Migration of silver from commercial plastic food containers and implications for consumer exposure assessment

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Food storage containers with embedded silver as an antibacterial agent promise longer durability of food. For risk assessment the release of this silver into the stored food and resulting human exposure need to be known. For the purpose of exposure assessment, silver migration from commercial plastic containers with declared content of ‘nano-’ or ‘micro-silver’ into different food simulants (water, 10% ethanol, 3% acetic acid, olive oil) was quantitatively determined by ICP-MS and the form of the released silver was investigated. The highest migration of silver was observed for the acidic food simulant with 30 ng silver cm⁻² contact surface within 10 days at 20°C. In a second and third use cycle, migration dropped by a factor of up to 10, so that the maximum cumulated release over three use cycles was 34 ng cm⁻². The silver release over time was described using a power function and a numerical model that simulates Fickian diffusion through the plastic material. The released silver was found to be in ionic form, but also in the form of silver nanoparticles (around 12%). Consumer exposure to the total amount of silver released from the food containers is low in comparison with the background silver exposure of the general population, but since natural background concentrations are only known for ionic silver, the exposure to silver nanoparticles is not directly comparable with a safe background level.

**Keywords:** silver; nanoparticles; food container; migration; food simulant

**Introduction**

Different types of silver (Ag) additives are used in commercial plastic products such as, for example, plastic food storage containers owing to the antimicrobial properties of Ag (Woodrow Wilson International Centre for Scholars 2012). The use of Ag in food storage containers is not prohibited in most countries including, for example, the United States. However, an agent that contains Ag in nanoparticulate form has to be registered in the United States (Environmental Protection Agency 2010). In the European Union certain Ag zeolites can be used for plastic food containers or in the rubber sealing based on national legislation (Art.7 in EU/10/2011, EC 2011, and provisional list of additives, European Food Safety Authority 2011) if the migration limits of 0.05 mg Ag kg⁻¹ food are observed (EC 2011), but the use of Ag in nano-form in plastic food containers is currently not authorised in the European Union (Art.9 in EU/10/201, EC 2011).

Like other plastic additives (e.g. the phthalates and brominated flame retardants) Ag is not covalently bound to the plastic matrix and can (and is intended to) be released during use (Chaudhry et al. 2008). For antimicrobial activity a small amount of Ag has to be present on the surface of the plastic material so that Ag ions can be formed in an aquatic environment (Kumar et al. 2005). Consequently, Ag is also available for oral intake with food that was in contact with this plastic surface. Ag ions ingested in small concentrations, e.g. at the level of dietary intake of 70–90 µg day⁻¹ are currently not considered as a health problem (Wijnhoven et al. 2009). However, associated with the registration of novel additives containing nanoparticles, risk assessments for Ag and Ag nanoparticles are required, which have to be based on exposure data.

Migration of Ag nanoparticles from plastics into food simulants was investigated by one study on the example of polyethylene bags, where they found a maximal migration rate of 8 ng cm⁻² after 10 days at 25°C for 4% acetic acid (Huang et al. 2011). Furthermore, in a student experiment on Ag-impregnated plastic food containers (Hauri & Niece 2011), a maximum Ag concentration of 0.9 µg l⁻¹ was determined in 5% acetic acid after 7 days. In this latter experiment the initial Ag content of the boxes was not determined. In both studies only total amounts of Ag were measured and the fraction of Ag in the form of nanoparticles had not been determined. Therefore, the human exposure to Ag (nanoparticles) resulting from Ag-doped food containers still remains largely unknown and the actual risk for the consumer is difficult to assess.

There are different possibilities of introducing the metal into the plastic material. Ag can be incorporated in a polymer in the form of Ag ions trapped in zeolites or related structures with adequate cavities. These zeolites can be added to the polymer suspension in the extruder, which
results in a homogeneous distribution of trapped Ag ions in the plastic or instead by incorporation into the food contact layer only (Quintavalla & Vicini 2002). Similarly, free Ag nanoparticles can be added to the polymer (Yeum et al. 2007; Chaudhry et al. 2008). Recently, Ag migrating from a future generation of biodegradable plastic material (a polylactide) with Ag zeolites to food simulants was studied (Fernandez et al. 2010). Also the effect of different filler types on Ag migration from a polyamide was reported and it was pointed out that the water diffusion characteristics of the emerging composite are decisive parameters for the antimicrobial properties (Kumar et al. 2005). However, in these studies the form of the released Ag was not investigated. It is assumed that Ag nanoparticles may exert a different toxicological response in biota compared with Ag ions (Wijnhoven et al. 2009), and at the same time are readily transformed into Ag ions. This creates a need to assess both the exposure to Ag ions and nanoparticles for further use in risk assessment. Additionally, for reusable food containers information on Ag migration under multiple use conditions is important for the assessment of a realistic consumer risk and benefit.

