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Nanosilver emissions to the atmosphere: a new challenge?

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Abstract. Atmospheric deposition of silver in Switzerland decreased significantly between 1995 and 2010, but recent increases in nanosilver production present a potentially new emission source of silver. While nanosilver is usually integrated in a robust matrix and its release is either controlled, dampened (highly diluted silver in nanosilver textiles) or prevented (computer modules), point source emissions of nanosilver can occur at the manufacturing sites. The emission of nanosize particles of particular concern because these particles penetrate deeply in the lungs, and have the potential of causing long-term adverse effects to humans. We investigated local silver emission patterns with bryophytes *Brachythecium rutabulum* and *Hypnum cupressiforme* and with bulk (dry and wet) deposition measurements of silver, using Bergerhoff samplers, close to a nanosilver manufacturer. With mean values of $0.033 \mu\text{g g}^{-1}$, the silver concentrations in the mosses were the same as the background concentration of Switzerland (141 sites). The spatial distribution revealed a decrease in the silver concentrations in moss as a function of increasing distance from the nanosilver manufacturer. The monthly collected bulk depositions were higher in the area of nanosilver production ($0.175 \pm 0.13 \mu\text{g m}^{-2} \text{day}^{-1}$) in comparison to rural ($0.105 \pm 0.08 \mu\text{g m}^{-2} \text{day}^{-1}$) and urban areas ($0.113 \pm 0.05 \mu\text{g m}^{-2} \text{day}^{-1}$) of Eastern Switzerland. Contrary to other areas, the larger monthly variability of the deposition values close to the production site points towards highly variable silver emissions. Subtraction of the silver background deposition results in approximately 60 g deposited silver per year within a perimeter of 4 km from the nanoparticle manufacturer. Along with bulk deposition of silver, we also studied potential morphological changes of the deposited nanosilver. We found silver nanoparticles in the form of environmentally stable silver iodide. We conclude that the applied methods are suitable for monitoring nanometal deposition. Dry nanoparticle production processes can generate atmospheric nanoparticle emissions but they appeared to be small in our investigated case.

Key words: Silver, nanoparticles, biomonitoring, deposition, bryophytes

Introduction

In this study, we focus on anthropogenic (nano)silver emissions to the environment. Historically, the photoindustry was the predominant source of silver emissions, with the waste water being the main pathway to the environment (Blaser et al., 2008). Nowadays, silver emission sources are more diverse: The photographic industry is responsible for no more than 8% of the total use, while electronics and catalyst industry together make up 55% of the use, ahead of jewelry & silverware (25%) (The Silver Institute, 2011). A minor share (0.5%) of the silver

used is incorporated in biocidal products. This value translates into about 28 tons of silver used in Europe, whereas 3.8 tons are applied to textiles, including species such as silver salts (79%), bulk (nano)silver metal (13%), and silver glasses and silver zeolites (8%) (Burkhardt et al., 2011). For Switzerland, these values can be estimated as 120 kg silver discharged to waste water and 40 kg disposed in incineration plants (Burkhardt et al., 2011). However, few nanosilver pathways have been investigated so far, such as the measured silver release into waste water (Kaegi et al., 2011). While indoor emissions from nanoparticle production processes can be measured

with commercial devices, nanoparticle emissions from production processes to the outdoor environment are yet to be studied. The growing concern over atmospheric deposition of heavy metals has led to an increase of the use of mosses to estimate deposition levels on continental (Harmens et al., 2008), country, regional, but also – less frequently – on local scale (Bargagli, 1998). Detailed reviews can be found in (Tessier et al., 1999; Onianwa, 2001; Zechmeister et al., 2003). As non-vascular plants, bryophytes accumulate metals from the air. They often show a high tolerance. Moreover, there is a correlation between accumulation and input to the ecosystem, e.g. (Berg et al., 1997). Thus, mosses can be used as bio-indicators, also for (nano)silver (Thöni et al., 1996). Nanosilver emissions are of environmental concern because of the high antimicrobial activity of released silver ions and the still unclear additional toxic action of the silver nanoparticles (Wijnhoven et al., 2009). Data on silver concentrations in mosses are available for Switzerland from 1995 (Thöni et al., 2008) and 2010 (data not yet published). In view of the growing nanosilver industry, it is of increasing importance to know the background level of silver in the ecosystem in order (i) to evaluate the current state of contamination, (ii) to control the evolution over time, and (iii) to predict the incidence of possible future silver emissions in order to establish the necessary interventions. Hence, additional measurement campaigns are required, taking into account the speciation of the nanosilver. Specific attention has to be paid to local pollution sources in order to take action at an early stage, if necessary.

