisms of degradation and the factors that determine are not well understood. Some biocides are metabolized by plants [7] and others are photo-degraded [8]. In addition, the knowledge on biocides in building material matrix is very limited and mainly restricted to wood [9] and antifouling paints in a minor extent. With respect to cement matrix, we may assume that additives in it will not easily decay by microorganisms because these microorganisms will not find the optimal conditions to live (moisture content, nutrient availability pH, etc).

2.2 *Propiconazole*

Propiconazole is chemically stable and will not undergo hazardous polymerization and can be only affected by oxidizing reagents, which will induce as decomposition products carbon monoxide, carbon dioxide, nitrogen oxides and hydrogen chloride gas. Although it can be metabolized by some species of microorganisms through oxidation reactions [7], a good evidence of its stability is the persistence in the environment, such as in surface waters and sediments [10]. In fact, studies of degradation in soil, where the concentration of microorganisms is higher than in building materials, show that the half-life of this biocide can exceed de duration of 1 year [11, 12]. The authors of the study suggested that the formation of bound residues of propiconazole contributes to the persistence of this fungicide in soil. The main factor affecting the degradation rate in soil is temperature: it increases about 3-fold as the temperature was increased from 5 to 18 °C. Decreasing of soil moisture to 60% field capacity only slightly slowed degradation12.

2.3 *Leaching of biocides into and from building materials*

There are few research studies that deal with leaching, migration and/or diffusion processes of biocides in building materials. Studies of biocides in wooden façade paints demonstrated that the biocide IPBC migrates towards the surface as well as into the wood. It is well known from antifouling that during normal use (e.g. paint on a ship's hull), biocides are directly released from the paint surface into the water and persist according to their physico-chemical properties and the conditions of the environment to which they are released.

Leaching of hazardous substances commonly contained in concrete was also investigated [13]. Leaching curves of different metals from concrete additives showed great variations when compared with one other, but a very uniform behaviour for different concrete types, which highlight the importance of the bonding characteristics between substances and material matrix. In addition, they found a lack of correlation between leachability and total concentration of the hazardous substances. In conclusion, study suggests that the leaching depends on the solubility and the way the substance is bound to the cement matrix.

A review by Hingston et al. [14] on leaching of Cr-Cu-As wood preservatives summarizes that leaching rate is dominated by salinity, pH, and the size of the wooden blocks used during laboratory leaching trials. The authors emphasize that direct comparison of results from laboratory and fieldwork is difficult, due to the varying effects of numerous parameters, particularly wood species, loading, and environmental conditions. But similarly to cement matrix, they could affirm that leaching of individual metal elements is not proportional to the concentration in the original formulation.

It can be concluded that many questions exists with respect to leaching of biocides in materials, and that not much studies have been performed, which forms the reason for this study. Consequently, in the next section the leaching of Propiconazole is evaluated in building materials.

3 Experiments to determine leaching-out and leaching-in

In this experiment the behavior of Propiconazole (active ingredient of Wocosen 50TK,) will be tested in gypsum blocks. The objective is to find if biocides besides leach from a plaster layer will also migrate from the plaster layer into the wall, “leaching in”. In order to test this, a leaching test has been devised. In the first section the preparation of the materials is described followed by a description of the used leaching setups. In the subsequent section, the preparation of samples and the chemical method to determine the concentration distribution of Propiconazole in the material is explained.

*3.1 **Experimental details***

To study the leaching into substrate materials, ten replicates have been made of each type of sample. The following types of samples were prepared;

A. A gypsum layer of $100 \times 150 \times 3\ mm^3$
B. An aerated concrete block of $100 \times 150 \times 50\ mm^3$ with on top a 3 mm thick gypsum layer.

To prepare the gypsum layers, a solution of Wocosen in ethanol is prepared, because of its low solubility in water. The following formulation was used:

- 75 g Wocosen EtOH, a solution of 2,16g Wocosen in 450g EtOH
- 165 g Demi-Water
- 360 g $CaSO_4 \cdot ½H_2O$

The biocide gypsum was poured into the used molds and the excess was removed. The gypsum was then dried for at least 3 days.

