

Release of Airborne Particles and Ag and Zn Compounds from Nanotechnology-enabled Consumer Sprays: Implications for Inhalation Exposure

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Revised manuscript ATMENV-D-16-01401

Supplemental Materials

January 2017

Design of the glove box and measurement of the released particles

All products were tested by spraying them into a specially designed 124 L glove box shown in Figure S1 (Supplemental Materials) and then measuring the size distribution and concentration of the released particles. The inner walls of the box were covered with conductive material to minimize static effects. The humidity inside the glove box was ~50%. A conductive sampling port was installed on one side of the box and connected to aerosol instruments. Two air inlets were installed on one side of the box and perpendicular to the sampling inlet to replenish the volume of air removed by the aerosol instruments. The sprays were sprayed in the direction of the sampling port and from a short distance to the port (~30 cm). Thus, particle loss due to settling is expected to be minimal. The use of this experimental design allowed simulating an untreated aerosol that would be present near a consumer's breathing zone.

The released particles were measured using a Scanning Mobility Particle Sizer 3986 (SMPS) and an Aerodynamic Particle Sizer 3321 (APS) (both by TSI, Inc., Shoreview, MN). The SMPS was equipped with a 0.071 cm orifice impactor (cut-off diameter, or d_{50} , =1416 nm) and operated at 0.3 L/min, while the APS was operated at 1 L/min for aerosol sampling and 4 L/min for sheath air flow. The SMPS was set to measure particles in 14 nm – 700 nm range, while the APS counted and sized particles in 0.5 μm – 20 μm range. The combined sampling flow rate of both instruments (1.3 L/min) resulted in the effective air exchange rate of 0.63 h^{-1} inside the box. The aerosol stream sampled from the glove box was split using a splitter (model 3708, TSI, Inc.). All connecting tubing was conductive (TSI, Inc.) and as short as possible to minimize particle losses.

Aerosolization and capture of airborne particles for analysis by transmission electron microscopy (TEM)

Two Ag and two Zn products of interest were selected to investigate the presence of nanoparticles and/or their agglomerates in the airborne phase. The products were aerosolized and the resulting particles captured using an experimental setup shown in Figure 2 (bottom drawing). Here, liquids from S3CS, S13OS, Z2HS, and Z4HS were aerosolized by a three-jet Collison nebulizer with a precious fluid bottle (both Mesa Labs, Butler, NJ) at 5 L/min and 13 psi air pressure. The resulting aerosol stream was diluted with particle-free air at a flow rate of 100 L/min. The combined air flow passed through a flow laminarizer (honeycomb) and entered the flow chamber, from where aerosol particles were sampled by an electrostatic precipitator (ESP) built in-house. The high dilution air flow was needed to remove the liquid aerosol component so that only solid particles would be captured onto the TEM grids. A commercial nebulizer was used instead of sprayers supplied with the investigated products so that a steady aerosol concentration could be maintained for ~ 45 min while the particles were being deposited on TEM grids.

A schematic of the used ESP is shown in Figure S2 (top drawing). The particles entering the ESP were charged by ions emitted by a carbon fiber brush (diameter and length of each fiber is 7 μm and 2.5 cm, respectively; Fu Fong Enterprises Co., Ltd, Taiwan) connected to a high voltage power supply (Bertan[®] 205B, Spellman Corp., Hauppauge, NY) and then deposited onto two HC300-Cu TEM grids (Electron Microscopy Sciences Inc., Hatfield, PA) secured onto a TEM grid holder (modified PELCO unit, Redding, CA). The ESP sampled aerosol at a flow rate of 1 L/min provided by an AirLite pump (SKC, Eighty Four, PA). Based on our preliminary

investigation of the ESP's collection efficiency, it was operated at a collection voltage of negative 12.5 kV and the distance between the fibers and the TEM grids was approximately 2.5 cm. The aerosolization and sampling lasted 45 minutes for each product to accumulate sufficient particle concentration on the TEM grids. A long sampling time needed to collect sufficient amount of material onto the TEM grids was indicated by other studies as well (Lorenz et al., 2011).

