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

Supplemental Information

Comparative Life Cycle Assessment of Silver Nanoparticle Synthesis Routes

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Table S1. Life cycle inventory of CR-TSC synthesis route.

Method	Section	Material	Amount	Unit	Corresponding LCI unit process	Comment
1 kg AgNP CR with trisodium citrate	Input	Silver nitrate	1.57	kg	Created, see below	Sileikaite et al., 2006
		Trisodium Citrate	0.80	kg	Created, see below	Sileikaite et al., 2006
		Water	9277	kg	Water, deionized, at plant/US*	Sileikaite et al., 2006 Reaction water + dissolution water
		Heat	2912179	kJ	Heat, unspecific, in chemical plant/US-US-EI U	Solution heated to 100 C Values checked with Aspen Plus
	Output	Citric acid	0.59	kg	Emissions to water> Citric acid	Sileikaite et al., 2006
		Sodium Nitrate	0.79	kg	Emissions to water> Sodium nitrite	Sileikaite et al., 2006
		Hydrogen	0.006	kg	Emissions to air> Hydrogen	Sileikaite et al., 2006
		Oxygen	0.12	kg	Emissions to air> Oxygen	Sileikaite et al., 2006
1 kg Silver nitrate	Input	Nitric acid	0.49	kg	Nitric acid, 50% in H2O, at plant/US	3Ag + 4HNO3 (cold and diluted) --> 3AgNO3 + 2H2O + NO
		Silver	0.64	kg	Silver, at regional storage/US	3Ag + 4HNO3 (cold and diluted) --> 3AgNO3 + 2H2O + NO
	Output	Water	0.07	kg	Emissions to air> Water	3Ag + 4HNO3 (cold and diluted) --> 3AgNO3 + 2H2O + NO
		Nitrogen monoxide	0.06	kg	Emissions to air> Nitrogen monoxide	3Ag + 4HNO3 (cold and diluted) --> 3AgNO3 + 2H2O + NO
1 kg Trisodium citrate	Input	Citric acid	0.74	kg	Created, see below	C6H8O7 + 3NaOH --> Na3C6H5O7 + 3H2O
		Sodium hydroxide	0.46	kg	Sodium hydroxide, production mix, at plant/kg NREL/RNA	C6H8O7 + 3NaOH --> Na3C6H5O7 + 3H2O
	Output	Water	0.26	kg	Emissions to air> Water	C6H8O7 + 3NaOH --> Na3C6H5O7 + 3H2O
1 kg Citric Acid	Input	Sugar	0.94	kg	Sugar, from sugarcane, at sugar refinery/US US-EI U	C6H12O6 + 3/2 O2 --> C6H8O7 + 2 H2O , (Verhoff et al.)
		Oxygen	0.25	kg	Oxygen, liquid, at plant/US*	C6H12O6 + 3/2 O2 --> C6H8O7 + 2 H2O , (Verhoff et al.)
		Lime	0.57	kg	Lime, hydrated, loose, at plant/US*	3 Ca(OH)2 + 2 C6H8O7 --> Ca3(C6H5O7)2.4 H2O + 2 H2O , (Tariq et al.)
		Sulphuric acid	0.76	kg	Sulhuric acid, liquid, at plant/US	3 H2SO4 + Ca3(C6H5O7)2.4 H2O --> 2 C6H8O7 + 3 CaSO4.2 H2O + 2 H2O (Tariq et al.)
	Output	Water	0.37	kg	Emissions to air> Water	Sum of water output water from above reactions. The initial acid production by fungi is an exothermic reaction.
		Gypsum	1.06	kg	Disposal, gypsum, 19.4% water, to sanitary landfill/US*	3 H2SO4 + Ca3(C6H5O7)2.4 H2O --> 2 C6H8O7 + 3 CaSO4.2 H2O + 2 H2O (Tariq et al.)

Table S2. Life cycle inventory of CR-SB synthesis route.

Method	Section	Material	Amount	Unit	Corresponding LCI unit process	Comment
1 kg AgNP CR with sodium borohydride	Input	Silver nitrate	1.57	kg	Created, see Table S1	Solomon et al., 2007
		Sodium borohydride	0.35	kg	Created, see below	Solomon et al., 2007
		Water	13915	kg	Water, deionized, at plant/US*	Solomon et al., 2007 Dissolution water
		Water for cooling	0.024	m^3	Water, cooling, unspecified natural origin/m3	Ecoinvent average cooling water
	Output	Hydrogen	0.009	kg	Emissions to air> Hydrogen	Solomon et al., 2007
		Diborane	0.13	kg	-	Solomon et al., 2007
		Sodium Nitrate	0.79	kg	Emissions to water> Sodium nitrite	Solomon et al., 2007
1 kg Sodium borohydride	Input	Trimethyl borate	2.74	kg	Trimethyl borate, at plant/GLO	B(OCH3)3 + 4NaH --> NaBH4 + 3NaOCH3
		Sodium hydride	2.54	kg	Sodium hydride, production mix, at plant/kg NREL/RNA	B(OCH3)3 + 4NaH --> NaBH4 + 3NaOCH3

Table S3. Life cycle inventory of CR-EG synthesis route.

