

Supplemental Information for

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

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1. Product and packaging information for products A-D



Figure S 1: Product information for product A



Figure S 2: Product information for Product B



Figure S 3: Product information for Product C



Figure S 4: Product information for Product D

2. Laser ablation (LA)-ICP-MS

Transient signals of the LA-ICP-MS experiments including about 30 seconds of gas blank and about one minute of ablation are shown in Figures S5 and S6. Figure S5 shows a line scan of the surface of product A and Figure S6 shows a hole drilling experiment on the product A, which corresponds to a crater depth of about 50 μm .

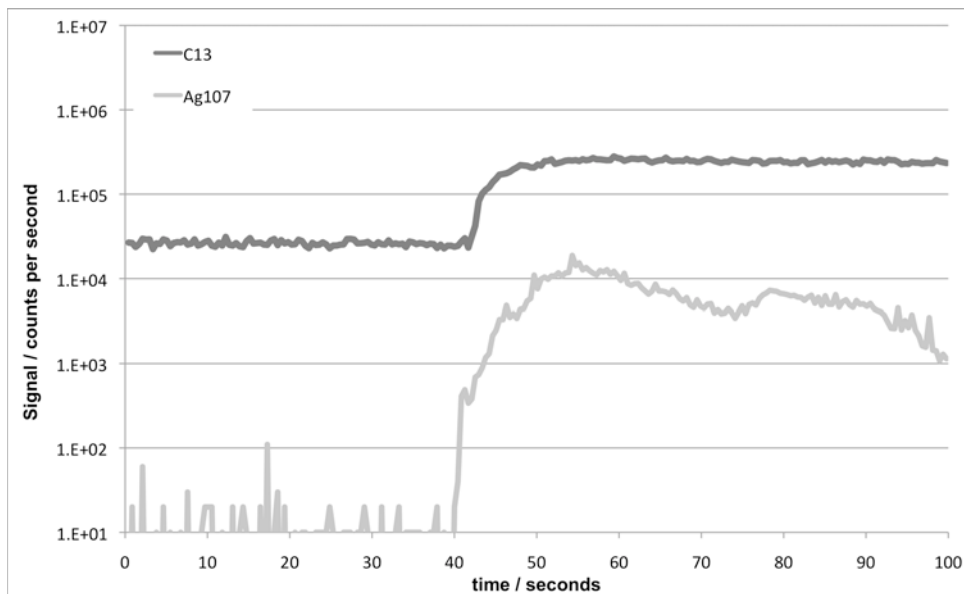


Figure S 5: LA-ICP-MS line scan (0.6 mm) on the surface of product A

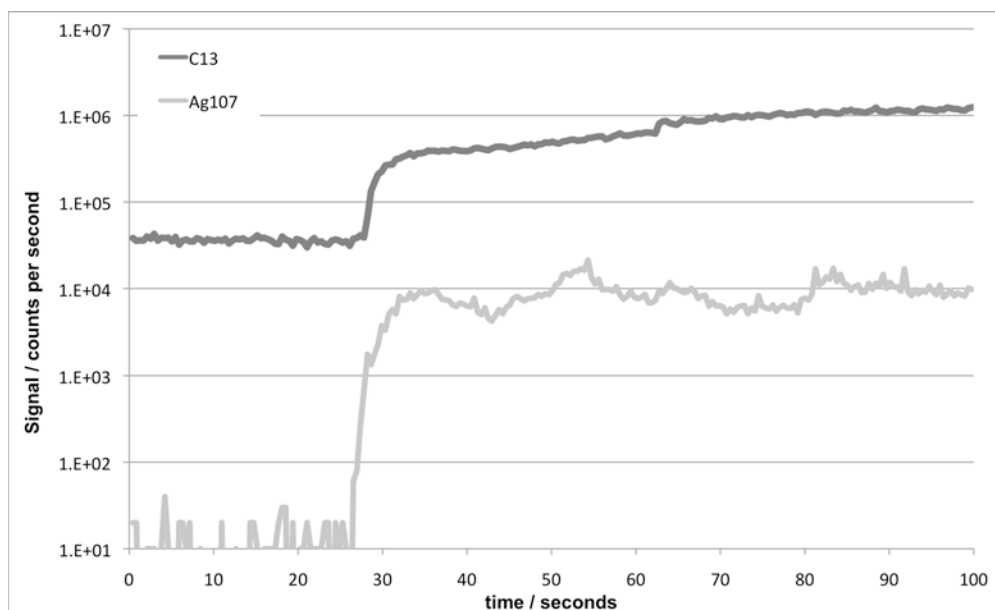


Figure S 6: LA-ICP-MS drilling experiment with product A (crater depth 50 μm)

3. Scanning electron microscopy (SEM)

We generated a concentrated sample by incubating one sample of product A (type A1) with a high polymer/food simulant ratio ($>10 \text{ cm}^2/\text{mL}$) for 4 days (food simulant: distilled water). Droplets of the obtained solution were shot on a fast spinning silica waver, thereby drying it with an even spread on the surface. This sample was analyzed by scanning electron microscopy (SEM, Zeiss Gemini). The results are given in Figure S7 (EDXS was not possible, because of interference of the silica waver).

