

# Analytical decision tool for risk assessment of ENMs to biological systems

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# Are there nanoproducts in South Africa?



- Development of a database of nanoproducts
- Examine for national and international sources of products in South African market
- Apply a set of criteria to determine which nanoproducts to be entered into our database...
- Database provides .... solid basis to consider the question of ECW streams

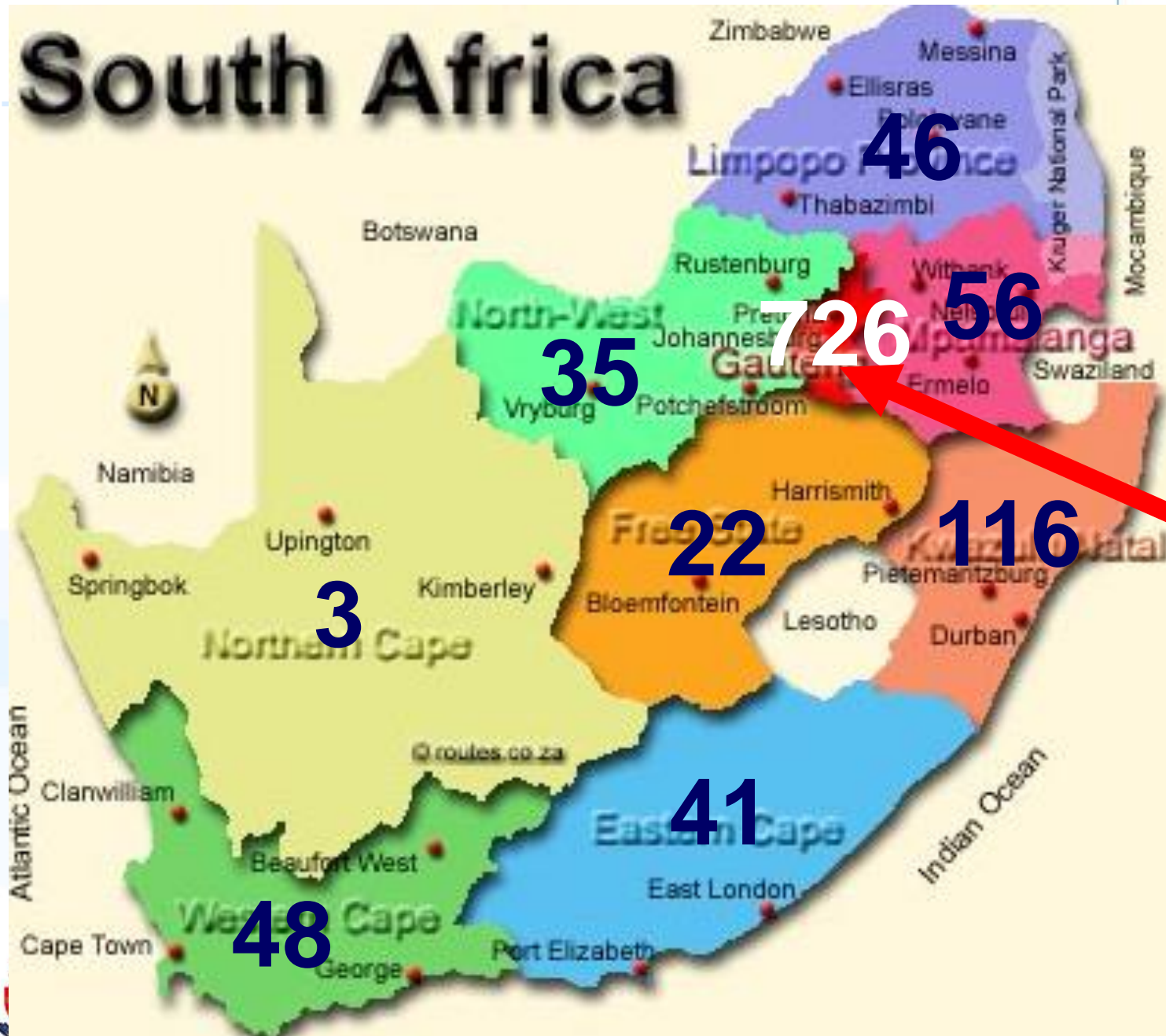


# Social, demographic, and economic data

Province	Area (Km <sup>2</sup> )	Population	Pop. Density (per/km <sup>2</sup> )	Relative Region income to RSA
<b>Gauteng</b>	<b>18 178</b>	<b>13 200 349</b>	<b>726</b>	<b>1.51</b>
Western Cape	129 462	6 200 098	48	1.39
Northern Cape	372 889	1 185 628	3	0.83
Kwa-Zulu Natal	94 361	10 919 077	116	0.81
Mpumalanga	76 495	4 283 888	56	0.75
Free State	129 825	2 817 941	22	0.73
North West	104 882	3 706 962	35	0.68
Eastern Cape	168 966	6 916 185	41	0.63
Limpopo	125 754	5 726 792	46	0.55
South Africa	1 220 812	54 956 920	45	-