Method	Section	Material	Amount	Unit	Corresponding LCI unit process	Comment
1 kg AgNP CR with ethylene glycol	Input	Silver nitrate	1.57	kg	Created, see Table S1	Slistan-Grijalva et al., 2005
		Ethylene Glycol	29.1	kg	Ethylene glycol, at plant/US	Slistan-Grijalva et al., 2005 90% recycling conidered
		PVP	47.2	kg	Created, see below	Slistan-Grijalva et al., 2005
		Water	261	kg	Water, deionized, at plant/US*	Slistan-Grijalva et al., 2005 Dissolution water
1 kg PVP	Input	1,4-butanediol	0.8	kg	Butane-1,4-diol, at plant/US	C4H10O2 --> C4H6O2 + 2H2 , (dehydrogenation of 1,4-butanediol over copper at 200 C forming gamma-butyrolactone)
		Ammonia	0.15	kg	Ammonia, liquid, at regional storehouse/US*	C4H6O2 +NH3 --> C4H7NO + H2O , (gamma-butyrolactone reacting with ammonia yields pyrrolidone)
		Acetylene	0.23	kg	Acetylene, at regional storehouse/US*	C4H7NO + C2H2 --> C6H9NO , (subsequent treatment of pyrrolidone with acetylene gives VP monomer)
		Hydrogen	0.04	kg	Emissions to air> Hydrogen	C4H10O2 --> C4H6O2 + 2H2
		Water	0.16	kg	Emissions to water> Water	C4H6O2 +NH3 --> C4H7NO + H2O

Table S4. Life cycle inventory of CR-Starch synthesis route.

Method	Section	Material	Amount	Unit	Corresponding LCI unit process	Comment
1 kg AgNP CR with soluble starch	Input	Potato starch	90	kg	Potato starch, at plant/US**	El-Rafie et al., 2011
		Water	10000	kg	Water, deionised, at plant/US*	El-Rafie et al., 2011
		Silver nitrate	1.57	kg	Created, see Table S1	El-Rafie et al., 2011
		Heat	1915027	kJ	Heat, unspecific, in chemical plant/US- US-EI U	El-Rafie et al., 2011 Heat for bringing to 70 C Checked with Aspen Plus

Table S5. Life cycle inventory of FSP synthesis route.

Method	Section	Material	Amount	Unit	Corresponding LCI unit process	Comment
1 kg AgNP FSP	Input	Oxygen	33.4	kg	Oxygen, liquid, at plant/US	Walser et al, 2011
		Methane	1.53	kg	Methane, 96 vol-%, from biogas, at purification/US*	Walser et al, 2011
		Water	62.8	kg	Water, deionised, at plant/US*	Walser et al, 2011
		Silver octanoate	2.35	kg	Created, see below	Walser et al, 2011
		2-ethylhexanoic acid	6.29	kg	Created, see below	Walser et al, 2011
		Xylene	6.29	kg	Xylene, at plant/US	Walser et al, 2011
		Electricity	25.10	kWh	Electricity, medium voltage, at grid/US	Walser et al, 2011
	Output	Nitric oxide	0.4	kg	Emissions to air> Nitric oxide	Walser et al, 2011
		Carbon dioxide	43.9	kg	Emissions to air> Carbon dioxide, fossil	Walser et al, 2011
		Water	16.8	kg	Emissions to water> Water	Walser et al, 2011
		Wastewater treatment	0.06	m3	Emissions to water> Waste water/m3	Walser et al, 2011
1 kg Silver octanoate	Input	Coconut oil	2.7	kg	Crude coconut oil, at plant/PH	Walser et al, 2011
		Silver nitrate	2.57	kg	Created, see Table S1	Walser et al, 2011
		Sodium hydroxide	0.38	kg	Sodium hydroxide, 50% in H2O, production mix, at plant/US	Walser et al, 2011
		Water	0.9	kg	Water, deionised, at plant/US*	Walser et al, 2011
1 kg 2-ethylhexaxnoic acid	Avoided product	Steam	0.0007	kg	Steam, for chemical processes, at plant/US	Walser et al, 2011
	Input	n-butyraldehyde	1.02	kg	Created, see below	Walser et al, 2011
		Transport	10.8	tkm	Transport, lorry 16-32t, EURRO 5/US	Walser et al, 2011
	Output	Carbon dioxide	0.05	kg	Emissions to air> Carbon dioxide, fossil	Walser et al, 2011
1 kg N-butyraldehyde	Input	Propylene	0.58	kg	Propylene, at plant/US	2CH3CH = CH2 + 2CO + 2H2 --> CH3(CH2)2CHO + (CH3)2(CH)2O (N to iso ration is 4:1, hence, iso is neglected) , (Walser et al.)
		Carbon monoxide	0.38	kg	Carbon monoxide, CO, at plant/US	2CH3CH = CH2 + 2CO + 2H2 --> CH3(CH2)2CHO + (CH3)2(CH)2O (N to iso ration is 4:1, hence, iso is neglected) , (Walser et al.)
		Hydrogen	0.03	kg	Hydrogen, liquid, at plant/US	2CH3CH = CH2 + 2CO + 2H2 --> CH3(CH2)2CHO + (CH3)2(CH)2O (N to iso ration is 4:1, hence, iso is neglected) , (Walser et al.)

Table S6. Life cycle inventory of AP synthesis route.

Method	Section	Material	Amount	Unit	Corresponding LCI unit process	Comment
1 kg AgNP AP	Input	Silver	1.00	kg	Silver, at regional storage/US	Zhou et al., 2009
		Argon	7.4	kg	Argon, liquid, at plant/US	Zhou et al., 2009
		Electricity	41.67	kWh	Electricity, medium voltage, at grid/US	Zhou et al., 2009

Table S7. Life cycle inventory of RMS-AR-N synthesis route.

Method	Section	Material	Amount	Unit	Corresponding LCI unit process	Comment
1 kg AgNP RMS-Ar-N	Input	Silver	1.00	kg	Silver, at regional storage/US	Pierson et al., 2005
		Argon	123.6	g	Argon, liquid, at plant/US	Pierson et al., 2005
		Nitrogen	10.4	g	Nitrogen, liquid, at plant/US	Pierson et al., 2005
		Electricity	27.8	kWh	Electricity, medium voltage, at grid/US	Pierson et al., 2005

Table S8. Acticoat 7 wound dressing material composition.

