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## Release and environmental impact of silver nanoparticles and conventional organic biocides from coated wooden façades



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## ABSTRACT

This study represents for the first time a comprehensive assessment of functionality and environmental impacts of metallic silver nanoparticles (Ag-NP) compared to conventional organic biocides. Four different transparent, hydrophobic coatings of wooden outdoor façades were tested during one year outdoor weathering.

The total silver release from products with Ag-NP was proportional to the overall erosion of the coating. The results indicate that the Ag-NPs are likely transformed to silver complexes, which are considerably less toxic than ionic silver. The protective effect of the silver containing coatings against mold, blue stain and algae was insufficient, even in immaculate and non-weathered conditions. The release of organic biocides from conventional coatings was dependent on the weather conditions, the type of biocide and the use in the base or top coat. The conventional coating showed a good overall performance free from mold, blue stain and algae until the end of the test period.

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### 1. Introduction

About 8 million square meters of façades treated with biocidal coatings are built in urban agglomerations in Switzerland every year (Burkhardt, 2006). With 16% for new houses and 29% for reconstructions, wood is the second most common façade building material behind plaster (Andexlinger, 2006). The use of water-based coatings for façades increases the consumption of biocides, as nearly all water-based coatings contain at least in-can preservation substances. Additionally, the trend to increase energy efficiency of buildings by using thick thermal insulation layers results in colder external surfaces and consequently enhances moisture condensation on the outer building envelope. Therefore the demand of functional coatings to avoid settlement and growth of microorganisms is increasing.

In wood coatings, mainly fungicides such as IPBC, propiconazole, tebuconazole, tolylfluanid or dichlofluanid are used. Limited information is available about the release of these biocides out of wood coatings during service life, and only little knowledge exists

about their fate and behavior in the urban storm sewer and the environment. Previous investigations have shown that especially IPBC (3-Iodo-2-propynyl butyl carbamate) was released very easily out of water-soluble coating systems on wood (Bjurman, 1995; Lindner, 1998; Volkmer and Schwarze, 2008). Biocides such as diuron, carbendazim and irgarol were detected in treated waste water and sewage sludge as well as in natural waters in Switzerland (Burkhardt et al., 2005).

Regarding the general environmental discussion about biocides, the industry is looking for alternatives to replace conventional biocides in coating systems. Based on its strong toxicity among a wide range of microorganisms combined with a low toxicity to humans, silver appeared to be a possible alternative.

The global production of silver is about 28 000 tons per year, with 0.5 percent in biocidal products. A survey in 55 companies, which trade with biocidal products, indicated that about 91% of the silver is used in ionic form and only about 9% in form of Ag-NPs (Kemper, 2008).

Nowadays several silver containing coatings for indoor and outdoor application exist, but represent still a niche market. Typically, silver concentrations up to 20 000 ppm are used to achieve antibacterial properties of products. In contrast the silver content in transparent coating systems is only around 100 ppm (Hund-Rinke et al., 2008), what might limit its antimicrobial efficiency.

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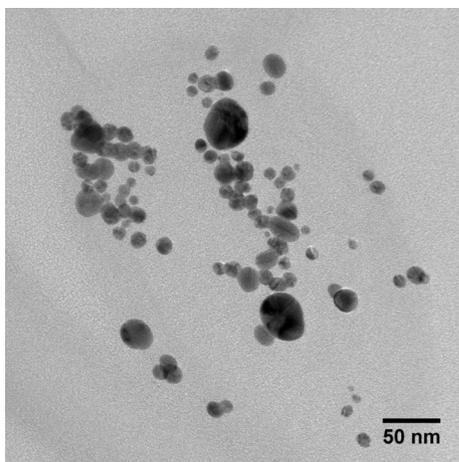


Fig. 1. Representative TEM image of Ag-NP in the coating formulation HySiwAg.

A comprehensive overview about the environmental and health effects of nanomaterials in textiles and façade coatings is given in Som et al. (2011). Different studies describe the toxic effect of Ag-NPs mainly on bacteria but also on other organisms such as fungi or algae (Marambio-Jones and Hoek, 2010; Fabrega et al., 2011; Musee et al., 2011). Thus it is still unproved, if Ag-NP can act as a suitable fungicidal agent in wood coatings. First results of another study indicated that presently the protective effect of Ag-NPs in wood coatings is not comparable with conventional biocides (Plaschkies et al., 2010).

Very limited information is available about the release of Ag-NPs out of façade coatings and their fate and behavior in the environment. To our knowledge, only one study (Kaegi et al., 2010) investigated the release of Ag-NPs from mineral façades during weathering. It was found that after only one year 30 percent of the Ag-NPs were released to the environment. Monodispersed carbonate-coated Ag-NPs agglomerated in natural water within a few days (Piccapietra et al., 2012). Agglomerated Ag-NPs seem to be more stable in natural water than single Ag-NPs, thus release silver at a faster rate (Li and Lenhart, 2012).

An integrative and comprehensive study on both, functionality and environmental safety of Ag-NPs in façade coatings was never carried out. Thus and to extend the knowledge about applications on wooden façades, we investigated the functionality and the safety

of Ag-NP-containing, hydrophobic and transparent coating systems for outdoor applications on wooden façades.

