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Release of Conventional and Nano-Sized Biocides from Coated Wooden Façades during Weathering: Consequences for Functionality and Aquatic Environment

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Abstract

Different transparent, hydrophobic wood coatings with conventional organic formulations as biocides and nanosilver were exposed to natural and artificial weathering. Run-off water was collected and analyzed, to assess toxicological effects on the aquatic environment. Furthermore, the coatings were evaluated for overall performance and for their protective effect against different microorganisms.

The coating with conventional biocides released the biocides slowly over the exposure time, depending on the weather conditions, especially the intensity of rainfall, but showed a good overall performance free from mould, blue stain and algae.

The products with nanosilver released a small amount of silver, correlating with the overall erosion of the coating. The small quantity and the fact that silver in the run-off water was not ionic and not particulate lead to the assumption, that the risk of these emissions for the aquatic environment is low. On the other hand the protective effect against mould, blue stain and algae seems to be insufficient.

Key words nanosilver, biocide, façade, leaching, wood coating

Introduction

Nanotechnology provides many opportunities to improve materials properties, performance and sustainability. The current applications of engineered nano particles (ENPs) span a wide range of industrial and consumer sectors. At the same time, the potential impact of these new materials on human health and the environment is viewed with apprehension. Therefore, the environmental and health consequences of these materials have to be carefully investigated and discussed.
In the context of the trend to increase energy efficiency of buildings by thermal insulation, the demand for protecting outside façade with functional coatings is increasing. Nanosilver as an ENP is proposed as a substitute for conventional organic biocides in coatings, because of its protective effect against bacteria. Some products are already on the market and in use.

A study about nanosilver as a biocide on mineral façades (Kaegi et al. 2010) came to the result that about 30 percent of the nanosilver was leached out during one year of natural weathering. To initiate a discussion about the benefit and risk of nanosilver in wood coatings more experimental data were needed.
The presented paper gives the first results of a current project initiated at Empa Duebendorf (CH) to address this needs. The final report will be published in spring 2011.

Materials and Methods

Materials. Industrial lamellas made of Norway spruce were used to produce laboratory scale façade elements (horizontal planking) for natural weathering (~1 m^2) and artificial weathering (~1.3 m^2). Four different transparent, hydrophobic coating systems were applied according to the manufacturer recommendations. The coating systems were:

- (A) - Hydrolysed silane with nanosilver
- (B) - Hydrolysed silane without nanosilver
- (C) - Oily alkyd resin with nanosilver
- (D) - Alkyd/acryl resin with propiconazole and IPBC (3-Iodo-2-PropynylButylCarbamate)

Methods. The coated façades were evaluated for overall performance and for their protective effect against different microorganisms. Run-off water after rainfall and artificial weathering was collected and analyzed, to assess the toxicological effect on the aquatic environment.

Natural weathering	June 2009 – June 2010, vertical alignment, direction SW (220°), location at Empa Duebendorf (CH)
Artificial weathering	(I) 113 cycles à 3 h UVA/UVB, ½ h sprinkling (40 l), 2½ h recovery (II) 113 cycles à 3 h heat (40°C), ½ h sprinkling (40 l), 2½ h recovery
Analysis run-off water	ICP-OES (Plasma Optical Emission Spectrometry), ICP-MS (Plasma Mass Spectrometry), LC-MS/MS (Liquid Chromatography with Tandem Mass Spectrometry), TEM (Transmission Electron Microscopy)
Acute Toxicity	Collected run-off water tested on algae (Combined Algae Test with *Pseudokirchneriella subcapitata*) and *Daphnia magna* (Immobilisation Test acc. to OECD 202)

Overall performance	Characterisation of the coating film / surface with different methods: Dry film thickness (ISO 2808, 6A), Adhesion (EN 2409), Contact angle, Colour measurement (ISO 7724), water and water-vapour permeability (EN 927-5/4), General appearance (EN 927)
Protective effect	Antimicrobial effect against mould (acc. to Empa SOP 4349), blue stain (acc. to EN 152.1) and algae (acc. to Empa SOP 4350) tested on reference samples

Results

Overall performance of the tested wooden façades. All four coating systems were tested at the original stage as a reference and after 1 year natural weathering. Results are shown in Table 1.

