

Nanoparticles in waste incineration

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In the past, waste incineration processes had been identified as an important source of ultrafine air pollutants resulting in elaborated treatment systems for exhaust air. Today, these systems are able to remove around 99.99% of all ultrafine particles as measured in a Swiss waste incineration plant [1]. However, the fate of ultrafine particles caught in the filters has received little attention until now. Studies investigating the size distribution of fly ash from waste incineration plants so far focused on micro-sized particles [2]. Based on the recent developments in nanotechnology and the resulting increase in the application of engineered nanomaterials (ENM), it can be expected that not only combustion generated nanoparticles are found in fly ash but also ENM. This study aimed at identifying the nano-fraction (weight and particle number) of fly ash from waste, wood and sludge incineration in Switzerland. In addition, first measurements were made to analyze the size distribution of fly ash before and after acid washing. The results obtained were compared to the modeled input of ENM into waste and sludge incineration to estimate their importance for waste streams in Switzerland.

Method

In the measuring part, samples from different waste, wood and sludge incineration plants were pre-fractionated at 2 μm . The mass fractions were determined by weighing and a Laser Diffraction Particle Size Analyzer was used to determine the particle size distribution (mass and particle number) before and after pre-fractionation. A more detailed analysis of the size distribution for the below-2- μm fraction was performed using a powder disperser for powder distribution and measurements for size distribution by scanning mobility particle sizer (SMPS) for the size fraction between 15 and 6600 nm and by an aerodynamic particle sizer (APS) for the size fraction from 0.5 to 20 μm . The data from both methods were fitted to receive an overall size distribution curve. In the modeling part, a model was generated which allowed a quantitative prediction of the expected ENM flows to waste incineration and landfills. The input flows were taken from Gottschalk et al. The model- and substance-specific coefficients were extrapolated based on the limited literature available.

Results

Figure 1 shows an example for a merged curve from SMPS and APS measurements (fly ash sample after acid washing). Based on the respective curves the mass fraction and number percentage of the fly ash particles <100 nm were calculated (Table 1). In average about 0.00079wt% of the fly ash samples are nano-sized.

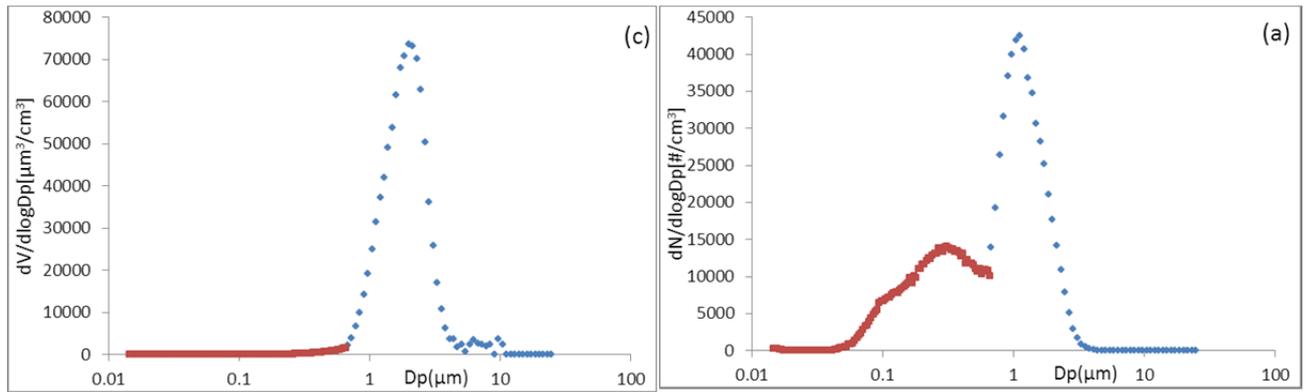


Figure 1: Fitted spectrum of the APS and SMPS results according to merging data routine. The final optimum fitting results are presented for (a) number and (c) volume for the fly ash sample WaSA

Table 1: Summary of mass and number percentage of all the fly ashes, based on the mass percentage calculated after the fractionation (Tab. 5) and the mass and number percentage results obtained from the merged SMPS and APS spectrums. Data rounded to two significant digits (max. 3 decimals).

Sample Number	Input material	Mass % fraction <2 μm	Mass% <100 nm of fraction <2 μm	Mass % <100 nm of full sample	Number % <100 nm of full sample
WaS1	waste, sludge	11	0.011	1.2E-03	1.0
WaS2	waste, sludge	8.5	0.005	0.42E-03	14
WaSA	Ashes of WaS1 & WaS2 after acid washing	19	0.002	0.35E-03	5.2
Wa1	waste	11	0.001	0.11E-03	3.7
Wa2	waste	25	0.004	1.1E-03	9.2
Wa3	waste	9.7	0.008	0.74E-03	18
Wo	wood	56	0.007	3.9E-03	16
WoS	wood&sludge	0.96	0.0004	3.1E-06	2.2
S	sludge	9.9	0.002	0.15E-03	8.9

Despite several differences between the models for nano-TiO₂, nano-ZnO and nano-Ag (e.g. partial dissolution of nano-ZnO in acid washing), it is shown that the major ENO-flow goes from the WIP to the landfill as bottom ash (Fig. 2 & 3). All other flows within the system boundary are about one magnitude smaller than the bottom ash flow. A different ENO distribution was found for CNT. CNT as carbon-based material is burned to a large extent (94%) so that only insignificant amounts remain in the system.

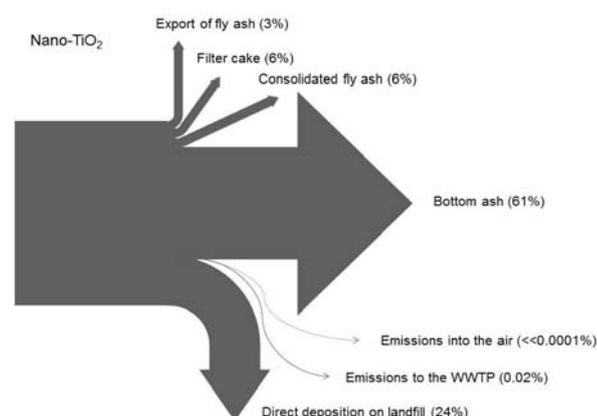
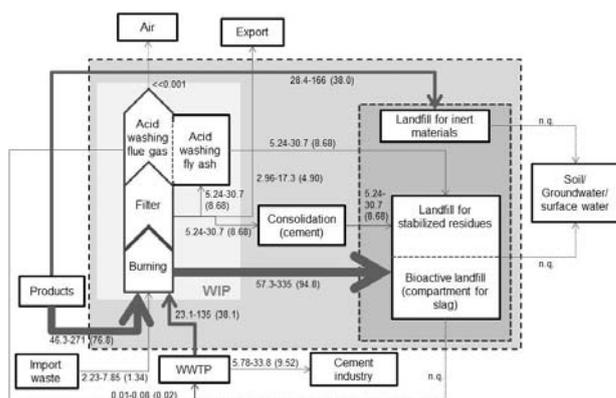


Fig. 2: Nano-TiO₂ flows to the landfills (15-85 percentile (mode value)) in t/a. The strength of the arrow is proportional to the respective ENO flow (mode-value).

