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Exposure to nanomaterials in consumer spray products available in the UK

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Background

- Nanomaterials are being used in an increasing range of consumer products, but the public health risks associated with exposure to engineered nanoparticles in such products remain to some degree uncertain. Inadvertent inhalation exposure is a particular concern.

- Assessment of risk requires consideration of both hazard and exposure. PHE has a programme of studies to explore potential toxicity (hazard).

- This project relates to the assessment of exposures from engineered nanomaterials in consumer spray products. To provide:
  - Input to policy decisions relating to risk management and regulation of engineered nanomaterials
  - Information on materials used, and realistic exposure levels to input to toxicity studies

Objective

Estimate inhalation exposures to UK consumers arising from the use of spray products containing engineered nanomaterials

Stage 1. Identify and purchase representative products available in the UK

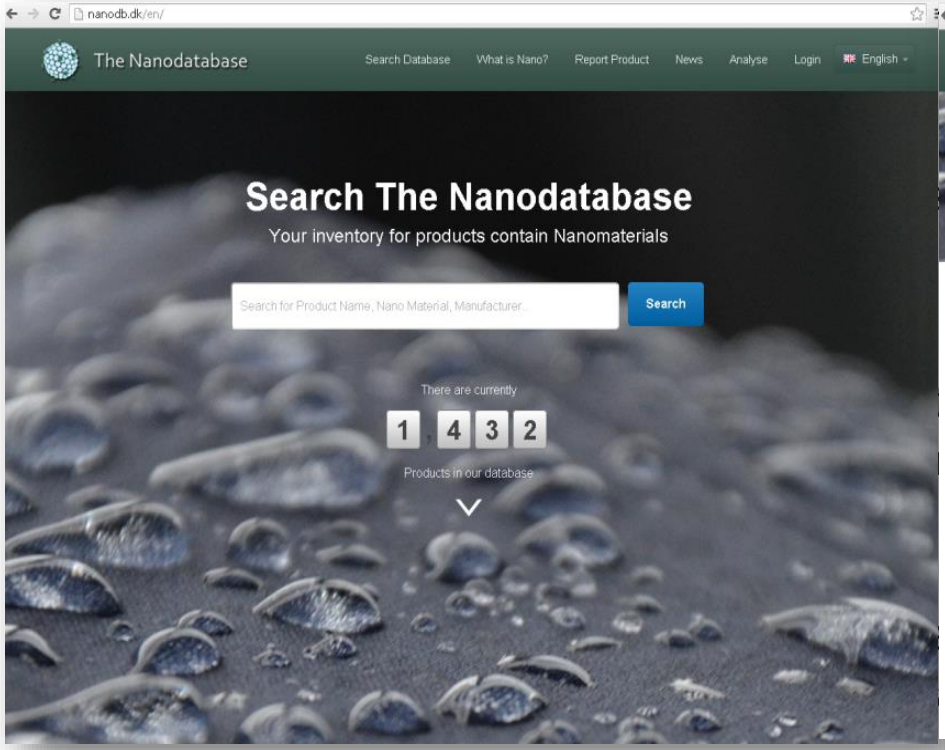
Stage 2. Analyse content of products and choose subset for aerosol analysis