Product	Section	Material	Amount	Unit	Corresponding LCI unit process	Comment
Acticoat7	Input	3 layers of HDPE mesh	0.69	g	Created, see below	Smith & Nephew
		2 layers of non-woven rayon/polyester	0.7	g	Created, see below	Smith & Nephew
		Silver	0.13	g	Modeled using one of the eight synthesis routes	Parsons et al., 2005
		Packaging, 2 layers of supercalendered paper	3.13	g	Paper, wood-containing, supercalendred (SC), at regional storage/US*	Estimation
		Transport	0.000052	tkm	Transport, lorry >16t, fleet average/US	Estimation
1 kg HDPE	Input	Polyethylene	1.05	kg	Polyethylene, HDPE, granulate, at plant/US	Assumed 5% loss of plastic, (adapted from Walser et al., 2011)
		Heat, natural gas	9.7	MJ	Heat, natural gas, at boiler modulating <100kW/US	Assumed HDPE fibers require the same heat input as PET fibers, (adapted from Walser et al., 2011)
		Water	26.04	kg	Water, deionised, at plant/US*	Assumed HDPE fibers require the same water input as PET fibers , (adapted from Walser et al., 2011)
		Electricity	5.9	kWh	Electricity, medium voltage, at grid/US	Assumed HDPE fibers require the same electricity input as PET fibers, (adapted from Walser et al., 2011)
	Output	Polyethylene	0.05	kg	Disposal, polyethylene, 0.4% water, to municipal incineration/US*	Assumed 5% loss of plastic, (adapted from Walser et al., 2011)
		Water	0.026	m^3	Treatment, sewage, to wastewater treatment, class 3/US*	
1 kg Polyester	Input	Polyethylene terephthalate	1.05	kg	Polyethylene terephthalate, granulate, bottle grade, at plant/US	Walser et al., 2011
		Heat, natural gas	9.7	MJ	Heat, natural gas, at boiler modulating <100kW/US	Walser et al., 2011
		Water	26.04	kg	Water, deionised, at plant/US*	Walser et al., 2011
		Electricity	5.9	kWh	Electricity, medium voltage, at grid/US	Walser et al., 2011
		Transport lorry	9.7	tkm	Heat, natural gas, at boiler modulating <100kW/US	Walser et al., 2011
		Transport freight	0.2	tkm	Transport, freight, rail/US	Walser et al., 2011
	Output	Polyethylene terephtalate	0.05	kg	Disposal, polyethylene terephtalate, 0.2% water, to municipal incineration/US*	Walser et al., 2011
		Water	0.026	m^3	Treatment, sewage, to wastewater treatment, class 3/US*	Walser et al., 2011

Table S9. Comparative TRACI environmental impacts of all methods.

IMPACT CATEGORY	UNIT	CR-EG	CR-SB	CR-TSC	CR-STARCH	FSP	RMS-AR-N	AP
OD	kg CFC-11 eq	2.27E-05	1.45E-05	2.92E-05	3.58E-05	3.87E-05	9.47E-06	1.00E-05
GW	kg CO2 eq	4.32E+02	1.32E+02	4.54E+02	4.34E+02	5.43E+02	1.28E+02	1.41E+02
PS	kg O3 eq	3.40E+01	2.34E+01	3.10E+01	3.34E+01	9.90E+01	2.30E+01	2.36E+01
AC	kg SO2 eq	4.55E+00	2.48E+00	4.64E+00	4.72E+00	9.75E+00	2.45E+00	2.54E+00
EU	kg N eq	7.19E+00	6.70E+00	6.93E+00	8.06E+00	2.57E+01	6.71E+00	6.75E+00
HHC	CTUh	6.00E-05	5.06E-05	5.45E-05	5.86E-05	1.92E-04	5.00E-05	5.07E-05
HHNC	CTUh	1.74E-04	1.59E-04	1.78E-04	2.11E-04	6.00E-04	1.56E-04	1.57E-04
HHCR	kg PM2.5 eq	3.76E-01	2.40E-01	3.79E-01	3.89E-01	9.05E-01	2.36E-01	2.42E-01
EC	CTUe	2.34E+03	2.09E+03	2.27E+03	5.31E+03	7.98E+03	2.08E+03	2.09E+03
FF	MJ surplus	7.69E+02	1.49E+02	6.69E+02	5.92E+02	6.42E+02	1.39E+02	1.48E+02