Fig. 3: Waste disposal as input-output system for nano-TiO₂. Total input: 155 t/a

Discussion

In Switzerland about 80'000 t of fly ash are produced per year [3]. According to the measurements in this study, a fraction of about 0.00079wt% of the fly ash is <math><100\text{ nm}</math>, which results in 704 kg per year. In contrast, the modeling calculates an amount of 22 t/a TiO₂-ENO, 0.8 t/a ZnO-ENO, 160 kg/a Ag-ENO and 4.9 kg/a of CNT in fly ash, which is significantly higher than the measured total nano-fraction in the fly ash. This discrepancy can be explained by the measurement method and the morphology of nano-objects [4]. Ultrafine particles such as ENO tend to agglomerate very quickly and form stable agglomerates of several hundred nanometers [5, 6]. This proclivity has been confirmed by TEM-analyses of ENO after incineration [7]. Since the measurements in this study were based on size fractionation without prior breaking of agglomerates, agglomerates were measured as large particles. Hence, the number and mass of NP in our measurements is probably significantly underestimated whereas the modeling calculates the mass of primary ENO, which might in fact be existent as agglomerates. TEM-analyses of the fly ash samples taken are needed to complement the results of the measurements.

References

1. Burtcher, H.; Zürcher, M.; Kasper, A.; Brunner, M., Efficiency of flue gas cleaning in waste incineration for submicron particles. In *Proc. Int. ETH Conf. on Nanoparticle Measurement*, Mayer, A., Ed. BUWAL: 2002; Vol. 52.
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Nanoparticles in waste incineration



Conference on Combustion Generated Nanomaterials, June 25th 2012

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Background:

- Engineered nanoparticles (NP) end up in landfills to a large extent after waste incineration.
- In combustion additional NP are produced which also end up in landfills.

Hypotheses:

Combustion generated NP contribute more to the overall NP fraction in fly ash than engineered NP.

Project plan:

- Total nanosized fraction of fly ash (Measured)
- Input of engineered nanoparticles into landfills (Modeled)

Literature review

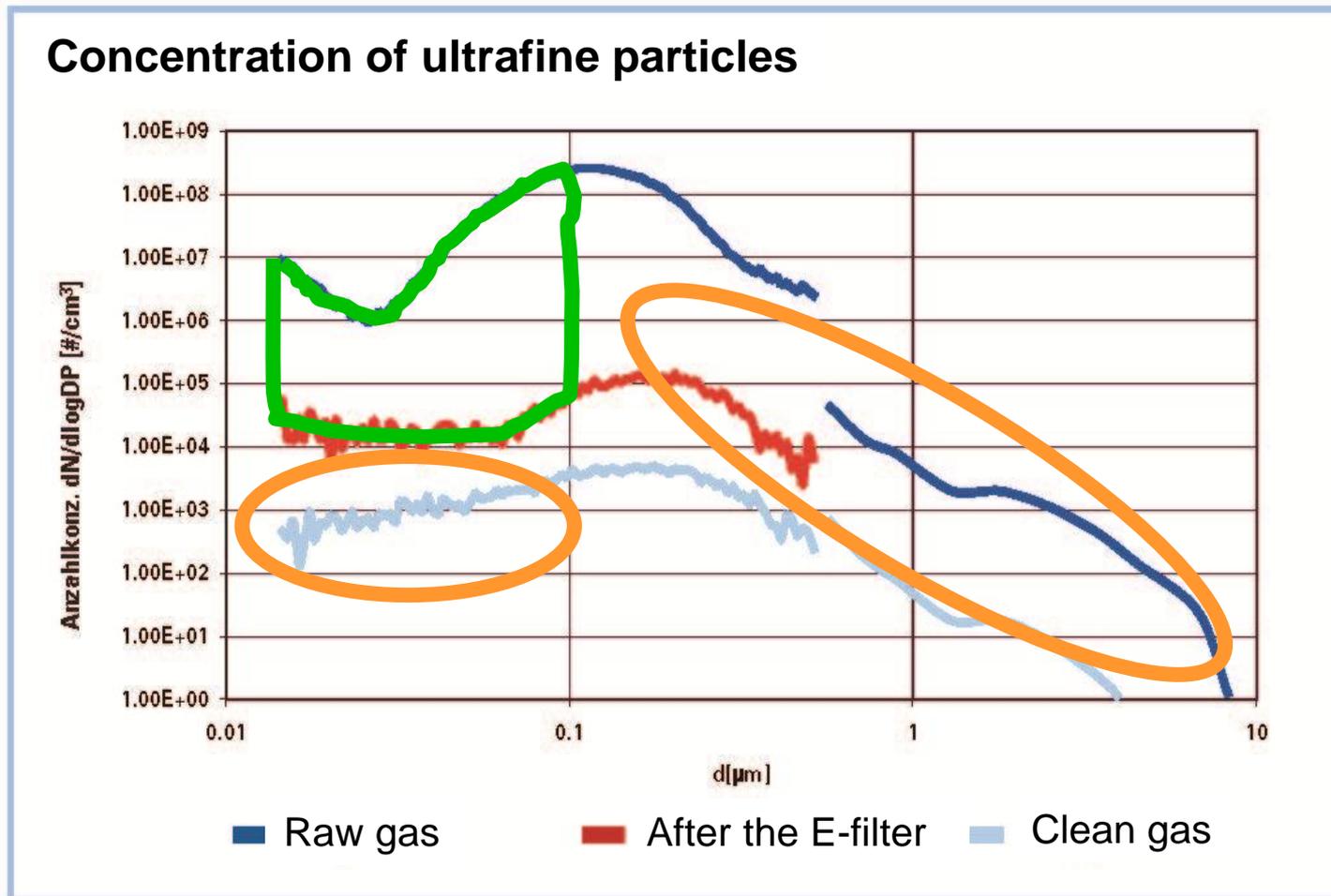


Abb. 1

Source: Burtscher, H.; Zürcher, M.; Kasper, A.; Brunner, M., Efficiency of flue gas cleaning in waste incineration for submicron particles. In *Proc. Int. ETH Conf. on Nanoparticle Measurement*, Mayer, A., Ed. BUWAL: 2002; Vol. 52.