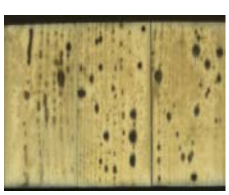
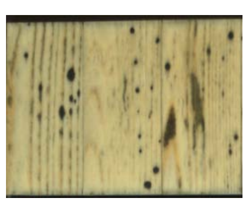
Table 1: *Tested parameters for the reference samples and 1 year natural weathered samples; (upper line = reference sample; lower line = weathered sample)*

	A	B	C	D
Dry film thickness [µm], mean	No film No film	No film No film	24 ± 4 19 ± 4	37 ± 5 39 ± 6
Colour [ΔE* a b (SCE)]	/ 20.8 ± 2.7	/ 15.6 ± 1.9	/ 17.7 ± 4.2	/ 11.3 ± 2.6
Adhesion	Not tested	Not tested	0 (No delamination) 2 (~5% delamination)	0 (No delamination) 2-3 (5-15% delamination)
Contact angle [°]	138 ± 8 130 ± 7	141 ± 5 133 ± 5	94 ± 3 85 ± 4	103 ± 2 102 ± 1
Water-vapour permeability [$g/(m^2 *\sqrt{h})$]	47 ± 1 41 ± 1	39 ± 1 40 ± 3	26 ± 1 31 ± 3	30 ± 2 29 ± 1
Liquid water permeability [g/m^2] after 72h	649 ± 6 864 ± 10	642 ± 9 994 ± 47	166 ± 17 434 ± 136	243 ± 15 209 ± 16

After one year natural weathering all systems showed a significant change in colour with ΔE* (SCE) between 11 and 21.

The **Silane coatings** (A, B) showed a slightly reduced contact angle (~ 6%) after one year natural weathering, while the hydrophobic effect was still very high. The coatings A and B offer no protection against water-vapour absorption. The results are comparable with untreated Norway spruce (43 ± 3). The protection against liquid water absorption is also insufficient because of the high water-vapour permeability and is in the range of untreated wood after one year. This explains why the façade elements showed wet surfaces after strong rain, even if there was a high hydrophobic effect.
The **Oily alkyd resin** coating with nanosilver (C) forms a film on the wood surface with a mean thickness of 24 µm. The coating showed insufficient overall performance after weathering. The hydrophobic effect was reduced by about 10 %. The water-vapour permeability increased by about 19 % and the liquid water permeability was 2.6 times higher than on the original reference samples.
The **Alkyd/Acryl resin** (D) with conventional biocides was completely intact after one year natural weathering. The hydrophobic effect and the water-vapour permeability stayed constant after one year weathering, while the liquid water permeability is slightly decreased.

Antimicrobial effect. After one year **natural weathering** the beginning of microbial growth was visible on product (A) and (B), mainly on the edges, knots and cracks. The decay on the Product (A) with nanosilver seemed to be a little time-delayed compared to the same product (B) without nanosilver. Product (C) with nanosilver showed a strong erosion and intense microbial decay. Only the product (D) was completely intact without showing any microbial decay.
The **laboratory test** results corroborated the observations made during the natural weathering of the façades. The samples treated with product (D) were free from mould, blue stain and algae. The other three tested coatings (A, B, C) were affected even in the original stage. There was no difference between the product (A and C) with nanosilver and (B) without nanosilver. Microscopic analysis of the affected surfaces showed that microorganisms were growing through the coatings into the wood structure. A visual overview about the laboratory test results is given in Figure 1.

	A	B	C	D
Mould				
Blue stain				

Algae

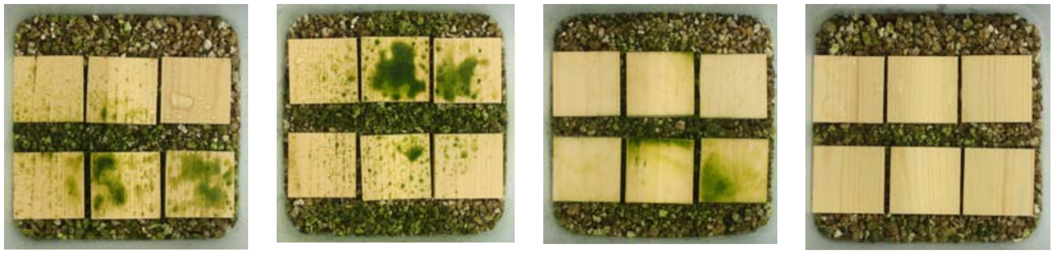


Figure 1: *Microbiological growth on reference samples*

Leaching. During the one year of natural weathering 33 rain events (total ~ 946 mm rain or 106 l/m^2) were sampled. In general the amount of run-off water is depending on the exposure conditions like amount of rainfall, wind speed and wind direction and also on the structural environment like roof overhang or geometry and wind flow conditions of the façade.

