

Chemical characterisation, antibacterial activity, and (nano)silver transformation of commercial personal care products exposed to household greywater

Maryam Khaksar,^a Sotirios Vasileiadis,^{a,b} Ryo Sekine,^{a,c} Gianluca Brunetti,^a Kirk G Scheckel,^d Krasimir Vasilev,^e Enzo Lombi,^a and Erica Donner^{*a}

* Corresponding author

^a Future Industries Institute, University of South Australia, Building X, Mawson Lakes Campus, South Australia 5095, Australia

E-mail: erica.donner@unisa.edu.au

^b Department of Biochemistry and Biotechnology, University of Thessaly, Larissa, 41500, Greece

^c Environmental Futures Research Institute, Griffith University, Gold Coast Campus, Southport, QLD 4222, Australia

^d National Risk Management Research Laboratory, US Environmental Protection Agency, 5995 Centre Hill Avenue, Cincinnati, OH 45224, USA

^e School of Engineering, University of South Australia, Building J, Mawson Lakes Campus, South Australia 5095, Australia

The Electronic Supplementary Material (ESI) contains 9 pages consisting of 4 figures and 4 tables.

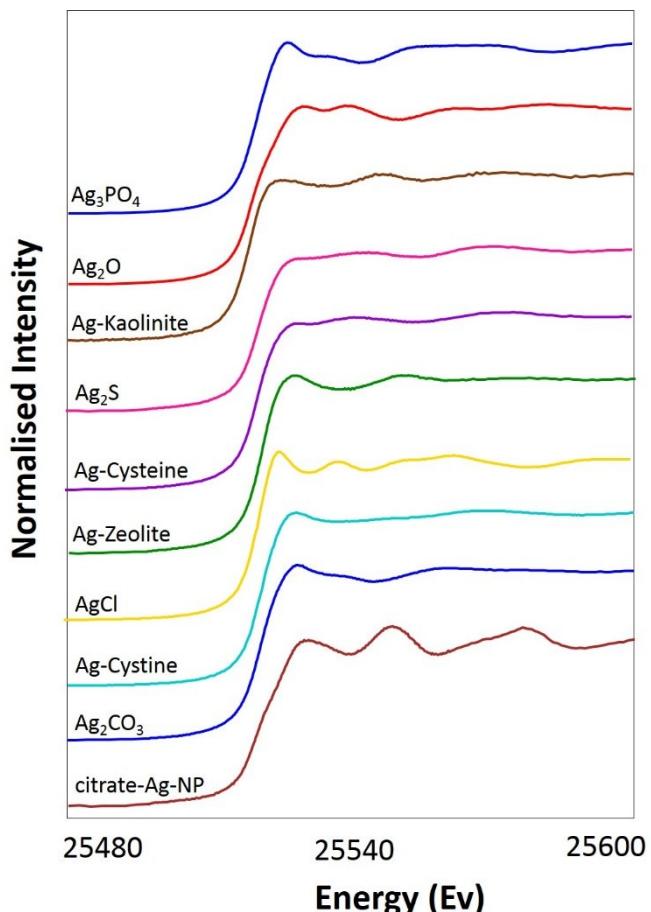


Figure S1 XANES spectra of Ag standards used in principal component analysis (PCA), target transformation (TT) and linear combination fitting (LCF) of Ag containing personal care products exposed to greywater.