Samples:

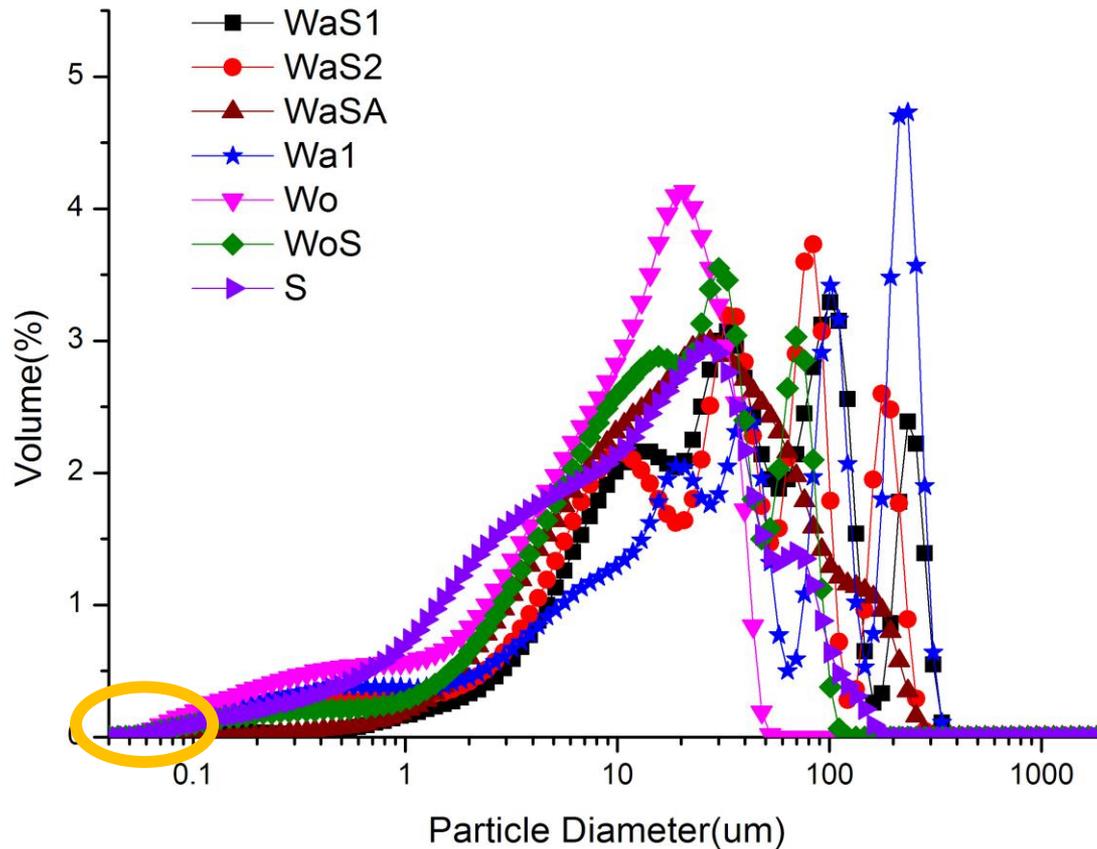
- Waste incineration (Wa1, Wa2, Wa3)
 - Waste and sludge incineration (WaS1, WaS2)
 - Sludge incineration (S)
 - Sludge and wood incineration (SWo)
 - Wood incineration (Wo)
-
- Mixed sample of WaS1 and WaS2 after acid washing of fly ash

Measurements:

- LS (Laser Diffraction Particle Size Analyser: before and after prefractionation at $2\mu\text{m}$)
- SMPS (Scanning Mobility Particle Sizer: only aerolized fraction $< 2\mu\text{m}$)
- APS (Aerodynamic Particle Sizer: only aerolized fraction $< 2\mu\text{m}$)

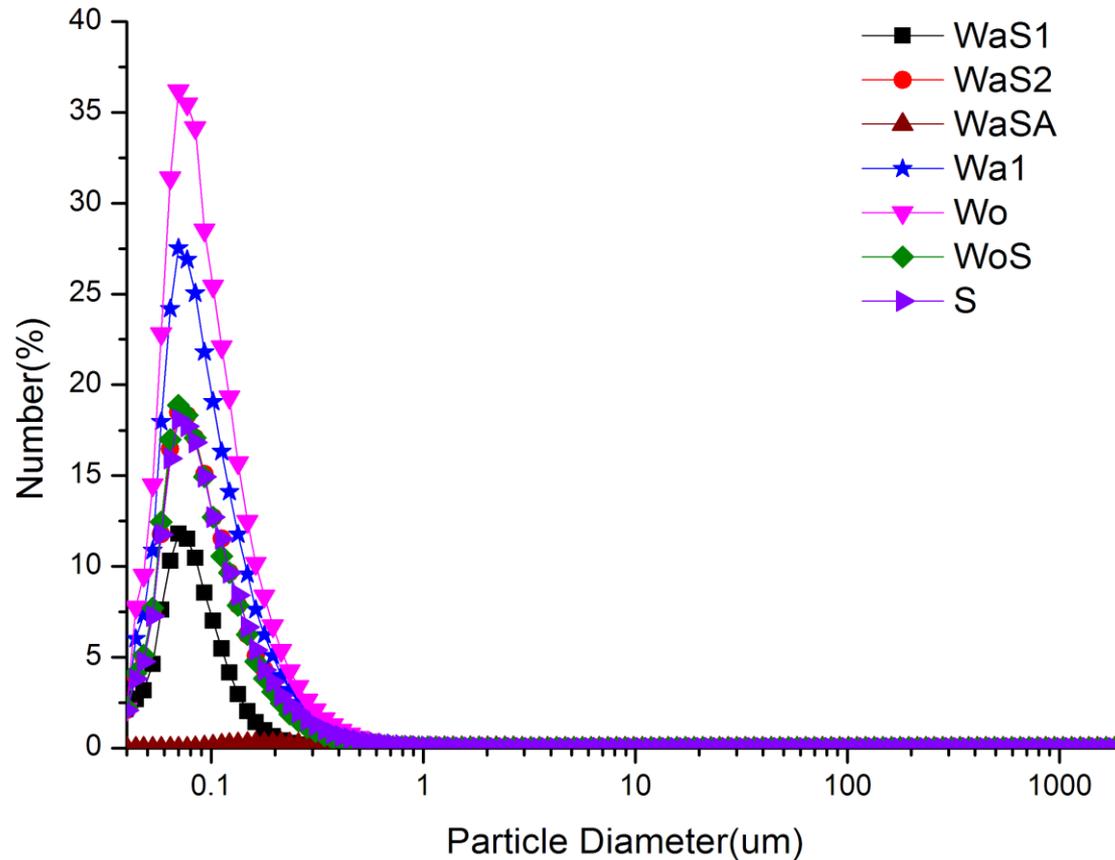
Size distribution (volume)