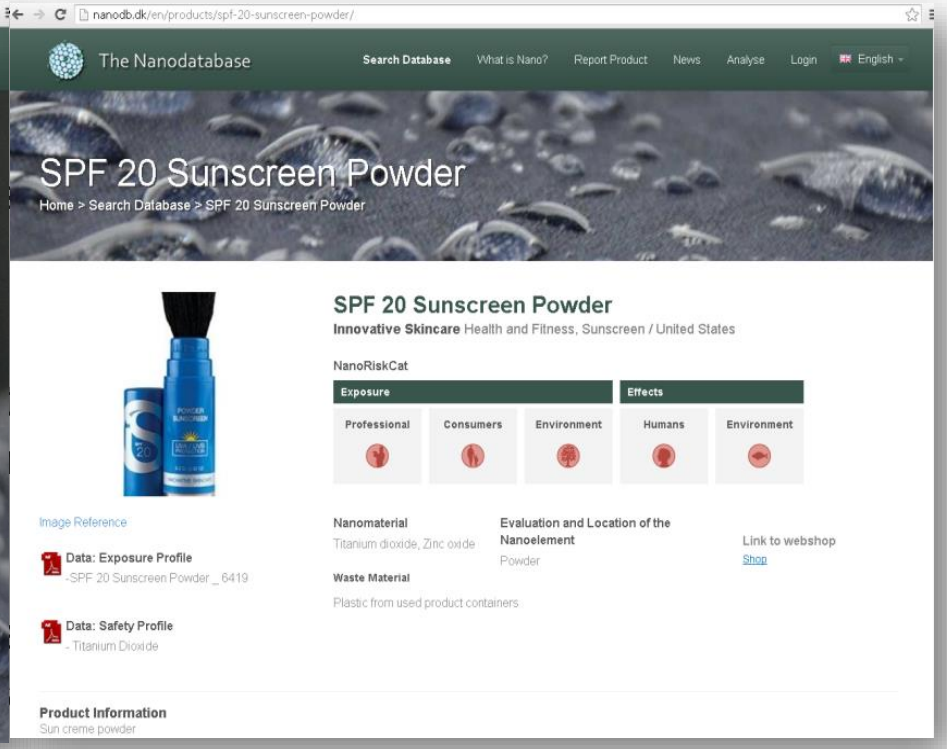
Stage 3. Characterise aerosol produced by selected products

Stage 4. Estimate levels of consumer exposures

Stages 1 and 2

Nanodatabase (www.nanodb.dk)
Online database developed by the Danish Consumer Council and the Danish Ecological Council in cooperation with the Technical University of Denmark (DTU)





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Product characteristics

#	Product	Replicates	Batches	Composition (manufacturer)	Application
1	Livoa Vital	3	2	Ag (10 ppm)	Health spray/supplement
2	Cicasilver (propellent)	3	2	Ag	Medical
3	NanoTec	3	-	Ag (5 ppm)	Furniture cleaner
4	M2 Beauté	2	-	Au	Beauty product
5	Squatty Potty Unicorn Gold	6	-	Au	Bathroom spray
6	Showerguard	3	-	Si	Glass treatment

Product characterisation

Summary of particle characterisation, total metal concentrations and pH of all suspensions

		DLS		NTA				splCP-MS			ICP-MS (ppb)		ICP-AES (ppb)	pH
Sample		Z-Av. (nm)	PDI	Mean (nm)	Mode (nm)	sd (nm)	PNC (#/mL)	Mean (nm)	sd (nm)	PNC (#/mL)	Ag	Au	Si	
Colloidal	1	79	0.44	78.4	45.2	61	2.71E+10	38	11	1.40E+09	9813 ± 411	-	1.3	8.20
	2	140	0.27	296.2	267.8	119.1	1.78E+11	29	4	2.29E+08	7615 ± 143	-		8.21
	3	202	0.27	139.4	103.6	54.9	3.38E+08	31	8	2.36E+08	7463 ± 95	-		8.28
CicaSilver	1	2376	0.93	356	237	185	7.21+E08	78	12	1.08E+05	1659 ± 391	-	16	-
	2	2030	0.74	216	156	92	2.85E+08	71	23	5.47E+05	1134 ± 102	-		-
	3	4472	0.53	309	206	160	1.44E+08	101	21	3.39E+06	3366 ± 520	-		-
Signo	1	283	0.13	354.2	273.5	131.8	1.51E+11	-		-	-	-	13	-
	2	206	0.09	350.9	395	70.8	2.04E+11	-		-	-	-		-
	3	211	0.10	315.1	194	151	3.40E+11	-		-	-	-		-
Au NP Standards:											Suppliers information PNC (#/mL)	Au (ppm)		
30nm Au		41.5	0.20	36.9	35.2	7.4	4.36E+11	40.4	11	6.10E+09	1.83E+11	50		
60nm Au		63.4	0.12	65.4	65.0	7.4	1.36E+11	67.6	17	2.59E+09	2.29E+10	50		
80nm Au		86.5	0.08	91.0	92.4	14.7	9.78E+10	80.6	23	2.09E+09	9.65E+09	50		