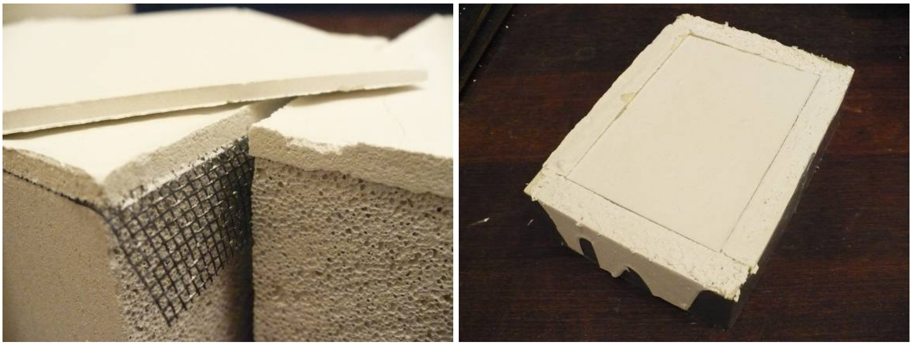

Figure 2. Left side, close up of the types of samples, right side a gypsum block in Styrofoam mold with biocide gypsum layer

3.2 ***Leaching method***

The artificial rain setup (Figure 3) consists of a water reservoir tank, a clock timer, two water pumps, eight spray heads, a large mesh (±1cm), a small mesh (±1mm), sample stage and a water drainage system. The clock timer is programmed to turn on the pumps for two minutes every day at 2 am and 2 pm. The water is then pumped from the reservoir tank to the rain setup. Eight spray heads, located at the top of the setup, spray 4.5 l/min of water. The water runs through a large mesh and then through a small mesh. The mesh is used to create a homogenous distribution of the rain. The rain then wets the samples and drains out through the drainage system. To dry the samples two 375 Watt lamps were fixed at both sides of the setup. These were turned on constantly and were turned off during raining. One sample was taken out of the artificial rain setup every week after 14 leaching

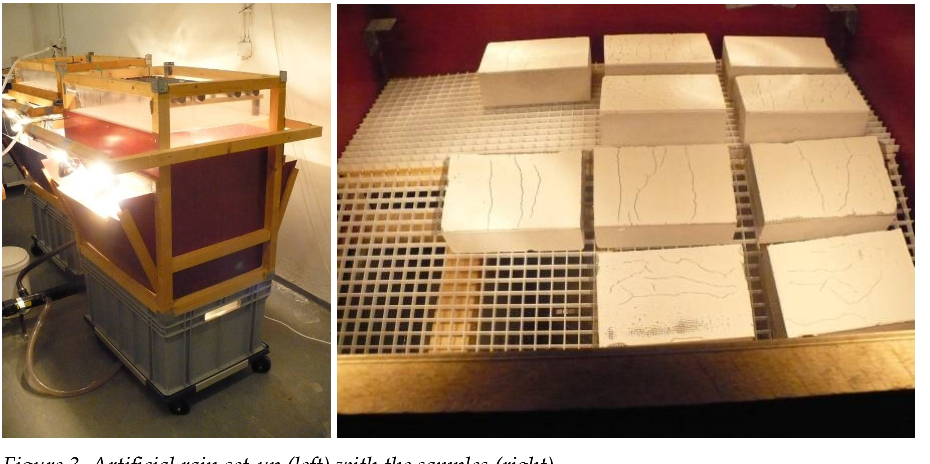

Figure 3. Artificial rain set-up (left) with the samples (right)

cycles. The samples were coded with the week number (1-10) followed by the sample type code (A, B). The samples were then prepared for analysis using HPLC as described in the next section.