## 2. Experimental methods

### 2.1. Experimental setup for weathering tests

Industrially manufactured lamellas made of Norway spruce (*Picea abies*) were used to produce laboratory scale façade elements (horizontal planking) with an area of  $0.75 \times 1.44 \text{ m}^2$ . Four different water-based, transparent and hydrophobic coating systems were selected and applied according to the manufacturer recommendations. The two silane based, non-film forming agents are comparable coatings in terms of hydrophobicity. The two alkyd based coating systems are film forming and less hydrophobic. All four products are available on the market and except (HySi) labeled as antimicrobial. Product (AARwB) contains IPBC and propiconazole, two of the mostly used fungicides in wood coatings. The coating systems were:

- **Hydrolysed Silane with 46 mg/kg Ag-NP (HySiwAg)**
- **Hydrolysed Silane without Ag-NP (HySi)**
- **Oily Alkyd Resin with 2 mg/kg Ag-NP (OARwAg)**
- **Alkyd/Acryl Resin with organic Biocide (2.28 w% propiconazole and 0.18 w% IPBC) (AARwB)**

The silver and the organic biocide content of the coatings were determined before application (Chapter 2.4.1 and 2.4.2). Nano silver, as shown in Fig. 1, with a diameter range of mainly 10–30 nm was used in the tested coating HySiwAg.

The façade elements were installed vertically on metal racks at Empa premises. They were exposed to the direction SW ( $220^\circ$ ) from June 2009 to June 2010. Climatic parameters were monitored continuously on a nearby weather station.

### 2.2. Erosion rate of the coating

The erosion rate of a façade coating is the overall material loss during a defined time period and includes all processes that can lead to a loss of material (e.g. weathering, mechanical abrasion, deterioration by microorganism). The material loss was assessed by measuring the coating thickness and/or quantification of

**Table 1**  
Test conditions and rating factors; antimicrobial effect of the coatings.

	Blue stain	Mold	Algae
Microorganisms	<i>Aureobasidium pullulans</i> , <i>Sclerophoma pithyophila</i>	<i>Aspergillus versicolor</i> , <i>Cladosporium sphaerospermum</i> , <i>Penicillium purpurogenum</i> , <i>Phoma sp.</i> , <i>Alternaria sp.</i>	<i>Chlorella vulgaris</i> , <i>Chlorella emersonii</i> , <i>Stichococcus bacillaris</i> , <i>Pleurococcus sp.</i> , <i>Anacystis montana</i>
Samples	6	6	6
Incubation time	6 weeks	6 weeks	12 weeks
Condition	22 °C, 70% rH	23 °C, 70% rH	Room temp. and humidity; location: window to north
<b>Rating</b>			
0	No affection	No affection	No affection
1	Minor affection, max. 10 single spots smaller than $\varnothing$ 2 mm	Mold only visible under microscope	Algae only visible under microscope
2	Visible affection, up to 50% of the tested surface	Visible affection, up to 25% of the tested surface	Visible affection, up to 25% of the tested surface
3	Visible affection, more than 50% of the tested surface	Visible affection, up to 50% of the tested surface	Visible affection, up to 50% of the tested surface
4	–	Visible affection, more than 50% of the tested surface	Visible affection, more than 50% of the tested surface
5	–	Visible affection, 100% of the tested surface	Visible affection, 100% of the tested surface

representative elements (Si for coating HySiwAg and HySi, Co for coating OARwAg).

### 2.3. Functional performance test/antimicrobial effect

The protective effect against three groups of representative microorganisms was tested on original (non-weathered) and on two month weathered samples. First of all, the samples were stored for 2 weeks under controlled climate conditions (20 °C, 65% rH). Afterward test samples were sterilized with ethylene oxide for 1 h under vacuum (0.65 bar, 55 °C) and then placed in the test vessels on Vermisol® Vermiculite. The pretreated samples were inoculated with the microorganisms and incubated and controlled during a defined time period. The test conditions and the rating factors are listed in Table 1. At the same time, growth and activity samples were run additionally to control the vitality of the used microorganisms. More detailed information is given in Künniger (2011).

### 2.4. Analytical investigation of the runoff water

The runoff water was dissipated over stainless steel gutters into glass bottles and collected after each rainfall event during one year. The runoff was stored in VWR® sterile sampling bags in the freezer at –20 °C for chemical analysis of the organic biocides and for toxicological tests. In addition separate runoff samples were filled in centrifuge tubes and used for chemical analysis (see 2.4.1) and microscopic investigations of the Ag-NP.

#### 2.4.1. Chemical analysis of the organic biocides

After thawing the frozen runoff at room temperature, the biocides IPBC and propiconazole were analyzed by LC–MS/MS (liquid chromatography–mass spectrometry/mass spectrometry Agilent 1290/6460) after adding an isotopically labeled standard (<sup>2</sup>H<sub>5</sub>-propiconazole) to the solution. Samples with a concentration above the linear range had to be diluted with H<sub>2</sub>O–Millipore before chemical analysis. The compounds were separated on a reversed phase column (type RP-18) using a methanol/water gradient. Ionization was achieved by electrospray in the positive mode. Two collision induced transitions were monitored for each compound; one was used as quantifier, the other as qualifier.

The same procedure was used to determine the initial content of the organic biocides in the original coatings.

To quantify the residual biocide content of the coatings on the wood samples, about 400 μm of the surface (wood including coating) were removed using a microtome. The samples were extracted two times with methanol in an ultrasonic bath. After preparation, the solutions were analyzed as described above.