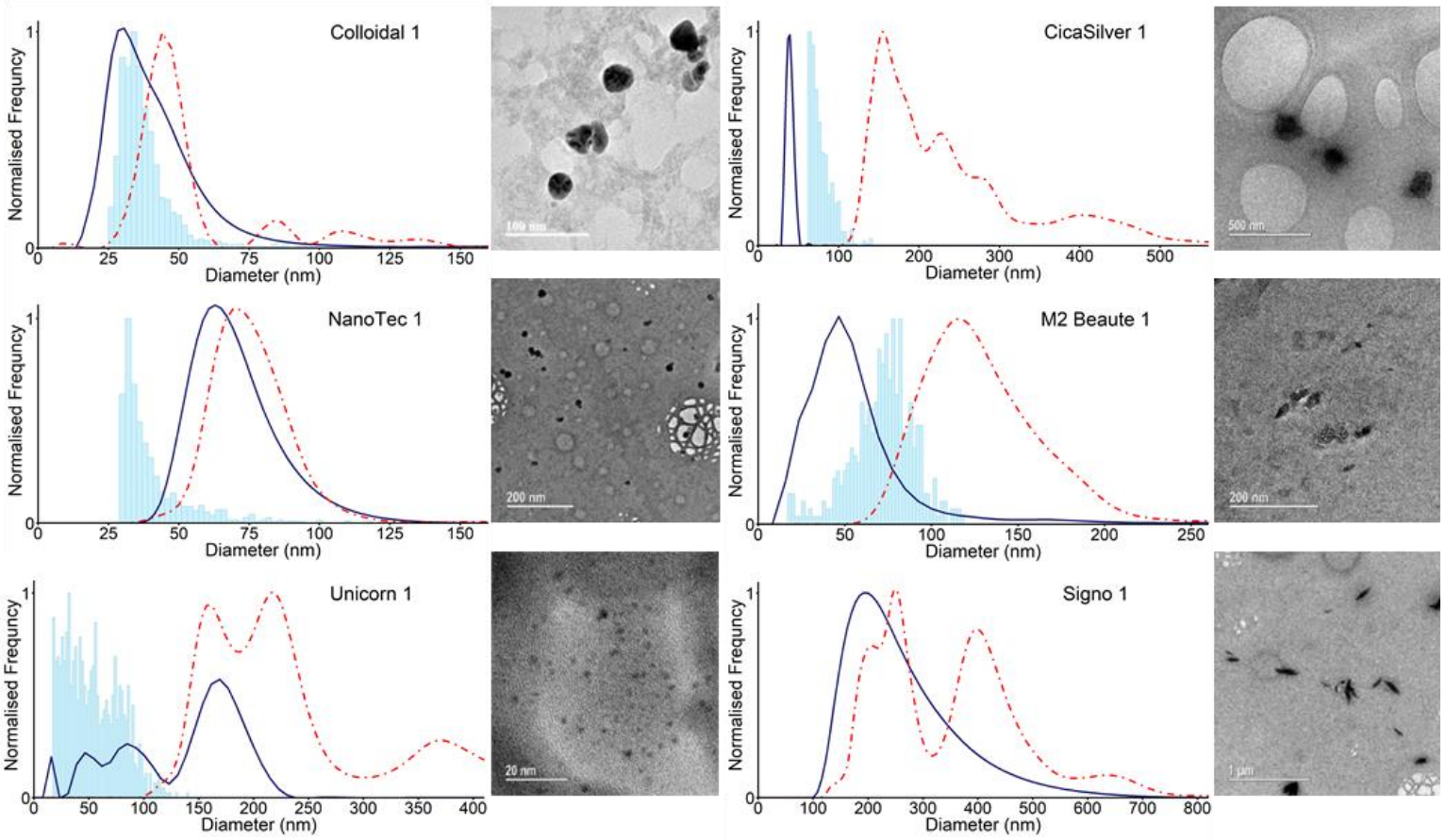
Products generally did contain at least some amount of the stated ingredients