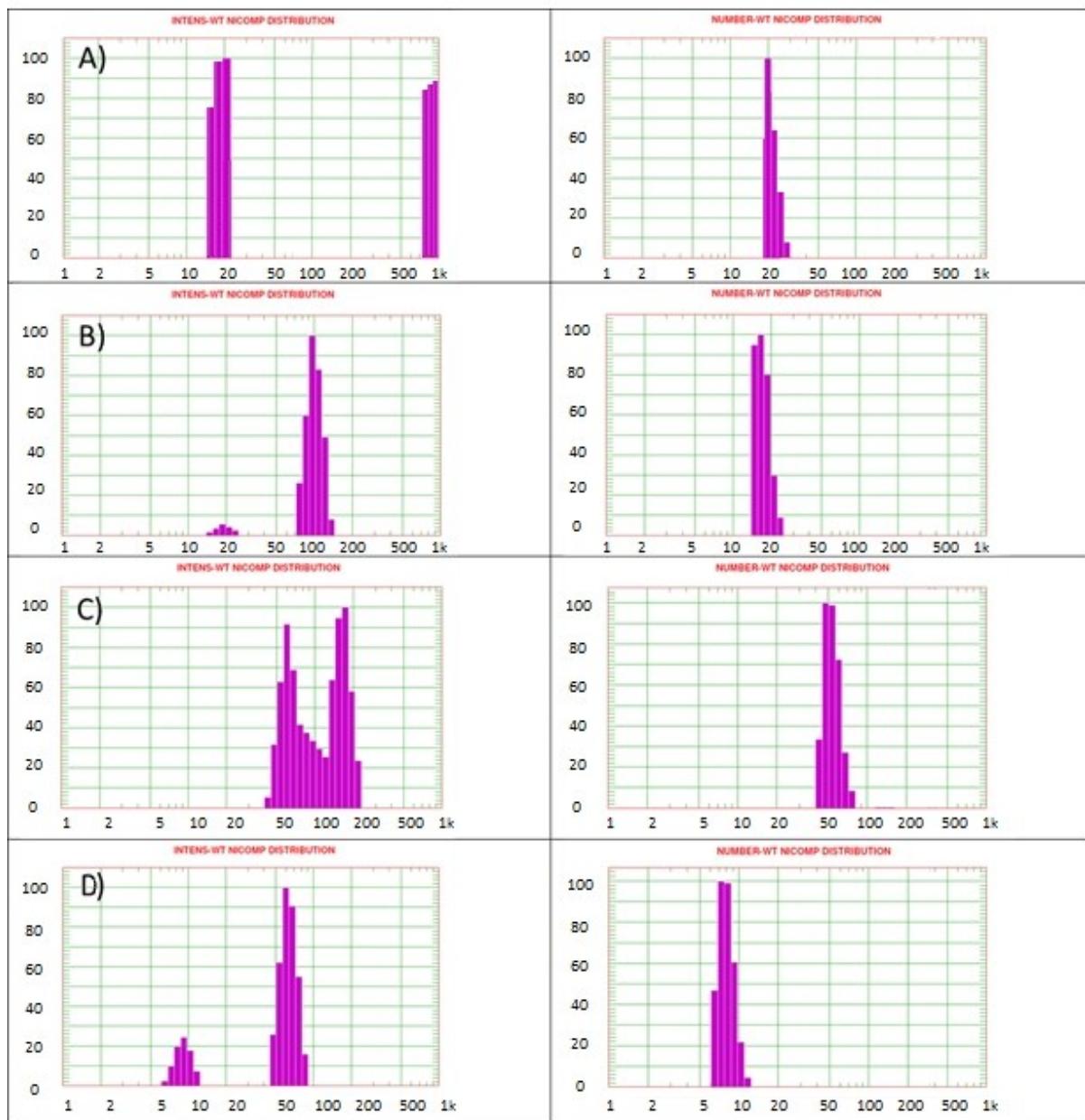


Figure S2 Intensity-weighted and number-weighted size distributions of Ag nanoparticles in: A) PCP5, B) PCP6, C) PCP7, and D) PCP8, as measured by DLS.

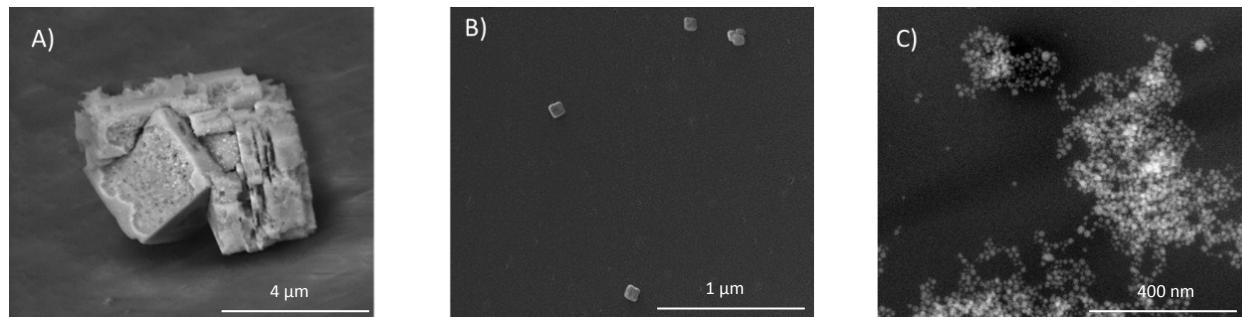


Figure S3 Representative SEM images of A) PCP2, B) PCP5 and C) PCP7.