Analysis of particles using STEM-EDX

In addition to TEM EDX (discussed in the main body of the paper), using STEM-EDX it is possible to obtain spatially resolved EDS maps of specific nanoparticles. Using STEM, the electron beam is converged to a small probe (<0.5 nm) and scanned across the sample. As well as acquiring a high-resolution image, site-specific EDS analysis can be carried out with a spatial precision of <10 nm (depending on experimental requirements). For our purposes, it meant we could gain an idea of the size, morphology, and chemistry of specific particles within the spray products. One example of the elemental maps obtained from a region is presented in Figure S3. The long thin particles are predominantly made up of Zn, S, and O, while many of the smaller particles are aluminum particulates. It is also clear that while there is some silicon present all over the sample, there is also one specific particle in this particular airborne phase that is Si-rich. This type of approach could aid future studies into the exact chemical makeup of the particles that humans come into contact with.

Table S1. Description of investigated spray products containing silver.

Product Code	Description	Brief description*	Advertised Contents	Density, g/cm ³ , [#]
S1CS	Used as cosmetic spray, dermatologic application	Skin spray	99.99% Pure, Colloidal Silver, Demineralized Water	1.01 ± 0.01
S2HO	Used orally (ingested) to prevent diseases	Ingestible dietary supplement	1.7-10 ppm silver, Water	1.00 ± 0.01
S3CS	Used to prevent unpleasant odors in shoes	Shoe deodorizer	0.001 % Silver, Ethanol (other components are unknown)	0.79 ± 0.00
S4HO	Used orally (ingested) as a health supplement	Ingestible dietary supplement	22 µg/ml of Silver, Water	0.99 ± 0.00
S5CS	Used for skin enhancement	Skin spray	Water, Nano Silver, 1, 3 Butylene Glycol, Sorbitol, Cucumber Extract, Diglycerin, Dipropylene Glycol, Aloe Vera Extract, PEG-60 Hydrogenated Castor Oil, Tetrasodium EDTA, Dipotassium Glycyrrhizin Extract, Methylparaben, Propylparaben	1.00 ± 0.02
S6CS	Used to clean skin	Skin spray	Water, Nano Silver, Sorbitol, 1, 3 Butylene Glycol, Dipropylene Glycol, PEG-60 Hydrogenated Castor Oil, Essential Oil, Tetrasodium EDTA, Methylparaben, Propylparaben	1.00 ± 0.01
S7HS	Used dermatologically as antifungal spray	Antifungal skin spray	Deionized Water, 20 ppm of Colloidal Silver	1.03 ± 0.01
S8HS	Used to improve breathing	Breathing enhancer	10 ppm of Colloidal Silver, Deionized Water.	1.02 ± 0.01
S9HS	Used as dietary supplement	Sprayable dietary supplement	2 µg/ml Silver, Pharmaceutical-Grade Purified Water	1.03 ± 0.00
S10OS	Used to prevent unpleasant odors in shoes	Shoe deodorizer	Isopropyl Alcohol, Water, Peppermint Essential Oil, Colloidal Silver	0.90 ± 0.01
S11CS	Used as cosmetic for skin protection	Skin spray	99.99% Pure Silver (water is added by consumer)	0.99 ± 0.01
S12HS	Used orally as a dietary supplement	Skin spray	10 ppm of Silver, Deionized Water	1.03 ± 0.00
S13OS	Used to clean surfaces	Surface cleaner	Nano polymer, Nonionic Surfactants, Citric Acid, Monohydrate, Alcohol, C9-11, Ethoxylated, Quaternary Coco Alkyl Methyl Amine Ethoxylate Methyl Chloride)	1.05 ± 0.00

[#]: Determined in this study by weighing 1 ml of product.

*: used in figure and table captions.

Table S2. Description of investigated spray products containing zinc compounds.