# South Africa



Region of focus

# Criteria used to include a given product in the database.... Nationally manufactured



- Source claiming that the product or application is available in the South African market (✓)
- The product should have nanoparticles which are nanotechnology - based produced, declared by manufacturer (✓)
- The particle size of the ENM is reported in (1 – 100 nm) (X)
- The product should not be a 'dead product', implying that it is currently available in the market (X)
- ENMs matrix type should be given (✓)

**Hansen et al. (2016); Vance et al. (2015)**

# Criteria used to include a given product in the database.... Imported to RSA



- Web searching through South African store websites
- Web searching through online shopping websites commonly used by South Africans (like the Amazon and eBay)
- Web searching for availability of brand outlets of products manufactured internationally

**Note: Products produced and manufactured by multinational companies meet the same standards --- and variability of Musee (2011 & 2016)**

# Model assumptions...



- Probability for any sub-product in a given product category as equal unless differentiated by the number of sub-products and the types of ENMs used
- Market penetration equals to population percentage with ability to purchase a given sub-category product is dependent on price, and therefore, levels of market penetration varies from product to product dependent on price
- Fate and behaviour aspects of the ENMs once released into the environment was not included in the model
- Model aimed to provide insights based on worst case scenario

# Nanoproducts categorization/classification in RSA



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- Nanoproducts identified were 178 (total)
- Types of nano
- Nanoproducts contained single (167 nanoproducts ( $\approx 94\%$ )) and multiple ENMs (11 nanoproduct  $\approx 6\%$ )
- Major ENMs in RSA Market: (where they contribute  $\geq 2\%$ )

ENMs	Percentage
Si	<b>9.6%</b>
Unknown	17.4%
Ti	<b>37.6%</b>
Ag	<b>10.7%</b>
Al	<b>2.2%</b>
CNT	<b>6.7%</b>
TiO <sub>2</sub> /ZnO (mixture)	2.8%