Quantities sometimes did (Livoa Vital Spray 1: **10 ppm** claimed, **9.8 ppm** measured) and

sometimes did not (NanoTec Spray 5: **5 ppm** claimed, **0.6 *ppb*** measured)

match

Product particle size

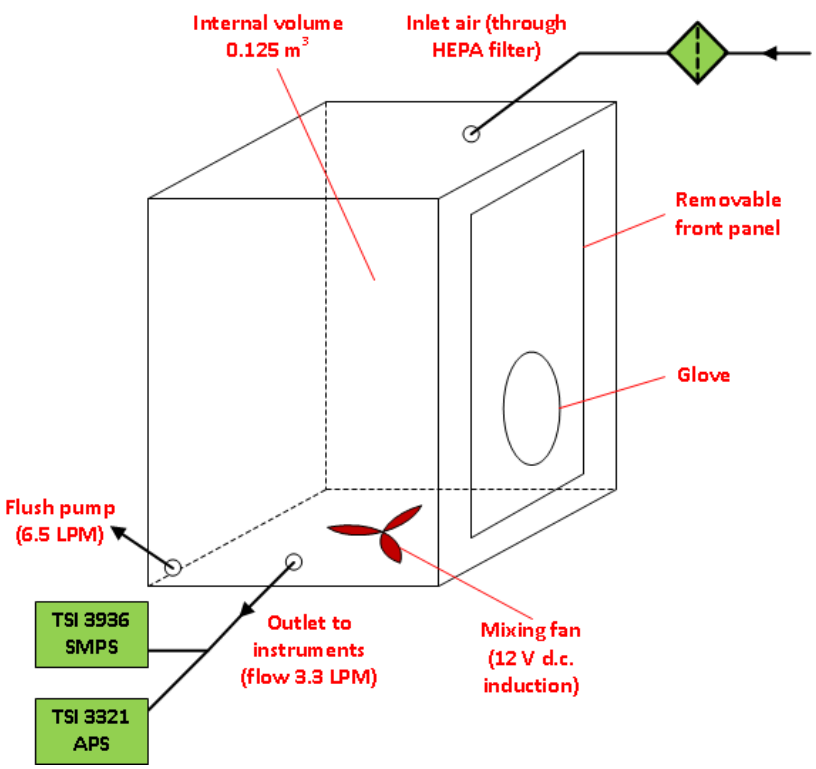


Full line – DLS (Malvern, Zetasizer)