#### 2.4.2. Chemical analysis of the Ag-NP

To analyze the silver content, 0.5 ml nitric acid (Suprapur®, 65% w/w) was added to centrifuge tubes (50 ml Cellstar® Greiner Bio-One, polypropylene) containing 50 ml of runoff water. The acidified samples were measured using a Perkin Elmer/Sciex Elan 6000 inductively coupled plasma mass spectrometer (ICPMS) against external calibration. All metal standards were produced from single element standards. Rhodium was used as an internal standard.

To determine the initial content of silver in the original coatings the same procedure was applied.

To quantify the residual silver content of the coatings on the wood samples, about 400 μm of the surface (wood including coating) were removed using a microtome. The silver containing samples were digested in an acid mixture prepared from 5 ml nitric acid and 2 ml hydrochloric acid (both from Merck, Suprapur® quality) and analyzed by ICPMS.

Beside the total silver content, it was interesting to identify possible transformation processes such as dissolution of the Ag-NP in the runoff as well as in the original coatings. Therefore, three additional methods were applied.

First, an optical characterization was performed, to identify Ag-NP. Runoff water was deposited directly onto TEM grids (Formvar–Carbon coated Cu-grids). To increase the particle concentration, some were placed by centrifuge 4–5 ml runoff water onto the Cu-grids using a swinging bucket rotor (2 h at 4300 rpm). The coating HySiwAg was also deposited directly onto the TEM grids as received, while coating OARwAg had to be diluted with hexane at a ratio of 1:1 before depositing onto the grid. The grids were investigated using a TEM (Transmission Electron Microscope Jeol FS 2200) operated at an acceleration voltage of 200 kV in the scanning mode. The Ag-NPs were localized using a HAADF (High-Angle Annular Dark Field) detector and identified with an EDX (Energy Dispersive X-Ray) system (EDAX).

Second, to determine the size and size distribution of the Ag-NPs in the suspension, the NTA (Nanoparticle Tracking Analysis) method was applied. The runoff samples were injected into a viewing chamber. The particles contained in the samples are visualized by virtue of the light they scatter when illuminated by laser light. The light scattered by the particles is captured using a scientific digital camera and the motion of each particle is tracked from frame to frame. This rate of particle movement is related to a sphere equivalent hydrodynamic radius as calculated through the Stokes–Einstein equation.

Finally the DGT (Diffusive Gradients in Thin films) technique was applied for the *in situ* measurement of dissolved free Ag ions and labile Ag complexes, representing the bioavailable silver in the runoff, which can cause environmental damage. The DGT consists of three layers, which are the filter, the diffusion layer made of polyacrylic-hydrogel and the metal binding ion-exchange resin (Zhang, 2003). The DGT unit was exposed to the runoff solution. The established concentration gradient drives the silver from the solution to the ion-exchange resin. After 24 h, the ion-exchange resin was removed and the silver was eluted with nitric acid over a period of 24 h and afterward measured by using an Agilent 7500cx ICPMS (see above).

### 2.5. Toxicity tests

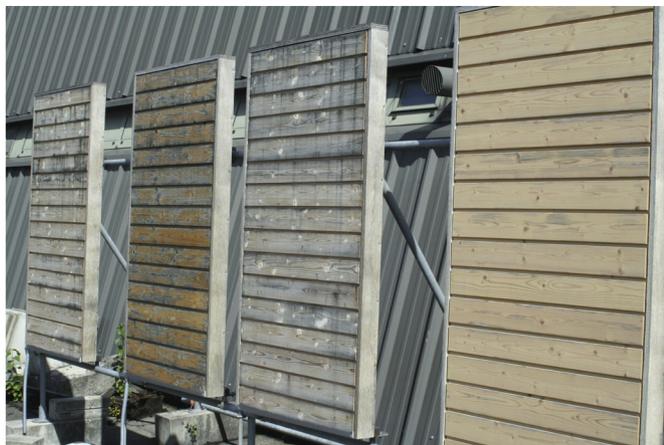
The aquatic toxicity of selected runoff samples was assessed by standard tests on three different water organisms.

- Algae (combined algae test with *Pseudokirchneriella subcapitata*).

This test measures the inhibition of the photosystem II (an effect often evoked by herbicides) and also growth inhibition as a measure for unspecific toxicity. The runoff and test medium were mixed 1:4. The inhibition of the photosystem II was measured after 2 and 24 h, the inhibition of growth after 0, 3.25, 18.5 and 23.5 h. Diuron

**Table 2**  
Antimicrobial effect, tested on origin (non-weathered) and outdoor weathered samples.

Samples	Blue stain after 6 weeks		Mold after 6 weeks		Algae after 12 weeks	
	Origin	2 month weathered	Origin	2 month weathered	Origin	2 month weathered
HySiwAg	2.5	3.0	3.5	4.75	2.75	2.5
HySi	2.5	3.0	4.5	5.0	2.5	2.5
OARwAg	2.5	3.0	4.5	4.5	2.75	2.5
AARwB	0.0	0.0	0.0	0.5	0.0	1.5



**Fig. 2.** Façades after 2 years outdoor weathering (from left: formulation HySiwAg, OARwAg, HySi, AARwB).

was used as a positive control, water as a negative control. For details see: [Quayle et al. \(2008\)](#).