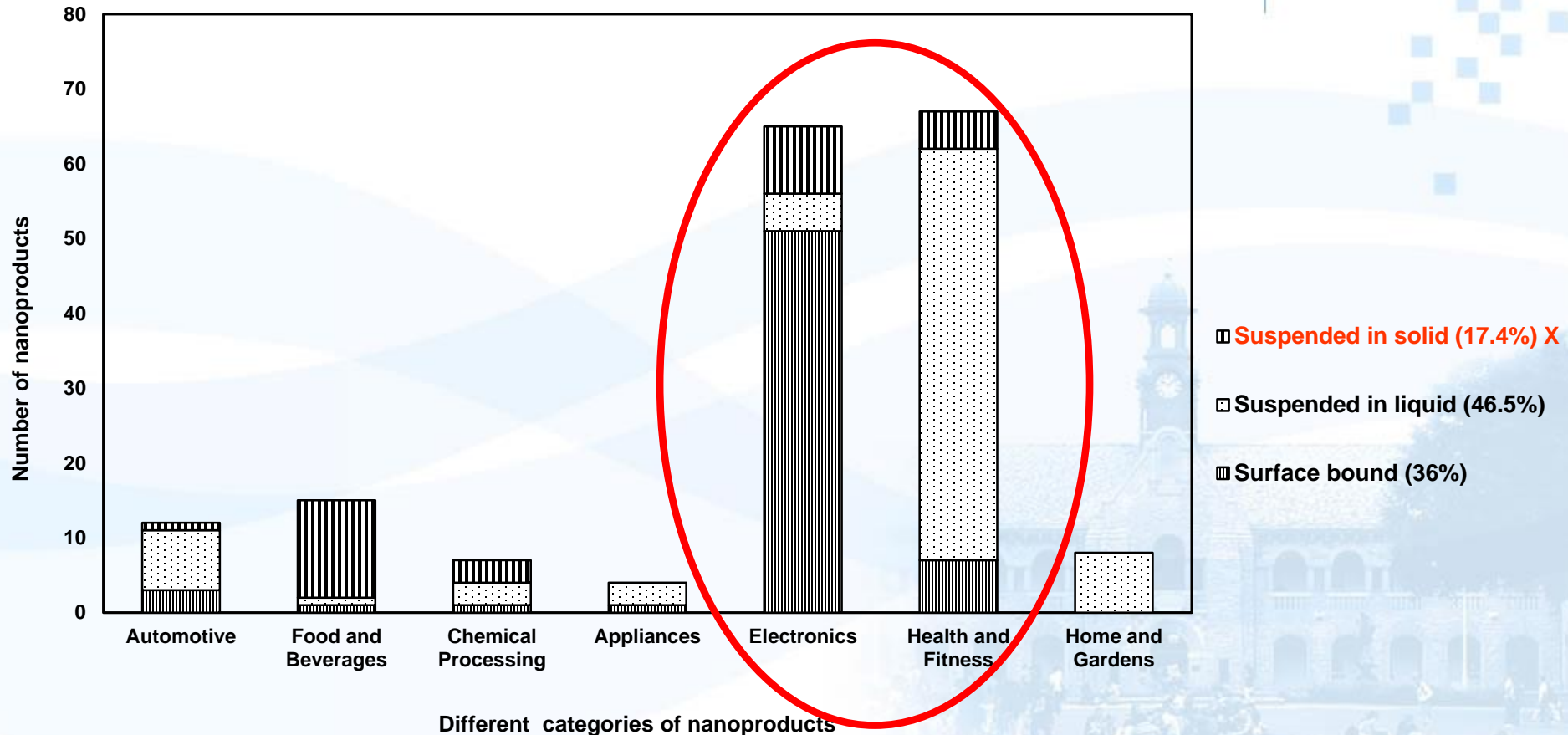
# Nanoproducts Categories...



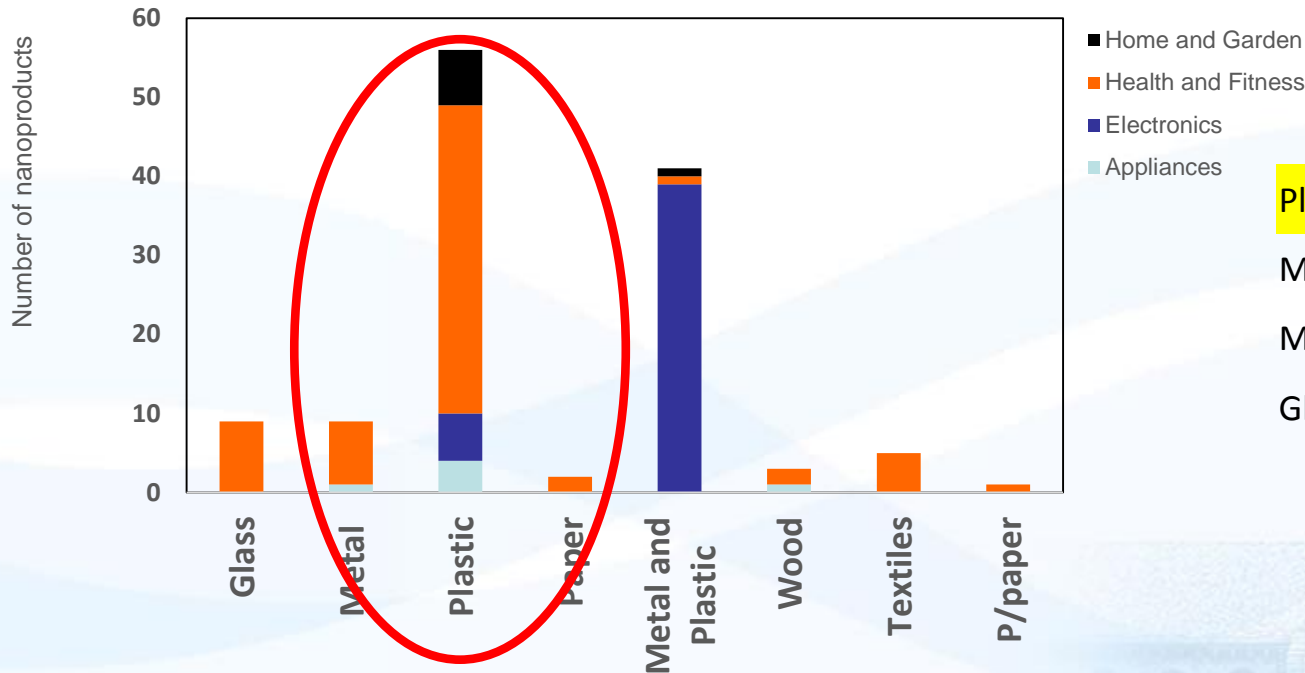
- Nanoproducts identified were 178 (total)
- Types of nanomaterials : CBNs, and inorganic ENMs
- Nanoproducts contained **SINGLE** (167 nanoproducts ( $\approx 94\%$ )) and **MULTIPLE** ENMs (11 nanoproduct  $\approx 6\%$ )
- Major ENMs in RSA Market are: (where they contribute  $\geq 2\%$ )