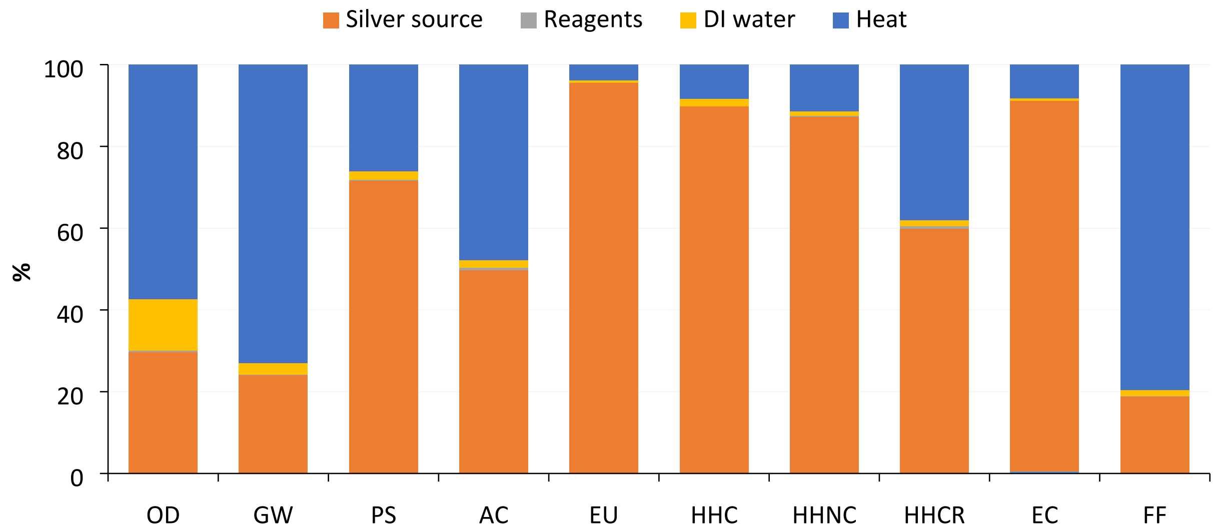

Figure S1. Process contribution for all TRACI impact categories of CR-TSC synthesis route (silver source is silver nitrate, reagent is trisodium citrate).

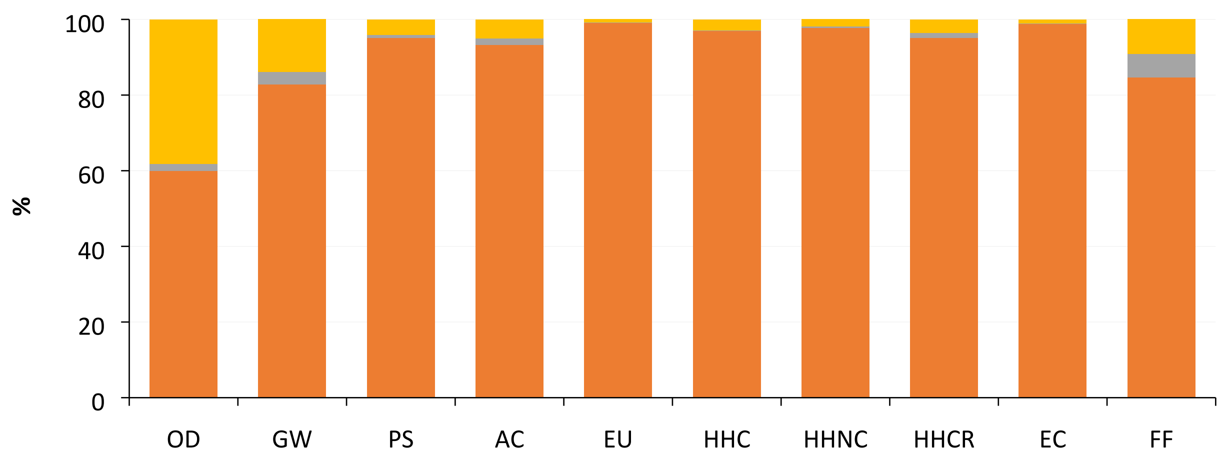

Figure S2. Process contribution for all TRACI impact categories of CR-SB synthesis route (silver source is silver nitrate, reagent is sodium borohydride).

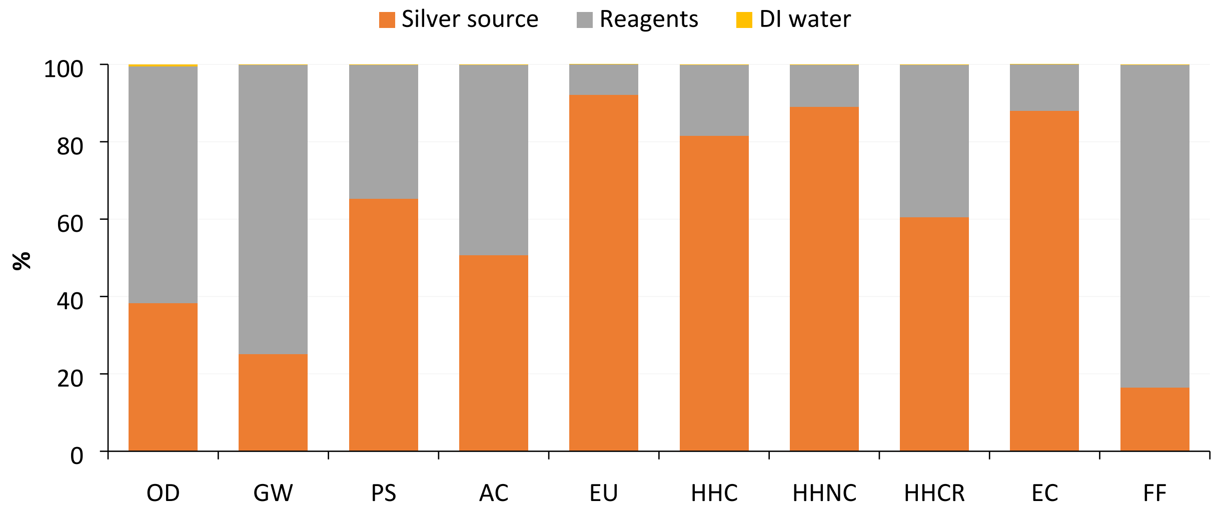

Figure S3. Process contribution for all TRACI impact categories of CR-EG synthesis route (silver source is silver nitrate, reagents are ethylene glycol and PVP).