- Bacteria (bacterial bioluminescence inhibition test with *Vibrio fischeri*).

This test determines the general, non-specific toxicity of the samples to bacteria. The runoff and test medium were mixed 1:4. The inhibition of the bioluminescence was measured after an incubation of 30 min. 3,5-Dichlorphenol was used as a positive control, water as a negative control (for details see: [Richter et al. \(2008\)](#)).

- Daphnia (acute immobilization test on *Daphnia magna*).

The test measures the acute toxicity on Daphnia. Undiluted runoff was used for the test with juvenile daphnia (<24 h of age). The immobilization was rated after 24 and 48 h. Water was used as a negative control (for details see OECD 202).

### 3. Results

#### 3.1. Protective effect against different microorganisms

The protective effect of the coatings against different microorganisms was tested on non-weathered samples and samples after 2

month outdoor weathering. Results are given in [Table 2](#) (for the rating rate see [Table 1](#)).

All coatings, except AARwB showed no protective effect against the tested microorganisms. Only the formulation AARwB with organic biocides was not affected by the studied microorganisms. These results from laboratory tests were confirmed by the observations made on samples during outdoor weathering ([Fig. 2](#)).

The use of the silane based coatings on wood leads to a time delayed affection of microorganisms compared to natural wood during outdoor weathering. This effect was also observed on other materials ([MacMullen et al., 2012](#)).

#### 3.2. Façade runoff

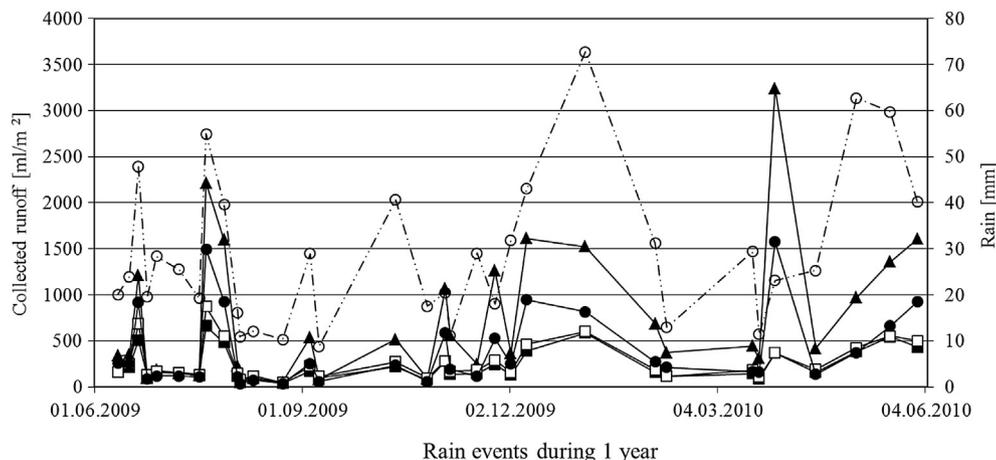
During a period of one year, the façade runoff from all rain events was collected. There were 33 rain events and the total rain amount was  $946 \text{ mm y}^{-1}$ . The mean pH-value for collected runoff water samples was  $\text{pH } 5.2 \pm 0.95$ . The samples were weighted and analyzed chemically for silver or organic biocides, depending on the coating.

[Fig. 3](#) shows the runoff volume ( $\text{ml/m}^2$ ) over the entire duration of the outdoor weathering. The collected runoff volume generally correlates with the amount of rainfall. The hydrophobic character of the façade surface influenced the runoff volume significantly. On the very hydrophobic surfaces HySiwAg and HySi, with initial contact angle of  $\sim 140^\circ$ , the total annual runoff volume was about  $8 \text{ l/m}^2$ , which corresponds to 1% of the total rain on a horizontal surface. On the less hydrophobic surface OARwAg (initial contact angle of  $\sim 94^\circ$ ), the total runoff volume was about three times higher ( $24 \text{ l/m}^2$ , 2.5% of the total rainfall on horizontal surface).  $13 \text{ l/m}^2$  were collected on coating AARwB, which had an initial contact angle of  $\sim 103^\circ$ .

#### 3.3. Release of organic biocide and silver

The organic biocide concentrations measured on the individual runoff events are given in [Fig. 4](#). While the IPBC concentration (contained in the top coat) strongly decreased during the first three rain events, the concentration of released propiconazole (contained in the base coat) stayed relatively constant during the one year of exposure. In total, 4.8 mg IPBC and 28.4 mg propiconazole could be detected in the runoff from  $1 \text{ m}^2$  façade with coating AARwB during the experiment, which corresponds to about 1% of the initial biocide amount contained in the applied coating.