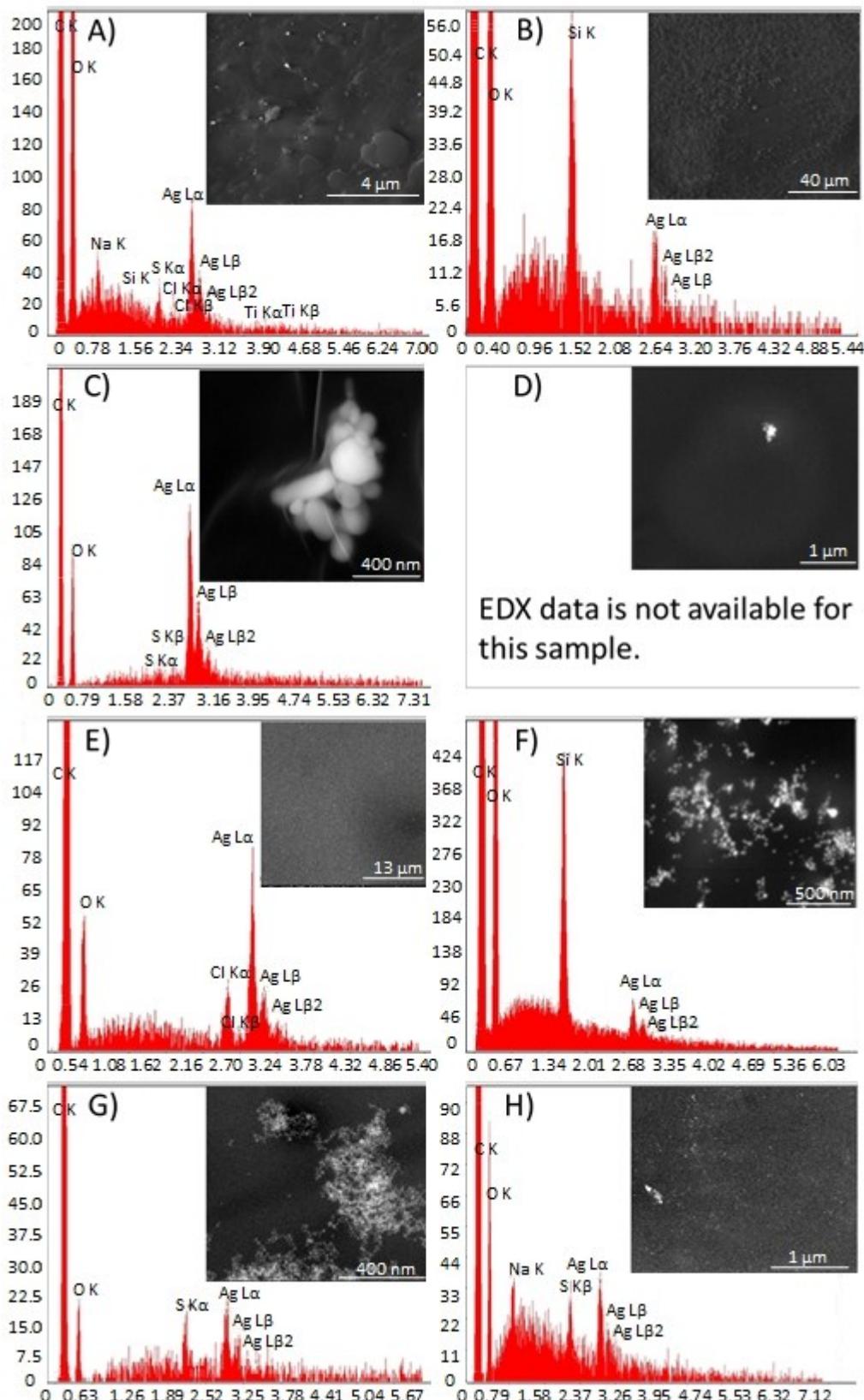


Figure S4 Sample Scanning Electron Microscopy (SEM) images of Ag (nano)particles in the commercial personal care products examined, and information from Energy Dispersive X-ray (EDX) spectra. A to H correspond to PCP1 to CP8.