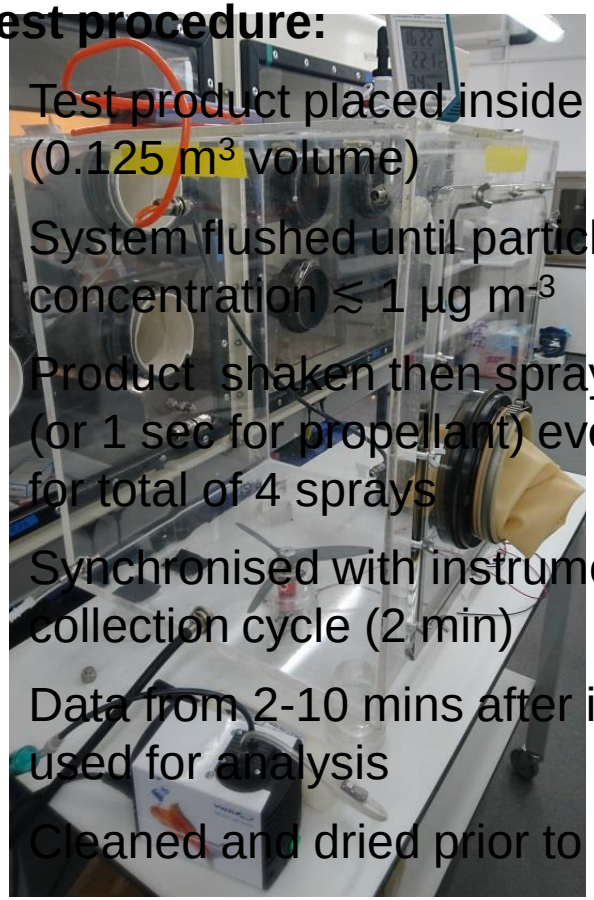
Dashed line – NTA (Malvern, Nanosight)

Histogram – single particle ICP-MS

Test chamber and procedure



Test procedure:

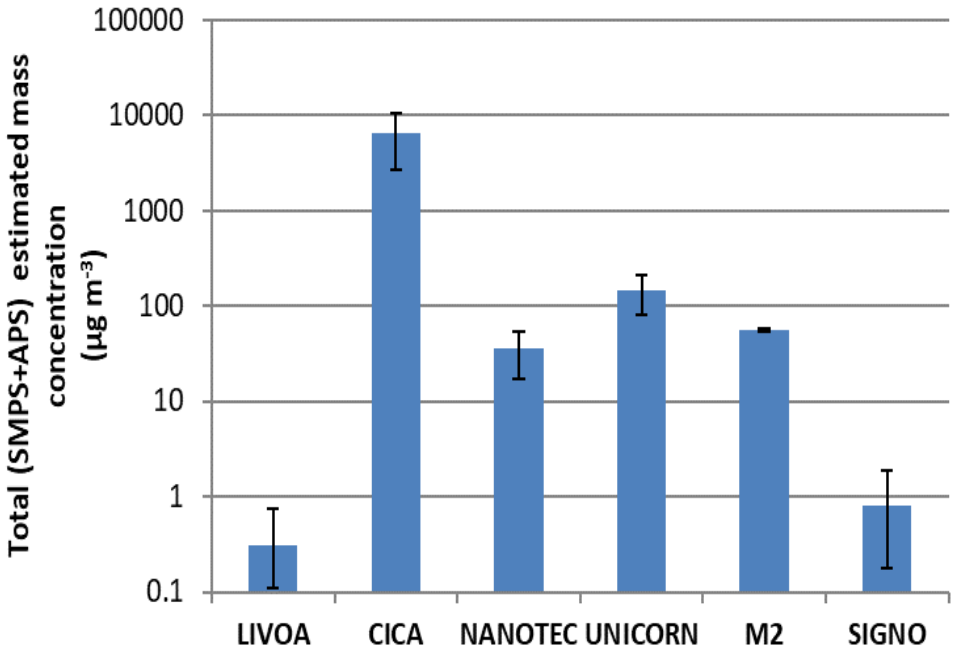


- Test product placed inside glovebox (0.125 m^3 volume)
- System flushed until particle mass concentration $\lesssim 1\ \mu g\ m^{-3}$
- Product shaken then sprayed once (or 1 sec for propellant) every 30 sec for total of 4 sprays
- Synchronised with instrument data collection cycle (2 min)
- Data from 2-10 mins after initial spray used for analysis
- Cleaned and dried prior to next test
- 3 repeat tests (for most products)