In contrast to the very low organic biocide concentration measured in the runoff, a residual content determination of the



**Fig. 3.** Collected runoff during one year outdoor weathering per  $\text{m}^2$  façade element and rain event Rainfall in mm ---○---; runoff in ml on coating HySiwAg —■—; HySi —□—; OARwAg —▲—; AARwB —●—

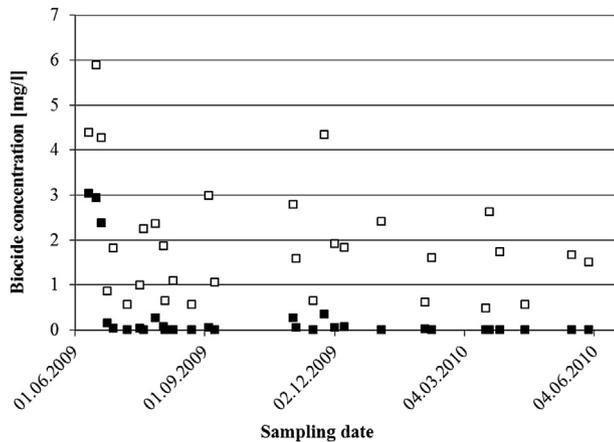


Fig. 4. Biocide concentrations of the runoff events during one year exposure of façade coating AARwB; ■ IPBC and □ propiconazole.

façade coating AARwB showed a 99% loss of IPBC and 36% loss of propiconazole after one year exposure (Fig. 5). The mass imbalance might be explained by transformation of the biocides (Directive-98/8/EC, 2007, 2008; Huang et al., 2008). Such transformation products are known to be less toxic and therefore they were not analyzed within this study.

The silver concentrations measured in the individual runoff events are given in Fig. 6. The Ag concentration in the runoff events of coating HySiwAg strongly decreased during the first three months. The concentration determined in the single rain events scattered between 1 µg/l and 21 µg/l. After the first three months until the end of the experiment, an average silver concentration of 0.67 µg/l in the runoff was measured.

In contrast the Ag concentration in runoff events of coating OARwAg was rather low with an average content of 0.1 µg/l during the first three months. During the next five months, the Ag concentration increased and varied between 0.08 and 0.86 µg/l. During that time also a visual degradation of the façade was observed. After a period of eight months, the Ag content in the runoff was below the detection limit of 0.01 µg/l.

The total amount of released silver in the runoff from 1 m<sup>2</sup> façade during the experiment was 15.7 µg for coating HySiwAg and

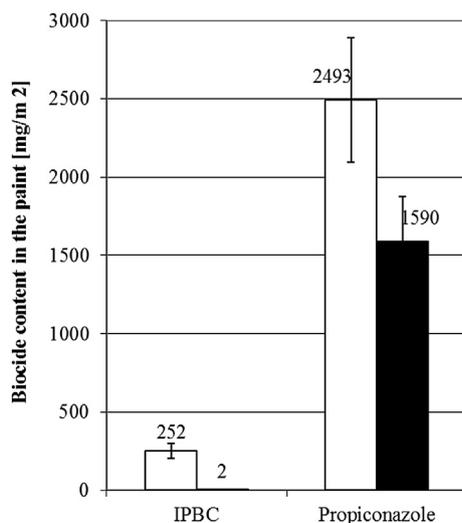


Fig. 5. Biocide content in coating AARwB measured on reference samples ( $n = 4$ ) and aged samples ( $n = 4$ ); □ reference samples and ■ samples weathered for 1 year.

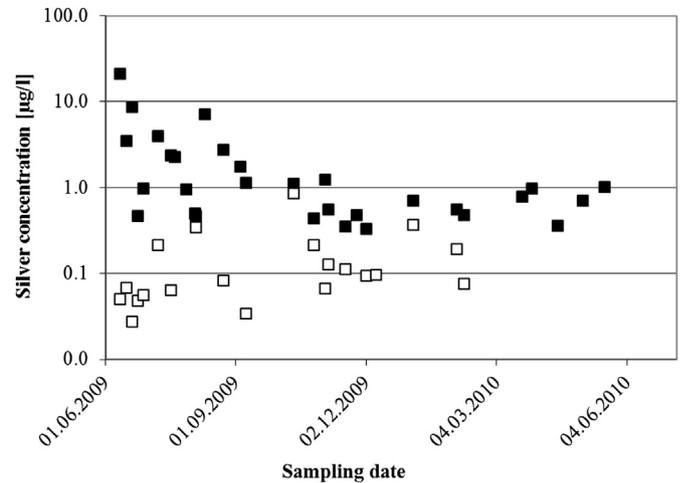


Fig. 6. Silver concentrations in runoff samples of all rain events during one year exposure of façade coatings ■ HySiwAg and □ OARwAg.

1.7 µg for coating OARwAg. In both cases, this was less than 1% of the initial silver amount in the coating.

The comparison of the residual silver content and the initial concentration showed a 34% loss of silver in coating HySiwAg after one year exposure (Fig. 7). This amount corresponded to the high erosion of coating HySiwAg during the weathering test. Fig. 8 shows an element mapping of silica before and after two month outdoor weathering, which indicates clearly a substantial loss of the coating.

The 9% loss of silver in coating OARwAg was low, and corresponded to a nearly unchanged coating thickness after one year of exposure. Cobalt as the reference element for the coating showed a comparable loss of 12% during weathering. These results suggest that the loss of silver corresponds to the overall erosion of the tested coatings. But the results also raise the question, why only a very small amount of silver (~1%) was detected in the runoff. The main explanation for the incomplete mass balance is the fact, that we only determined one possible pathway into the environment; which is the transport of material by rain into the aquatic compartment. Other mechanisms, which are the transport by wind or the movement by gravity force into the surrounding area, were not taken into account.

Neither by NTA method nor by TEM, could particulate silver be detected in the runoff water. Tests with artificial reference solutions, containing 2 µg/l silver nanoparticles, showed clearly that this concentration would be easily detected by TEM. Therefore, we assume that there were no silver nanoparticles in the runoff. Particles and agglomerates in the runoff contained mainly iron, silica, aluminum and calcium and their oxides.