This study aims at quantifying consumer exposure to total Ag and Ag nanoparticles in commercial plastic food containers, which are necessary data for the assessment of consumer risk. Plastic additives migration to food is often studied by using food simulants because this allows one to standardise the experimental conditions and to facilitate analysis (EC 1997). Therefore, we investigated the total Ag migration over time from Ag-doped plastic food containers into food simulants to identify food properties that might influence the migration. Additionally, the form of the released Ag was studied by using single-particle inductively coupled plasma mass spectrometry (SP-ICP-MS) to distinguish nanoparticles and ions using the method described by Gschwind et al. (2011).

Materials and methods

Analysis of Ag content and topography of the boxes

Four commercial plastic food containers labelled or marketed as containing ‘nano-’ or ‘micro-Ag’ were investigated (for further information, see the Supplementary Information). We qualitatively determined the Ag content of the commercial products, including a test for the homogeneity of Ag in the raw material with laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) (Stehrer et al. 2010). The containers were ablated from the outside and from the inside of the original container in order to check for the existence of a coating layer on the plastic surface by a 193 nm ArF excimer laser (Compex, Lambda Physics, Göttingen, Germany) using the following conditions: spot size, 95 µm; repetition rate, 10 Hz; scanning speed, 10 µm s⁻¹; line length about, 1 mm; and energy density, 20 J cm⁻². The measurement parameters of the ICP-MS (ICP-MS 7500cs; Agilent Technologies, Tokyo, Japan) are summarised in Table 1.

Furthermore, we quantitatively determined the Ag content of the commercial products by digesting triplicate samples of the polymers and quantifying by solution nebulisation inductively coupled plasma mass spectrometry (SN-ICP-MS) (for the parameters, see Table 1). About 10 mg of the polymers per sample were dissolved in 2 ml of nitric acid (sub-boiled, pro analysis; Merck, Darmstadt, Germany) and 2 ml of hydrogen peroxide (trace select ultra; Fluka, Sigma-Aldrich Corporation, Buchs, Switzerland) by a microwave-assisted pressure digestion procedure (ultraCLAVE II; MLS GmbH, Leutkirch, Germany, 60 min with up to 200°C and 80 bar). The method allowed complete digestion of the polymers and clear solutions without residuals were obtained. The digestion solutions were transferred into 10 ml water and then diluted by a factor of 10 using 2% nitric acid. The ICP-MS was calibrated with Ag standard solutions of 0.2, 1 and 5 ng g⁻¹ (prepared from a silver ICP standard, 1000 mg l⁻¹ Ag in 2% HNO₃; Merck). Indium was used to determine the recovery of the digestion procedure and yttrium served as an internal standard for the ICP-MS measurements. The method allowed the detection of Ag with an LOD of 0.1 µg g⁻¹ plastic (derived from the instrumental LOD and sample preparation as described in the Supplementary Information).

The topography of the food boxes was determined by atomic force microscopy (MFP3D) (Asylum Research,

| Table 1. Measurement parameters for the LA-, SN- and SP-ICP-MS experiments. |
|-----------------|-----------------|-----------------|
| **RF power (W)** | **1400**        | **1400**        | **1400**        |
| **Carrier gas (He) (l min⁻¹)** | **1.0 L/min** | **–**          | **0.35**         |
| **Nebuliser gas (Ar) (l min⁻¹)** | **0.75**      | **0.85**        | **0.85**         |
| **Auxiliary gas (Ar) (l min⁻¹)** | **0.7**        | **0.7**         | **0.8**          |
| **Plasma gas (Ar) (l min⁻¹)** | **17.5**       | **17.5**        | **17.5**         |
| **Isotopes measured** | **¹³C, ²³Na, ⁵⁶Zn, ¹⁰⁷Ag, ¹⁰⁹Ag** | **⁸⁹Y (internal standard), ¹⁰⁷Ag, ¹⁰⁹Ag, ¹¹⁵In** | **¹⁰⁷Ag** |
| **Dwell time (ms)** | **10**          | **100**         | **1**            |
| **Total integration time** | **30 s background, 90 s signal** | **5 × 10 s**    | **5 min**        |
| **Scan mode** | **Peak hopping** | **Peak hopping** | **–**            |
Santa Barbara, CA, USA). Tapping-mode atomic force microscopy (AFM) imaging was conducted using silicon nitride cantilevers (OMCL-AC160TS – Olympus microcantilevers; Olympus, Tokyo, Japan) with a spring constant of 26 N m\(^{-1}\) and a resonant frequency of 300 kHz in air under ambient conditions. The AFM (height) images were evaluated with WSxM (Horcas et al. 2007).