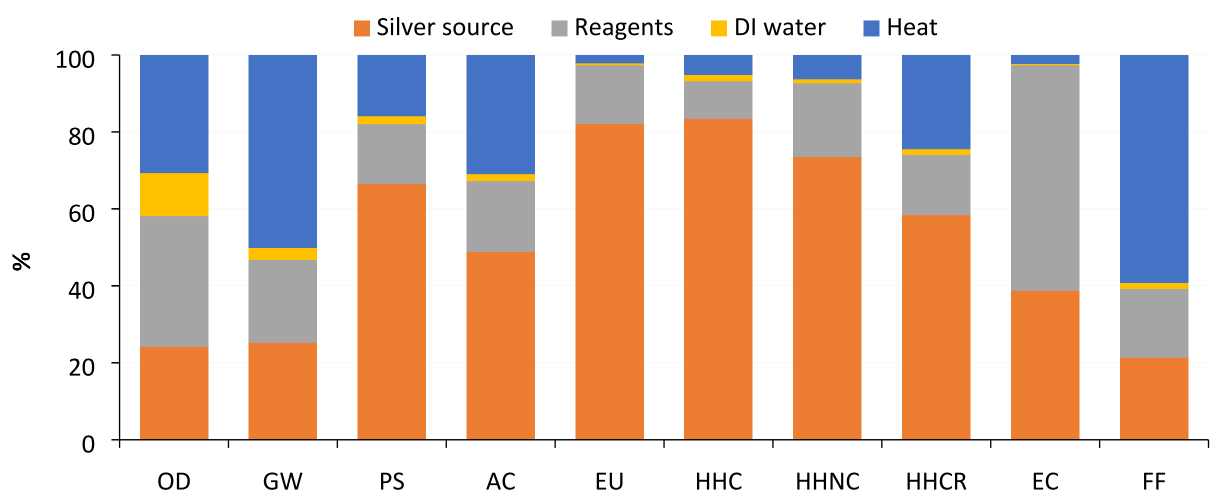

Figure S4. Process contribution for all TRACI impact categories of CR-Starch synthesis route (silver source is silver nitrate, reagent is soluble starch solution).

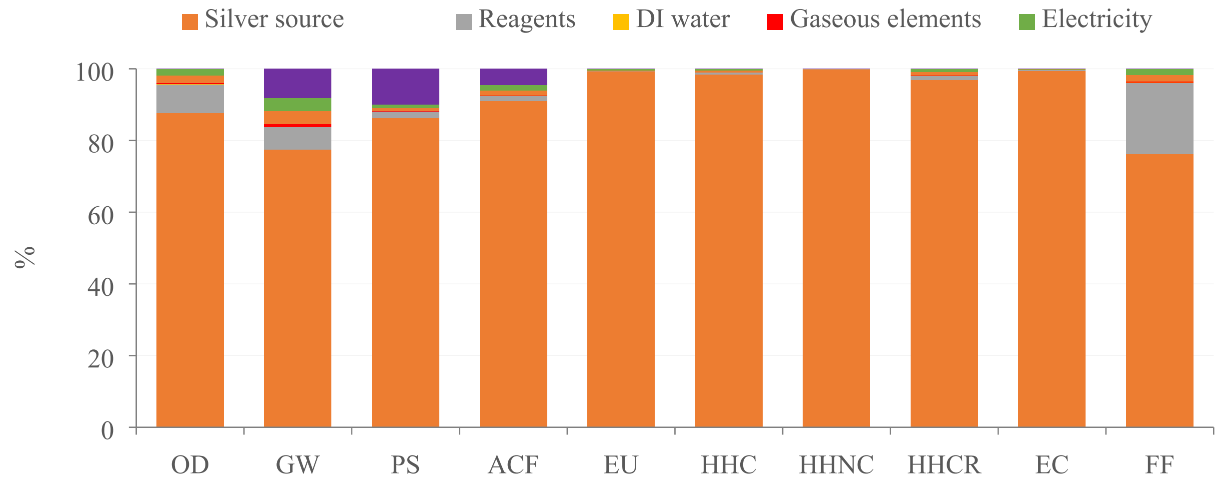

Figure S5. Process contribution for all TRACI impact categories of FSP synthesis route (silver source is silver octanoate, reagents are 2-ethylhexanoic acid and xylene, gaseous elements are oxygen and methane).

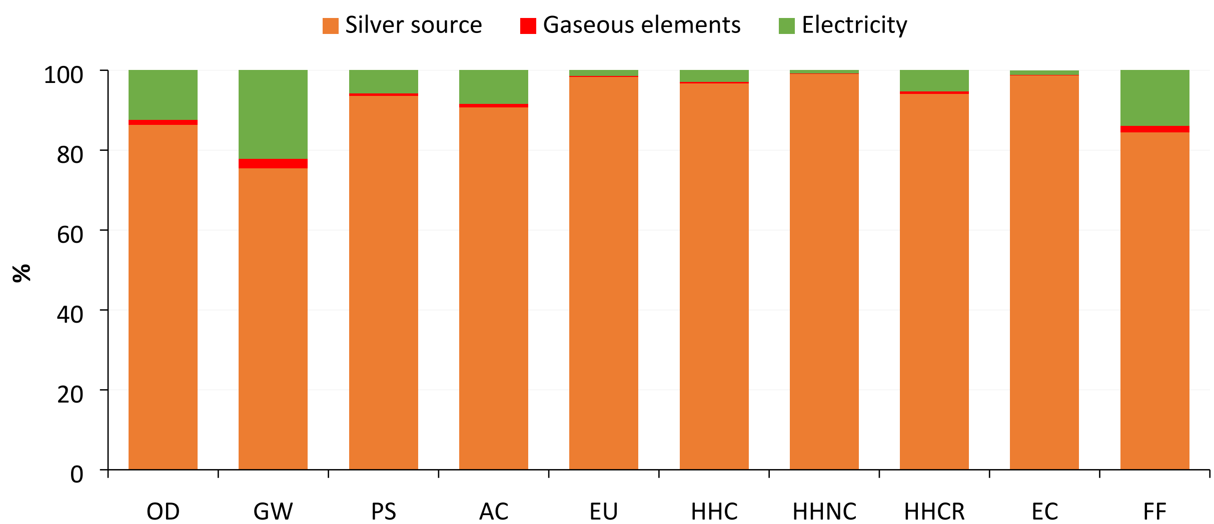

Figure S6. Process contribution for all TRACI impact categories of AP synthesis route (silver source is solid silver, gaseous elements are argon and nitrogen).