Determination of ionic silver in runoff samples by the DGT method showed that only less than 2% of the detected silver was available in ionic form.

### 3.4. Toxicity of façade runoff

For the toxicity tests, the runoff samples with the highest concentrations of silver were chosen as a worst case. Runoff water with a maximum silver concentration of 7.17 µg/l for the tests on bacteria and algae, as well as a maximum of 21.08 µg/l for the tests on daphnia showed no toxic effect on the tested water organisms.

As expected the runoff samples of façades coated with the formulation AARwB with higher concentrations of organic biocides affected the tested organisms. In the following only IPBC will be

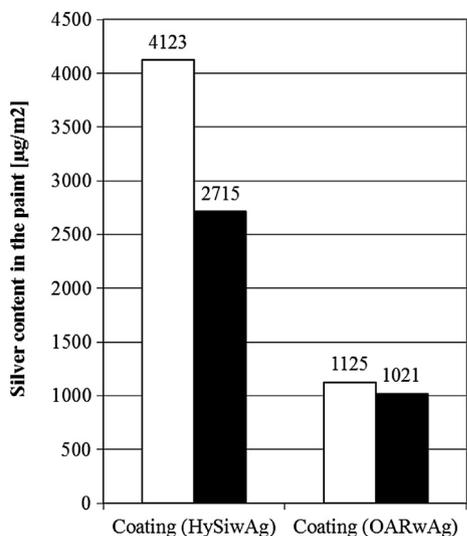


Fig. 7. Ag content in coating HySiwAg and OARwAg measured on reference samples and aged samples (each with  $n = 3$  analyzed as on mixed sample); □ reference samples and ■ samples weathered for 1 year.

discussed, because IPBC is more toxic to the tested aquatic organisms than propiconazole (Kegley et al., 2011).

As seen before in Fig. 4, the IPBC concentration during the first three rain events was high (between 2.56 and 3.27 mg/l) and therefore significantly affected the daphnia. Runoff water of four more rain events during the one year experiment showed IPBC concentrations between 0.16 and 0.37 mg/l, which is around the 48 h  $EC_{50} = 0.558$  mg/l (PAN, Pesticide Database) level. An immobilization of daphnia must also be expected for those samples. It can be assumed that all other runoff samples according to their low IPBC concentration ( $<0.07$  mg/l) beneath the 21-day  $LOEC = 0.099$  mg/l (Ward, 1991) would not have significantly affected daphnia.

Fig. 9 shows the effect of IPBC on Algae *Pseudokirchneriella subcapitata*. An IPBC concentration of 1.09 mg/l in the runoff induced a 97% inhibition of Photosystem II as well as a 83% inhibition of algae growth. According to this result, concentrations of IPBC in the first three rain events (between 2.56 and 3.27 mg/l) are high enough to completely inhibit the growth and photosystem II of the tested algae. Another four rain events (IPBC concentrations between 0.16 and 0.37 mg/l) would have affected the tested algae and inhibit the growth of up to 30%, while their photosystem II seems to be not influenced significantly due to that concentrations. It can be assumed that all other runoff samples, which had low IPBC concentration of less than 0.07 mg/l, would not have affected the tested algae significantly.

The inhibition of bioluminescence of bacteria *Vibrio fischeri* was tested up to highest test concentration of IPBC 3.27 mg/l (0.65 mg/l with 1:4 dilutions). This concentration resulted in a 27% inhibition of bioluminescence (Fig. 10). This implies that the undiluted first three rain events with IPBC concentrations between 2.56 and 3.27 mg/l would have affected the bacteria more intense. Since IPBC concentrations less than 0.1 mg/l showed no inhibition effect, concentrations of all other runoff samples might not cause significant inhibition of the bioluminescence.

#### 4. Discussion

The outdoor weathering tests and the laboratory functionality tests showed that only the organic biocides were efficient to protect a coating against affection by mold, blue stain and algae. The coatings with Ag-NPs failed in all laboratory tests and were also insufficient during outdoor weathering. However the affection by microorganisms was delayed on the silane based coatings during outdoor weathering. It can be assumed that this effect was rather induced by the hydrophobicity of the coating and/or the silane components than by the Ag content, because the non-Ag formulation showed almost the same performance.

The Ag content of the Ag-NPs containing coatings decreased proportional to the overall erosion of the coating. Over a year the Ag