**Determination of migration rates in different food simulants**

With the two plastic containers A and D that actually contained Ag (Table 2) we conducted migration experiments with food simulants. As recommended in Commission Directive 97/48/EC for food contact material investigations (EC 1997) the following four food simulants were used: distilled water, 3% w/v acetic acid (glacial, pro analysis; Carlo Erba Reagents, Milan, Italy), 10% v/v ethanol (absolute, analytical grade; Scharlau, Barcelona, Spain) and commercial olive oil.

For the migration experiments, weighed pieces of the commercial product A (type A1) with surfaces of 1–2 cm\(^2\) were placed into microtubes (2 ml volume, polypropylene) and 1.8 ml of the respective food simulant were added. The samples were incubated in the dark at 20°C for a period of 1 h to 10 days (data points at 1, 3, 6, 10 h, 1, 5 and 10 days) with three replicates for each datum point (according to European Commission guidelines – EC 1997 – 20°C is the worst-case temperature simulating storage in a refrigerator). After incubation, the plastic pieces were removed from the microtubes and the vials were sonicated. The migration samples with water and with 3% acetic acid were analysed by SN-ICP-MS after adding yttrium as an internal standard and diluting with 2% nitric acid without further treatment. For the migration samples with 10% ethanol (v/v), the ethanol was vaporised prior to analysis by ICP-MS in order to avoid instabilities of the nebuliser. The olive oil migration samples were digested using the same method as described for the polymer digestion and subsequently measured by SN-ICP-MS. The method allowed the detection of Ag with an LOD of 15 pg g\(^{-1}\) solvent for aqueous, ethanolic and acetic acid and 1 ng g\(^{-1}\) solvent for olive oil (derived from the instrumental LOD and sample preparation as described in the Supplementary Information).

**Characterisation of migrating Ag**

In order to distinguish between migrating Ag in ionic and in nanoparticulate form, samples with higher Ag concentration were generated by incubating product A (type A1) with the food simulant distilled water for 4 or 10 days by using a high polymer/food simulant ratio (>10 cm\(^2\) ml\(^{-1}\)). Droplets of a solution obtained after 4 days were shot on a fast spinning silica waver, thereby drying it with an even spread on the surface. This sample was analysed by
Assessment of migration under multiple-use conditions

For the combination of a food container/food simulant with the highest migration rates, an additional experiment was conducted to assess migration under realistic multiple-use conditions. Migration for intact food boxes was determined in two sets of three subsequent incubation experiments in order to simulate conditions of multiple use. For these experiments two boxes of type A2 and A3 were incubated for 10 and 4 days, respectively (samples 1a and 2a). They were filled to 1 cm height with the food simulant 3% acetic acid that showed the highest migration rates in the migration experiments. No sonication was performed prior to sampling since this might enhance the Ag release. In order to simulate a second use cycle, we stored the used boxes empty for 10 days in the dark at room temperature and then incubated each again with food simulant for 10 days (samples 1b and 2b). The third incubation followed directly on the second without storage (samples 1c and 2c).

Models

A model for migration of nanoparticles from plastic containers was derived from basic laws of diffusion kinetics for the case of non-steady diffusion from a solid–liquid interface (Simon et al. 2008). If the constant parameters are lumped together into the parameters \( a \) and \( b \), this model takes the form of a power function (1) with \( b = 0.5 \) and \( f(t) \) describing the number of particles migrating from the plastic container per surface:

\[
f(t) = at^b
\]

In this ideal case only particles of one size were assumed. In our case there is no information on the size distribution of the particles (be they nanoparticles or ions), but the shape of the curve may remain. By estimating \( a \) and \( b \) one can fit a power function to the migration values, which are given in mass of Ag per surface.

