Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Supporting Information

Release of Silver Nanomaterials from Textile:

Influence of Realistic Wearing on Nanomaterial Characteristics

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Table S1. List of ingredients in Tide Liquid Original Detergent*.

Alcohol Sulfate	Dimethicone	Mannanase
Alcoholethoxy Sulfate	Disodium Diaminostilbene Disulfonate	Polyethylene Glycol 4000
Alkyldimethylamine Oxide	DTPA	Polyethyleneimine Ethoxylate
Amylase	Ethanol	Propylene Glycol
Borax	Ethanolamine	Protease
Calcium Formate	Fragrance	Sodium Fatty Acids
Citric Acid	Laureth-9	Sodium Formate
Diethylene Glycol	Linear Alkylbenzene Sulfonate	Sodium Hydroxide
Diquaternium Ethoxysulfate	LiquitintTM Blue	Water

*https://www.pg.com/productsafety/ingredients/household_care/laundary_fabric_care/Tide/Tide_Liquid_Original.pdf

Table S2. Size of the standard Ag-NMs used to calibrate the SP-ICP-MS.

Methods	**Size (nm)**	**Details**
DLS	99±1	Z-average, PDI = 0.15
TEM	100±9	Average of 50 particles
TEM (from manufacturer)	100±8	Average (stated)

Table S3. Relevant instrument parameters used for SP-ICP-MS analysis.

Instrument Settings	**Values**
Dwell time	10 ms
Settling time	0 ms
Acquisition time	60 s
Scan mode	Peak hopping
Nebuliser	Meinhardt concentric
Spray chamber	cyclonic
Peristaltic Pump Settings	**Values**
Sample introduction rate	0.8 ml/min
Pump tubing	0.95 mm (ID)
Sample flush	60s @ 24 rpm (2% HNO_3)
Read delay	30s @ 5 rpm
Sample read	61s @ 10 rpm
Wash	45s @ 24 rpm

Table S4. Silver standard used in XANES measurements.

Compound	Cat. number	Manufacturer
Ag Glutathione*	PHR1359	Sigma Aldrich
Ag Histidine*	AAA1762718	Alfa Aesar
Ag Cysteine*	W326305	Sigma Aldrich
$AgNO_3$	209139	Sigma Aldrich
Ag_2SO_4	3443-04	J.T. Baker
Ag_2S*	89473	Alfa Aesar
AgCl	21127	ACROS Organics
Ag_3PO_4	11415	Alfa Aesar
Ag_2O	1192080025	Millipore Sigma
Elemental Ag-PVP 30 nm	0120XH	Skyspring Nanomaterials
Elemental Ag 30 nm	0118XH	Skyspring Nanomaterials

*Compounds were synthesised according to methods described in Wang et al., (2015)

Table S5. Proportion of of Ag^0, AgCl and Ag_2O in socks samples determined by LCF of XANES spectra.

Sock Sample[a]	Ag^0	AgCl	Ag_2O	R-factor
Unworn Control 1(BG) - Unwashed	100.0±0.0	0.0±0.0	0.0±0.0	0.0141
Unworn Control 1(W) - Unwashed	88.9±1.2	7.8±1.1	3.3±1.6	0.0017
Unworn Control 2 (BG) - Unwashed	98.0±0.9	2.0±0.9	0.0±1.3	0.0009
Unworn Control 2 (W) - Unwashed	83.0±1.7	13.8±1.7	3.2±2.4	0.0038
Unworn Control 3 (BG) – Wash Cycle 3	94.7±0.6	2.2±0.6	3.1±0.9	0.0005
Unworn Control 3 (W) – Wash Cycle 3	84.5±1.6	12.2±1.6	3.3±2.3	0.0032
Unworn Control 4 (BG) – Wash Cycle 3	79.5±2.7	17.0±2.5	3.5±3.7	0.0071
Walking 1 (BG) – Wash Cycle 3	97.4±1.3	2.5±1.2	0.1±1.7	0.0021
Walking 1 (W) – Wash Cycle 3	91.4±1.0	7.0±0.9	1.6±1.4	0.0011
Walking 2 (BG) – Wash Cycle 3	86.5±1.6	11.9±1.5	1.6±2.2	0.0027
Running 1(BG) – Wash Cycle 3	95.8±0.6	2.0±0.5	2.1±0.8	0.0003
Running 2(BG) – Wash Cycle 3	100.0±0.3	0.0±0.0	0.0±0.0	0.0033

[a] For some sock samples, two different sections were analyzed, as shown in Figure S3, where BG stands for "Black /Grey strip" and W for "White".

Table S6. Dimension of Ag sheet-like NMs (n=38)

	Minimum (nm)	Maximum (nm)	Mean (nm)
Thickness	9	308	67 ±56
Length	228	10898	2249 ±611
Width	125	3031	1085 ±1963

Table S7. Silver variation at 8 locations on the socks used for running after the 3rd cycle.

Location		Right Foot		Left Foot	
		Top	Sole	Top	Sole
Subject 1	Heel	-7%	-8%	15%	-34%
	Arch	7%	17%	-3%	-12%
	Pads	-9%	6%	10%	-4%
	Toes	-10%	6%	-3%	-3%
Subject 2	Heel	20%	-1%	21%	-3%
	Arch	-8%	-3%	-1%	-2%
	Pads	11%	-8%	3%	5%
	Toes	-14%	-11%	4%	5%
Subject 3	Heel	-2%	17%	13%	-3%
	Arch	9%	-3%	2%	-36%
	Pads	-3%	-15%	5%	0%
	Toes	0%	-4%	-11%	-38%

Pink - Ag loss; Blue - Ag gain; calculated for each location following this formula: (Initial Ag – Final Ag)/Initial Ag. Root mean square error (precision) of XRF measurements was 2.9%. The coefficient of variation between measurement after unfolding, shaking and refolding the sock was 3.3% (n = 10)

Table S8. Silver variation at 8 locations on the socks used for controls after the 3rd cycle.