Data from Laser Diffraction Particle Size Analyser

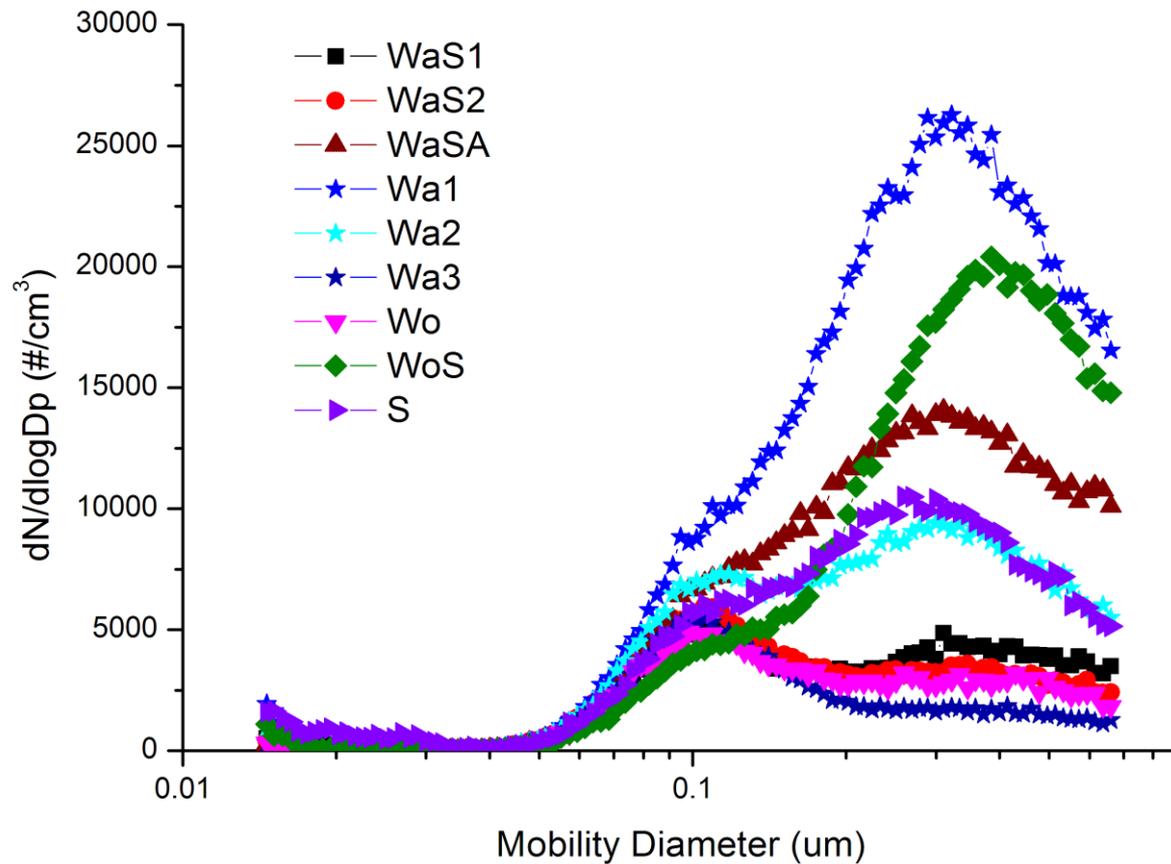


Size distribution (number)

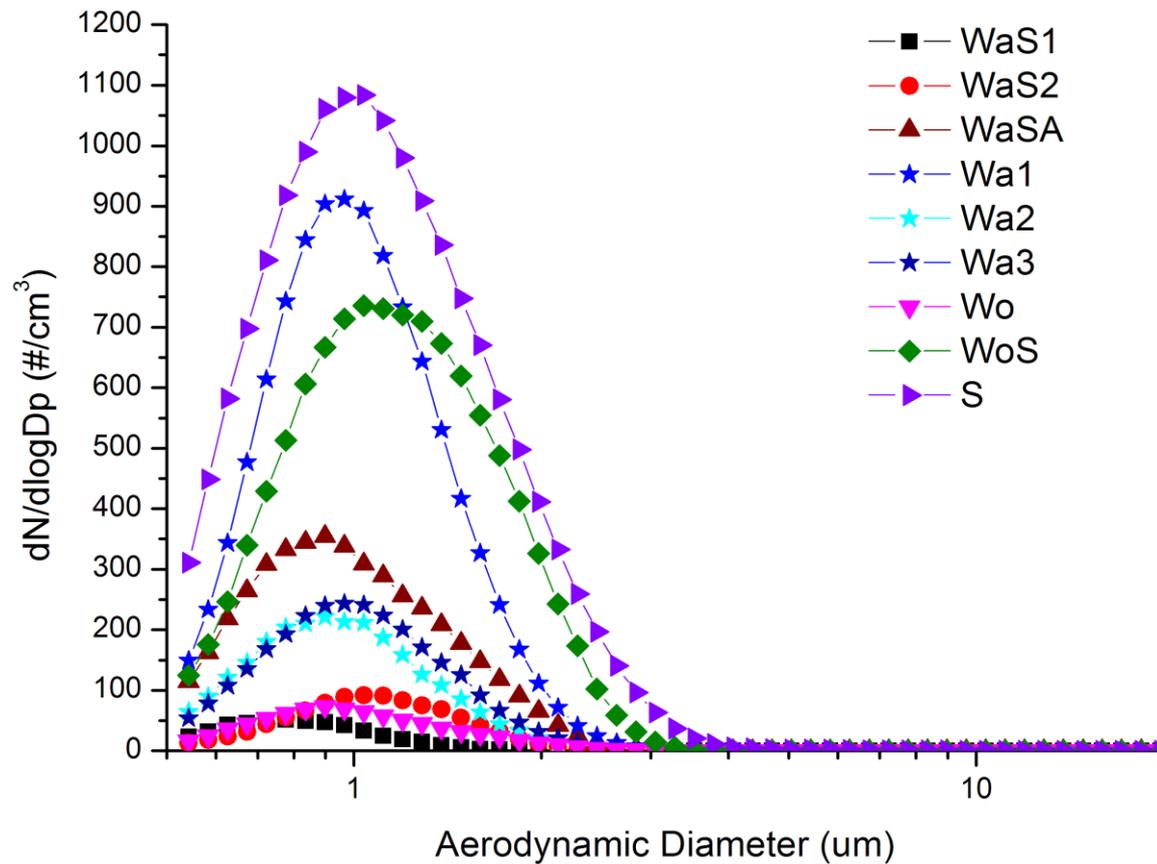
Data from Laser Diffraction Particle Size Analyser