Aerosol instrumentation

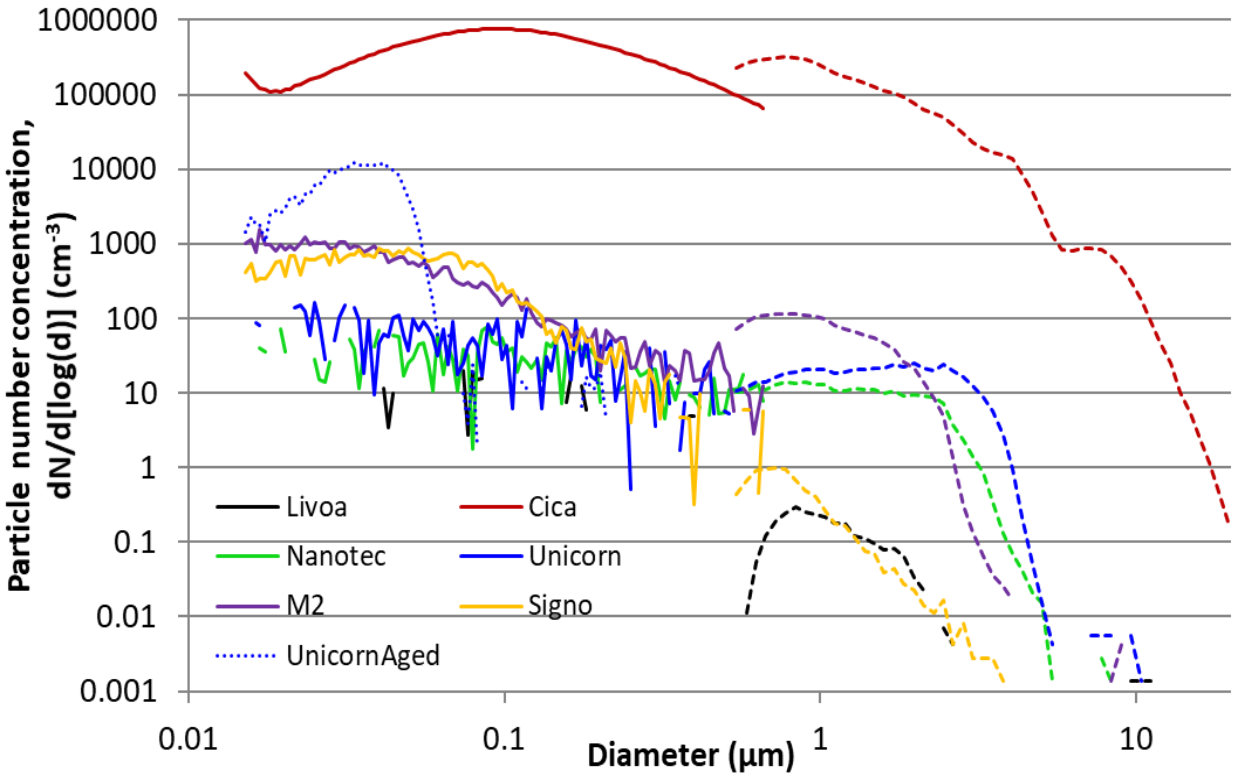
- Aerodynamic Particle Sizer (APS, TSI 3321) – Particle **aerodynamic diameter 0.5 – 20 µm**
- Scanning Mobility Particle Sizer (SMPS, TSI 3936) – Particle **mobility diameter 0.015 – 0.6 µm**

Aerosol mass concentration



- Mass estimated over whole size range measured (10 nm to 20 µm) by combining data from SMPS and APS (assuming unit particle density)
- Wide variation (over 4 orders of magnitude) in estimated mass concentration

Aerosol size distribution



- Propellant spray produces both highest mass and number concentrations
- 3 (?) products produce particles in ‘nano’ size range (< 100 nm)