Product Code	Description	Brief Description*	Advertised Contents	Density, g/cm ³ , [#]
Z1CS	Used as a sunscreen	Sunscreen	Zinc Oxide 19%, Aloe Vera, Gel Bladderwrack Extract, Caprylic Triglycerides, Caprylyl Glycol, Cucumber Extract, d-alpha Tocopherol, Grapefruit Seed Extract, Jojoba Oil, Magnesium Ascorbyl Phosphate, Sea Kelp Extract, Sunflower Oil	0.80 ± 0.01
Z2HS	Used as a skin protectant	Skin protectant	Zinc Pyrithione (0.25%), SDA-40 Alcohol, Isopropyl Myristate, SLS Needles, Undecylenic Acid	0.78 ± 0.01
Z3CS	Used as a sunscreen	Sunscreen	Aqua (Water), Caprylic/Capric Triglyceride, Zinc Oxide, Dicaprylyl Carbonate, Mentha Piperita Water, Alcohol, Glycerin, Titanium Dioxide, Lauryl Glucoside, Polyglyceryl-2 Dipolyhydroxystearate, Pongamia Glabra Seed Oil, Cocos Nucifera (Coconut Oil), Gardenia Tahitensis, Glyceryl Isostearate, Polyhydroxy Stearic Acid, Cetearyl Glucoside, Cetearyl Alcohol, Tocopherol, Parfum (Natural Fragrance), Xanthan Gum, Glyceryl Caprylate, Alumina, Stearic Acid, Citric Acid, Polyepsilon-Lysine, Sodium Benzoate, Potassium Sorbate, Benzyl Benzoate, Benzyl Salicylate, D-Limonene, Linalool	0.98 ± 0.01
Z4CS	Used as skin protectant	Skin protectant	Zinc Pyrithione (0.25%), Isopropyl, Myristate, SD Alcohol 3C, Sodium Lauryl Sulfate, Simethicone USP	0.78 ± 0.05
Z6HS	Ingested orally as a dietary supplement	Ingestible dietary supplement	0.0975 mg/ml of Zinc (Gluconate), Purified Water, Vegetable Glycerin, Soy Lecithin, PEG-40 Castor Oil, Menthol, Peppermint Oil, Clove Bud Oil, Slippery Elm Extract, Stevia Extract, Echinacea Extract, Elderberry Extract, Wild Cherry Bark Extract	1.06 ± 0.01

[#]: Determined in this study by weighing 1 ml of product.

*: used in figure and table captions.

Table S3. Size distribution parameters of aerosolized Ag- and Zn-based products. All values are in nanometers and represent aerodynamic diameters. The upper size limit of the measured aerosol was 20 µm. The averages and standard deviations are based on at least three repeats.

Product type	Parameter / Metric	Median ± Std. Dev.	Mean ± Std. Dev.	Geometric Mean ± Std. Dev.	Mode ± Std. Dev.
Silver	Number-based	193.86 ± 160.83	328.82 ± 275.31	174.44 ± 142.15	264.55 ± 365.65
Zinc		128.59 ± 153.19	276.72 ± 203.61	127.75 ± 106.46	110.50 ± 165.68
Silver	Mass-based	3,879.47 ± 3,077.87	4,554.32 ± 2,953.20	3,565.71 ± 2,646.79	5,913.43 ± 5,890.47
Zinc		10,730.70 ± 4,907.56	10,347.53 ± 4,449.25	8,545.58 ± 3,980.09	16,552.60 ± 7,283.77

Table S4. Number concentrations (particles/cm³) of aerosolized Ag-based products. The numbers represent averages and standard deviations based on at least three repeats. Spray products: S1CS: Skin spray, S2HO: Ingestible dietary supplement, S3CS: Shoe deodorizer, S4HO: Ingestible dietary supplement, S5CS: Skin spray, S6CS: Skin spray, S7HS: Antifungal skin spray, S8HS: Breathing enhancer, S9HS: Sprayable dietary supplement, S10OS: Shoe deodorizer, S11CS: Skin spray, S12HS: Skin spray, S13OS: Surface cleaner.