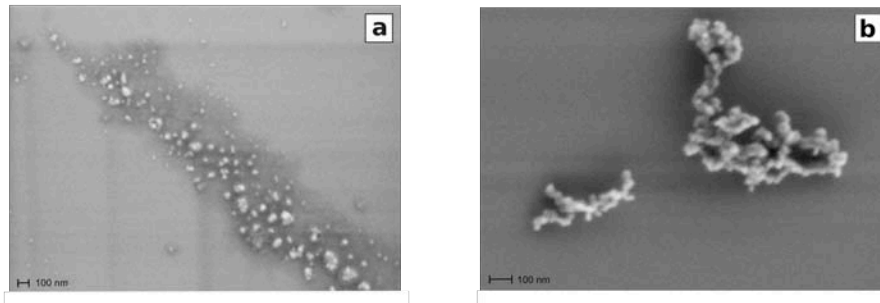


Figure S 7: Nanoparticulate structures in concentrated solution (food simulant: dist. water) observed by SEM

4. Determination of the chemical identity by TEM-ED

In Figure S8 four electron diffractograms (ED's) of different regions of the TEM grid are shown. In ED001 two rings are marked that can be attributed to metallic silver (reflex 111 (2.239 Angström) and reflex 220 (1.44 Angström)). Inside the inner circle further reflexes can be seen that cannot be attributed to metallic silver. Both reflexes for metallic Ag also appear in ED003. Here, a further strong reflex was detected (reflex 200 (2.83 Å, theoretical: 2.77 Angström)), which can be attributed to AgCl.

Further reflexes can be found that cannot be attributed to either metallic Ag or AgCl. The same is true for ED004 and ED007. From TEM-EDXS and TEM-ED together it can be concluded that Ag is present in different forms, at least as metallic Ag, and probably also as AgCl and AgS.

The formula for the analysis of ED's for a picture width of 9 cm is:

$$\text{measured value [mm]} \times d \text{ value [Angström]} = 35.6 \text{ [Angström mm]}$$