The aims of this study were (i) to quantify silver deposition in the immediate surroundings of a nanosilver production company, in terms of concentration in mosses as well as by measured deposition rates, (ii) to analyze spatial deposition patterns with increasing distance from the potential emission source, (iii) to investigate the morphology of the detected silver nanoparticles, (iv) to compare and assess historical silver concentrations with current silver concentrations in Switzerland, and (v) to put the results into the context of current (nano)silver flows in Switzerland.

Materials and Methods

The investigations of the morphology and elemental composition of the primary and secondary nanoparticles were performed by means of a Transmission Electron Microscope (TEM, Tecnai F30, FEI; field emission gun; SuperTwin lens; resolution ca. 0.1 nm; additionally equipped with an energy-dispersive X-ray spectrometer (EDXS) for qualitative elemental analyses). Moss leaves were analyzed with scanning electron microscopy (SEM, FEI Quanta Q200), which allowed the investigation of heavy metals on the surface of the mosses. The primary nanoparticles were also characterized by their size (Fig. 4). In the field work, we collected the pleurocarp moss species *Hypnum cupressiforme* Hedw. s.l and *Brachythecium rutabulum* (Hedw.) Bruch, Schimp. & Gümberl at 8 sites within a radius of <1 km from the nanoparticle production company (Fig. 1). Three more samples were taken 1–10 km from the potential silver emission source. The mosses were collected from the ground or on surfaces of

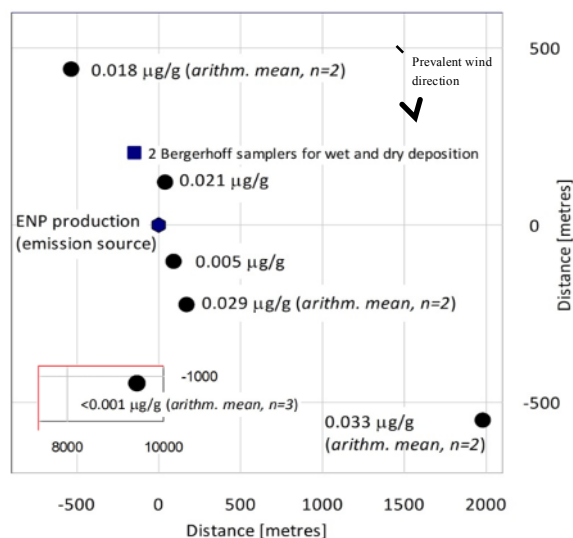


Figure 1. Sampling grid of the mosses in the area of the nanoparticle production firm. The concentrations values indicate silver mass per dry mass of moss.

decaying stumps, at least 5 m away from the nearest tree. Long-term weather data (wind, rain) for the particular location were taken into consideration. In addition to the local field campaign, the silver monitoring in Switzerland was continued by collecting mosses in 2010 at the same 141 sites as in the previous monitoring period (1995, approximately five moss samples per 1000 km²) in order to account for the background concentration as well as for the trend in silver deposition.

The moss samples were cleaned, and the stems of the last three years' growth removed. Then, this plant material was digested in a high pressure microwave oven, with concentrated HNO₃ and H₂O₂, for further analysis with ICP-MS (Varian 920). Zero controls and comparisons to reference materials were carried out for quality control.

In addition to the deposition measured by examining the mosses, we measured the bulk (dry and wet) silver deposition with the Bergerhoff (Verband Deutscher Ingenieure, 2010) in 1994 (Thöni, 1999) and 2008 at 5 sites sampled quarterly across Eastern Switzerland. In addition, we installed two Bergerhoff samplers close to a nanosilver production site over a 1 year period with monthly change of the sampling devices.