ENMs	Percentage
Si	<b>9.6%</b>
Unknown	17.4%
Ti	<b>37.6%</b>
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TiO <sub>2</sub> /ZnO	2.8%

# ENMs in different products matrixes available in SA



# Distribution of waste per nanoproducts category....



Plastics	44.40%
Metal and plastics	32.50%
Metals	7.10%
Glass	7.10%

**> 91% of waste**

Note: Automotive, and Chemical Processing have not been included based on the fact that this is industrial manufacturing processes and not domestic used products.

Nanoproducts in the food and beverage category not included in the analysis. ENMs were in the food, and the link to how they can be transferred onto packaging form of waste streams could not be ascertained.

# Distribution of ENMs in Health and fitness category



Product	Others	CNTs	Au	TiO2	Ag	Si	Totals	%
Cosmetics	20	1	2	2	1	3	29	43
Sunscreen	1			7	1		9	13
DUP	2			11	2	1	16	24
Textiles	0	1			4		5	7
Fitness	2	6					8	12
Sub-totals	25	8	2	20	8	4	67	100%

**DPU: razor blades, shampoo, shoe polishers, creams, cleansing bars, moisturizers, deodorants, toothpaste, powders**

# Daily use products (DPU)...



Razor blades	2	Unknown
Shampoo	3	TiO <sub>2</sub>
Shoe polish	1	TiO <sub>2</sub>
Creams	4	TiO <sub>2</sub>
Moisturizers	1	Si
deodorants	1	Ag
Toothpaste	1	TiO <sub>2</sub>
Lotion	1	Ag
Cleansing	2	TiO <sub>2</sub>

# Trigger(s) based mass of ENMs for data registration

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- How will different ENMs be dealt with when considering the trigger tonnage mass e.g. AgNPs reported lower masses but has shown to induce effects at very low concentrations
- What tonnage threshold will be applicable for ENMs as opposed to the values set for bulk materials?
- Test the likely effect of using current mass based thresholds. On waste management it will have no effect when considering the level of risk a given waste stream is likely to trigger



- Based on REACH: For exposure information: among the information required include: information on waste quantities and composition of the waste resulting from manufacture and/or use of the products (scarcely lacking: both for products imported and manufactured with ENMs (both for industrial and consumer uses)
- Mass as a trigger to evoke need for data collection to carry out risk assessment is linked to production of a given chemical; and in turn, current set values are unlikely to be reached soon by ENMs

# Mass as a trigger: the scoring approach



Bulk chemicals mass based classification		
Production volume (kg)		
< 11 340 (1.1 tonnes)	Very low	1
≥ 11 340 < 453 590	Low	3
≥ 453 590 < 45 359 000	Medium	5
≥ 45 359 000	High	7
Mass for nanoforms		
< <b>113.4</b>	<b>Very low</b>	<b>1</b>
≥ <b>113.4</b> < <b>4535.9</b>	<b>Low</b>	<b>3</b>
≥ <b>4535.9</b> < <b>453 590</b>	<b>Medium</b>	<b>5</b>
≥ <b>453 590</b>	<b>High</b>	<b>7</b>

According to Malkiewicz, et al. Nanomaterials in REACH — project report; 2011. Three categories for chemicals registration: Substances imported/produced:

- >1000 tonnes per annum must have been registered by 30th November 2010
- > 100 tonnes by 31st May 2013
- > 1 tonne by 31st May 2018.
- Proposition for Nanoforms:  
=> **1tonne/100 =10 kg**