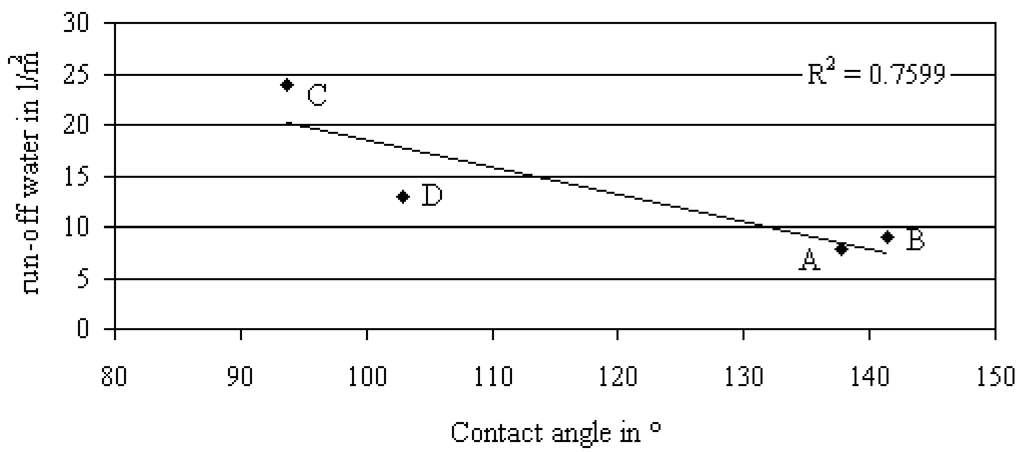


Figure 2: *Relationship between contact angle of surfaces and the amount of run-off water collected during one year of natural weathering*

The different quantity of run-off water collected from the façade was depending on the hydrophobic character of the coated surfaces (see Figure 2). On the super hydrophobic façades (product A and B) only around 8 l/m^2 façade were collected in the container over the year, compared to the less hydrophobic façades (C) with nearly triple the amount (~ 24 l/m^2) of run-off water. This can be explained by the effect, that water droplets bounced off the super hydrophobic surfaces much more than on less hydrophobic surfaces, especially in windy weather.