3.3 *Preparation for HPLC analysis*

From samples of type B, 4 layers have been taken which have been analysed. The samples were cut using a diamond blade circular saw. The samples were cut without water cooling, so that no extra leaching could occur. The saw used was not able to cut through a 5 cm high sample so the samples have first been cut into 3-4 cm wide strips. Then Layers B1, B2, B3 and B4 were cut out of the strips and stored in plastic sealed bags. The width of the saw blade was taken into account. The layers were numbered 1 to 4, respectively top to bottom. The obtained layers were crushed manually using a steal mortar. The concentration of Wocosen in the powder was then analysed, following the procedure described in section 3.4. All layers were crushed individually.

3.4 *HPLC analysis*

In order to quantify the amount of residual Wocosen in the gypsum samples an ethanolic extraction was used. Previous experiments have shown that an ethanolic extraction does not produce high recovery. The reason for a low recovery using only ethanol is that biocide encapsulated inside the gypsum crystalline lattice will not be recovered. A method was developed that results in the total dissolution of the gypsum matrix using a di-sodium EDTA / ammonium carbonate solution.

3.4.1 *Procedure of HPLC analysis*

The gypsum sample is weighed into a glass jar. Subsequently a weighed amount of di-sodium EDTA / ammonium carbonate (consisting of 150 g di-sodium EDTA, 100 g ammonium carbonate and 1000 ml demi-water) is added (approx. 100 g). This mixture is stirred overnight in the closed jar to obtain virtually complete dissolution of the gypsum matrix material. Subsequently 50 g of Ethanol is added to ensure complete dissolution of Wocosen. After this, a sample is taken from the extraction liquid and filtered over a 0,45 μm syringe filter. This sample is analysed using a Waters HPLC apparatus with an omnispher 5 C18 column and a UV detector operating at dual wavelengths of 220 and 270 nm.

4 Results

The results from the HPLC analysis are given in mg/g. However, this does not provide a good representation of the Wocosen distribution in the sample. As layers A and B1 are made out of gypsum their density is much higher then that of layers B2, B3 and B4 which consist of aerated concrete (Table 2). If a layer of gypsum and a layer of aerated concrete contain the same mg/g Wocosen, the layer of gypsum will contain more Wocosen. For this reason all data have been converted to mg Wocosen per layer. Using the density the weight of material in each layer is calculated (Table 3). In order to obtain the amount of Wocosen per layer the amount mg/g is multiplied by the weight of each layer (Table 4).

The amount of Wocosen per layer is shown in Figure 4. Sample A, which is only a biocide containing gypsum layer, shows a fast decrease in Wocosen concentration in the first 3 weeks. This proves the biocide is soluble in water and leaches out from the gypsum.

Table 2: Density of the material

	Gypsum	Aerated concrete	unit
Volume	45	343.75	cm^3
Weight	69	121.8	g
Density	1.5	0.4	g/cm^3

Table 3: Weight of each layer

layer	A	B1	B2	B3	B4	unit
Volume	45	45	45	45	45	cm^3
Density	1.53	1.53	0.35	0.35	0.35	g/cm^3
Weight	69	69	15.94	15.94	15.94	g

Tabel 4: mg Wocosen per layer

weeks	0	1	2	3	4	5	6	7	8	9
A	40.39	25.00	4.85	2.18	1.33	0.00	0.00	1.41	1.56	0.00
B1	14.57	10.49	6.86	6.26	7.24	7.07	6.00	5.48	5.28	3.54
B2	1.47	0.00	3.47	1.39	1.32	1.40	1.44	1.33	1.51	0.71
B3	0.00	1.12	0.72	0.25	0.42	0.50	0.56	0.53	0.80	0.19
B4	0.00	0.00	0.00	0.10	0.33	0.31	0.39	0.30	0.37	0.09