Size\ Product	S1CS	S2HO	S3CS	S4HO	S5CS	S6CS	S7HS	S8HS	S9HS	S10OS	S11CS	S12HS	S13OS
14 - 100 nm in aerody- namic diameter	(8.4±6.6) ×10 ²	(1.1±0.7) ×10 ⁵	(1.1±2.4) ×10 ⁵	(3.9±3.0) ×10 ²	(1.4±1.5) ×10 ²	(2.0±0.7) ×10 ³	(5.8±2.5) ×10 ²	(3.1±1.8) ×10 ²	(2.4±1.3) ×10 ²	(1.4±0.2) ×10 ⁴	(1.6±0.5) ×10 ³	(2.2±1.4) ×10 ²	(4.8±1.0) ×10 ³
0.1 - 2.5 µm in aerody- namic diameter	(1.4 ± 0.6) ×10 ³	(3.1±1.3) ×10 ⁴	(7.4±2.1) ×10 ³	(6.8±3.6) ×10 ²	(9.7±4.3) ×10 ²	(2.1±0.6) ×10 ³	(1.7±0.3) ×10 ³	(1.6±0.3) ×10 ³	(5.6±1.8) ×10 ²	(1.4±0.3) ×10 ⁴	(3.8±0.5) ×10 ³	(1.1±0.3) × 10 ³	(6.3±0.9) ×10 ³
2.5 - 10 µm in aerody- namic diameter	(3.7±1.3) ×10 ¹	(4.4±1.9) ×10 ¹	(5.6±0.9) ×10 ²	(5.3±2.8) ×10 ⁰	(1.3±0.2) ×10 ²	(3.2±0.2) ×10 ²	(1.9±0.3) ×10 ⁻¹	(7.0±0.1) ×10 ⁻¹	(7.8±1.6) ×10 ⁻²	(2.4±0.5) ×10 ⁰	(1.2±0.4) ×10 ¹	(4.3±1.0) ×10 ⁻¹	(7.1±2.9) ×10 ¹
Total number concentra- tion (0.014 – 20 µm in aerody- namic diameter)	(2.2±1.2) ×10 ³	(1.4±0.8) ×10 ⁵	(1.2±2.4) ×10 ⁵	(1.1±0.7) ×10 ³	(1.2±0.6) ×10 ³	(4.5±1.3) ×10 ³	(2.3±0.6) ×10 ³	(1.9±0.5) ×10 ³	(7.9±3.1) ×10 ²	(2.8±0.5) ×10 ⁴	(5.5±1.0) ×10 ³	(1.4±0.4) ×10 ³	(1.1±0.2) ×10 ⁴

Table S5. Number concentrations (particles/cm³) of aerosolized Zn-based products. The numbers represent averages and standard deviations based on at least three repeats. Spray products: Z1CS: Sunscreen, Z2HS: Skin protectant, Z3CS: Sunscreen, Z4CS: Skin protectant, Z6HS: Ingestible dietary supplement.

Size\Product	Z1CS	Z2HS	Z3CS	Z4HS	Z6HS
14 - 100 nm in aerodynamic diameter	(1.7±1.7)×10 ²	(1.2±0.3)×10 ⁴	(2.4±0.7)×10 ³	(2.0±0.4)×10 ⁴	(1.4±2.0)×10 ⁴
0.1 - 2.5 µm in aerodynamic diameter	(7.1±2.5)×10 ²	(5.7±0.8)×10 ³	(2.4±0.5)×10 ³	(8.9±1.6)×10 ³	(8.3±2.3)×10 ²
2.5 - 10 µm in aerodynamic diameter	(3.0±1.9)×10 ¹	(1.2±0.1)×10 ²	(3.4±0.7)×10 ²	(1.9±0.2)×10 ¹	(2.8±2.3)×10 ¹
Total number concentration (0.014 – 20 µm in aerodynamic diameter)	(9.1±4.4)×10 ²	(1.8±0.3)×10 ⁴	(5.2±1.3)×10 ³	(2.9±0.5)×10 ⁴	(1.5±2.0)×10 ⁴