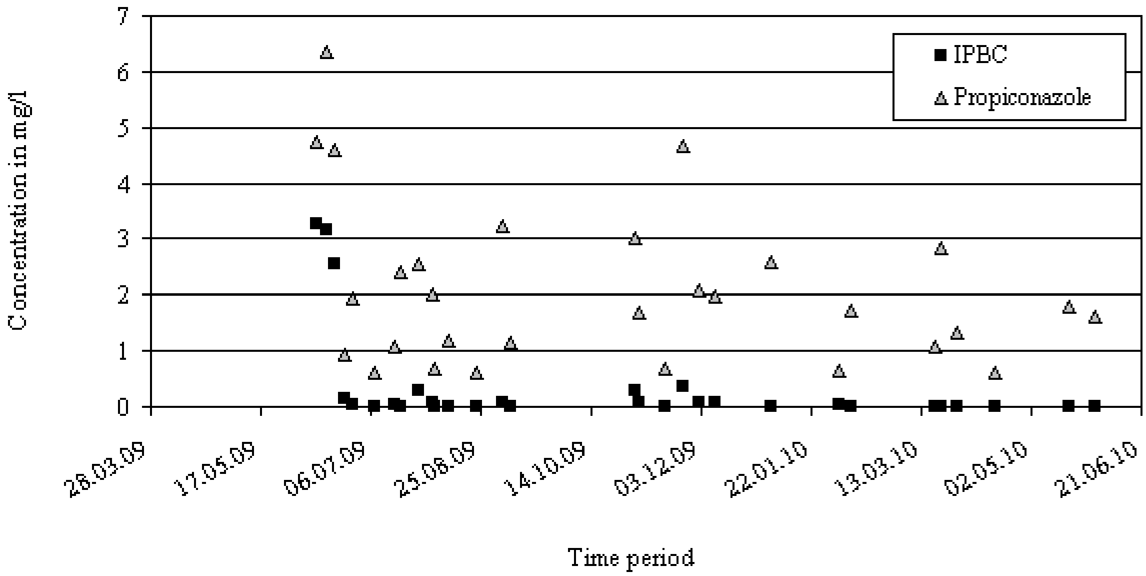


Figure 3: *Release of IPBC and propiconazole from coated façade (product D) during 1 year natural weathering; concentration of the collective samples*

The amount of water that runs over the surface influenced the amount of leached conventional biocide. After one year natural weathering with a total collected run-off water of 13 l/ m^2, only around 1% of the applied biocides (product D) were detected in total. The highest concentrations of IPBC above 2 mg/l (between 2.5 to 3.3 mg/l) were found only during the first three rainfall events. Thereafter, IPBC concentrations decreased rapidly and were always below 0.4 mg/l. After six months, IPBC concentrations fell below the detection limit of 0.001 mg/l. Propiconazole seemed to leach constantly over time (Figure 3).

The same type of façade emitted 48% of IPBC and 18% of propiconazole during one month of artificial weathering with a total collection of 4700 litres (Figure 4).

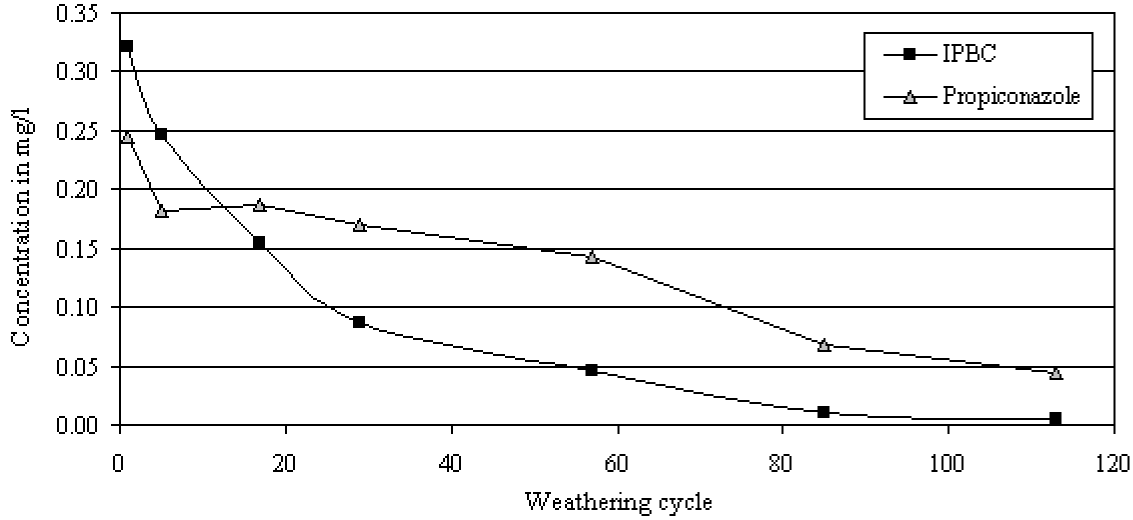


Figure 4: *Release of IPBC and propiconazole from coated façade (product D) during one month (113 cycles) artificial weathering; concentration of the collective samples*

The tested samples with nanosilver as a biocide contain a maximum of 2.5 mg particulate nanosilver /m^2 façade. The nanosilver particles were well dispersed in the liquid coating (Figure 5), but were not visible on the coated surfaces of the façades.

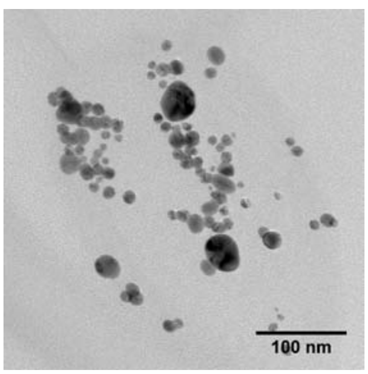


Figure 5: *TEM image of nanosilver particles in coating (A)*

After nine months of natural weathering less than 3% of the total silver was detected in the run-off water. The current data allows the assumption that the nano-sized silver particles are well fixed in the tested coating matrix and don't migrate to the surface. The amount of released silver correlates with the overall erosion of the coating layer during weathering (see Figure 6). The detected silver in the run-off water was not particulate (NTA Nanoparticle Tracking Analysis; www.nanosight.com) and not available in ionic form (DGT Diffusive Gradients in Thin Films). It is supposed that the silver and sulphur compounds in the rainwater oxidize on the façade surface to silver sulphide.