Size distribution (number) SMPS

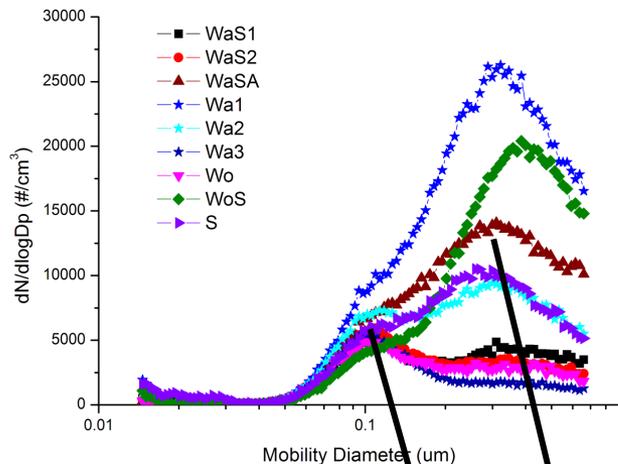


Size distribution (number) APS

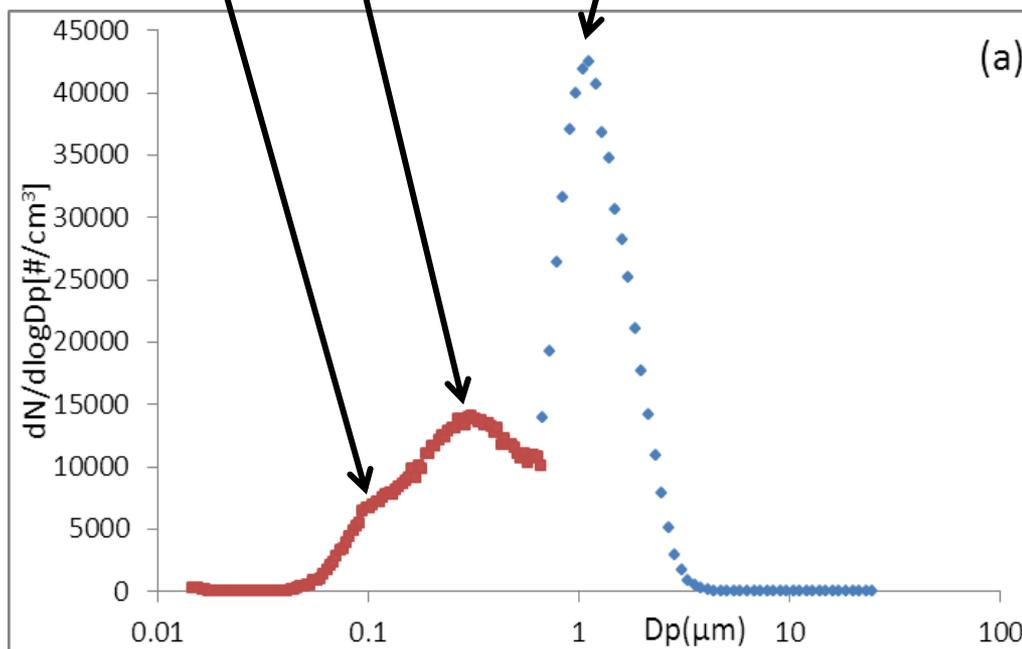
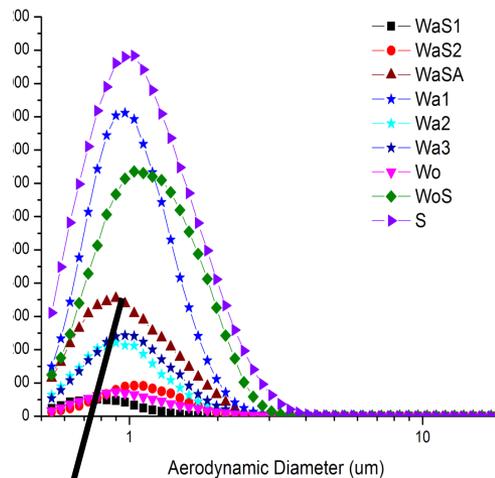


Size distribution (number)