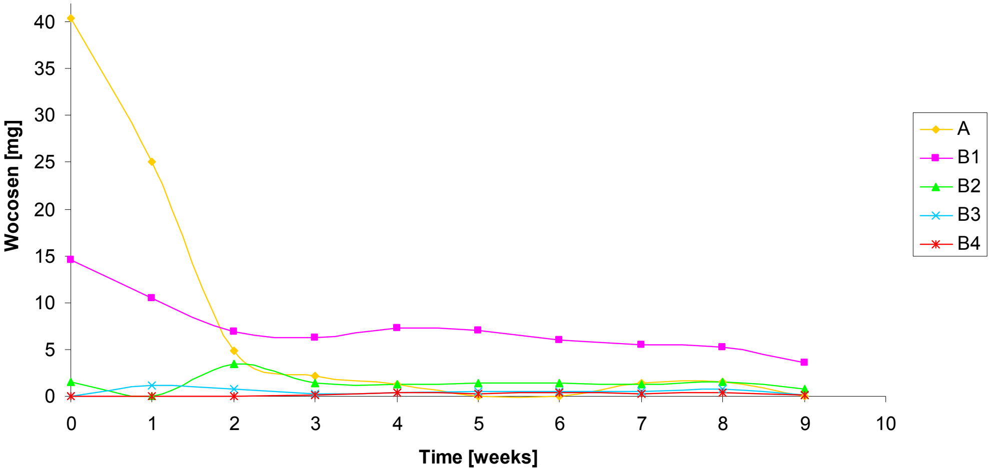

Figure 4. Amount of Wocosen in time in sample A and B

Sample B1 is a 3 mm thick gypsum layer containing Wocosen, which has been applied to an aerated concrete block. It was expected layer B1 would show the same amount of Wocosen at $t = 0$ compared to sample A, which is not the case. The explanation for this is that the gypsum layer containing biocide has been applied to a dry aerated concrete block. The dry aerated concrete acts like a sponge and so instantly takes up a volume of liquid containing Wocosen, thus extracting some Wocosen from gypsum layer B1 during application. This then also explains the Wocosen present in sample B2 at $t = 0$.

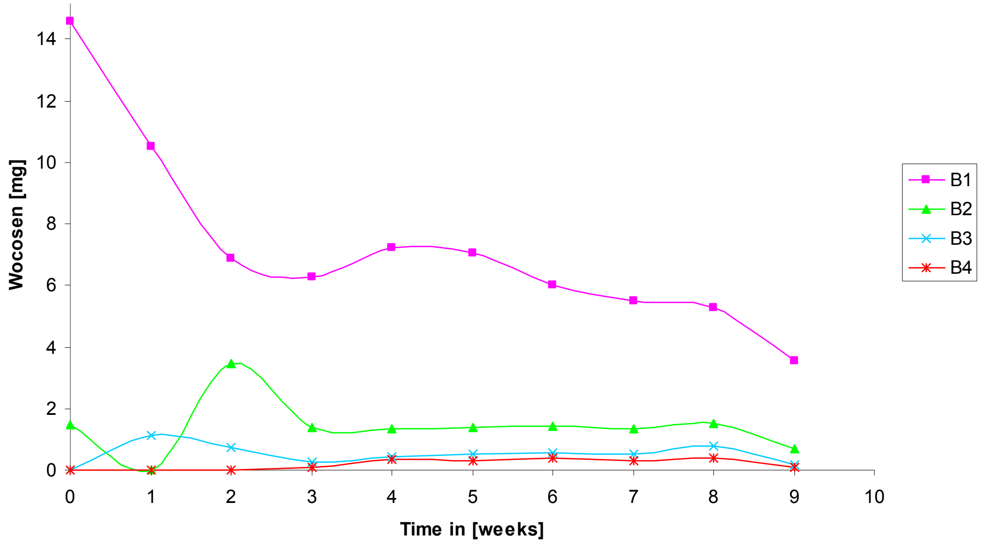

Figure 5. Amount of Wocosen in time in sample B

Figure 5 shows the amount of Wocosen in the layers of sample B only. After one week of artificial rain layer B3 starts to show an amount of Wocosen, this implies that the biocide has travelled through layers B1 and B2 down into layer B3.
The same can be said for layer B4. This layer does not show any Wocosen for 3 to 4 weeks of leaching. After 4 weeks of rain a small amount of Wocosen can be detected. This also implies the biocide has travelled from layers B1 and B2, through layer B3 into layer B4. Thus the biocide has "leached into" the sample.