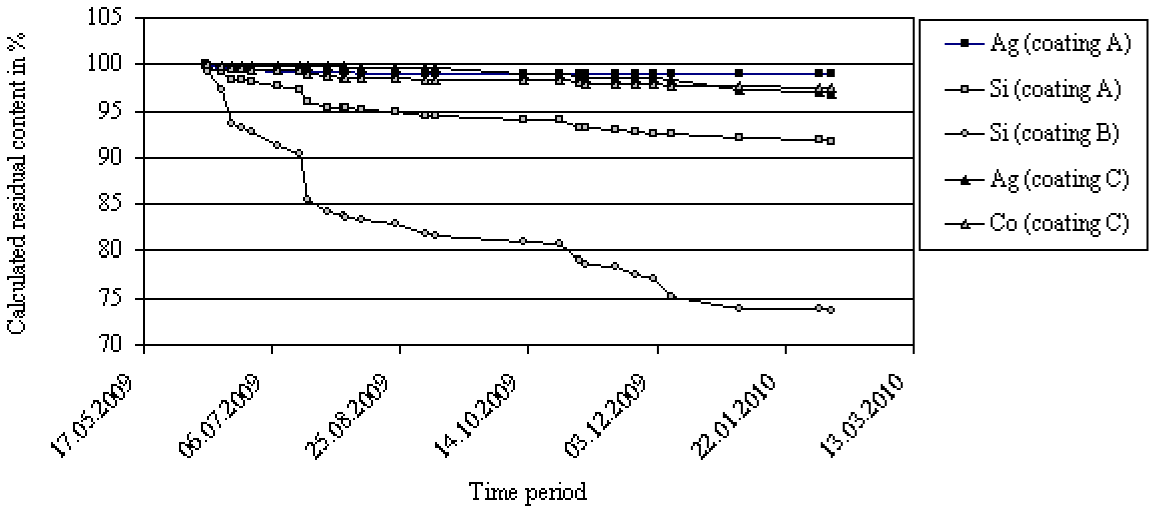


Figure 6: *Calculated residual silver content of the coating films after nine months of natural weathering (in percent)*

Based on the first results of the ongoing artificial weathering tests we expect at the same type of façades about 50 to 60% silver emission during 1 month of artificial weathering with a total collection of about 4700 litres (Figure 7).

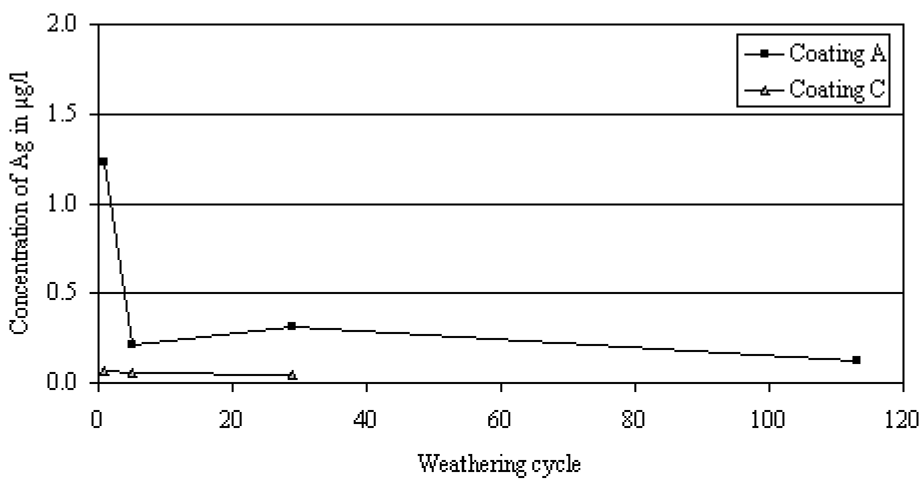


Figure 7: *Release of total silver from coated façades (products A and C) during one month (113 cycles) artificial weathering; concentration of the collective samples*

Tests to determine the residual content of biocide or nanosilver in the coatings after weathering are in progress. These results will allow compiling a mass balance of the discussed components.