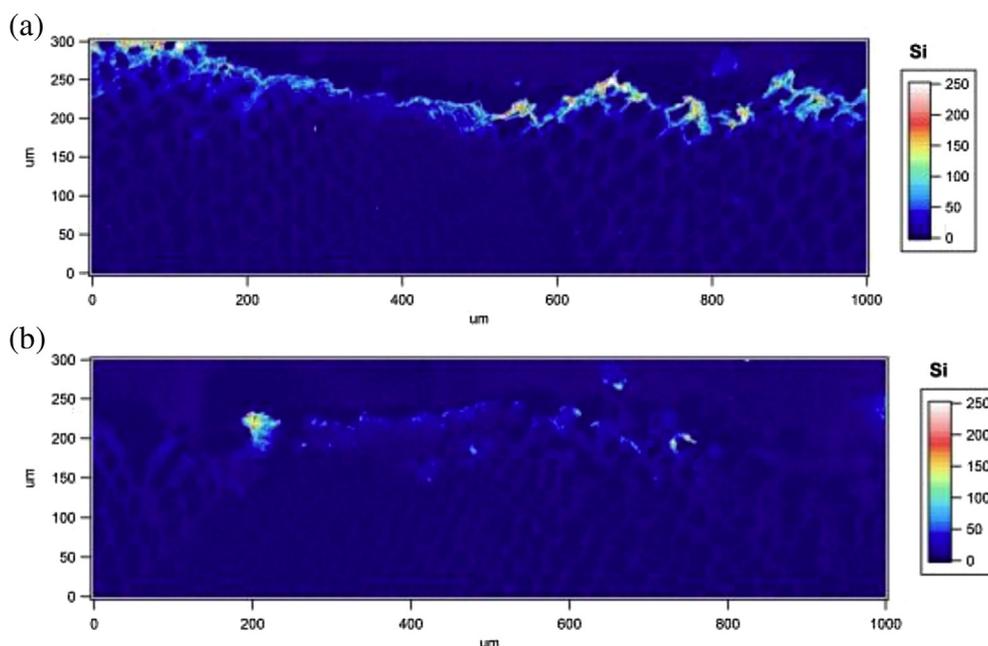


Fig. 8. Element mapping of silicium on non-weathered (a) and 2 month weathered (b) samples with coating HySiwAg.

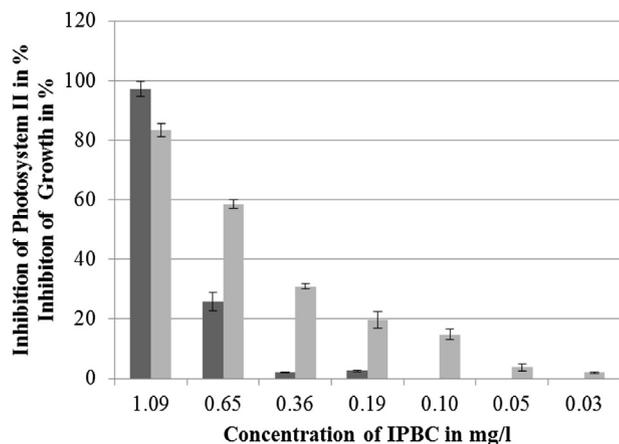


Fig. 9. Inhibition of photosystem II and growth of algae after 24 h exposure to runoff from outdoor weathering; Photosystem II and Growth.

content in the coating layers, evaluated by residual content determination of the coating, decreased by 35% for HySiwAg and 10% for OARwAg, but only a minor portion was detected in the runoff. In contrast to a study about mineral façades (Kaegi et al., 2010), Ag was not observed as nanoparticles in the runoff; neither separate nor attached or embedded to small particles of organic binder. Further investigations are needed to answer the open questions:

- Which are other pathways of silver and the eroded coating material into the environment except runoff water? It is well known from visual observations that there is a transport of already eroded surface material by wind and/or gravity into the surrounding area. But this process has been never investigated quantitatively and therefore also the parameters, which govern this process, are not known.
- Are the Ag-NPs transformed already on the façade to hardly or insoluble and therefore considerably less toxic forms such as  $\text{Ag}_2\text{S}$  or  $\text{AgCl}$ ? (Leygraf and Graedel, 2000). A calculation (Pourbaix diagram) of the Ag speciation, based on realistic conditions with rainwater, fog and/or dew on the façade, corroborates this theory: Fig. 11 shows the prospective reaction products in the presence of rainwater, which are  $\text{Ag}_2\text{S}$  and  $\text{AgCl}$ . The same results were obtained also for fog and dew.

The concentrations of both organic biocides in the façade decreased over the one year testing period; however, at a very

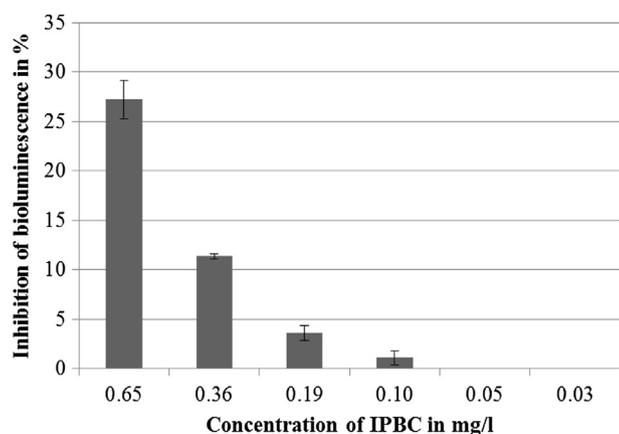


Fig. 10. Inhibition of bioluminescence after 30 min exposure of bacteria to runoff from outdoor weathering (no effect for concentrations  $\leq 0.05$  mg/l).