Location		Right Foot		Left Foot	
		Top	Sole	Top	Sole
Control 1	Heel	21%	0%	10%	-7%
	Arch	14%	-5%	-1%	-14%
	Pads	-6%	-3%	7%	2%
	Toes	-11%	-13%	-3%	-3%
Control 2	Heel	-13%	14%	7%	-3%
	Arch	-1%	10%	11%	-2%
	Pads	6%	-8%	-1%	-7%
	Toes	-16%	5%	2%	-11%
Control 3	Heel	9%	-3%	16%	-9%
	Arch	15%	1%	3%	-16%
	Pads	7%	-9%	6%	-8%
	Toes	-7%	-6%	0%	-8%

Pink - Ag loss; Blue - Ag gain; calculated for each location following this formula: (Initial Ag – Final Ag)/Initial Ag. Root mean square error (precision) of XRF measurements was 2.9%. The coefficient of variation between measurement after unfolding, shaking and refolding the sock was 3.3% (n = 10)

Table S9. Silver variation at 8 locations on the socks used for walking after the 3rd cycle.

Location		Right Foot		Left Foot	
		Top	**Sole**	**Top**	**Sole**
Subject 1	**Heel**	-28%	-22%	-24%	-24%
	Arch	-12%	-16%	-30%	-30%
	Pads	-30%	-44%	-19%	-19%
	Toes	-31%	-34%	-33%	-33%
Subject 2	**Heel**	-32%	-6%	-33%	-33%
	Arch	-21%	-25%	-47%	-47%
	Pads	-30%	-34%	-23%	-23%
	Toes	-28%	-31%	-30%	-30%

Pink - Ag loss; Blue - Ag gain; calculated for each location following this formula: (Initial Ag – Final Ag)/Initial Ag. No measurements were completed for subject 3. Root mean square error (precision) of XRF measurements was 2.9%. The coefficient of variation between measurement after unfolding, shaking and refolding the sock was 3.3% (n = 10)

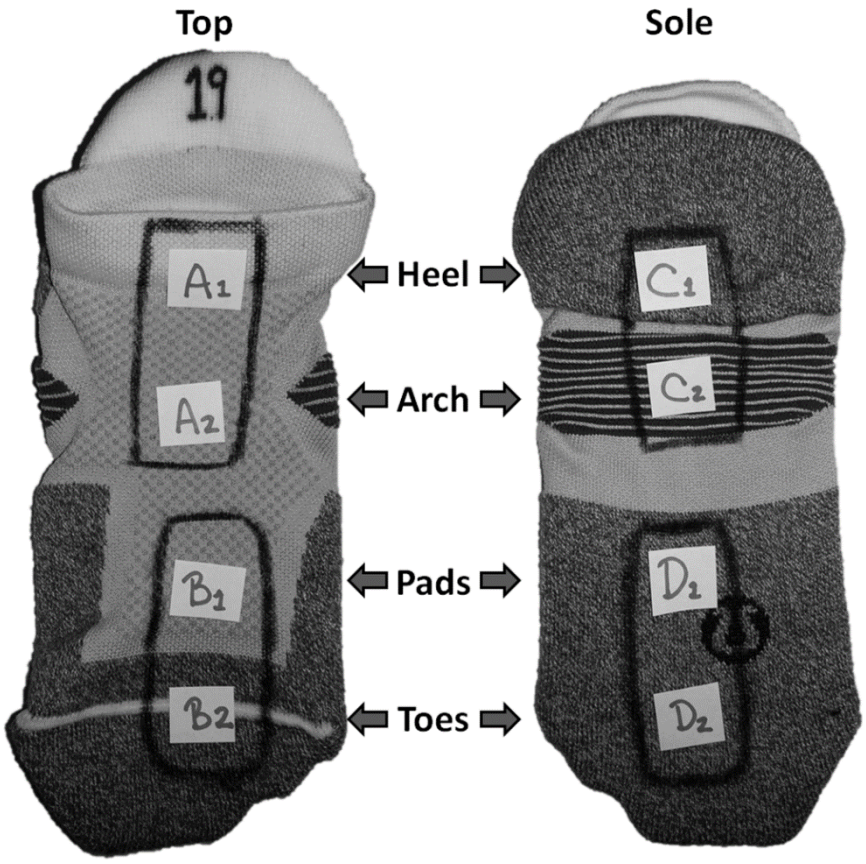


Figure S1. Locations of XRF measurements on the top and sole of the sock. Black rectangular marking represent the alignment of the XRF analyser on the socks. The letters and numbers represent the 8 positions of the XRF measurement which had an area of 1.5 x 1.5 cm.