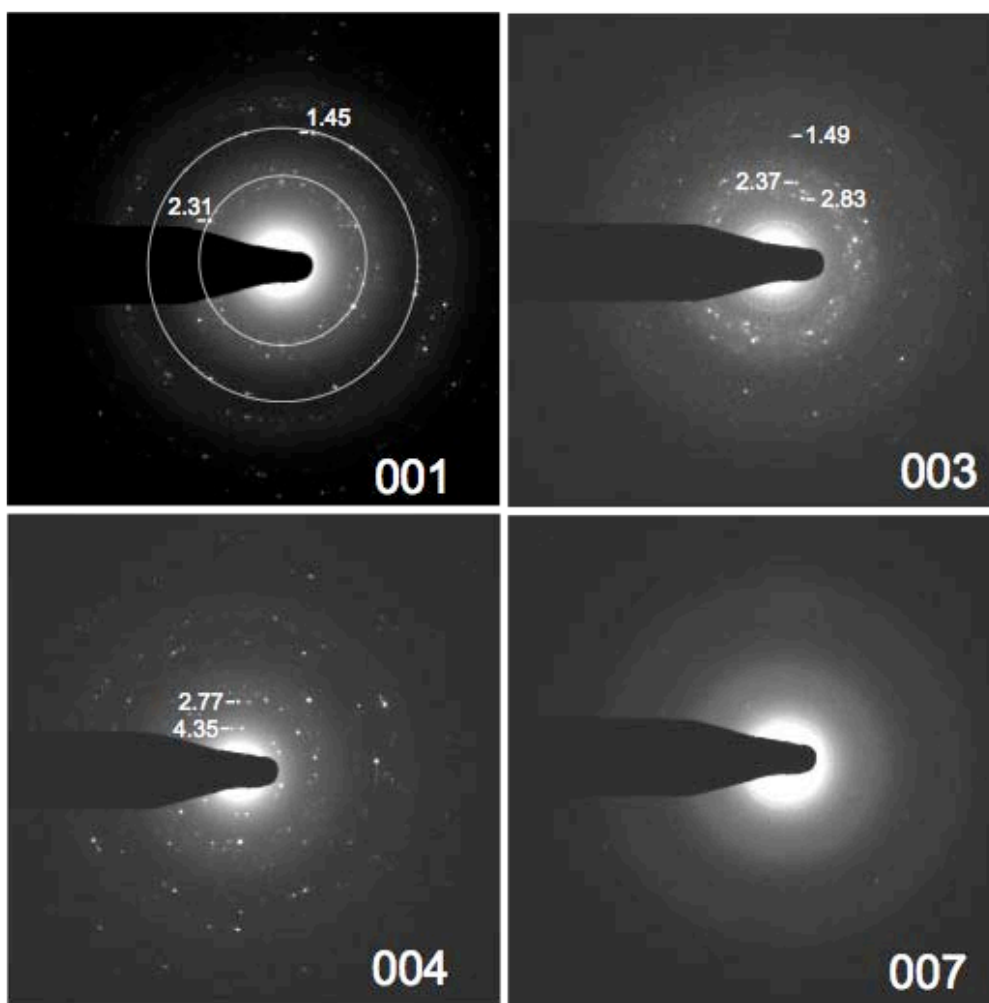


Figure S 8: Electron diffraction (ED) from different regions on the TEM grid

5. Analytical performance for silver quantification

a) Quantification of silver in polymers after digestion

For the polymer digestion recoveries were found to be between 95 and 105% using Indium as recovery standard. Repeatability of the following SN-ICP-MS analysis for a single solution was within 2% standard deviation. Digestion replicates resulted in higher

standard deviations of up to 20%. This variable silver distribution is in agreement with the LA-ICP-MS experiments.

The instrumental limit of detection (LOD) of silver in solutions was determined as 10 pg/g. Polymer digestions and solution preparation lead to a 10^4 overall dilution, which results in a limit of detection of 0.1 μg silver/ g polymer.

b) Quantification of silver in migrations solutions

The limit of detection of silver for the SN-ICP-MS measurements was estimated to be 10 pg/g. Migration solutions in water and acetic acid were diluted by a factor of 1.5 by using 2% nitric acid prior to the SN-ICP-MS measurement. The acetic acid was shown not to significantly change the sensitivity of the system. Ethanolic migration solutions were concentrated by solvent evaporation to half their volume and then diluted with 2% nitric acid resulting in an overall dilution of 1.5. Therefore LODs of silver in aqueous, ethanolic and acetic acid migration solution resulted in 15 pg/g food simulant.