Acute toxicity of the collected run-off water tested on daphnia and algae. The run-off water with conventional biocides (coating D) showed some toxic effects against ***Daphnia magna*** dominated by the concentration of the agent IPBC (Figure 8). These results correspond to literature data, which show that IPBC (LC50=0.645 mg/l;(Henderson 1992)) is 10 times more toxic to *Daphnia magna* than propiconazole (LC50=5 mg/l; (Kast-Hutcheson, Rider et al. 2001)).

Run-off water of the other coatings (A-C) showed no effect on *Daphnia magna*, even not at the highest analyzed concentrations of total silver (21µg/l).

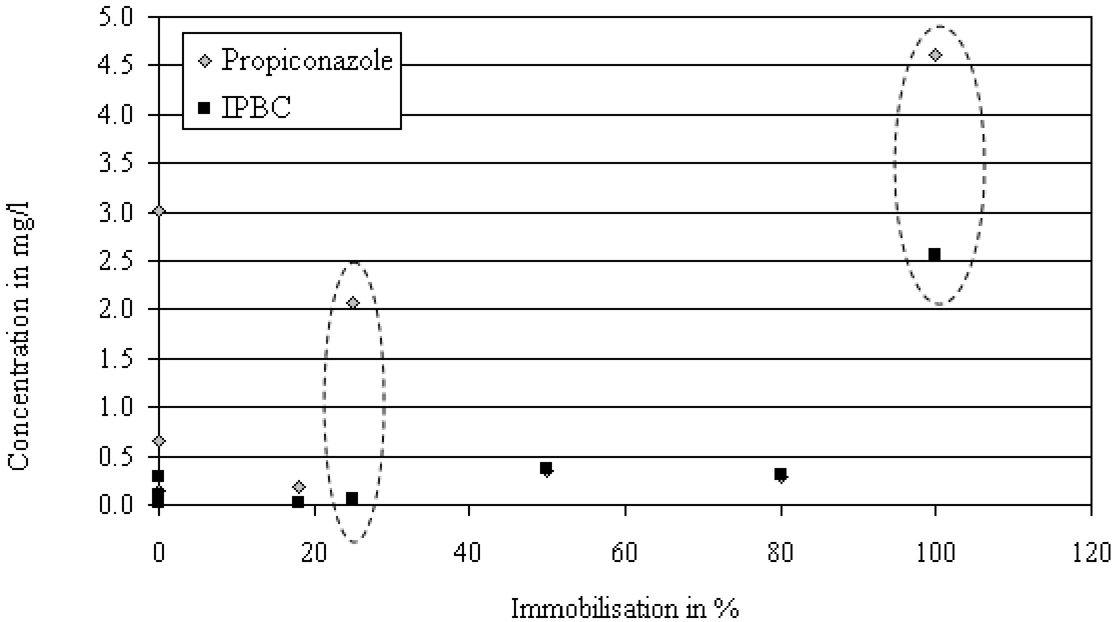


Figure 8: *Immobilisation of Daphnia magna after 48 h exposure to run-off water (Natural and artificial weathering coating D) with different original concentrations of IPBC and Propiconazole; Samples from Natural weathering are separate marked with a circle*

Test on algae ***Pseudokirchneriella subcapitata*** were only effective with the run-off water from coating D with conventional biocides. On the concentration of IPBC (3.27 mg/l) and propiconazole (4.73 mg/l) a nearly 100% inhibition of the photosystem II and 80% growth inhibition stands for an acute toxic effect against the tested algae (Figure 9 and 10).