It has to be kept in mind, however, that a power function has no limit value, and therefore is only valid if the thickness of the diffusion medium can be assumed as being infinite or if the incubation interval is much smaller than the interval needed for complete diffusion. In order to reflect the limited availability of Ag nanoparticles or ions for migration from the plastic material, we adapted a 2D Lagrangian Particle Tracking Model (LPTM) (Weitbrecht 2004) to account for 1D diffusion. Further information on this model is given in the Supplementary Information. For model comparison, we fitted both the power function and the numerical model to the migration data.

Results

In two out of four tested food containers Ag was detected at significant signal intensities by LA-ICP-MS. Scanning and hole-drilling LA-ICP-MS experiments on the inside and outside of the containers provided similar Ag signals (for representative graphs, see the Supplementary Information), which indicates that the Ag is contained in the bulk material and not in a coating layer on the polymer. The signal characterising the inside of the polymer (spatial resolution of 120 µm) varied within one order of magnitude for different locations of the containers.

For all containers A–D the Ag content was quantitatively determined by SN-ICP-MS after acid digestion of the food containers. For the food boxes A, boxes of different sizes A1–A3 contained different amounts of Ag. In the two food containers A and D Ag at concentrations of 9.7–23 and 37 µg g\(^{-1}\), respectively, were quantified. For the containers A the SD of three ICP-MS measurements from different places at the bottom and the walls is 16–22% (Table 2), which gives an indication that the Ag may not be evenly distributed in the plastic. Such an inhomogeneous Ag distribution is in agreement with the conducted LA-ICP-MS experiments. The Ag concentrations of the other two containers B and C were below the LOD of 0.1 µg g\(^{-1}\) plastic (Table 2).

The results of the migration experiments for the food boxes A1 are summarised in Figure 1; the fitting parameters and the goodness of fit for the migration curves are given in the Supplementary Information. The concentration of Ag in the food simulants increases with incubation time and
depends on the respective food simulant. The largest migration of 9.5 ng cm$^{-2}$ after 10 days was found for the most acidic food simulant 3% acetic acid. For water and 10% ethanol v/v, half as much migration after 10 days was observed. For olive oil no migration was found (LOD = 1 ng g$^{-1}$ oil).

For the plastic bags D only negligible migration of the contained Ag was detected: the maximum was 0.5 ng cm$^{-2}$ after 10 days for acetic acid; all other values were below the LOD (0.5 ng cm$^{-2}$).

For the food boxes A, a concentrated migration solution was prepared by using a larger polymer/food simulant ratio (higher concentration needed for SEM and TEM/EDXS, as well as for SP-ICP-MS, since the sample uptake of the single droplet generator is in the pL range). In this solution, the presence of metallic nanoparticulate Ag could be proved by TEM/EDXS and TEM/ED (Figure 2 (a)–(f); the Ni signal in the EDXS plots originates from the TEM grid). It can further be derived that in addition nanoparticles are formed that probably consist of AgCl and AgS (for details, see the Supplementary Information). Nanoparticle agglomerates with primary particle sizes of 20–100 nm were found by SEM (Figure 2(g)).

The analysis by SP-ICP-MS with microdroplet dispenser also showed Ag in nanoparticulate form and was used to determine the ratio between ionic and particulate Ag (see Figure 2(h) and the Supplementary Information) as described in the following: Figure 2(h) represents the transient signal of an SP-ICP-MS measurement that shows constant signals of approximately 500 counts s$^{-1}$ (cps) and peaks above 2000 cps. The constant signals at 500 cps were generated from single droplets at intensities that correspond to Ag ions in solution, whereas the peak signals represent nanoparticles or nanoparticle agglomerates in the solution. Based on the number of peaks for each Ag form and the atomic mass of Ag it was estimated that 12% of the mass of Ag that is released from the food box is in nanoparticulate form (for details, see the Supplementary Information, ch. 6). By comparison with a calibration point, the detected events can be assigned to nanoparticles of 100–350 nm (see the Supplementary Information, ch. 6). However, it should be noted that also agglomerates as detected with SEM and TEM can cause the events >2000 cps, so that the primary particles may be smaller.