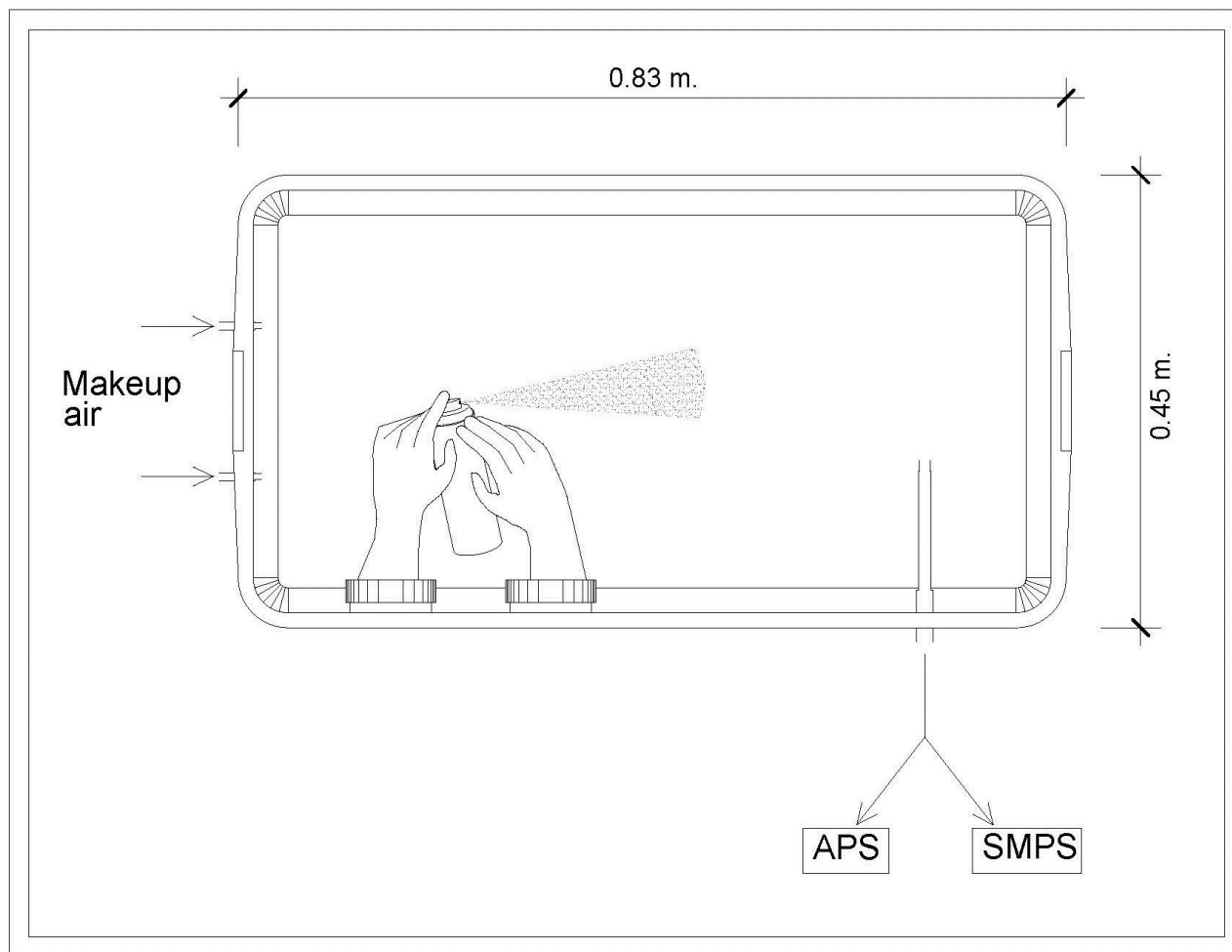


Figure S1. Top view of the test chamber. Products were sprayed by hand and then analyzed using an Aerodynamic Particle Sizer (APS) and a Scanning Mobility Particle Sizer (SMPS).