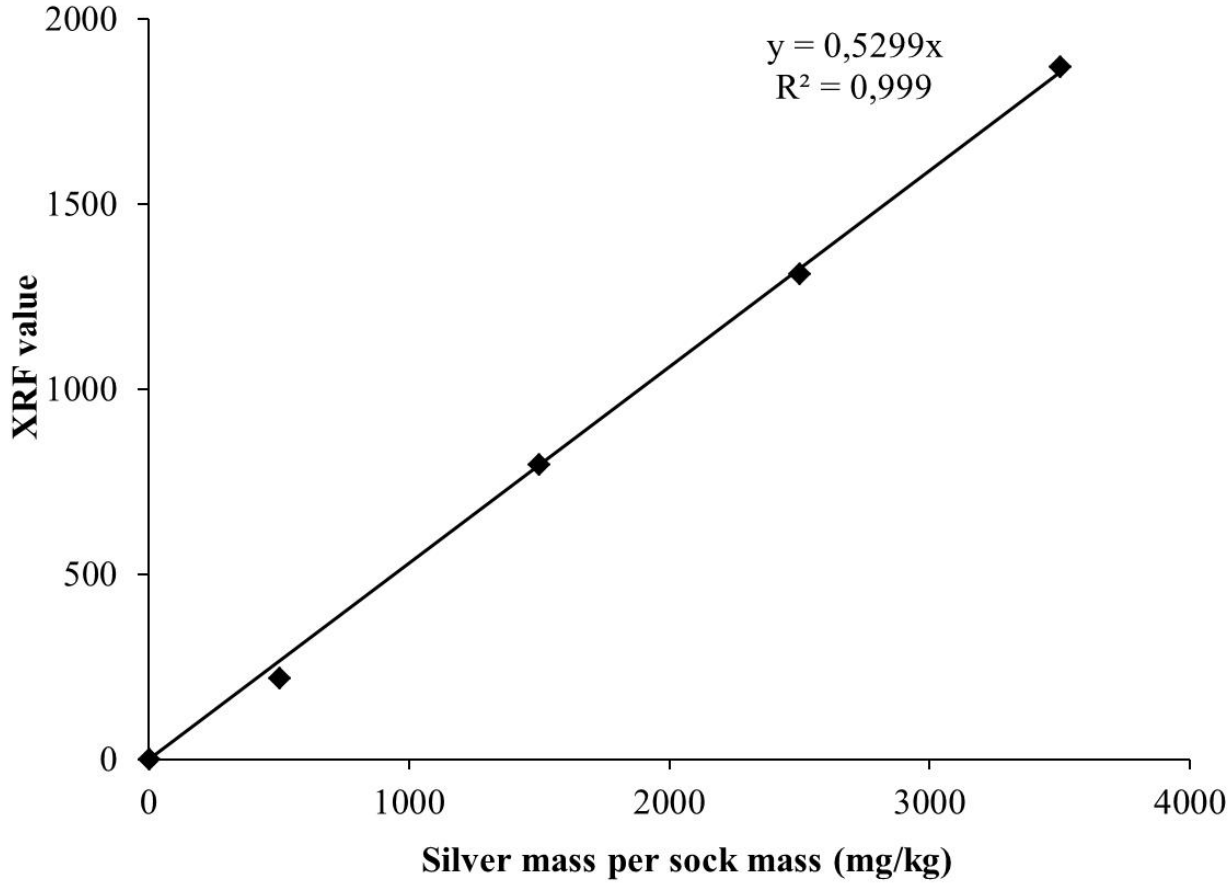


Figure S2. Calibration curve for the XRF according to mass of Ag per mass of sock.

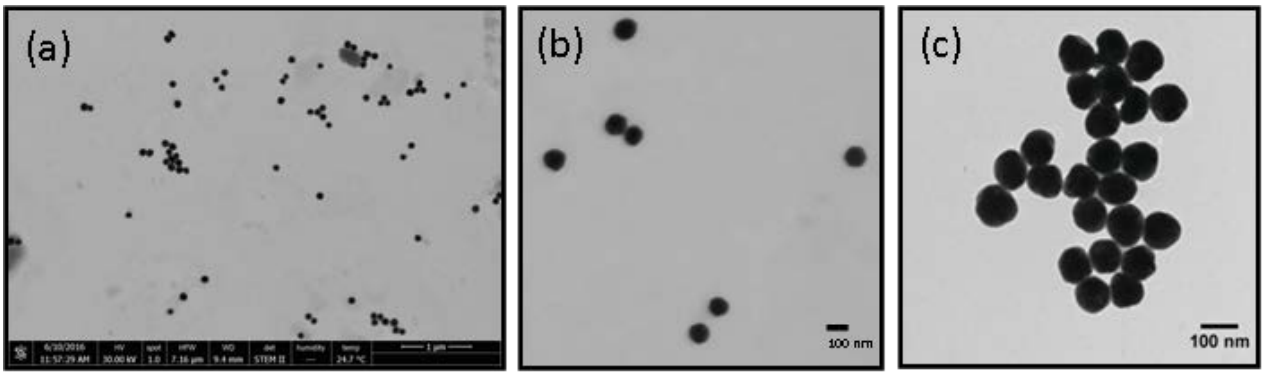


Figure S3. Imaging of the standard engineered nanomaterials used to calibrate the SP-ICP-MS (a) TEM image of the standard Ag ENMs, (b) a higher magnification, and (c) TEM image supplied by the manufacturer. The average of at least 50 particles was sized using the line tool in the free software ImageJ.

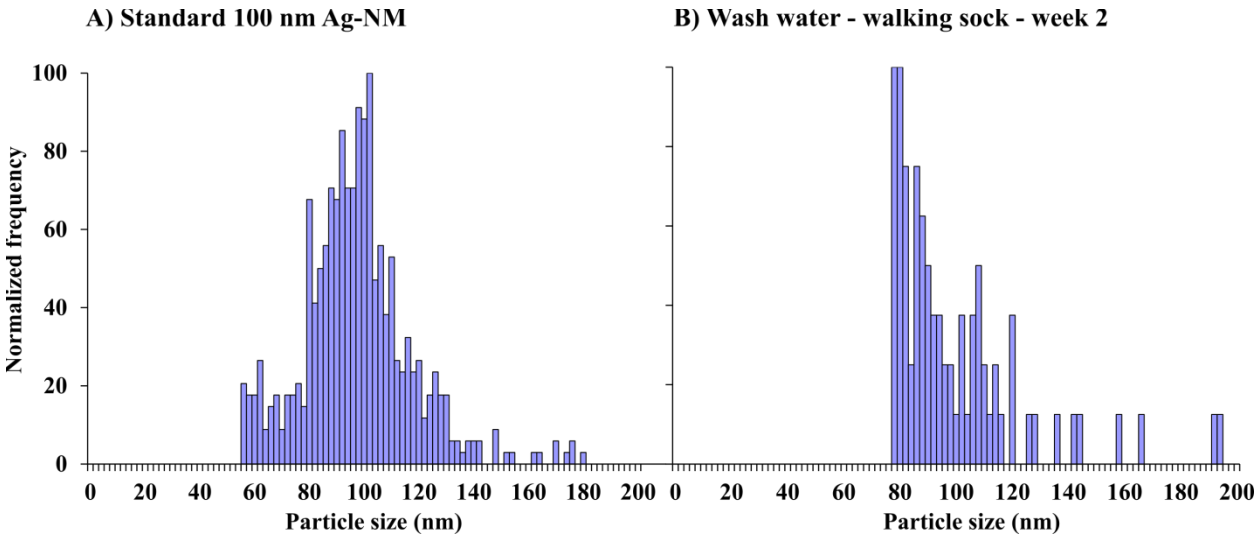
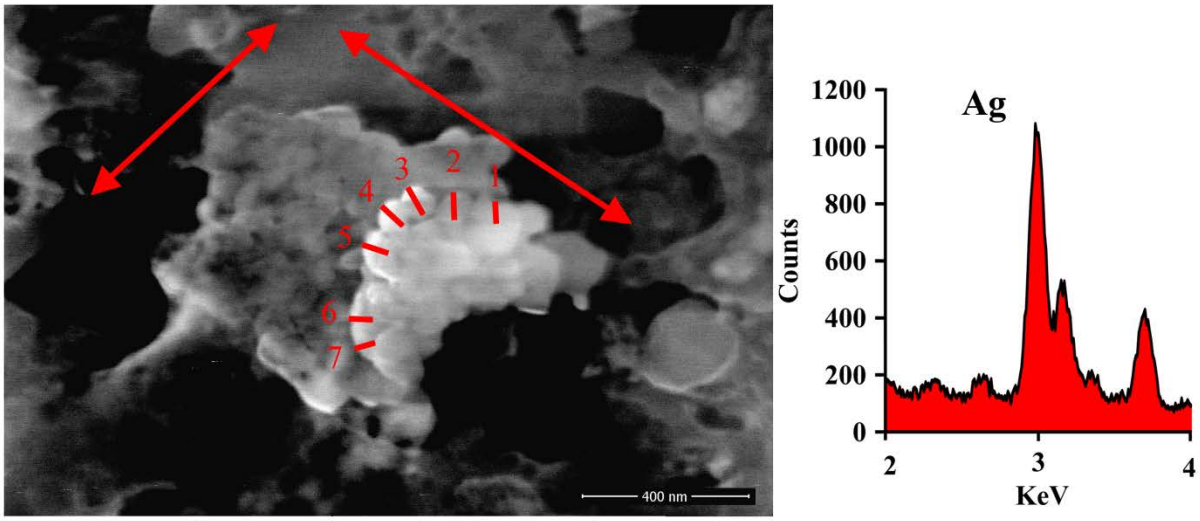