For comparison, the more realistic case of incubation in intact boxes was tested for the worst-case food simulant 3% acetic acid with boxes of the lowest (A2) and the highest (A3) Ag content. After 10 days we found a maximum migration of 30 ng cm$^{-2}$ for the new A3 box and 2 ng cm$^{-2}$ for the reused A3 box (Figure 3). Experiment 2 found that initially there is less leaching, but the sums of 1a–c and 2a–c are approximately the same (34 and 32 ng cm$^{-2}$, respectively), indicating that a defined amount of Ag may be available for leaching, regardless of the storage and incubation times. With an Ag amount per surface of 0.079 g cm$^{-2}$ for product A, we calculated that 2.0–2.9% (product A2) and 1.8–1.9% (product A3) of the initial Ag content leached out of the plastic in the multiple-use experiments.

Thus, we observed a rapid initial migration that appears to be restricted to a small percentage of the initial Ag content. In order to identify reasons for this behaviour, we studied the surface of the plastic boxes by AFM, which showed a rough surface with variations in height of up to 10 μm. Therefore, the actual surface area may be larger by a factor of about 100 (10 × 10 for two dimensions) compared with the nominal surface area (Figure 4).

**Discussion**

Out of four Ag-labelled products tested in this study, only two contained Ag in significant amounts. The other two
claimed to contain nano-Ag, but even with the sensitive techniques applied in this study, no Ag was detected.

Since the antimicrobial effect presumably is based on the release of Ag ions or nanoparticles into the stored food or onto the plastic surface, a considerable amount of Ag has to migrate from the plastic material in order to fulfil the product claim. Products A and D leached 30 and 0.5 ng cm$^{-2}$ in 10 days, respectively, and an effect against microorganisms normally is expected for a concentration of around 30 µg g$^{-1}$ solvent for Ag ions (EC$_{50}$ for

Figure 2. Identification of nanoparticles: transmission electron microscopy (TEM) images of nanoparticles from the dried migration solution (a, c, e) and corresponding ED (b) and EDXS (d, f) characterising two regions: (a–d) for region A and (e–f) for region B. SEM image (g) and Ag signal in the ICP-MS in counts s$^{-1}$ from introducing single droplets of a migration solution (h).
Escherichia coli) (Malachova et al. 2011). If the released Ag is assumed to penetrate food to a depth of 10 µm, then, assuming a density of 1 kg l\(^{-1}\) for the food and an even distribution within the film of 10 µm, 30 ng cm\(^{-2}\) amounts to the EC\(_{50}\) value of 30 µg g\(^{-1}\). This means that product A would have an antimicrobial effect and product D would not. The penetration depth, however, will depend on the physical and chemical characteristics of the food, as well as on the distribution and composition of the bacterial population, so that a general conclusion concerning the antimicrobial effect is difficult to draw.

In the recently published study on polyethylene (PE) bags of a different brand after 10 days at 25°C, a maximum of 8 ng cm\(^{-2}\) was found for migration into 95% ethanol (Huang et al. 2011). In our study we found substantially less migration (maximal 0.5 ng cm\(^{-2}\) in 3% acetic acid and <LOD for ethanol) for the PE bags (even considering the smaller Ag content of 37 µg g\(^{-1}\) in our study in contrast to 100 µg g\(^{-1}\) in Huang et al. 2011), but similar migration for the food boxes. In the experiment by Hauri and Niece (2011) the highest migration without heating was 0.9 µg l\(^{-1}\) after 7 days, presumably amounting to about 1.1 ng cm\(^{-2}\) (assuming 194.4 cm\(^2\) incubated surface from

Figure 3. Migration of Ag from intact boxes (A2 and A3) into food simulant 3% acetic acid in multiple-use experiments.

Figure 4. 3D image of the box surface for product A3 (left); and cross-section from the upper left corner to the lower right of the 3D image showing the height profile (right). Analysis by atomic force microscopy (AFM).
a comparison with similar boxes), which is substantially less than in our experiments. For the food storage container that contained leachable Ag, the migration rate was found to depend on the food simulants used. pH especially seems to have an important influence (the more acidic the simulant, the more leaching). The highest migration was found for 3% acetic acid (pH 3), which was also found by Hauri and Niece (2011) (compared with deionised and tap water) and has been reported previously for Ag-doped glass containers (AFC-Panel 2006).