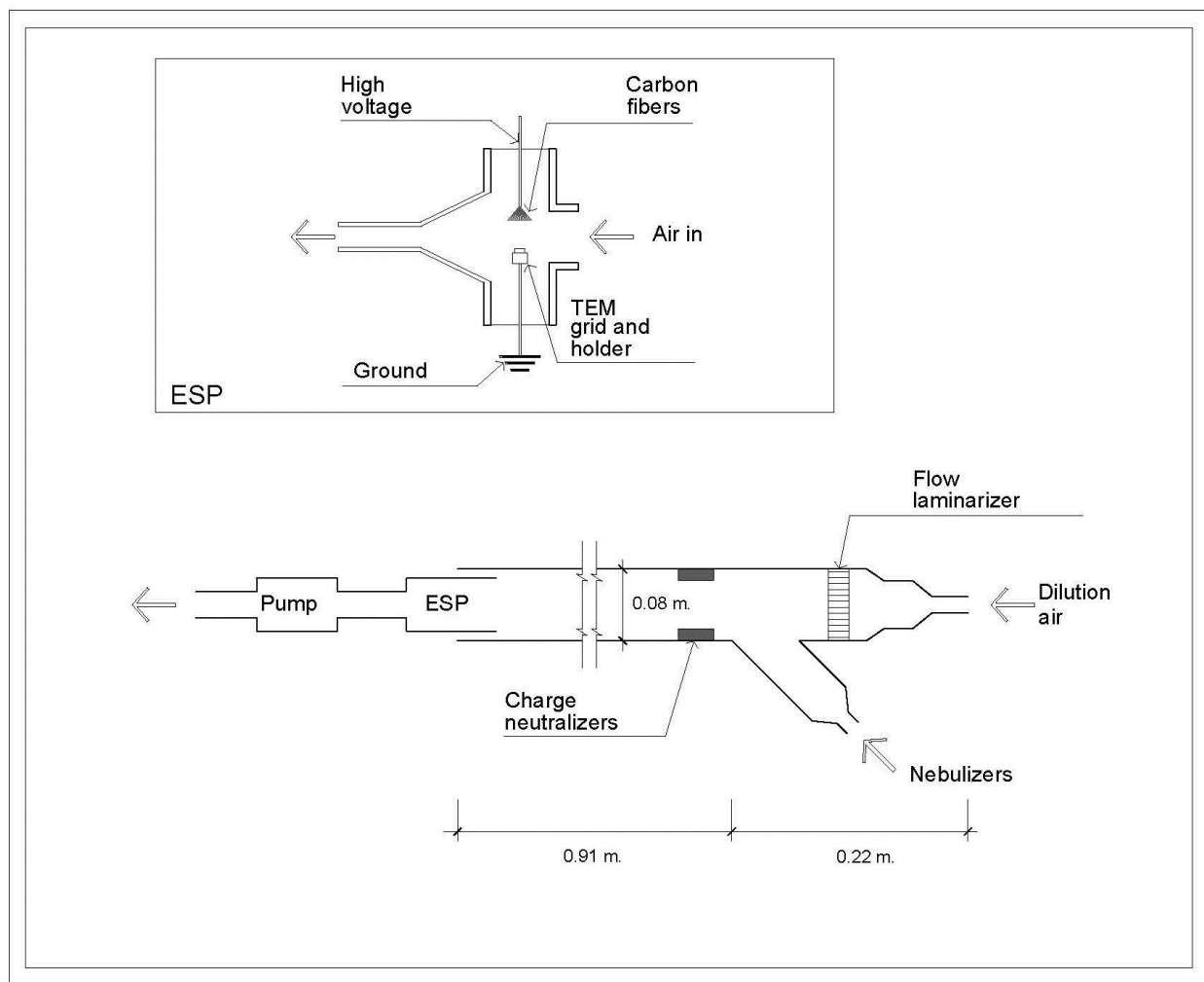


Figure S2. Experimental set up to aerosolize selected products using a nebulizer (bottom drawing). The airborne particles were then captured by a homemade electrostatic precipitator (top drawing) and then analyzed by transmission electron microscopy (TEM).