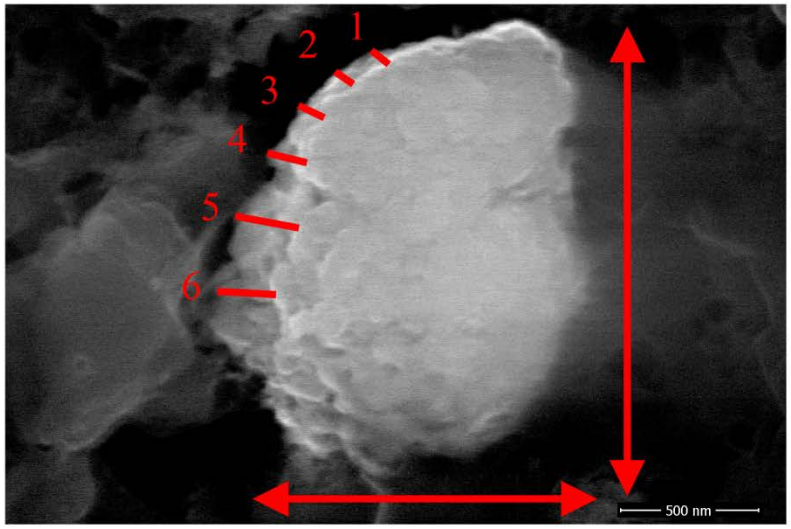
Figure S4. Normalized frequency of particle sizes in A) 100 nm Ag-NM standard and B) Ag-NM from the wash water of the walking sock experiment. Higher particle size cut-off in the wash water is cause by the ionic Ag background.