SMPS



APS



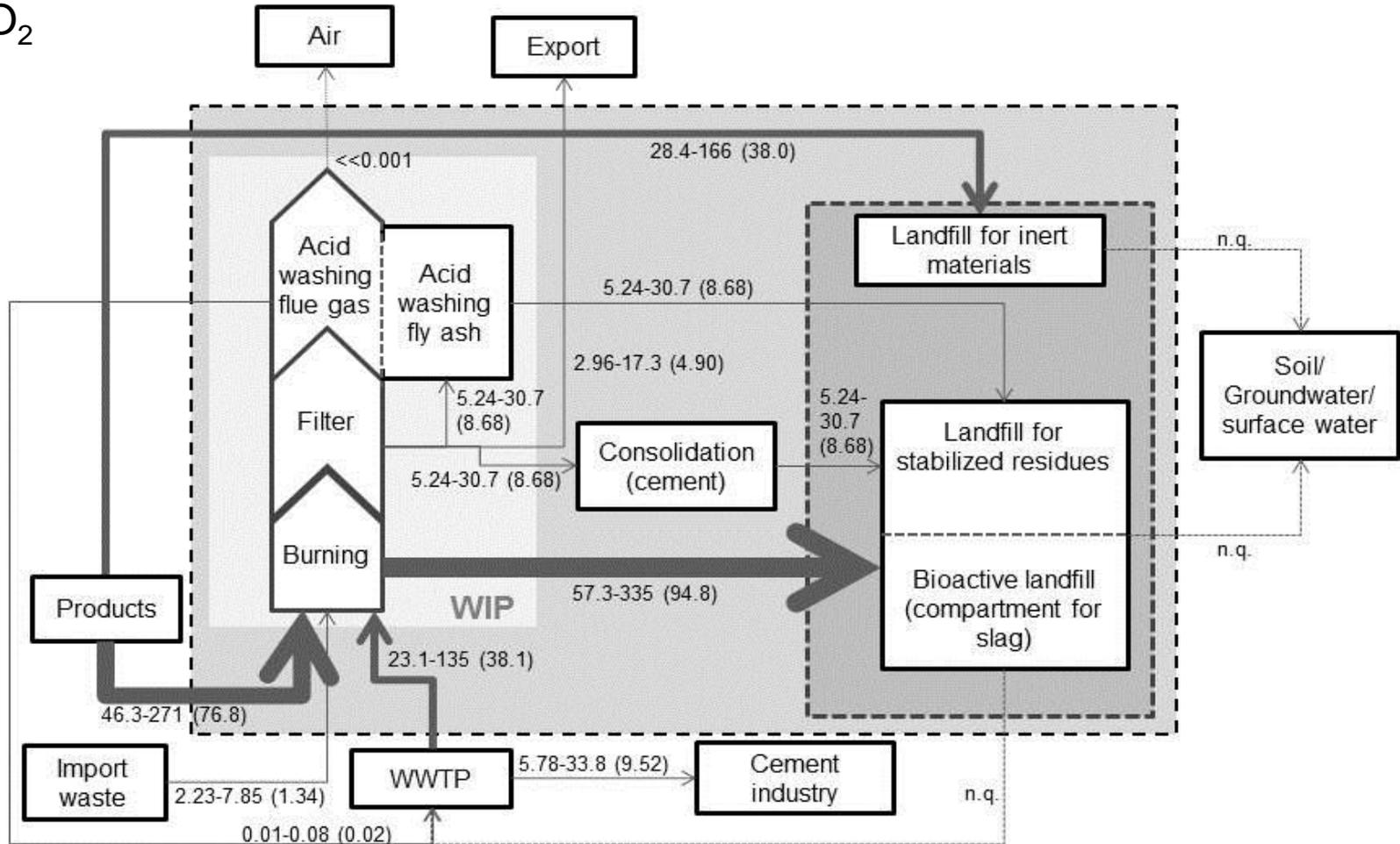
Sample WaSA

Nano-fraction in fly ash

Sample Name	Input material	Mass % <100 nm of full sample	Number % <100 nm of full sample
WaS1	waste, sludge	1.2E-03	1.0
WaS2	waste, sludge	0.42E-03	14
WaSA	Ashes of WaS1 & WaS2 after acid washing	0.35E-03	5.2
Wa1	waste	0.11E-03	3.7
Wa2	waste	1.1E-03	9.2
Wa3	waste	0.74E-03	18
Wo	wood	3.9E-03	16
WoS	wood&sludge	3.1E-06	2.2
S	sludge	0.15E-03	8.9