Results and Discussion

The primary particles consisted of 80% silica and 20% evenly distributed nanosilver with a size mode of 30 nm (Fig. 4). The nanoparticle production company is the only relevant source of atmospheric silver emissions in the investigated area. Hence, we assume that any significant increase in silver around the production site would be caused by that firm. Silver concentrations in the mosses were between 0.002 and 0.033 μg g⁻¹ (Fig. 1, 3). The silver concentration at the sampling point >8 km away from the production facility was below the quantification limit of 0.001 μg g⁻¹, indicating that the silver concentrations decrease with increasing distance from the production firm. We found higher silver concentrations in the prevalent wind direction. The bulk deposition rate of airborne silver was between 0.04 μg d⁻¹ - 0.44 μg d⁻¹

m^{-2} (Fig. 2) with an average value of $0.175 \pm 0.088 \mu\text{g d}^{-1} \text{m}^{-2}$ (95% CI). The monthly fluctuations of silver deposition were not correlated with the total dust deposition and the measured silver deposition showed a high variability (data not shown). These facts point towards a discontinuous silver emission source. Moreover, the average silver deposition was higher around the nanoparticle production site, but in the same order of magnitude as other areas of Switzerland ($0.108 \pm 0.0298 \mu\text{g d}^{-1} \text{m}^{-2}$ (95% CI)). In contrast, regarding the silver accumulation in the mosses, the silver concentrations did not differ significantly between the nanoparticle production area and other regions of Switzerland. From a temporal perspective for the entire area of Switzerland, we observe decreasing silver concentrations in mosses between 1995 and 2010 (Fig.3)

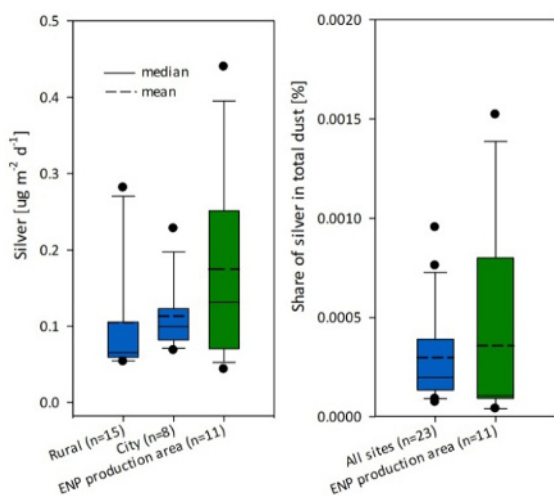


Figure 2. Left: Absolute (wet and dry) silver deposition close to the nanoparticle factory (monthly measurements). The results are shown together with absolute deposition values for rural and city sites in Switzerland. **Right:** The share of silver in the dust is higher around the production area in comparison to other areas in Switzerland.

The analysis with electron microscopy showed nanosilver particles of 80 nm diameter in the form of the environmentally stable silver iodide (Fig. 4). Not only the physical and chemical form, but also the total amount of deposited nanosilver is of interest for environmental fate and risk modeling. For the calculations, we took into account the estimated travel distance of the particles:

$$d_{99\%} = h_e \cdot v_w^{-1} \cdot \frac{\rho_p d_p^2 C_c g}{18\mu}$$

$d_{99\%}$ = distance, where 99% of emitted particles are assumed to be deposited; h_e = height of emission source; v_w = average wind speed; ρ_p = particle density; d_p = particle diameter; C_c = slip correction factor; g = gravity; μ = viscosity of air

We subtracted the silver background deposition and obtained the total silver deposition in the circle area within $d_{99\%}$ (4 km , $9.1 \cdot 10^{-5} \mu\text{g m}^{-2} \text{d}^{-1}$) from the nanoparticle production firm with the integral below and the known