Table S1: Composition of the synthetic greywater mixtures used to test the chemical transformation of Ag in personal care products.

Ingredient	Greywater 1	Greywater 2	Product Brand/ Grade
	Amount in 100 L (g)	Amount in 100 L (g)	
Moisturiser	1	1	Dove
Toothpaste	3.25	3.25	Colgate Maximum Cavity Protection
Deodorant	1	1	Mum
Shampoo/hand wash	72	72	Palmolive
Laundry detergent	15	-	Omo High Performance concentrate
Clay (Kaolinite)	5	5	Industrial grade
Vegetable oil	0.7	0.7	Coles Own brand
Na ₂ SO ₄	3.5	-	Analytical grade
NaHCO ₃	2.5	-	Analytical grade
Na ₂ PO ₄	3.9	-	Analytical grade
Boric acid	0.14	-	Analytical grade
Lactic acid	2.8	-	Analytical grade
Recycled (treated) wastewater from an urban wetland	2 L	2 L	-

Table S2 Labelled ingredients of the products used in the preparation of the synthetic greywater.

Product	Ingredients as per package	Comments
<i>Dove Protecting Moisturising Lotion</i>	Octyl methoxycinnamate (5.5%), Butyl methoxydibenzoylmethane (2.0%), Octyl salicylate (3.0%), Phenylbenzimidazol sulfonic acid (2.0%), Methylparaben, Propylparaben, Phenoxyethanol, Iodopropynyl butylcarbamate, Fragrance.	
<i>Toothpaste Colgate Maximum Cavity Protection, regular flavour, 140 g by Colgate (Customer info: Colgate Oral Care 1800 802 307)</i>	Sodium monofluorophosphate (0.76% w/w), Abrasives, Detergents, Humectants, sorbitol, and water. Thickeners, Preservatives, Flavouring agents, Colouring agents, Tartar control	<ul style="list-style-type: none"> • A common sweetener used is Saccharin. • Artificial dyes are used to colour red, green, and blue toothpastes. Titanium dioxide is used to make some toothpastes white. • Toothpaste that are designed for tartar control commonly contain pyrophosphate. • Abrasives: used to provide cleaning power, common compounds used are calcium carbonate, silica, calcium phosphate, and alumina. • Detergents are used to create the foaming action and keep it from dribbling. The most common detergent is sodium lauryl sulphate. • Common humectants are Glycerin • Common preservatives are sodium benzoate, methyl paraben, triclosan and ethyl paraben.
<i>Anti-perspirant Mum Dry Active, 24h by Procter and Gamble (Customer info: 1800 226 524)</i>	Aluminium chlorohydrate (22%w/w), Other common ingredients in anti-perspirants, Binders, pH agents.	
<i>Palmolive Soft Wash Milk and Honey 500 mL, made in Thailand (Customer info: 1800 802 307)</i>	Water, Sodium Laureth sulphate, Cocamidopropylbetaine, Cocamine DEA, Lauryl glucoside, Polyquaternium 7, Fragrance, Glycol distearate, Laureth-4, Sodium chloride, Sodium sulphate, Citric acid, Poloxamer 124, Sodium styrene/acrylates copolymer, DMDM Hydantoin, Methylchloroisothiazolinone, Methylisothiazolinone, Tetrasodium EDTA, Honey, Dry milk powder, Ci 19140, Ci 16035.	
<i>Omo High Performance concentrate 1kg, 5way cleaning action by Unilever (Customer info: 1800 225 508, www.omocareline.com.au)</i>	Anionic and non-ionic surfactants (Commonly used are alcohol ethoxylates and alkylphenol ethoxylates), Optical brightener/fluorescer, Enzyme (commonly used is proteinase), Alkalies, Sodium polyphosphate, Zeolite, Polymer, Perfume, Colour.	Alcohol ethoxylates and alkyl phenol ethoxylates are commonly used as surfactants.