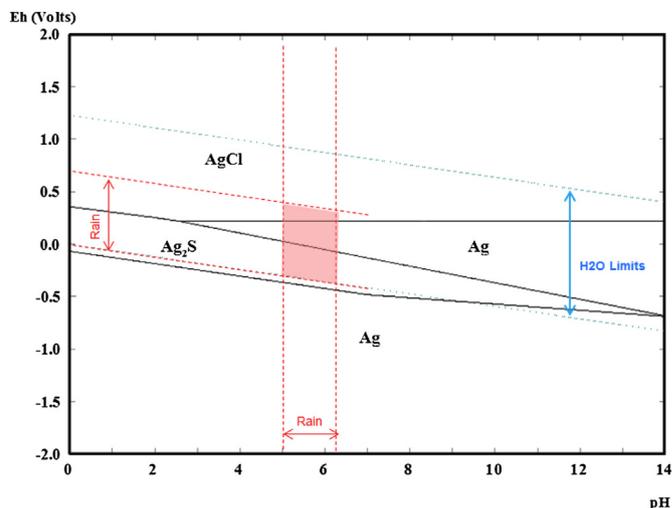


Fig. 11. Potential–pH equilibrium diagram for the system  $\text{Ag-Cl-N-S-H}_2\text{O}$  at 25 °C (calculated with HSC Chemistry software from Outotec Research Oy). The red area represents the reasonable conditions for rainwater in the tested region. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

different rate. Only 1% of IPBC was left in the façade, whereas 64% of propiconazole remained. As for both compounds, only small fractions were found in the runoff water, further elimination processes must have been present. IPBC is known to rapidly degrade under environmental conditions (Juergensen et al., 2000) Such transformations into less toxic compounds (European Chemicals Agency, 2012) likely took place on the façade. IPBC was applied to the coating, i.e. to the outermost layer of the façade. Within these exposed layers, photochemical and microbial transformation can take place, and these layers will also be more affected by erosion of the surface. More than 60% of propiconazole remained on the façade after one year, which might be explained by its application in deeper coating layers, which reduces evaporation and slows down losses by runoff water. The transformation of propiconazole is estimated to be slower than for IPBC (US EPA, 2012). Consequently rainwater will wash off especially the degradation products, and finally only small amounts of the initial biocides can be found in the runoff.

All organic biocides leached out, independent from the erosion state of the coating. A permanent high moisture content of façade increased the leaching (Künniger, 2011). At the same time a significant diffusion of the biocides into the wood structure was not observed.

The runoff water collected on façades with silver containing coating systems showed no acute toxicity for the tested water organisms. The reasons might be the very low concentration of silver in the runoff and the fact that the silver was not available in ionic form, which is the toxically most active species. On the other hand, the applied coatings with Ag-NP (<50 ppm) were not efficient against the tested microorganisms such as mold, blue stain and algae. The generally low silver concentration in combination with the insufficient availability of free silver ions on the surface might be the main reason for this functional failure.

As expected some of the runoff water samples with organic biocides harmed the tested microorganisms. The concentrations of IPBC in the runoff of the first three rain events were high enough to completely inhibit the photosystem II and growth of the tested algae, to affect bioluminescence of the bacteria and to immobilize the daphnia. All runoff water with IPBC concentrations less than 0.07 mg/l did not affect the tested microorganisms significantly.

Other aquatic organisms might react more sensitive even to those low concentrations. The NOEC of IPBC is reported with 0.05 mg/l for *Daphnia magna* (after 21 days) and 0.0046 mg/l for algae *Scenedesmus subspicatus* (Growth inhibition after 72 h).

On the other hand, the applied coating with organic biocide was very efficient against mold, blue stain and algae during natural weathering as well as on samples in laboratory tests.

## 5. Conclusion

This experimental study provides the first comprehensive assessment of both, functionality and environmental impact of Ag-NPs compared to conventional organic biocides.

First of all, experimental work pointed out that for an environmental impact assessment a chemical analysis of the runoff and a residual content determination of the coating are required, to assess and quantify the potential release behavior of the active substances. Beside the environmental impact assessment an evaluation of the coating functionality (e.g. the protective effect) and overall performance is mandatory for a sustainable product development before it comes to market.

Secondly, results of this study confirmed that the tested façade coatings showed different release dynamics of silver and organic biocides. The decrease of silver corresponded with the overall erosion of the coating, while organic biocides diffused to the surface and were release from the coating independent from the state of erosion.

Eroded material can enter the rain channel but might be also carried into the surroundings and deposited somewhere on the ground. A quantitative determination, how much of eroded material reached the other compartments of the environment, was unfortunately not part of the study, but the experience shows that this might be necessary for further investigations.

Silver was not observed as nanoparticles in the runoff; neither separate nor attached or embedded to small particles of organic binder.

Preventing a too fast release of organic biocides, representative for wood coatings, is still an issue which needs to be improved. In spite of the comparatively fast release, only a relatively small amount of the biocides could be detected in the runoff, because the organic biocides are degraded to less toxic compounds. For a risk assessment and a better mass balance, not only the release dynamics of the biocides but also the characteristic of possible degradation processes generated by chemical transformation and the detection of degradation products in the runoff should be included.

Finally the results of this study proved, that under the tested conditions Ag-NP did not protect the façades against fungal decay. Therefore a use of Ag-NP as alternative biocide in coatings is questionable. Even if no enhanced acute risk for the aquatic environment was observed for initial concentrations below 50 ppm in the coating, data about the chronically risk are still lacking. If a protective effect for the wooden façades is desired and necessary, conventional biocides in coatings can achieve this requirement for a limited time period. The selection of a fast degradable substance, such as IPBC probably minimizes the burden for the aquatic environment.

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In memory of Andrea Ulrich, who died in March 2013. We lost a confident high qualified colleague and a good friend.

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