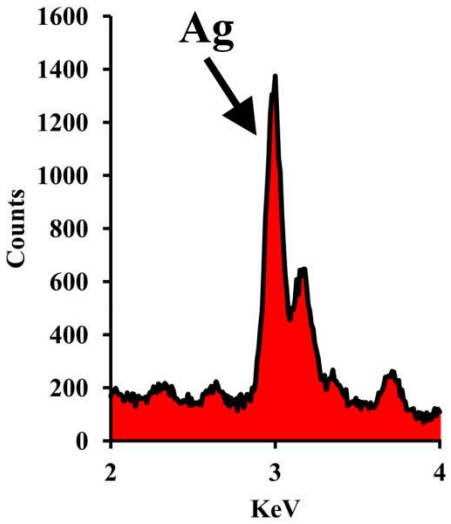


Dimensions	Size (nm)
Lenght	840
Width	608

Thickness	Size (nm)
1	59
2	66
3	77
4	70
5	61
6	53
7	48

Figure S5. Estimation of the nanoplate size using SEM image

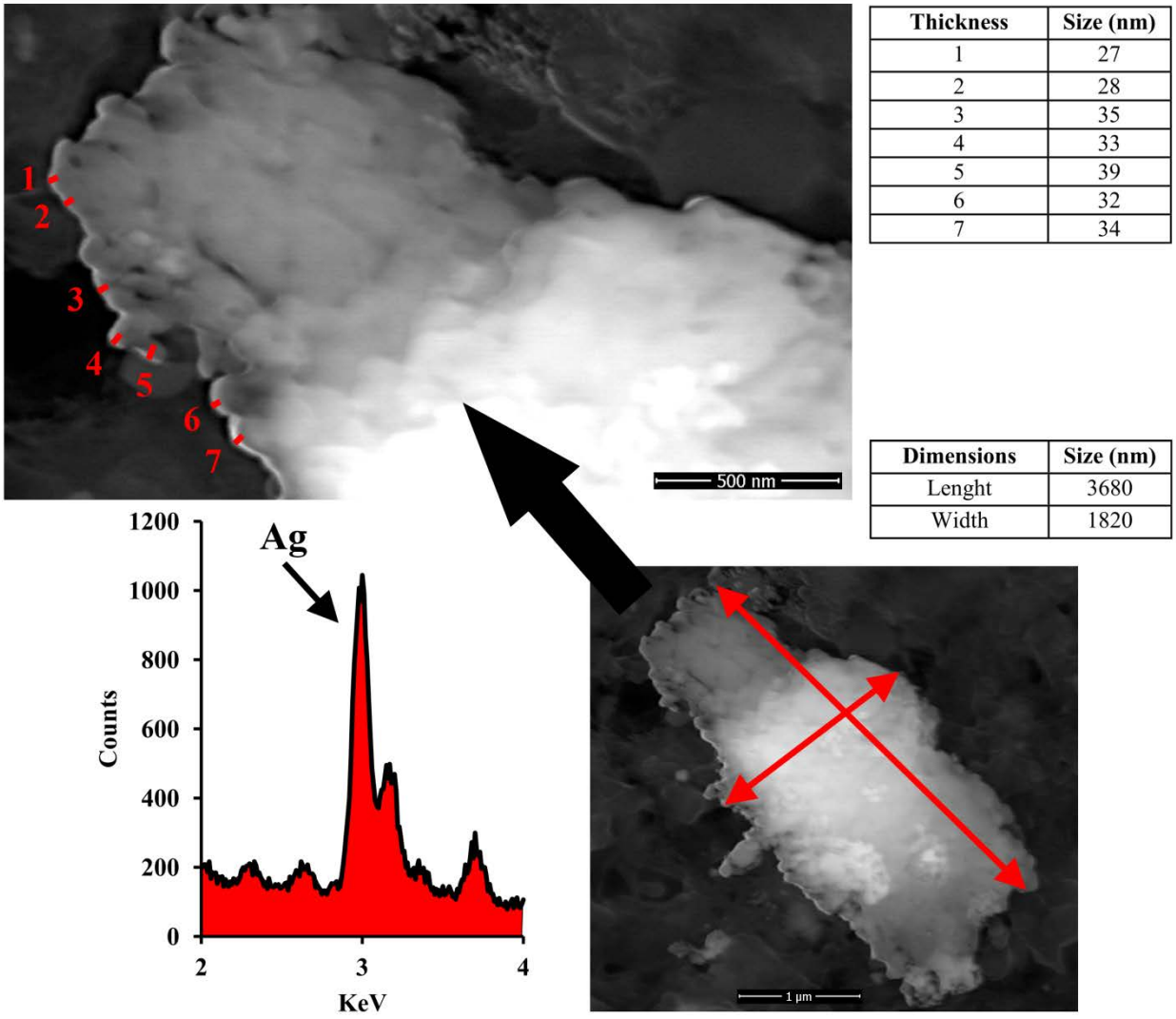




Dimensions	Size (nm)
Lenght	1688
Width	1233

Thickness	Size (nm)
1	81
2	78
3	98
4	114
5	232
6	206

Figure S6. Estimation of nanoplate size using SEM image



Thickness	Size (nm)
1	27
2	28
3	35
4	33
5	39
6	32
7	34

Dimensions	Size (nm)
Lenght	3680
Width	1820

Figure S7. Estimation of nanoplate size using SEM image

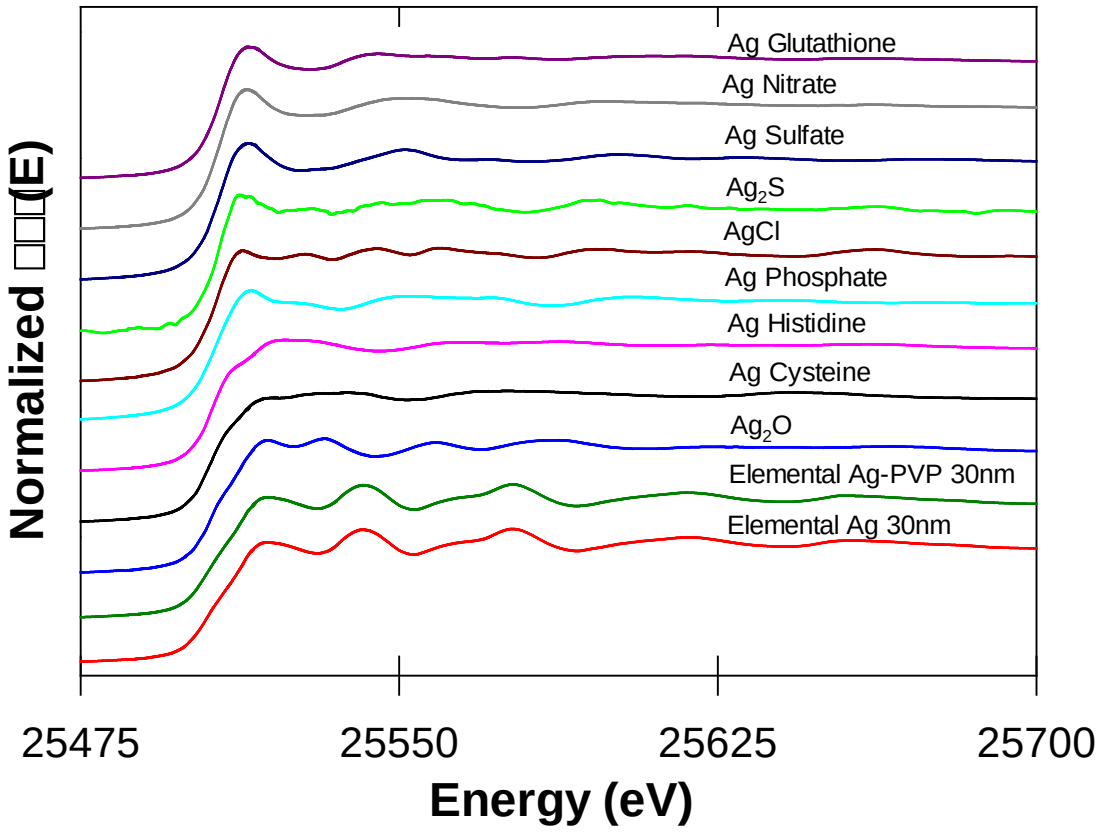


Figure S8. Normalized Ag K-edge XANES spectra of various Ag standards.