The oil migration solutions were digested prior to the analysis, which resulted in a dilution factor of 100. Therefore, with 1 ng silver/ g food simulant the LOD of silver in oil was higher than for the other food simulants.

6. Determination of particle fraction and size with ICP-MS

For standard SP-ICP-MS the determination of size and number of particles is hampered by differences in the transport efficiency of ions and particles (Pace et al. 2011). The method of using a microdroplet dispenser as published in Gschwind et al. 2011 achieves

100% transport efficiency, which means that ions and nanoparticles are both transported with the same rate and their signals can directly be compared.

The size of the individual Ag particles can be determined by comparing the signal heights to a calibration point. Spherical metallic Ag nanoparticles of 110 nm induce a signal intensity of around 3000 cps for ^{107}Ag (Gschwind et al., 2011). Therefore, supposed that the signals of the migration solution are produced by metallic Ag the detected events can be assigned to Ag nanoparticles of 100-350 nm (spikes of 2'000-110'000 cps). However, it should be noted that also agglomerates as detected with SEM and TEM can cause these events and the initially produced or migrated particles might be smaller. Figure S9 (left) shows a transient signal of an SP-ICP-MS measurement. Six SP-ICP-MS measurements were performed for our sample and summarized in the histogram in Figure S9 (right). This histogram includes 7500 droplet events in total and 40 peak signals >2000 cps (spikes) of varying intensity. The individual signals of each spike were summed up and the sum compared to the sum signal of the droplets to yield the mean particle fraction (illustrated in Table S1).

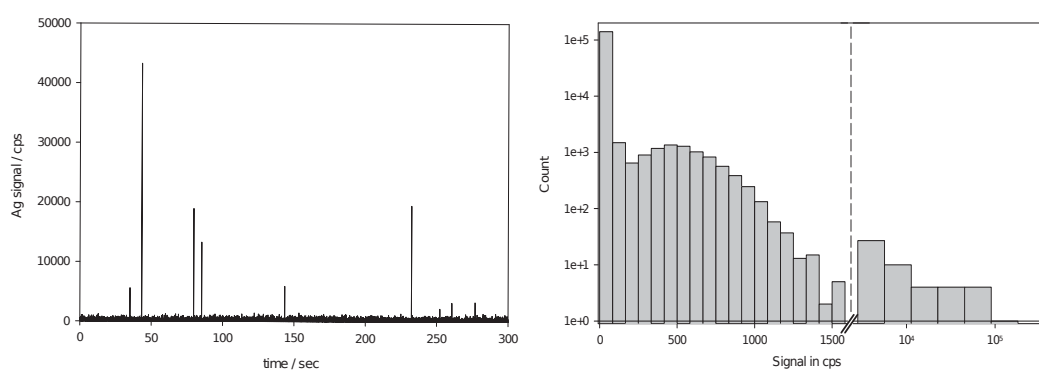


Figure S 9: Example of a transient signal of an SP-ICP-MS measurement (left) and histogram of six SP-ICP-MS measurements of the same sample (right). The break in the x-axis denotes a change in scale

Table S 1: Calculation of the particle fraction

	# events	Calculation	Counts Ag total	Fraction
Solution	7500 droplets*	500cps multiplied by number of droplets	3'750'000	88%
Particles	40 events >2000 cps	Sum of individual spikes > 2000 cps	500'000	12%

*Integration time: 5 x 300 s with 5Hz droplet dispenser frequency

7. The one-dimensional (1-D) Lagrangian-Particle-Tracking-Model (LPTM)

The 1-D-LPTM was adapted from a 2-D approach described by Weitbrecht, 2004.¹⁶ The model consists of a random walk simulation under the assumption that the spreading of the particle ensemble can be treated as a Fickian type of diffusion. Discrete particles are defined that move under the influence of general transport processes. Thereby, we simulate diffusion of silver inside the plastic phase towards the boundary where the particles migrate into the food simulant. A 1-D approach is used because only the particle movements towards the plastic/liquid interface, normal to the boundary, influence the migration speed. As initial condition a number of particles N are homogeneously distributed on a virtual line through the plastic material, normal to the boundary. At each simulation time step every single particle moves a certain distance, randomly distributed. If a particle crosses the plastic/liquid interface we assume that it migrates instantaneously into the food simulant. This process is simulated using an adsorptive boundary condition.