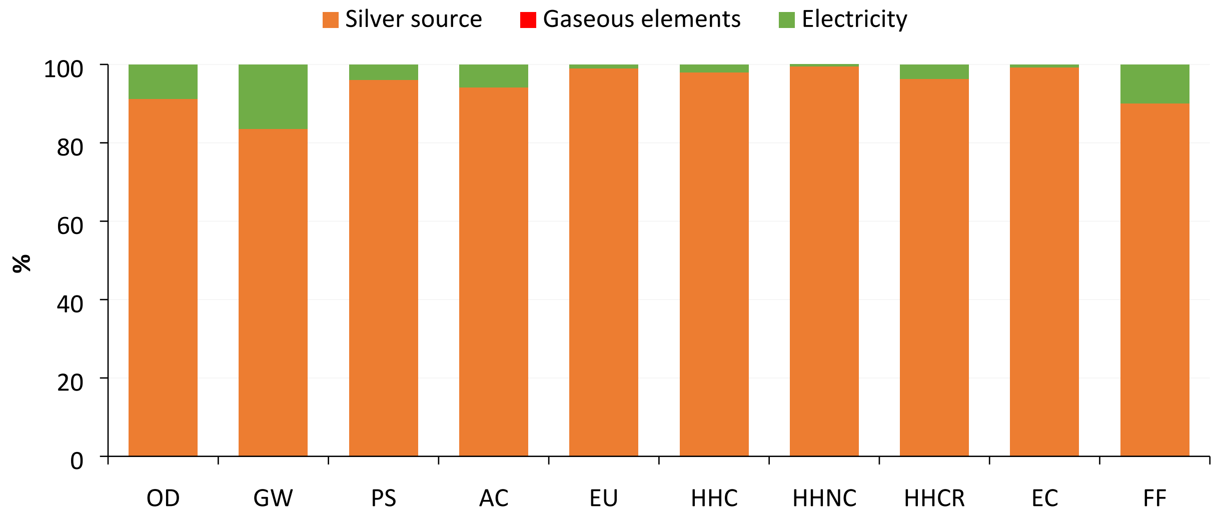

Figure S7. Process contribution for all TRACI impact categories of RMS-AR-N synthesis route (silver source is solid silver, gaseous elements are argon and nitrogen).

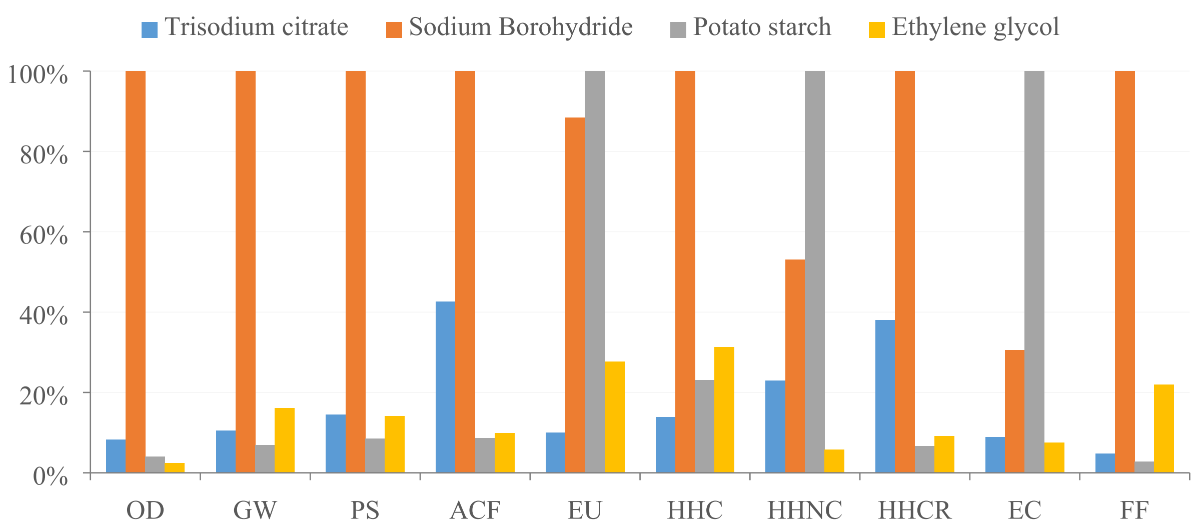

Figure S8. Comparison of reducing agents for all impact categories.