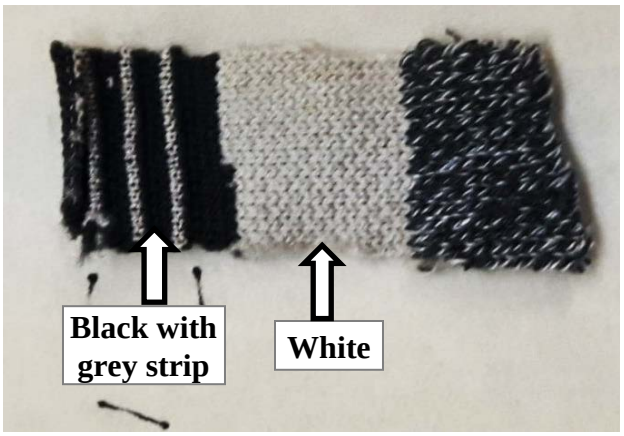


Figure S9. Sock sample showing the two sections that were analysed by XAS.

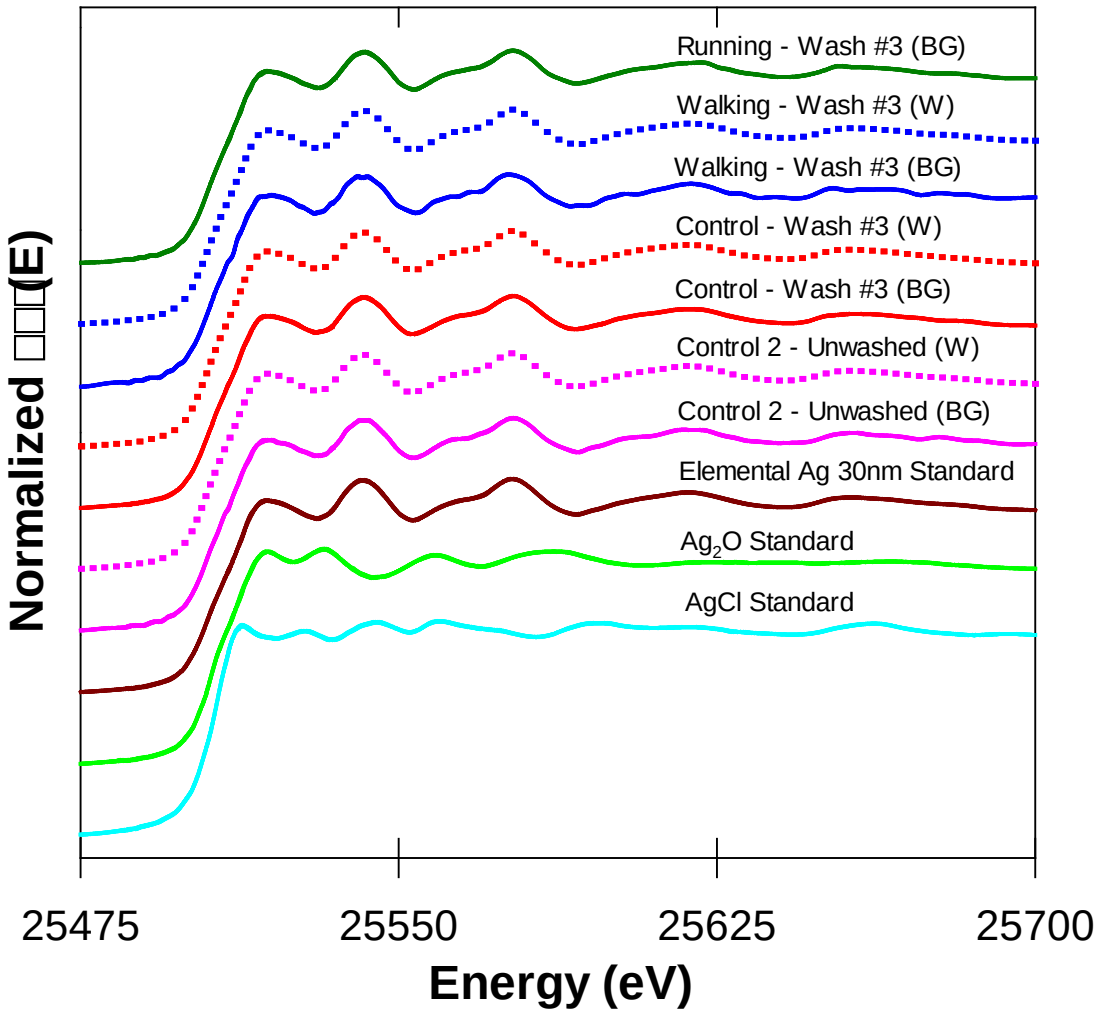


Figure S10. Normalized Ag K-edge XANES spectra of sock samples and selected Ag standards. For clarity, the spectra are plotted with an offset of 0.3. BG : black/grey striped section of the sock; W: white fabric sections of the sock