Table S3 Fundamental parameters of synthetic greywater at the beginning and at the end of Ag exposure.

Parameter	Greywater 1		Greywater 2	
	Start	End	Start	End
T (°C)	22.7 (± 1.1)	23.6 (± 1.7)	22.7 (± 0.9)	23.7 (± 1.8)
pH	9.1 (± 0.6)	8.5 (± 1.4)	7.9 (± 1.2)	7.9 (± 0.9)
Eh (mV)	175 (± 4)	172 (± 3)	261 (± 2)	214 (± 3)
EC (mS)	0.7 (± 0.1)	0.7 (± 0.1)	0.5 (± 0.2)	0.5 (± 0.1)
TDS (mg L ⁻¹)	0.3 (± 0.1)	0.3 (± 0.1)	0.2 (± 0.1)	0.2 (± 0.1)
Dissolved Oxygen (mg L ⁻¹)	23.1 (± 1.2)	8.4 (± 1.0)	22.9 (± 2.4)	9.9 (± 1.7)
Total dissolved Oxygen (mg L ⁻¹)	22.9 (± 1.3)	23.6 (± 0.8)	22.9 (± 0.9)	23.7 (± 1.6)
COD (mg L ⁻¹)		222 (± 7)		180 (± 4)

Table S4 LCF results of the Ag K-edge XANES spectra using the standards listed, as percentage composition and variability (in parentheses) of the total. R-factor indicates the quality of the fit.

	PCP1			PCP2			PCP3		
	Before exposure	GW1	GW2	Before exposure	GW1	GW2	Before exposure	GW1	GW2
Ag-NP (Ag^0)	69 (3)	--	--	31 (2)	--	--	26 (1)	23 (2)	--
AgCl	--	67 (3)	68 (6)	64 (2)	64 (4)	64 (4)	56 (1)	61 (1)	43 (3)
Ag-clay	16 (4)	16 (5)	15 (5)	--	--	--	--	--	28 (4)
Ag_2O	--	17 (2)	16 (3)	5 (3)	--	--	17 (1)	15 (2)	--
Ag_2CO_3	--	--	--	--	20 (7)	27 (6)	--	--	--
Ag-reduced sulfur	14 (5)	--	--	--	16 (4)	8 (4)	--	--	29 (2)
0.00018									
R-factor	0.000194	0.000133	0	0.000276	0.000281	8	0.000043	0.000109	0.000102
	PCP4			PCP5			PCP6		
	Before exposure	GW1	GW2	Before exposure	GW1	GW2	Before exposure	GW1	GW2
Ag-NP (Ag^0)	87 (4)	--	31 (3)	--	--	--	84 (5)	42 (5)	--
AgCl	--	39 (3)	69 (3)	80 (4)	61 (2)	63 (3)	--	35 (6)	44 (7)
Ag-clay	--	36 (4)	--	16 (4)	20 (3)	17 (4)	--	3 (9)	30 (3)
Ag_2O	12 (4)	24 (2)	--	3 (2)	18 (1)	18 (2)	--	18 (3)	16 (3)
Ag_2CO_3	--	--	--	--	--	--	--	--	--
Ag-reduced sulfur	--	--	--	--	--	--	16 (5)	--	8 (4)
0.00010 0.00011									
R-factor	0.000618	9	9	0.000479	2	7	0.000479	6	0.000070
	PCP7			PCP8					
	Before exposure	GW1	GW2	Before exposure	GW1	GW2			
Ag-NP (Ag^0)	86 (2)	21 (2)	--	91 (4)	--	--			
AgCl	--	18 (7)	56 (3)	--	59 (2)	60 (2)			
Ag-clay	--	23 (5)	24 (4)	--	28 (8)	23 (3)			
Ag_2O	--	--	18 (2)	9 (4)	12 (2)	15 (2)			
Ag_2CO_3	--	--	--	--	--	--			
Ag-reduced sulfur	13 (2)	35 (3)	--	--	--	--			
R-factor	0.000254	0.000056	0.000101	0.000459	0.000070	0.000078			