To determine the length of the diffusive step size L in each time step we use the following assumptions: The spreading of an instantaneous plane source driven by molecular diffusion, leads to a Gaussian concentration profile of the form:

$$f(x) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left[-\frac{(x-\mu)^2}{2\sigma^2}\right] \quad (1)$$

with σ = standard deviation and μ = location of the peak value. At the same time, the analytical solution of the advection diffusion equation for an instantaneous plane source leads to the following 1-D concentration profile (Boeker & van Grondelen, 2011):

$$c = \frac{m_a}{\sqrt{4\pi Dt}} \exp\left[-\frac{(x-\mu)^2}{4Dt}\right] \quad (2)$$

with: c = concentration, m_a = mass in the plastic per unit area, t = time, μ = location of the peak concentration and D = diffusion coefficient. Comparing the two expressions in square brackets of equation (1) und (2) it can be concluded with $4Dt = 2\sigma^2$, that the standard deviation of the particle distribution can be determined with

$$\sigma = \sqrt{2Dt} \quad (3)$$

The diffusive step size L for a single particle in our LPTM simulation at a certain time step is therefore given with

$$L = \sqrt{2D \Delta t} \quad (4)$$

The new position of the particle after a time step Δt is determined by:

$$x_{new} = x_{old} + Z L \quad (5)$$

with x as the position of the particle and Z the Gaussian distributed variate with a mean quantity of zero and a variance equal to one. Z is a new variable and not defined in (1). By using the number of particles N that are distributed along the 1-D-line and the apparent diffusion coefficient D as fitting parameters, we can fit the simulation results to our data (numerical model see Textbox S1). The actual number of particles is converted into mass per surface with a conversion factor that relates the maximal particle number available for leaching (N) with the Ag content found in the boxes. For model comparison, we fitted both the power function and our numerical model to our migration data (graphical representation see Figure 1, main text; parameters see Table S2).

Text box S1: One-dimensional (1-D) Lagrangian-Particle-Tracking-Method (LPTM), example for the solvent acetic acid

```

% Definitions
nstep = 2000;      % number of calculated time steps
Dy = DyP(1);      % First fitting parameter: molecular diffusion
                  % coefficient (mm2/s) (curvature of the function)
dt = 0.01;        % time step (s)
L = 1;            % simulation space (here: thickness of plastic) (mm)
P = DyP(2);       % Second fitting parameter N: total number available
                  % silver atoms/ions in the plastic layer (limit value
                  % of the function)
CF_time = 1.16;   %  $\times 10^{-5}$  conversion factor for converting seconds
                  % into days
CF_mass = 1.79;   %  $\times 10^{-13}$  conversion factor for converting maximal
                  % particle number into maximal ng/cm2 (Ag-ions with 107.89 g/mol)

% Distribute n particles evenly on a straight-line segment with 1 cm2
x = [0+L/P:L/P:L]'; % column vector with x positions of the single
ions
n = length(x);      % number of particles, length defines the maximum
                  % length of the vector (n elements)
part_loss = zeros(nstep,1); % column vector with number of lost
                  % particles for every time step
timeset = [dt:dt:nstep*dt];

% Start of simulation
for i = 1:nstep,
    sigma = sqrt(2*Dy*dt); % with normal distribution and sigma
as
                        % characteristic step size at each
                        % time
                        % step for Fickian type of diffusion
                        % (mm)
    k = randn(n,1).*sigma; % k: path length for every particle
    x(:) = x(:) + k;      % calculation of the new position of
                        % every particle

% Definition of boundary conditions
    for j = 1:n
        % left, adsorptive boundary
        if x(j)<0
            x(j) = NaN;
        %right, adsorptive boundary
        elseif x(j) > L,
            x(j) = NaN;
        end
    end
    part_loss(i) = sum(isnan(x)); % summation of NaN for time steps
end
part_loss_ng = part_loss*CF_mass; % conversion particles into
                                % 10-13 ng/cm2
timeset_day = timeset*CF_time;