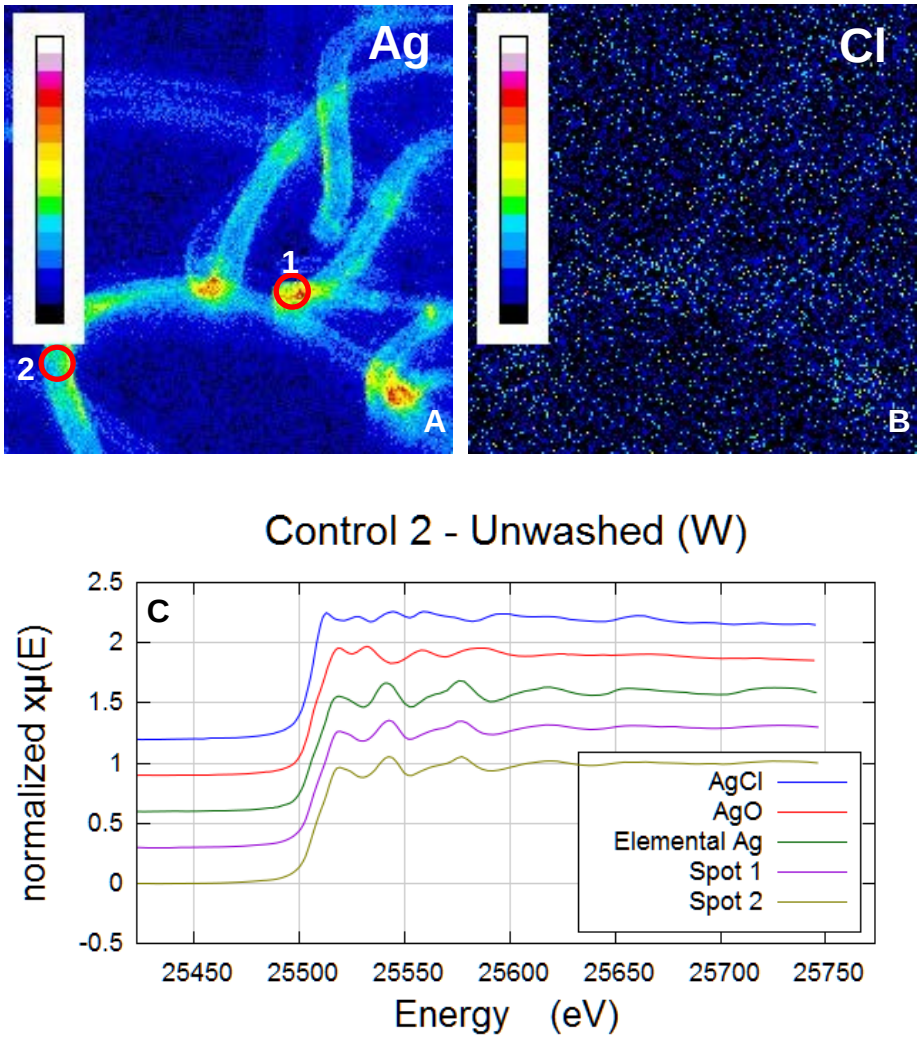


Figure S11. Elemental images by XAS of (A) Ag and (B) Cl and (C) XANES spectra of selected spots for an unwashed sock.

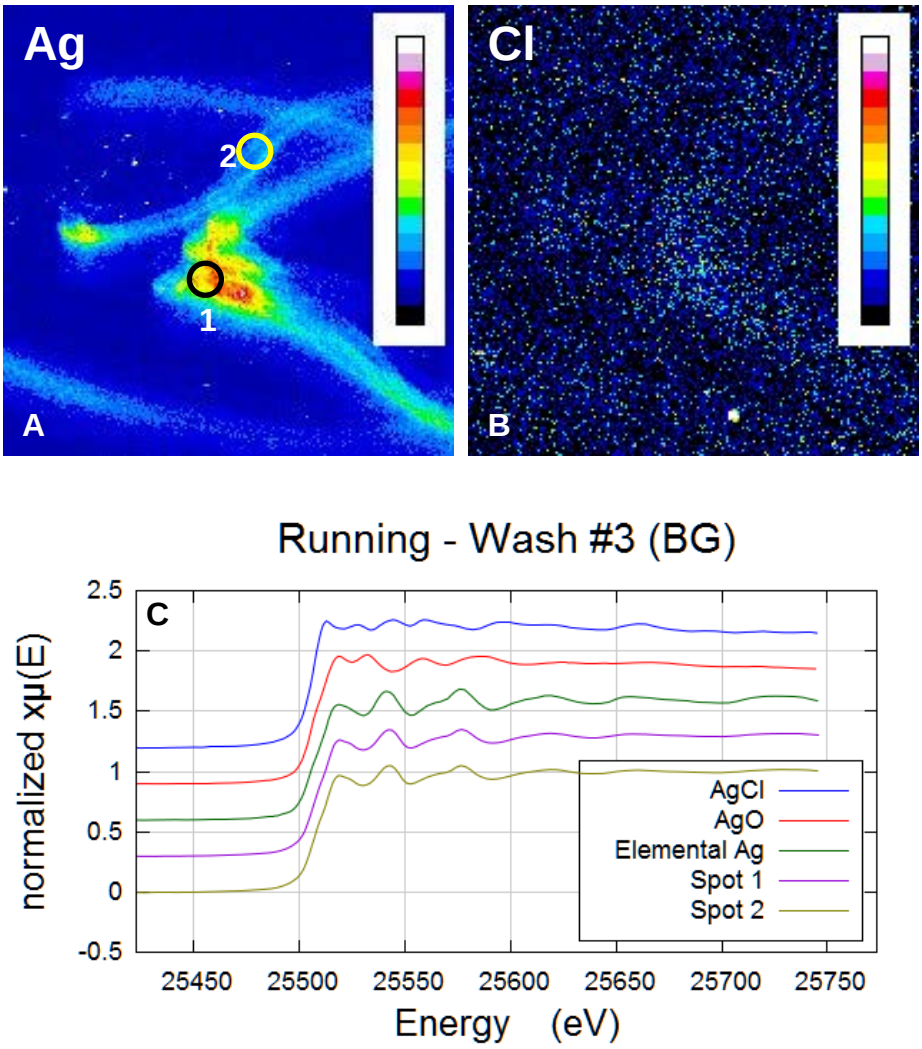


Figure S12. Elemental images by XAS of (A) Ag and (B) Cl and (C) XANES spectra of selected spots for a sock used for running.