1. Comparison of Green Synthesis using Soluble Starch (CR-Starch)

The method described in section 2.2.4[1] is compared here with another reported CR-Starch technique, the main difference being the temperature at which the reaction occurs.[2] AgNPs in this method are produced using soluble starch as both the reducing and stabilizing agent for the silver nitrate solution.[2] Here, soluble starch is added to deionized water and heated in microwave until complete dissolution. The dissolved starch is used to reduce a 100 mM silver nitrate solution. The particles were formed in an autoclave at 15 psi and 121°C after 5 minutes. Energy consumed by the microwave in order to dissolve the starch in water was calculated using the average gelatinization temperature of starch (70°C),[3–7] and an average efficiency for microwave equipment (50%).[8] Autoclave heat was also calculated for the solution mixture and checked for consistency using the chemical process optimization software Aspen Plus. Assuming 100% yield, to produce almost 1 kg of silver nano particles, 100 kg of potato starch is required alongside 1000 kg of water, to reduce 1.69 kg of silver nitrate. Life cycle inventory for this route can be found in Table S10. From figure S9, it can be seen that the significant heat and electricity consumption of this method outweighs the contribution of the other constituents. Figure S10 shows relative results between the two mentioned CR-Starch routes, and a scenario in which instead of autoclaving, the above reduction takes place at atmospheric conditions with a reaction temperature of 100C. The results emphasize the high dependency of impacts to the reaction conditions. For this synthesis route, changing the parameters such as temperature, heating duration, or silver nitrate concentration affects the diameter and the size distribution of the silver particles.[1] Lower temperatures and durations result in smaller particles. Modifications of the starch also directly affects its solubility in water, requiring less energy for dissolution. Hence, determining the application of these particles are crucial to estimating the overall cradle-to-gate impacts of their synthesis.

Table S10. Life cycle inventory of autoclaved CR-Starch synthesis route.

Method	Section	Material	Amount	Unit	Corresponding LCI unit process	Comment
1 kg AgNP CR with soluble starch	Input	Potato starch	100	kg	Potato starch, at plant/US**	Vigneshwaren et al., 2006
		Water	10000	kg	Water, deionised, at plant/US*	Vigneshwaren et al., 2006
		Silver nitrate	1.57	kg	Created, see Table S1	Vigneshwaren et al., 2006
		Heat	26205065	kJ	Heat, unspecific, in chemical plant/US- US-EI U	Vigneshwaren et al., 2006 Heat for bringing to 121 C @ 15 psi Checked with Aspen Plus
		Electricity	3833253	kJ	Electricity, medium voltage, at grid/US	Vigneshwaren et al., 2006 Microwave electricity concumptionn

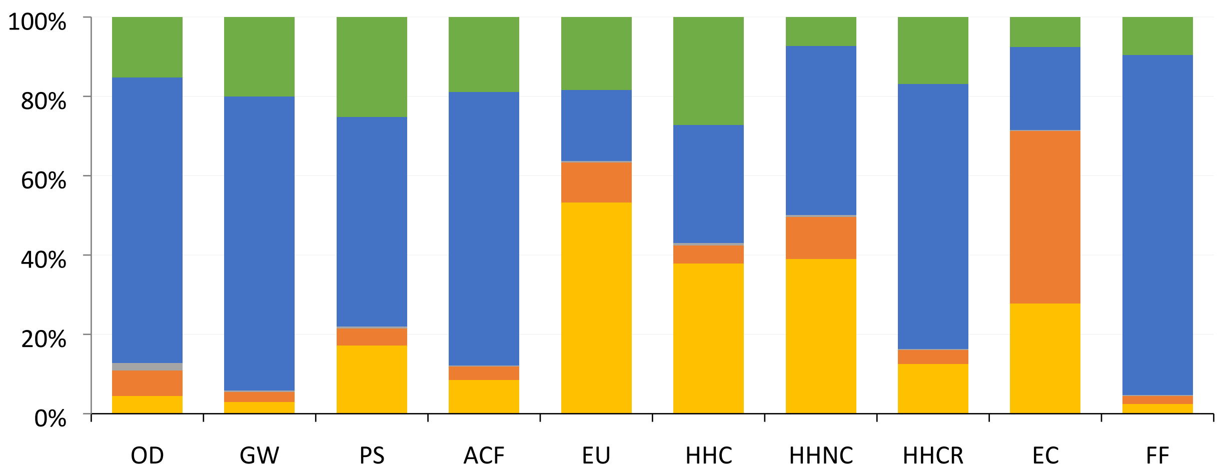

Figure S9. Process contribution for all TRACI impact categories of autoclaved CR-Starch synthesis route (silver source is silver nitrate, reagent is soluble starch solution).

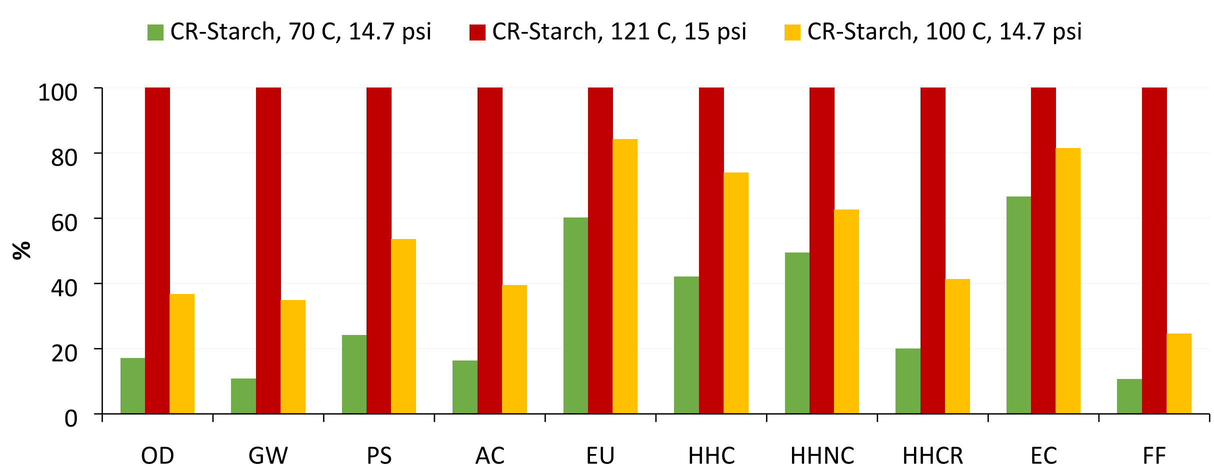

Figure S10. Comparison of CR-Starch routes for all impact categories.