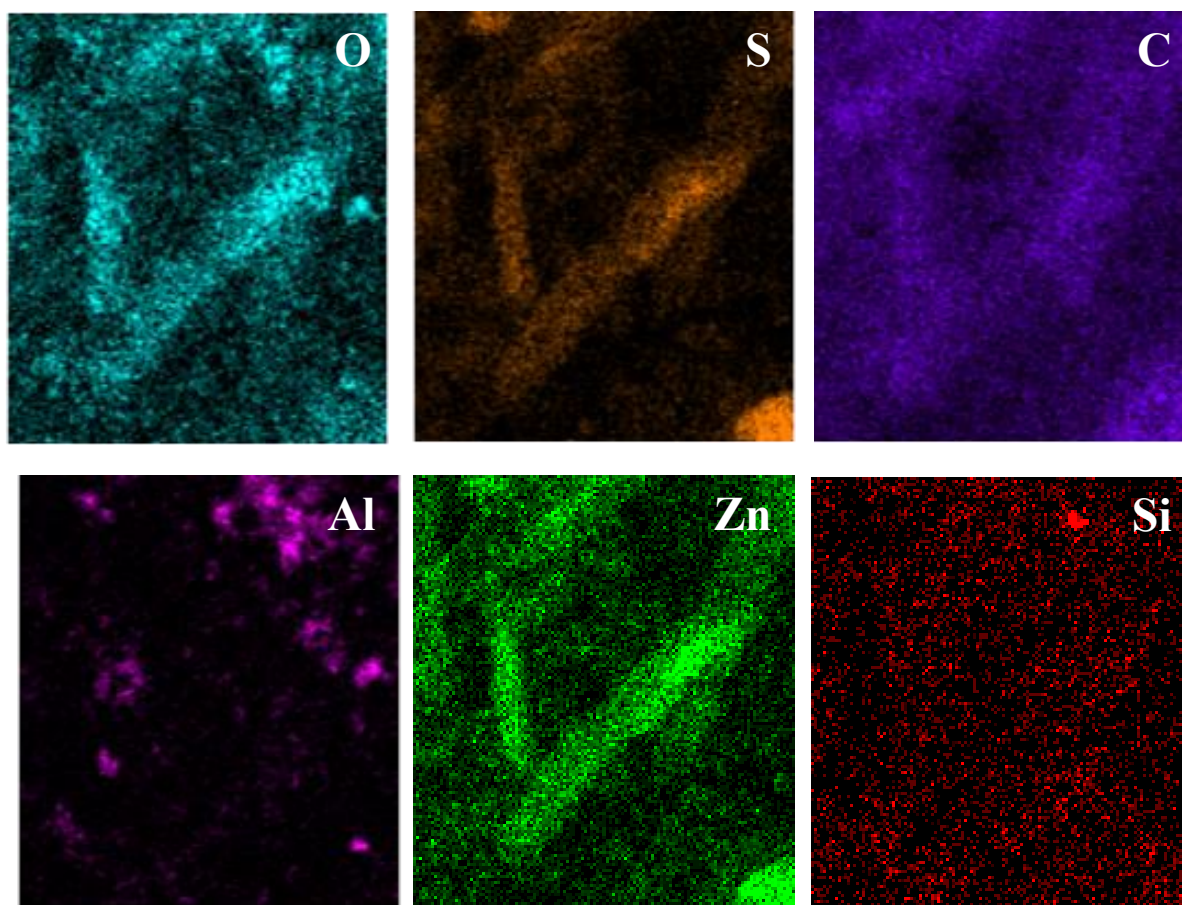
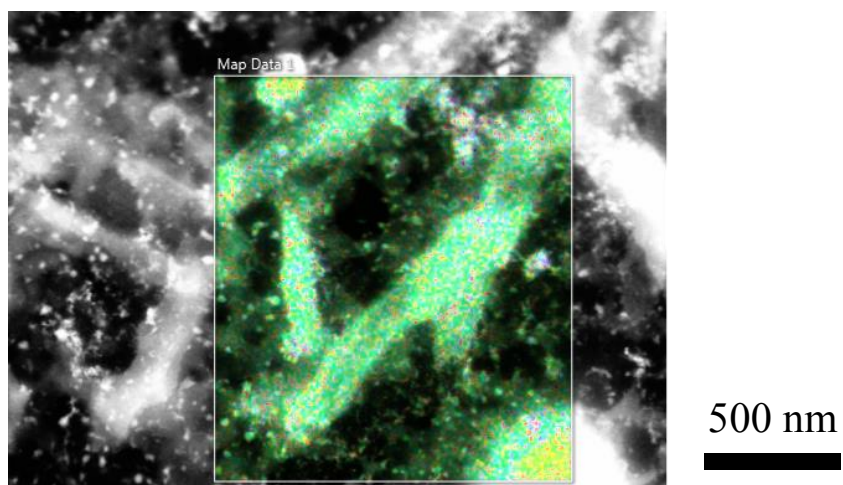


Figure S3. STEM image and corresponding EDS maps of the most abundant elements from a Z4HS (skin protectant) airborne sample illustrating the composition of different particulates in the sample.