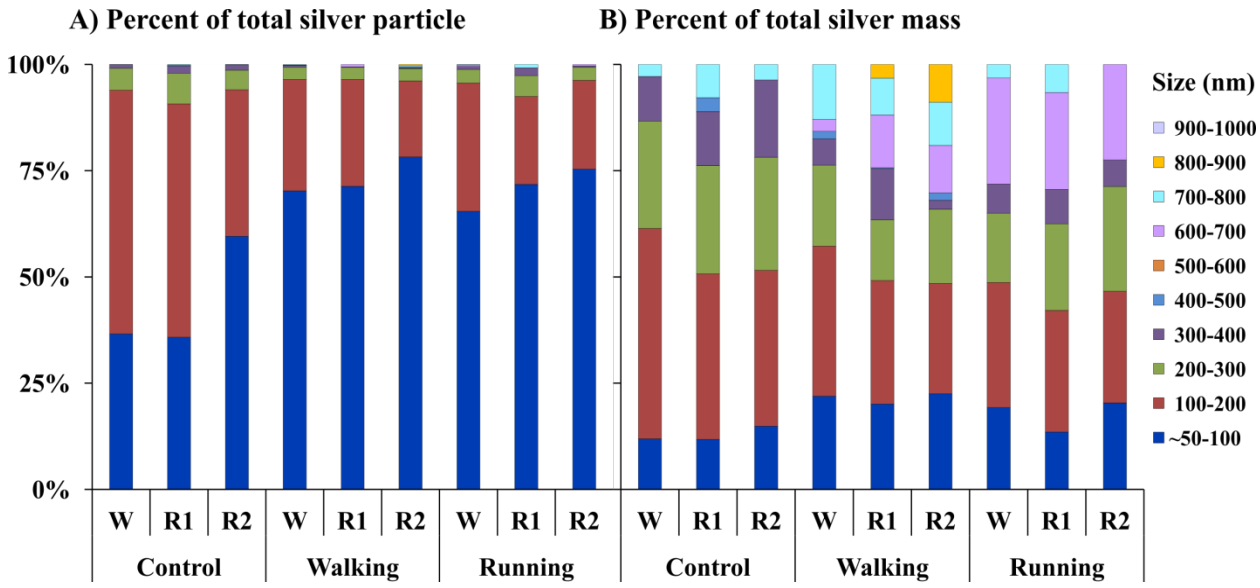


Figure S13. A) Number of Ag particles and B) Mass of total silver according to the particle size distribution in the wash (W) and rinse (R) water of unworn control and worn socks (walking and running). All values are from the average of three cycles.

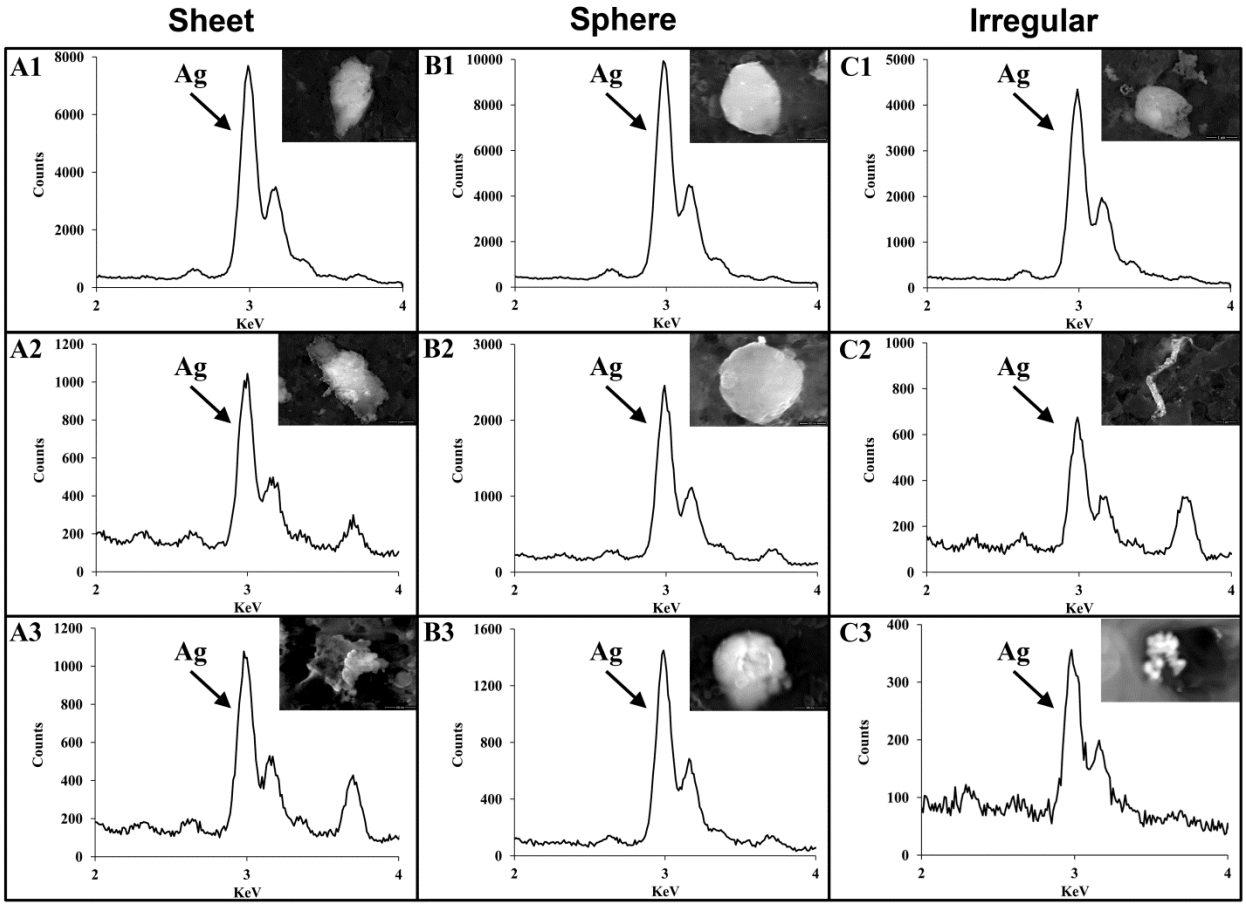


Figure S14. EDX spectra of incidental nanomaterial of A) Ag sheet, B) Ag sphere and C) other shape present in the wash water of an unworn sock

References

Wang P, Menzies NW, Lombi E, Sekine R, Blamey FPC, Hernandez-Soriano MC, et al. Silver sulfide nanoparticles (Ag_2S-NPs) are taken up by plants and are phytotoxic. Nanotoxicology 2015; 9: 1041-1049.