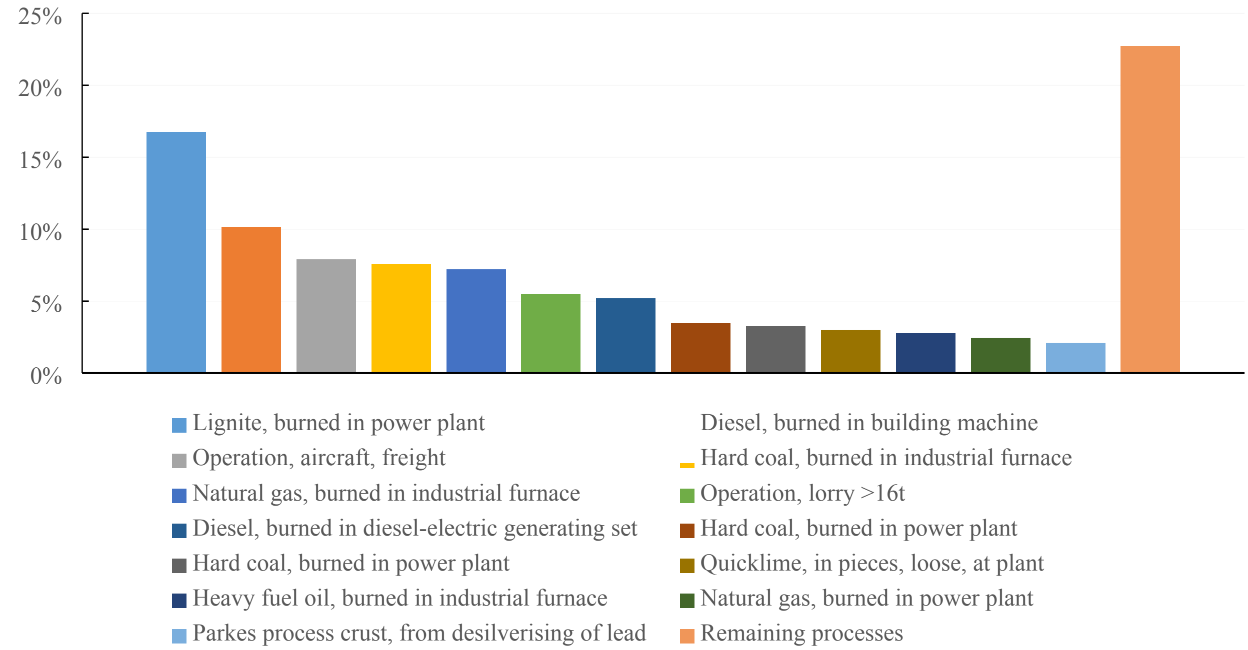

Figure S11. Process contribution to GWP for silver at regional storage.

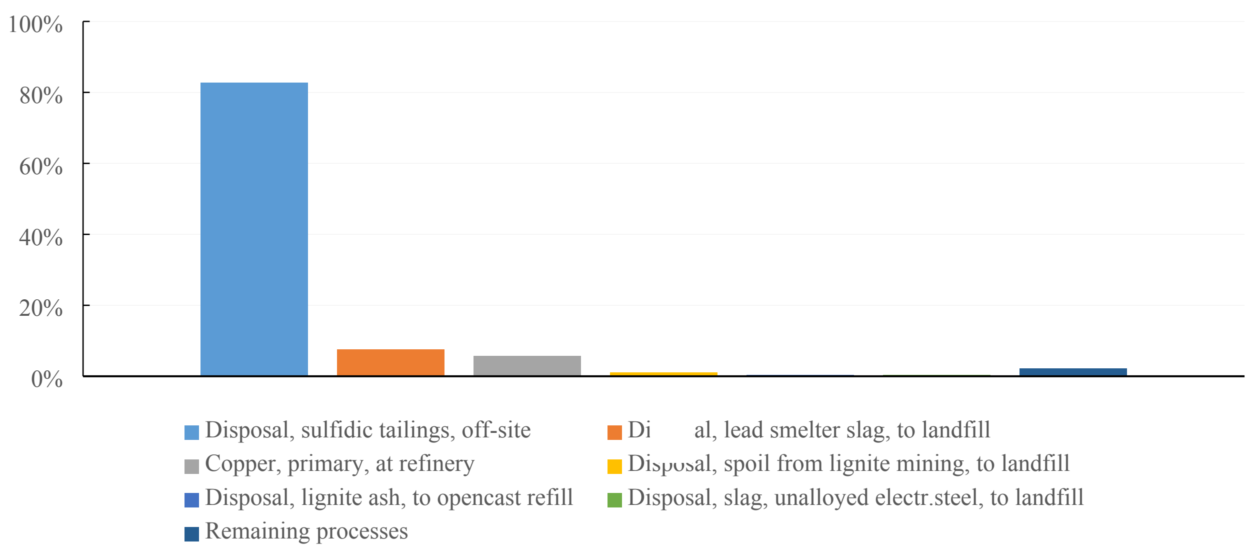

Figure S12. Process contribution to ecotoxicity for silver at regional storage.

Notes and References

(1) El-Rafie, M. H.; El-Naggar, M. E.; Ramadan, M. A.; Fouda, M. M.; Al-Deyab, S. S.; Hebeish, A. Environmental synthesis of silver nanoparticles using hydroxypropyl starch and their characterization. *Carbohydr. Polym.* **2011**, *86* (2), 630–635.

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