Particle emissions from shredding, sanding, and cutting of polypropylene containing carbon nanotubes and organic prigment nanomaterial

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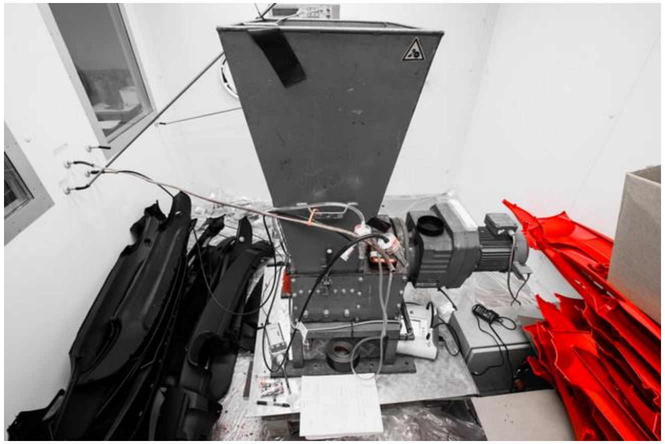
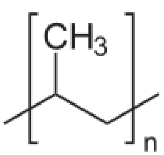
Outline

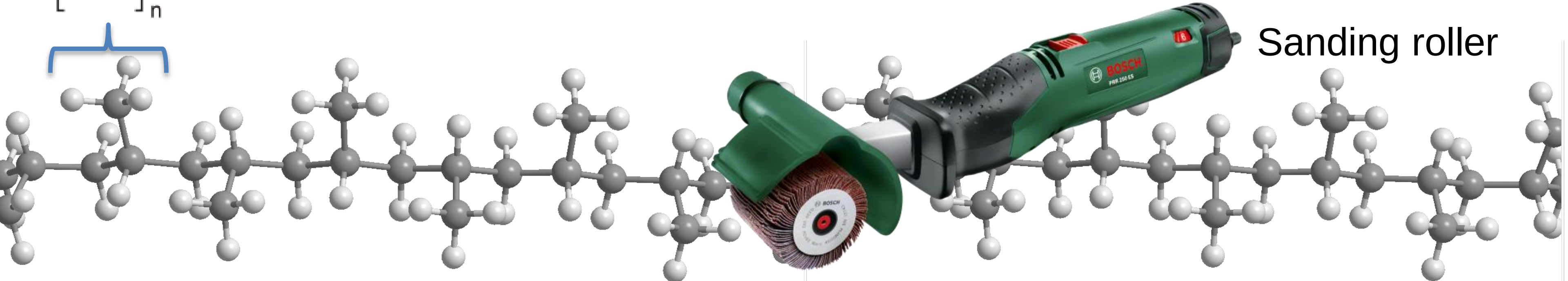
- Materials: polypropylene (PP) car bumpers
  - PP + 0.2 wt.% Organic Pigment
  - PP + 2.5 wt.% MWCNT
- PP particle emissions during
  - Cutting
  - Shredding
  - Sanding
- Exposure modelings