```

By fitting both models with least squares optimizing procedures we obtain the parameters summarized in Table S2.

Table S 2: Fitting parameters and goodness of fit (R^2) for the two models

Food simulant, box size	Fit with power function			Fit with LPTM		
Parameters	a [ng/cm^2]	b [-]	R^2	N [$1/\text{cm}^2$]*	D [cm^2/s]	R^2
Water, box pieces	2	0.35	0.99	300	0.00065	0.95
Ethanol 10%, box pieces (fit without outlier at day 10)	3.32	0.35	0.97	321	0.00072	0.91
Acidic acid 3%, box pieces	2.31	0.36	0.92	550	0.00050	0.94

* Particle numbers at different time steps are converted to ng/cm^2 for presentation in Figure 2 (using the molar mass of silver, and assuming particles of atomic silver)

For the power function a clear minimum existed. For the LPTM the results are not unambiguous: The optimized parameters depended on the initial values and are not independent from each other. Therefore a set of physically meaningful initial values was tested and the curve with the best R^2 was selected (for a representative sensitivity plot see Figure S1). We conclude that on the basis of this experiment alone it is not possible to derive a diffusion coefficient; also it is likely that other processes than diffusion are involved in the release of Ag to food simulants (see discussion in the paper). We therefore regard our parameters N and D as pure fitting parameters.

Our optimal N differs for the different food simulants, which should not be the case if purely diffusion through the plastic would be described. It should be kept in mind that since we are investigating a commercial product apart from the polymer and the added silver a wide range of additives are present in the plastic that may influence the processes involved in the release of Ag.

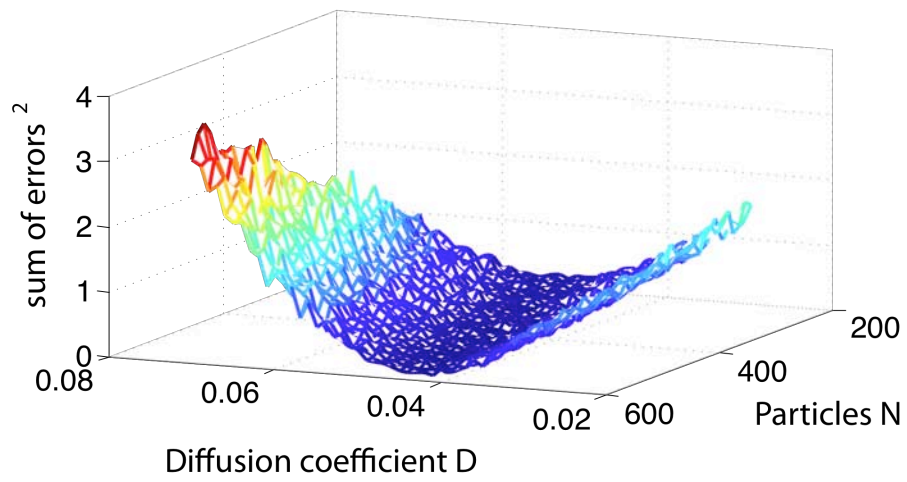


Figure S 10: Sensitivity plot for the optimization of parameters N (particles) and apparent diffusion coefficient D for ethanol

8. Supplemental reference

Boeker E. & Van Grondelle, R. Environmental physics: Sustainable energy and climate change, 2011, Wiley-Blackwell, 3rd ed