Figure 6 shows a concentration profile of sample B. Remarkable is that the lines level out as the time increases. The amount of Wocosen decreases but is also distributed over the entire sample. This can only happen when the Wocosen travels from layer B1 trough the sample to layer B4. Thus as the water is absorbed into layer B1 the Wocosen in that layer dissolves and travels along until the sample dries. This is another proof that the biocide does not only leach from the sample but also "leaches into" the sample.

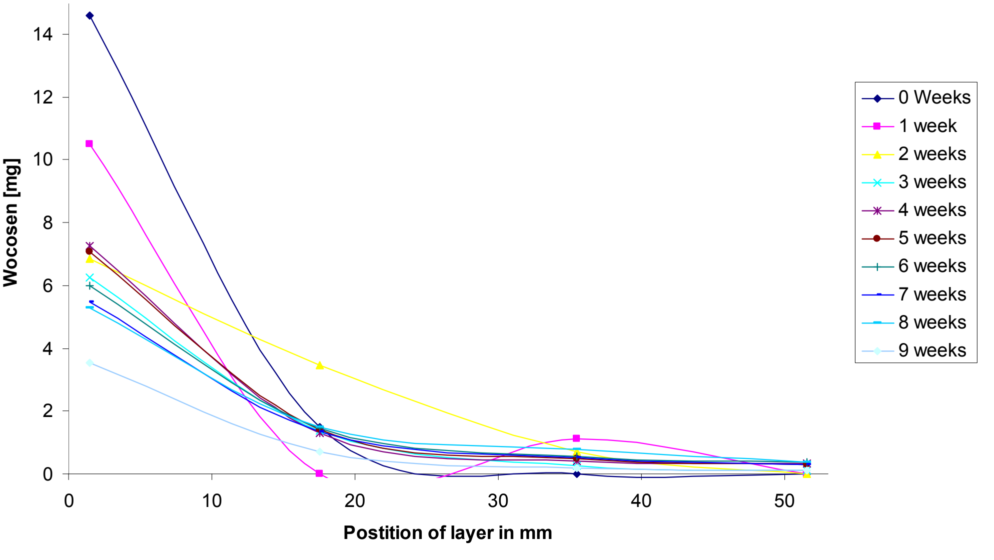

Figure 6. Concentration profile of sample B per week

5 Conclusions

Wocosen is soluble in water and water is absorbed by the gypsum layer and the gypsum block. As the water is absorbed by the top layer, it dissolves the Wocosen, travels further down the sample and transports the biocide to the lower regions of the sample. As the artificial rain is then stopped and the sample is allowed to dry, the water is removed and the Wocosen is left behind, in a new layer of the sample. After 1 week layer 3 shows an increase in Wocosen concentration, and layer 4 also shows a small increase after 3-4 weeks. As layers 3 and 4 did not contain Wocosen at the beginning of the test and did contain Wocosen after artificial rain, the Wocosen must have transported through the samples to the bottom, thus the Wocosen has leached into the sample.
The fact that this process happens, even directly after application of a wet layer, means that the effective concentration at the surface is lower. This process clearly depends on the sorption properties of the substrate applied on. Consequently, application of all kind of release technologies, under development (e.g. in Axioma project), could be hindered. Therefore, methods could be thought of to prevent leaching of biocides into a substrate material, e.g. introducing a hydrophobic layer or prevent initial water uptake by impregnating the substrate material.

6 Outlook

Investigations at TNO and within the European project “Axioma” on the field of modelling will contribute in understanding the above measured processes. With this knowledge the effective concentration at the surface can be modelled. Clearly, several factors play a dominant role:

1. Leaching of biocides to the environment
2. Degradation of biocides
3. Transport of biocides into substrate layers

In many cases we think that the latter process is forgotten and further research is needed to better understand this phenomenon.

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