Jigsaw



Down-scaled industrial shredder

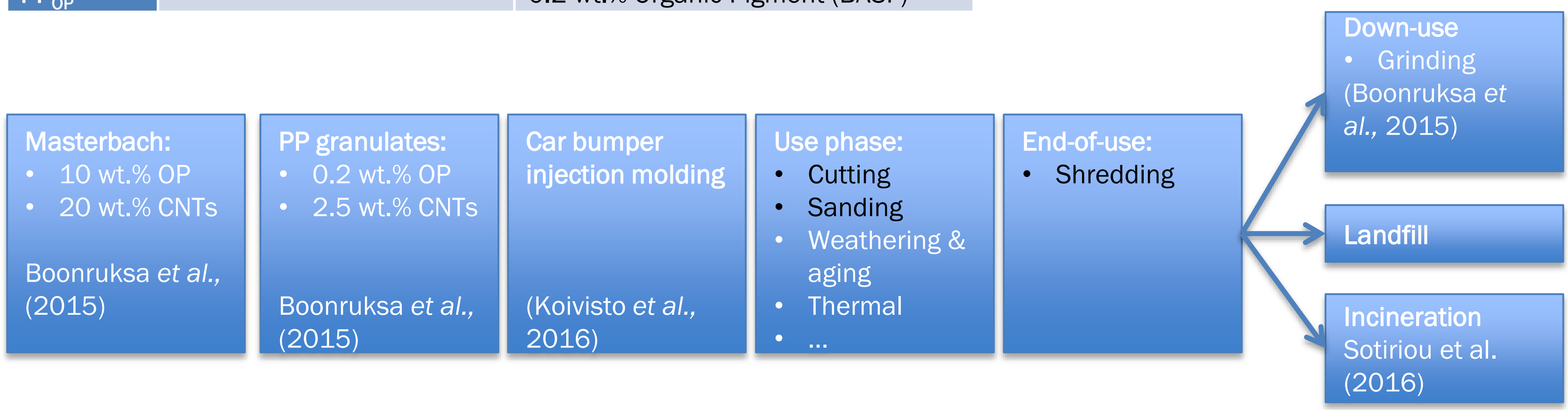




Sanding roller

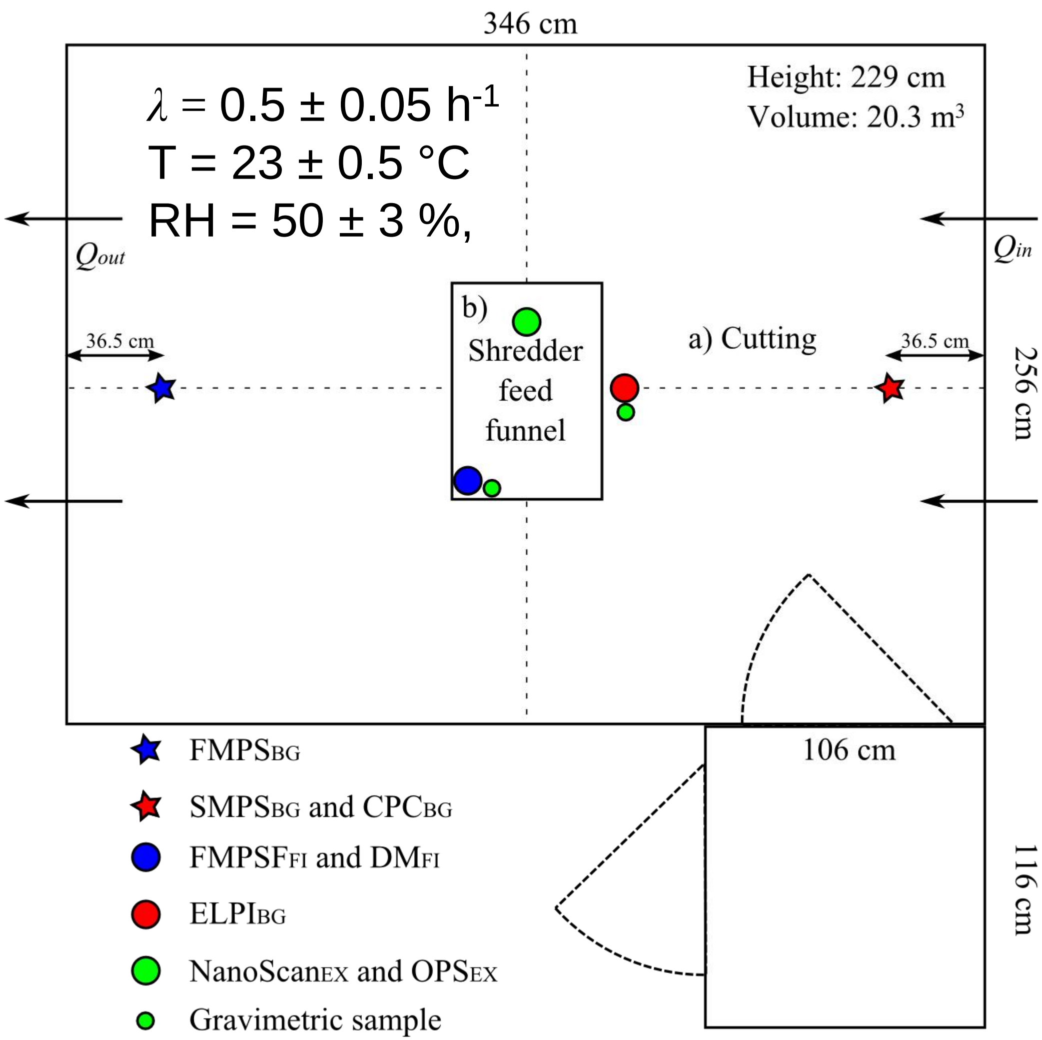
PP materials and life-cycle

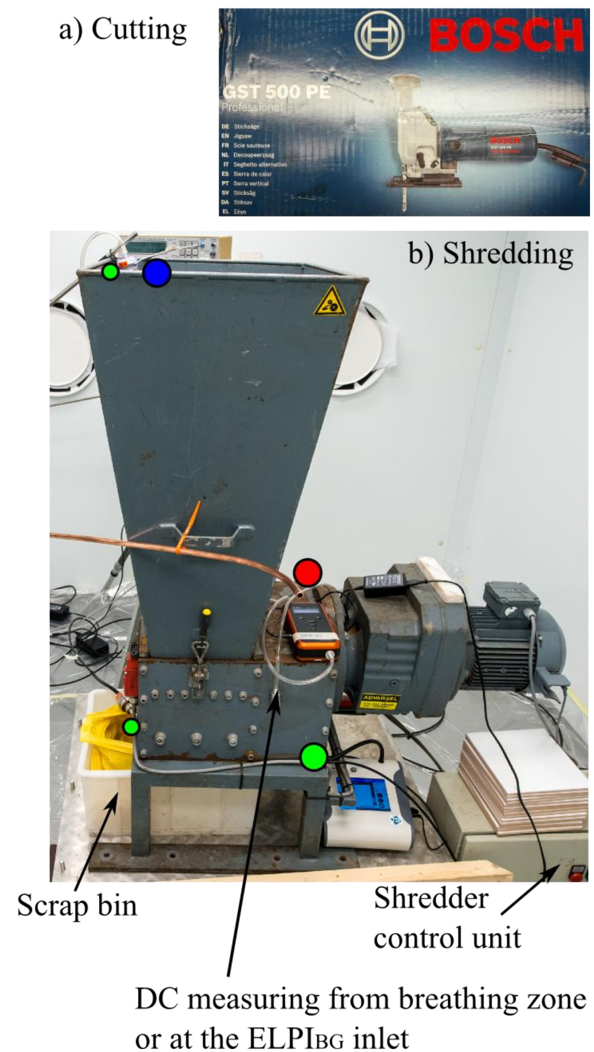
Material	Matrix	Nanomaterial
PP_0	Polypropylene (KSR4525, Borealis AG, Vienna, Austria)	-
PP_{CNT}		2.5 wt.% MWCNT (Nanocyl, NC7000)
PP_{OP}		0.2 wt.% Organic Pigment (BASF)