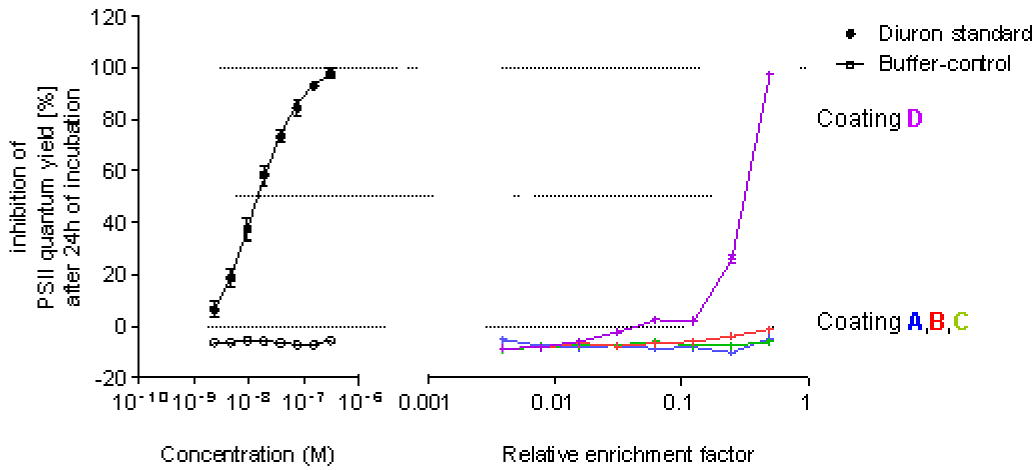


Figure 9: *Inhibition of photosystem II after 24 h incubation of Pseudokirchneriella subcapitata in run-off water from natural weathering; lowest dilution 1:4*

The run-off water with the highest content of silver (coating A with 7.2 µg/l) showed non effect neither on the photosystem nor on the growth of the algae. Run-off water of coating B inhibits the growth of the algae after 24 h exposure on about 15%, although there was no silver and no other biocide in it. This fact let suppose that there are other compounds in the water with a slightly toxic effect on algae. Tests with bacteria are in progress.

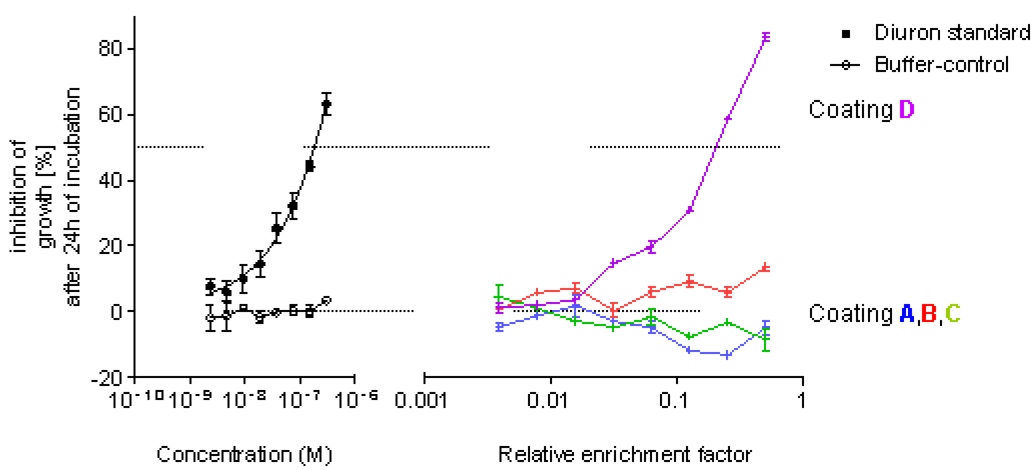


Figure 10: *Growth inhibition after 24 h incubation of Pseudokirchneriella subcapitata to run-off water from natural weathering; lowest dilution 1:4*

Conclusions

The current data allow the assumption that the nano-sized silver particles are well fixed in the tested polymer matrix of the coating and don't migrate to the surface. The quantity of total silver in the run-off water correlates with the surface erosion of the coating during weathering.

Run-off water with the highest analyzed content of total silver showed no effect against *Daphnia magna and Pseudokirchneriella subcapitata*. This corresponds to the result that the silver is not available in ionic form and also corroborates the theory of silver sulphide formation in the run-off water, because *Daphnia magna* react very sensitive to silver ions, but showed nearly no effect in contact with silver sulphide (Hund-Rinke et al. 2008).

The results of antimicrobial effectiveness tests of nano-sized silver as a biocide correlate with other studies (Plaschkies et al. 2010). Current concentrations of nano-sized silver in coatings (≤ 25 ppm) showed no protection effect against mould, algae and blue stain.

Acknowledgement

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