Implications for exposure

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- Small chamber, so concentrations higher than expected in ‘real’ product use
- However, an advantage is that (after correcting for wall loss and aerosol coagulation) can estimate an ‘emission factor’ for each product (future work)
- Amount and location of respiratory tract deposition determined by particle size
- Therefore linking claims/presence of NP within a product as a whole to potential risk needs assessment of their presence in particles of different sizes:
  - i) Is the material claimed by the manufacturer actually in the product, at the stated quantity, and in NP form? e.g. Spray 1 – **yes**: 10 ppm Ag; TEM
  - ii) In which sizes of particles are any NPs found and in what proportion? e.g. Spray 1 – very few particles; yet to assess NP content as function of size
- **Need for characterisation of emissions on a product-by-product basis**

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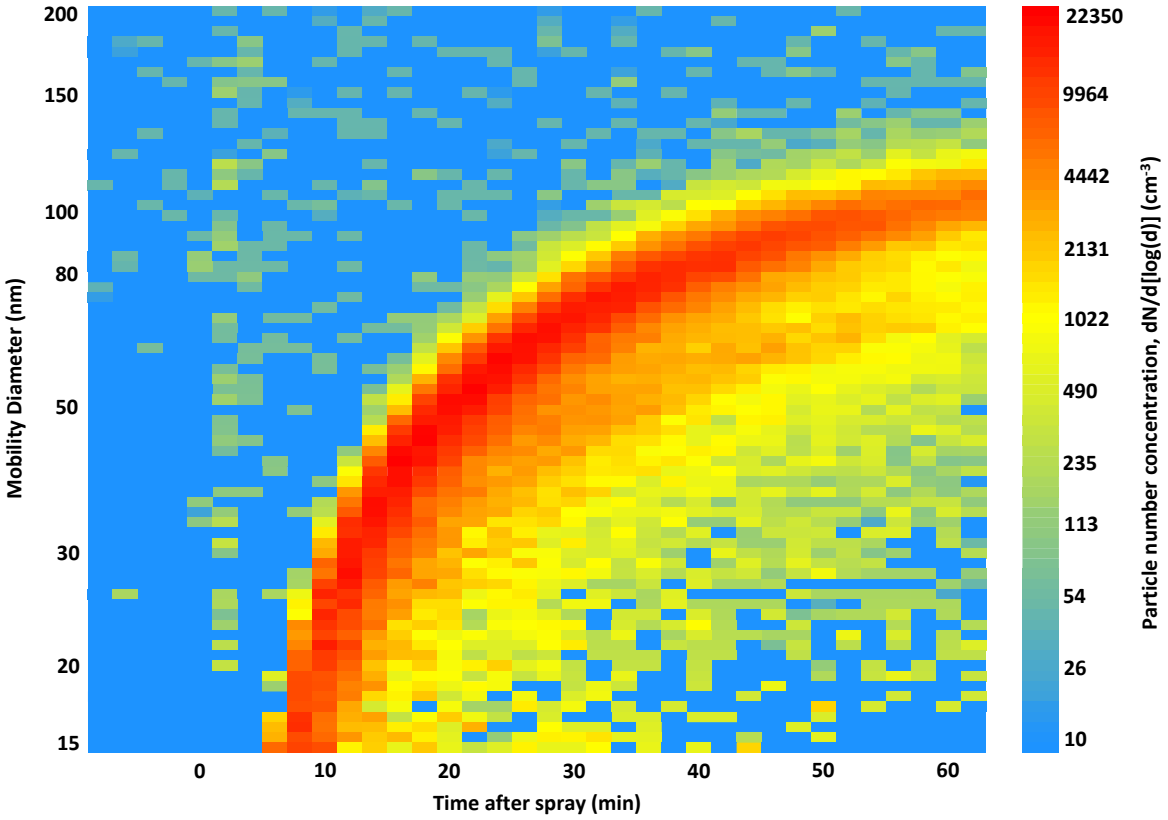
New particle ‘nucleation’



- Spray 2 did not initially produce nanoparticles, but high concentrations were observed after 5-10 minutes

Aerosol mass distribution