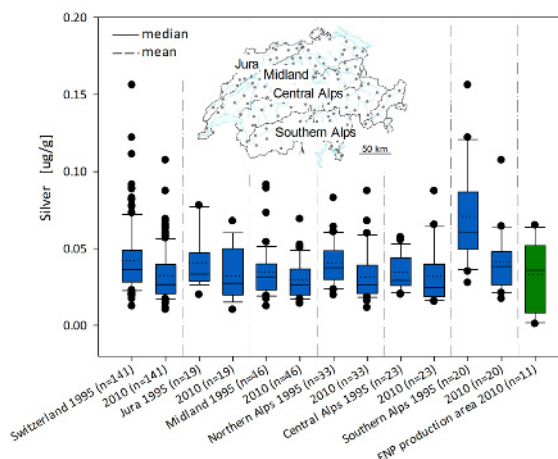


Figure 3. Silver concentrations in the mosses for Switzerland and further specified for different regions (blue). For comparison the silver concentrations in the moss around the nanoparticle production site (green). The Swiss map shows the sampling locations and

deposition value close to the emission source d_e ($0.067 \mu\text{g m}^{-2} \text{d}^{-1}$):

$$\int_{d_e}^{d_{99}} a \cdot e^{-bx} dx$$

With the values $a = 0.067 \mu\text{g m}^{-2} \text{d}^{-1}$ and the optimized value $b = 0.00165$, the estimation is valid for a total area of 50 km^2 where 99% of the silver deposition occurs. Solving the integral results in 60 g deposited silver per year.

Conclusions

Even though we did not observe increased silver concentrations in the bryophytes, the bulk silver deposition is elevated around the ENP production site in comparison to urban and rural areas in Switzerland. Hence, dry synthesis of nanosilver can lead to emissions to the atmosphere. However, the annual atmospheric silver deposition to the soil is small in view of the total soil content. The Earth's crust contains approximately $0.1 \mu\text{g g}^{-1}$ of silver and soils contain approximately $0.3 \mu\text{g g}^{-1}$ (Turekian et al., 1961). Moreover, the observed silver deposition rates in the vicinity of the nanoparticle production plant are in the same order of magnitude as in the background. However, the bioavailable fraction of the engineered nanoparticles might be higher than the natural background. Hence, nanoparticles from anthropogenic origin in ambient air or water are likely to be more problematic than those originating from bedrock, with slow weathering. From this perspective and by embracing the precautionary principle, a safe handling of engineered nanoparticles implies the complete prevention of nanoparticle emissions to the indoor and outdoor environment.

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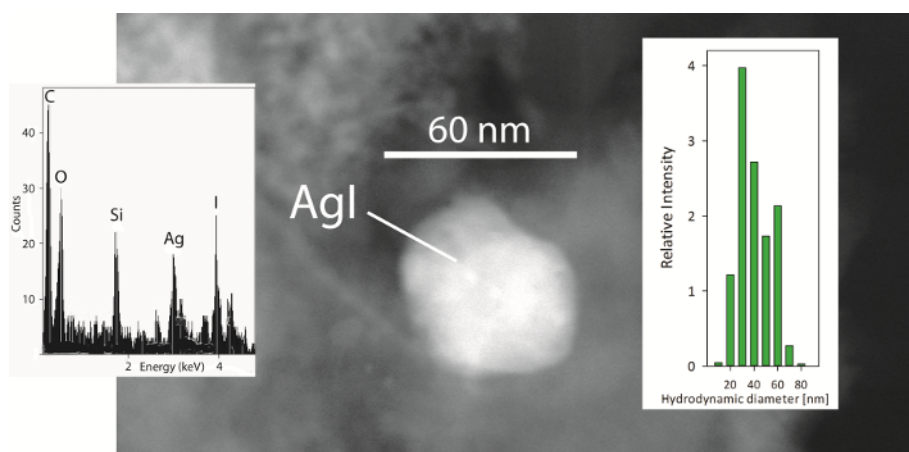


Figure 4. Nanosize silver iodide as detected in the deposited dust (TEM and EDXS). The inlet on the left shows the EDXS results while the inlet on the right shows the size distribution of the primary silver nanoparticles, embedded in a silica matrix.