Busolo et al. (2010) found that migration of Ag from polyactic acid coatings accelerated after 6 days. In our experiments we could not see such acceleration. Rather, a limit value was reached and under multiple-use conditions hardly any Ag leaches from the boxes in the follow-up experiments. Compared with the total content of Ag in the box, only a small amount of Ag is released (approximately 2%). It can be assumed that initially Ag leaches only from the easily accessible parts from the rough surface, but not from sites further inside the plastic. Pores in the surface of up to 10 μm increase the surface area so that the apparent diffusion rate per nominal surface area is higher than the real diffusion rate per actual surface area. With a migratability of 1.7 × 10−7 m per month as theoretically derived by Simon et al. (2008) for 5 nm nanoparticles in polypropylene at 25°C, a migrating flux of Ag of about 10−5 ng cm−2 day−1 can be calculated. However, our experimental results indicate a migration flux of up to 4 ng cm−2 day−1 for a smooth surface (Figure 2). Consequently, even by taking into account a factor of three to four for the rough surface, the maximum migration is much higher than predicted by Simon et al. (2008) so that it seems that no nanoparticles diffuse through the polymer, but Ag ions that are released either by nanoparticles or capturing structures such as zeolites.

Another experimental finding is that a small fraction of Ag indeed is released in the form of Ag nanoparticles, which suggests that the original polymer was produced by using Ag nanoparticles. However, we cannot exclude that secondary particles were formed as previously reported by Akaighe et al. (2011), but the reduction of Ag under our experimental conditions seems less likely than a release of nanoparticles from the plastic. Furthermore, it can also not be excluded that the high polymer surface-to-liquid ratio required for the SP-ICP-MS measurements influences the ratio of ionic to particulate Ag.

Under conditions of multiple use Ag migration into the food simulants decreases dramatically after the first use. In the subsequent incubation experiments up to one order of magnitude less Ag was released. We assume that Ag leaching occurs mainly from the uppermost layer of the plastic where the food simulant can enter the pores on the surface, thereby minimising the migration path inside the plastic. Food simulant might also enter into the plastic as postulated by Kumar et al. (2005), thus further enlarging the diffusion coefficient.

Interestingly, all equations describing migration from the small pieces were exponential equations to the power of about 0.35, which is in contrast to the theoretically derived exponent of 0.5 for nanoparticle migration in plastics (Simon et al. 2008). The deviation may imply that the observed Ag ions in the food simulants rather result from Ag ion migration in the water-saturated plastic zone (like that postulated for Ag ion migration in polyamide; Kumar et al. 2005) than from nanoparticle migration inside the plastic. This would mean that the dominating process may not be diffusion inside the plastic but oxidation of Ag-NP into Ag ions in the surface layer and subsequent dissolution (both steps are possibly pH dependent as found in our study). Therefore, the apparent diffusion coefficient $D$ from the numerical model is also the result of different unknown processes and cannot be used directly to characterise the diffusion process.

The fit with the numerical model is not significantly better than the fit with the power function. However, the numerical approach would allow implementation of further processes to test the above mechanistic conclusion of leaching from a confined surface layer. Further experiments that include samples with longer incubation times are required to validate this hypothesis and to set up an appropriate model.

**Exposure assessment**

For realistic consumer exposure to, for example, a piece of meat stored in a food container, we can deduce from our measurements that a worst-case acute exposure to 4.2 μg Ag can result from storage of 100 ml food in a new Ag-doped box of normal size (calculated for 30 ng cm−2 migration from a 140 cm2 surface). The Ag concentrations in drinking water in the United States for comparison ranged from 0.1 to 9 μg l−1 in 1969 (McCabe et al. 1970) and also food contains trace amounts of Ag. Therefore, from our study we conclude that consumer exposure to Ag from Ag-doped plastic containers such as the ones investigated in this study will be negligible in comparison with the background exposure of the general population (2 L of water alone may contribute 18 μg). Similarly, the exposure to Ag nanoparticles is quite low. However, due to methodological challenges, natural background levels of Ag nanoparticles yet remain to be measured. It has been shown that Ag nanoparticles can be formed under environmentally relevant conditions under the influence of humic acids (Akaighe et al. 2011) or can be formed by plants when exposed to elevated concentrations of Ag(0) (Gardea-Torresdey et al. 2003), but whether these reactions take place in the environment is not known. It is therefore not possible to compare the results for Ag nanoparticles with a safe background level. Considering also the uncertainties around the toxicological effects of Ag nanoparticles (Wijnhoven et al. 2009) and,
for example, the possibility of the Trojan horse mechanism (Kreuter 2004), a health risk from Ag nanoparticles migrating from Ag-doped food boxes seems unlikely, but cannot be excluded.

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