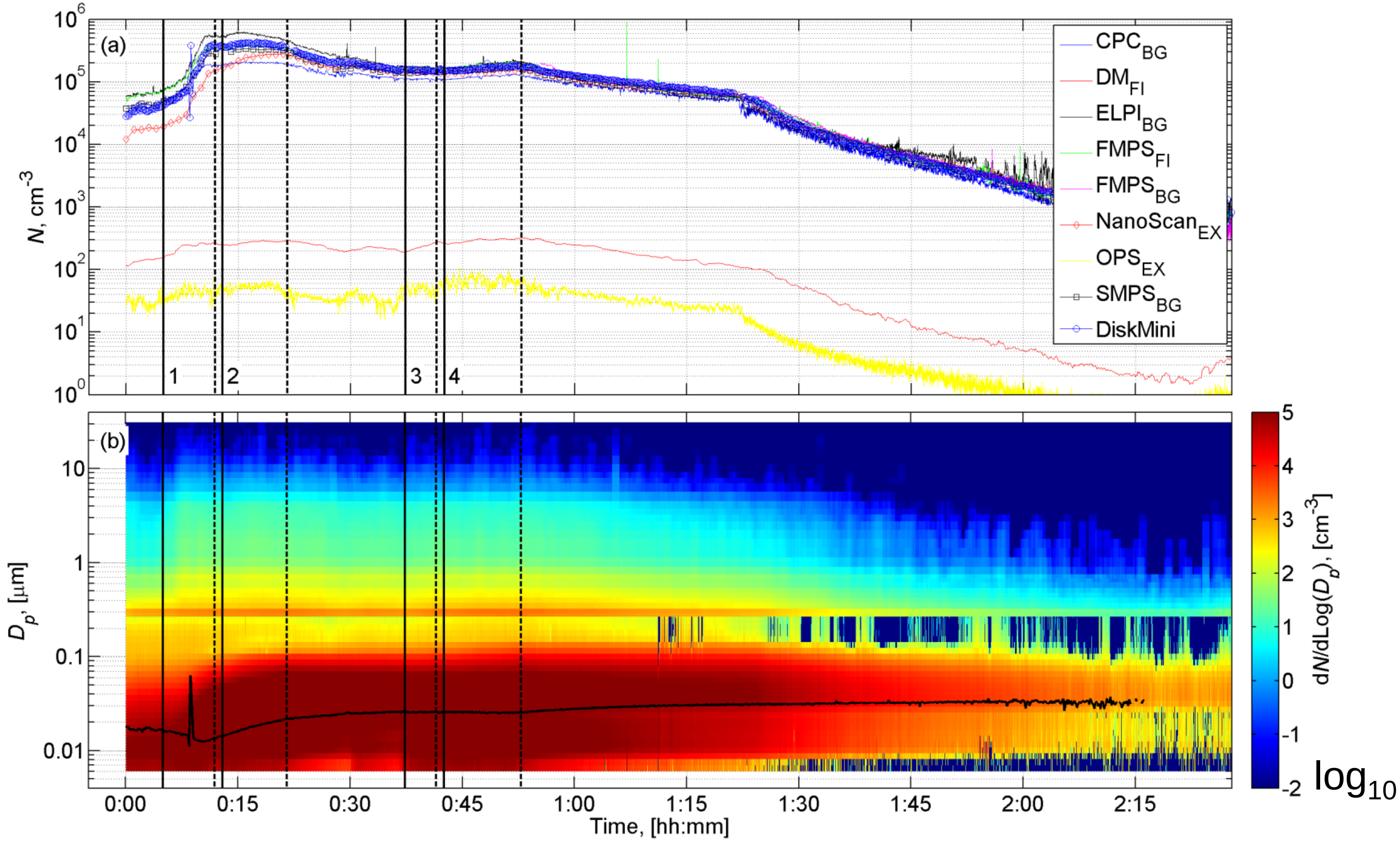
- Masterbach = filler mixed and homogenized in low-density polyethylene
- Extrusion with twin screw extruder into the final PP concentration, cooled, cut to granulates