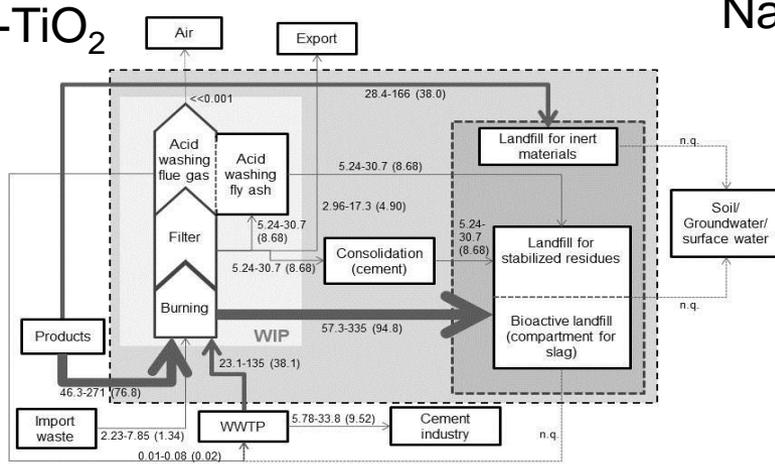
Quantified flows

Nano-TiO₂

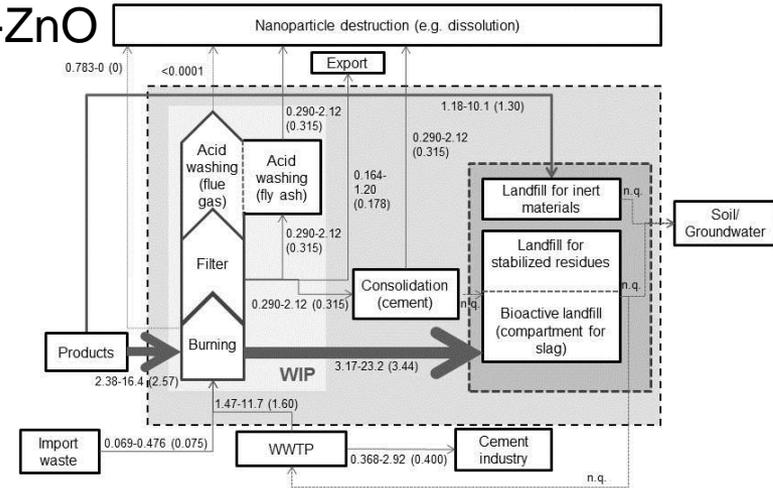


Quantified flows

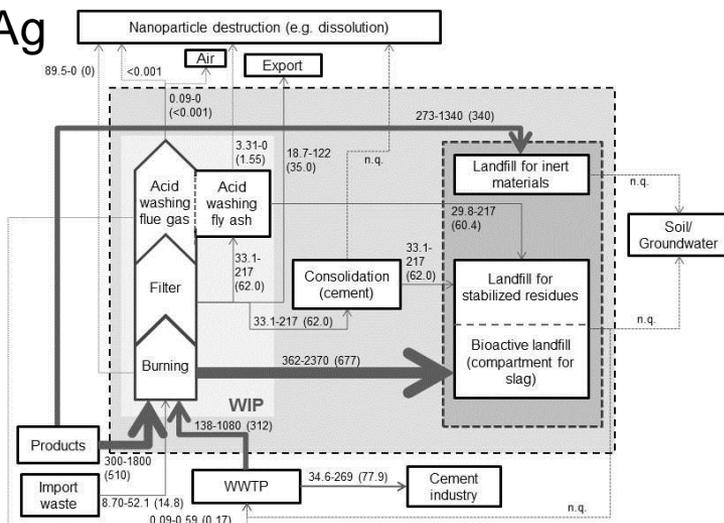
Nano-TiO₂



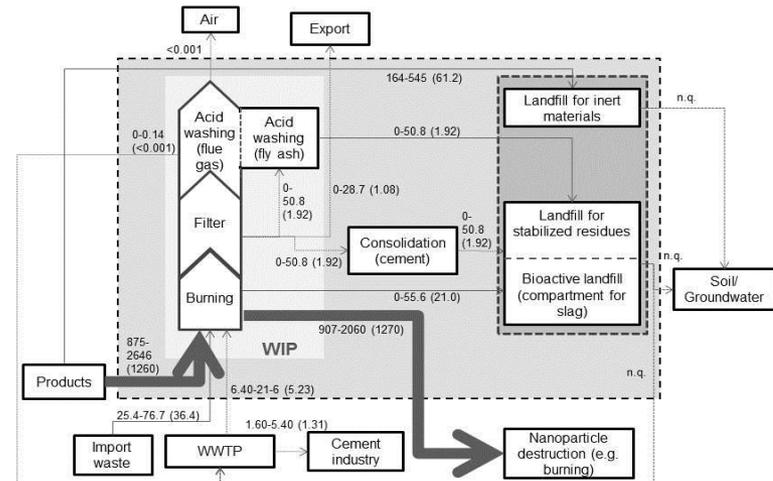
Nano-ZnO



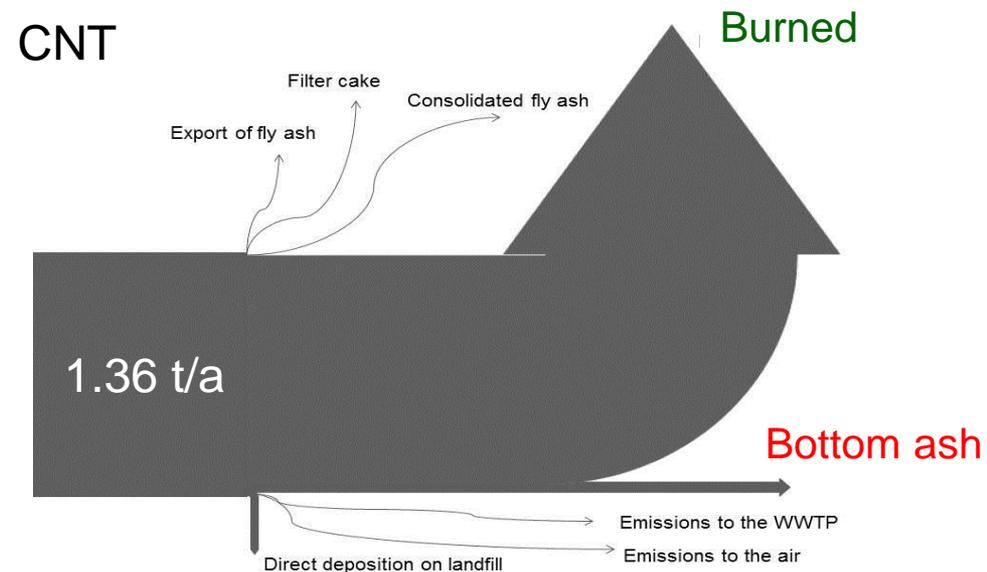
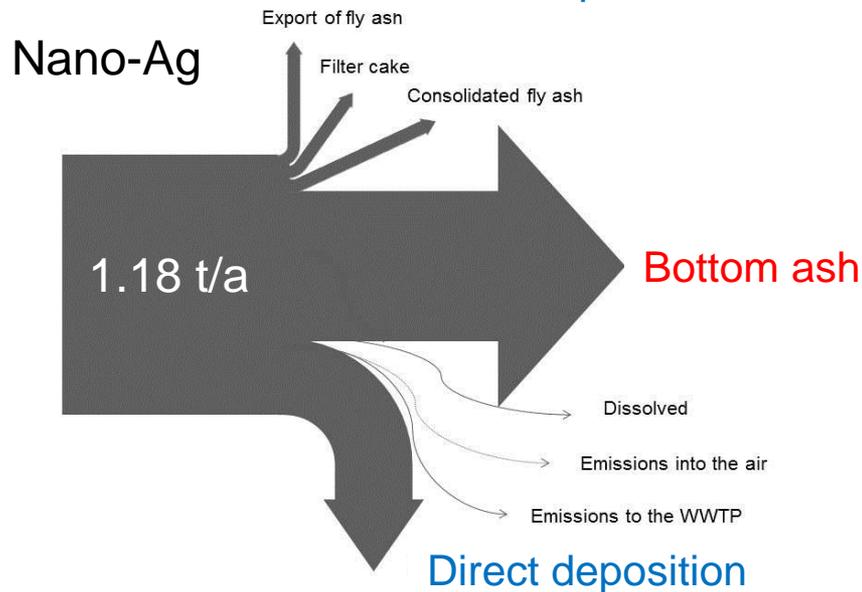
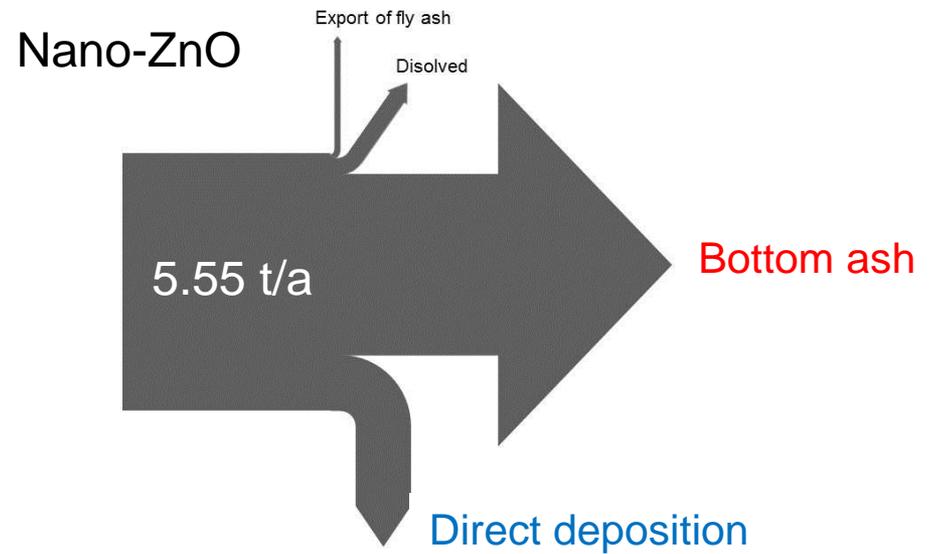
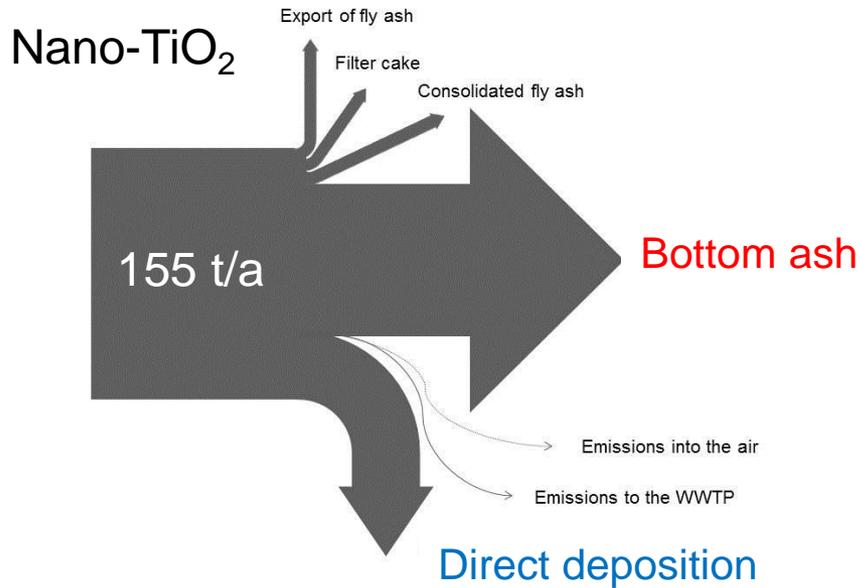
Nano-Ag