# Tonnage of ENMs....

ENMs	Mass (tons)	Mass (kg)	Ref.
Ag	550	$5.5 \times 10^5$	1
TiO <sub>2</sub>	201 500	$2.015 \times 10^8$	2
ZnO	33 400	$3.34 \times 10^7$	3
CNTs	3 000	$3 \times 10^6$	1
nC <sub>60</sub>	1 620	$1.62 \times 10^6$	1
Cu	10	$1 \times 10^4$	4
SiO <sub>2</sub>	1 590 000	$1.59 \times 10^9$	5
Al	5 500	$5.5 \times 10^6$	1
Au	3	$3 \times 10^3$	6

# Estimated mass of ENMs to solid waste landfills... in kg



ENMs	CNTs	TiO <sub>2</sub>	Au	Ag	Si
High	6.48	924.89	12.89	10.81	310.14
Medium	3.49	537.15	6.94	6.38	167.00
Low	1.92	273.91	3.82	3.20	91.85

Conventional chemicals (kg)	Mass (kg) [Nanoform]	Qualitative value	Score
< 11 340 (1.1 tonnes)	< 113.4	Very low	1
≥ 11 340 < 453 590	≥ 113.4 < 4535.9	Low	3
≥ 453 590 < 45 359 000	≥ 4535.9 < 453 590	Medium	5
≥ 45 359 000	≥ 453 590	High	7



# Classification of reported effects data for ENMs

Toxicity classes*	ENMs (toxicity classes)**	Fish [96-h LC <sub>50</sub> (mg/L)]	Crustaceans [48-h EC <sub>50</sub> (mg/L)]	Algae [72- or 96-h; EC50 (mg/L)]	Ranking scores for Toxicity
-----	Extremely toxic	≤ 0.1	≤ 0.1	≤ 0.1	9
Acute I/ Chronic I	Very toxic	≤ 1	≤ 1	≤ 1	7
Acute II/ Chronic II	Toxic	1 to ≤ 10	1 to ≤ 10	1 to ≤ 10	5
Acute III/ Chronic III	Harmful	10 to ≤ 100	10 to ≤ 100	10 to ≤ 100	3
Acute IV/ Chronic IV	Not classified/ not harmful	≥ 100	≥ 100	≥ 100	1

\*European Commission (EC) 2008. Regulation (EC) No 1272/2008

\*\*Chen et al. (2015) ATLA 43, 221–240

\*\*\*Studies of Nam et al., (2015) showed Au toxicity to most sensitive organisms.

# Classification of reported toxicity data for ENMs...



Toxicity classes*	ENMs (toxicity classes)	ENMs toxicity classification**	ENMs toxicity classification***	Scores for ranking
	Extremely toxic	Ag	Ag	9
Acute I/ Chronic I	Very toxic	CuO, ZnO	Cu	7
Acute II/ Chronic II	Toxic	TiO2	Zn, Ti, Se, Co, Ni	5
Acute III/ Chronic III	Harmful	MWCNTs, SiO2	Al, Au, Fe	3
Acute IV/ Chronic IV	Not classified/ not harmful	Au****	Si	1

\*European Commission (EC) 2008. Regulation (EC) No 1272/2008

\*\*Bondarenko et al. (2016) Nanotoxicology, 10:9, 1229-1242.

\*\*\*Chen et al. (2015) ATLA 43, 221–240

\*\*\*\*Studies of Nam et al., (2015) showed Au toxicity to most sensitive organisms

Values of toxicity vary consideration between organisms of the same ENPs

# ECW classes from personal care products....



ENMs	Mass of ENMs		Exposure score		Hazard score	Risk score
	High (kg)	Low (kg)	High	Low		
CNTs	7	2	1	1	1	2
TiO <sub>2</sub>	925	274	3	3	5	7
Au	4	3.82	1	1	3	4
Ag	11	3	1	1	9	10
Si	310	92	3	1	1	3






# RSA context ...

- Nanoproducts are in SA market but also ECW in the landfills!!
- Likely low masses of ENMs released into landfills
- Imported products are majorly the source of ENMs into the environment but with limited national capability to deal with such waste streams
- Increasing waste streams containing ENMs as products developed have shorter use span
- Need for monitoring of ENMs in landfills in SA

# .... and way forward



- Consider other trigger(s) besides mass to invoke data collection...
- Landfill will host multiple ENMs and therefore consideration for mixtures is essential
- Issue of using the toxicity factors between nanoforms and counterpart bulk materials to find new mass related trigger may be possibility...



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# Thank you

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