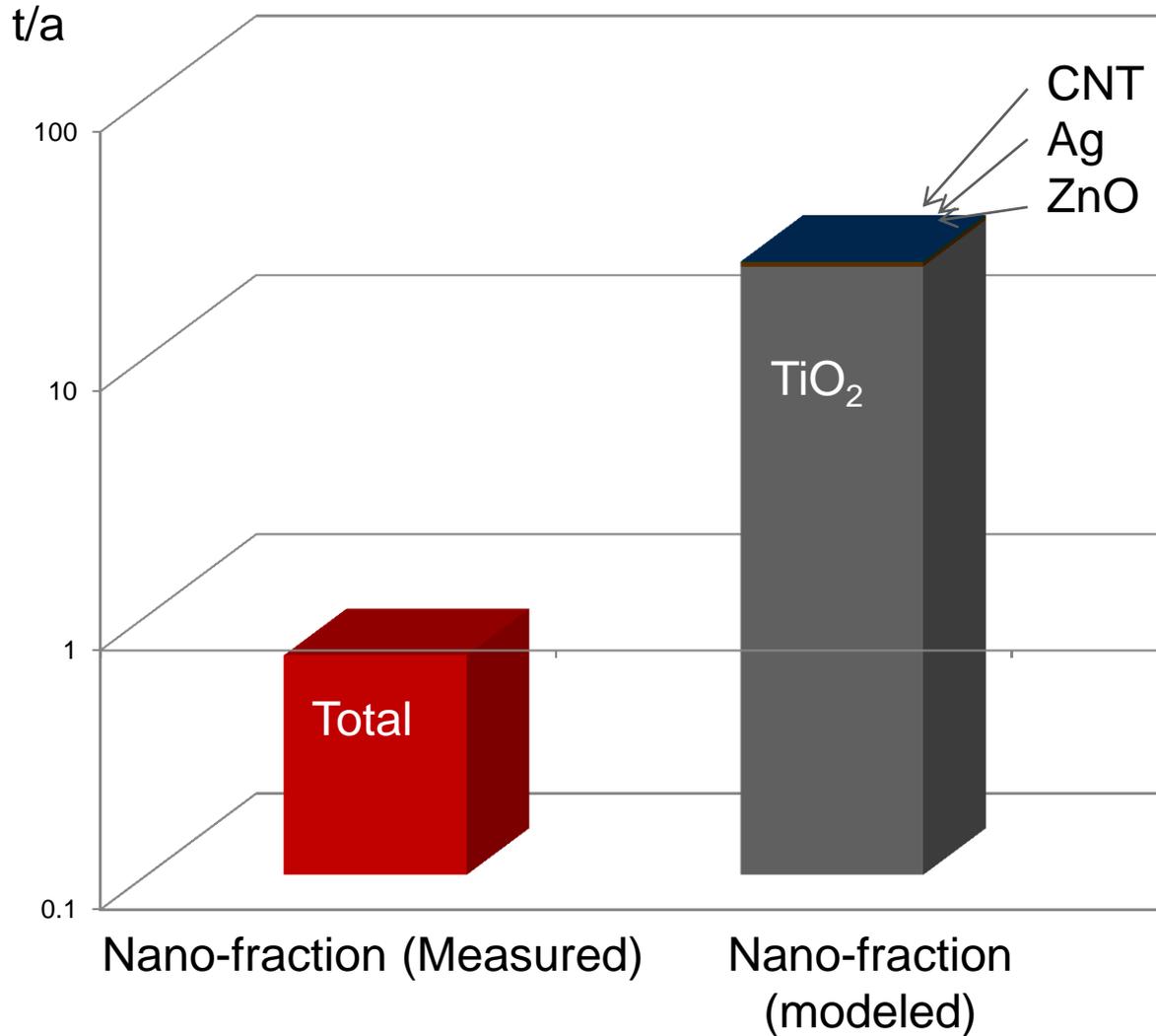
CNT



Input-Output Graphs



Comparison of measured and modeled data



Conclusion

Measurement:

- Mass-fraction of «loose» NP in fly ash is insignificant: 700 kg per year (0.0008% of 80'000 t of fly ash)

Modeling:

- Bottom ash is the predominant flow of engineered NP into landfills. Around 23 t/a of engineered NP are expected in fly ash in Switzerland.

Synthesis:

- NP in fly ash are present as agglomerates or attached to microsized particles.
- TEM/SEM-analyses are needed to complement the results.

Thank you for your attention!



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