Cutting and shredding studies



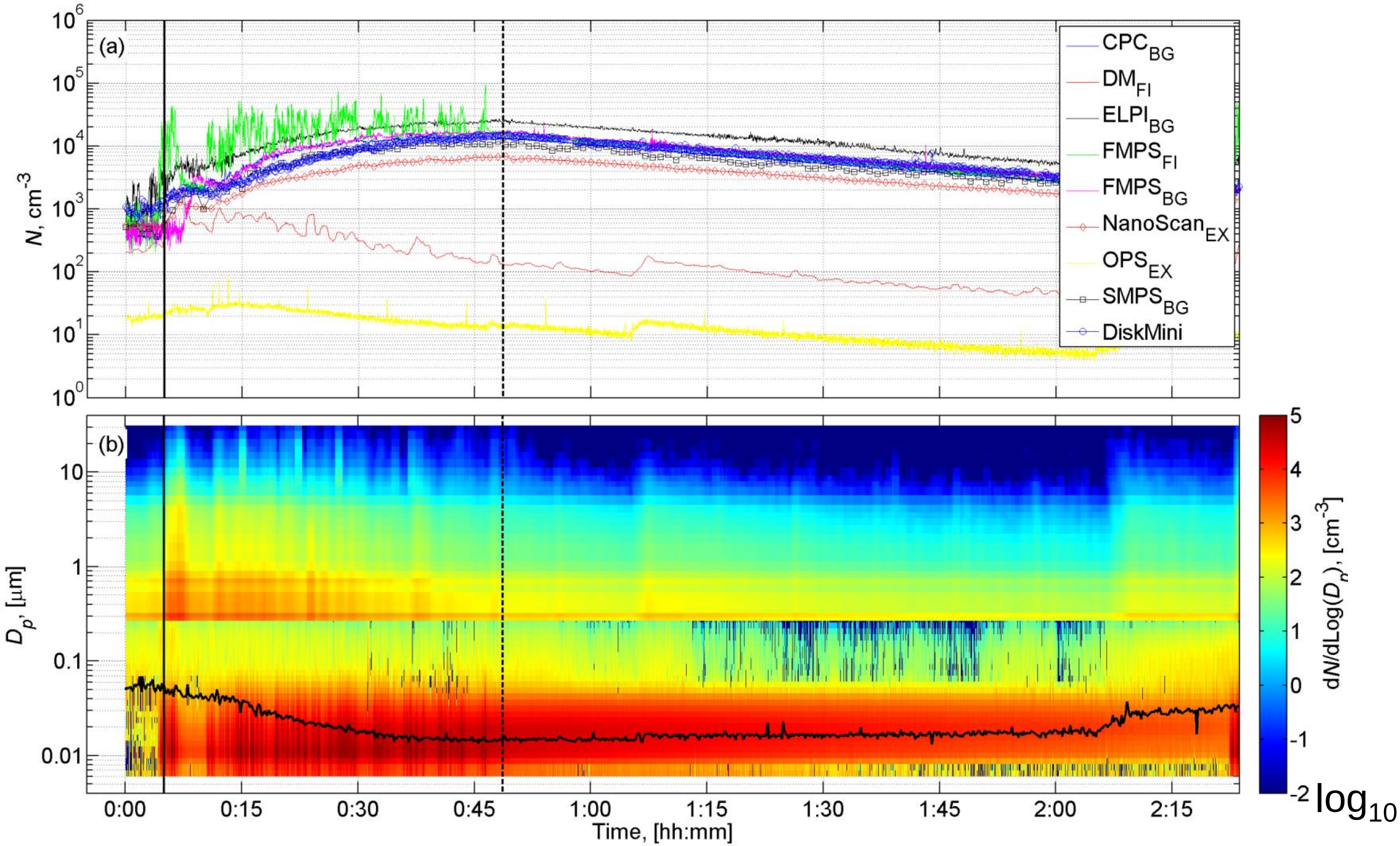


Cutting PP_{OP} and PP_{CNT} bumpers



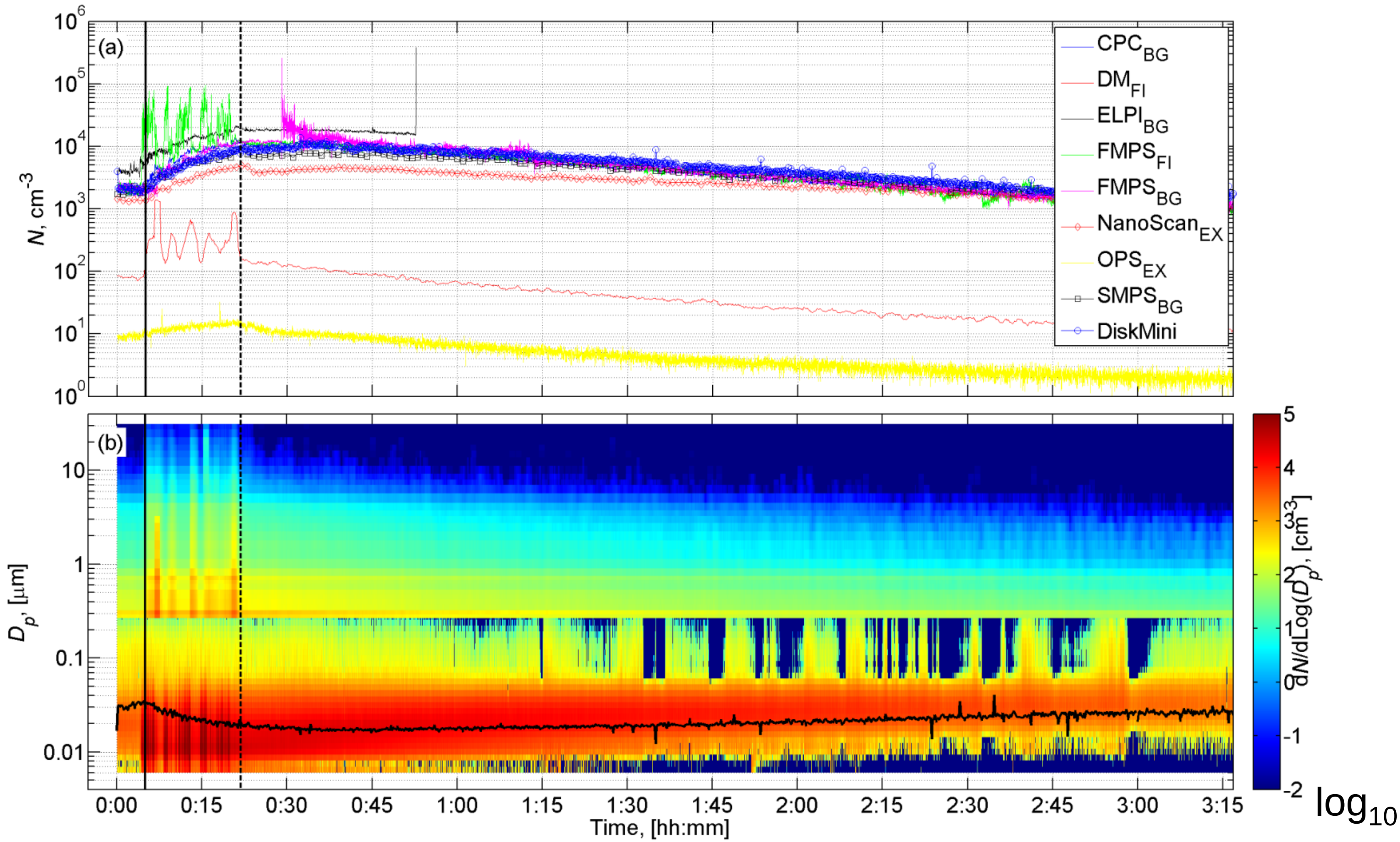
Cutting PP_{OP} (1-3) and PP_{CNT} (4) bumpers with jigsaw (include cutting machine emissions) Concentrations measured *ca.* 1.5 m from cutting site a) total particle number concentrations and b) particle size distributions.

Shredding PP_{OP} bumpers



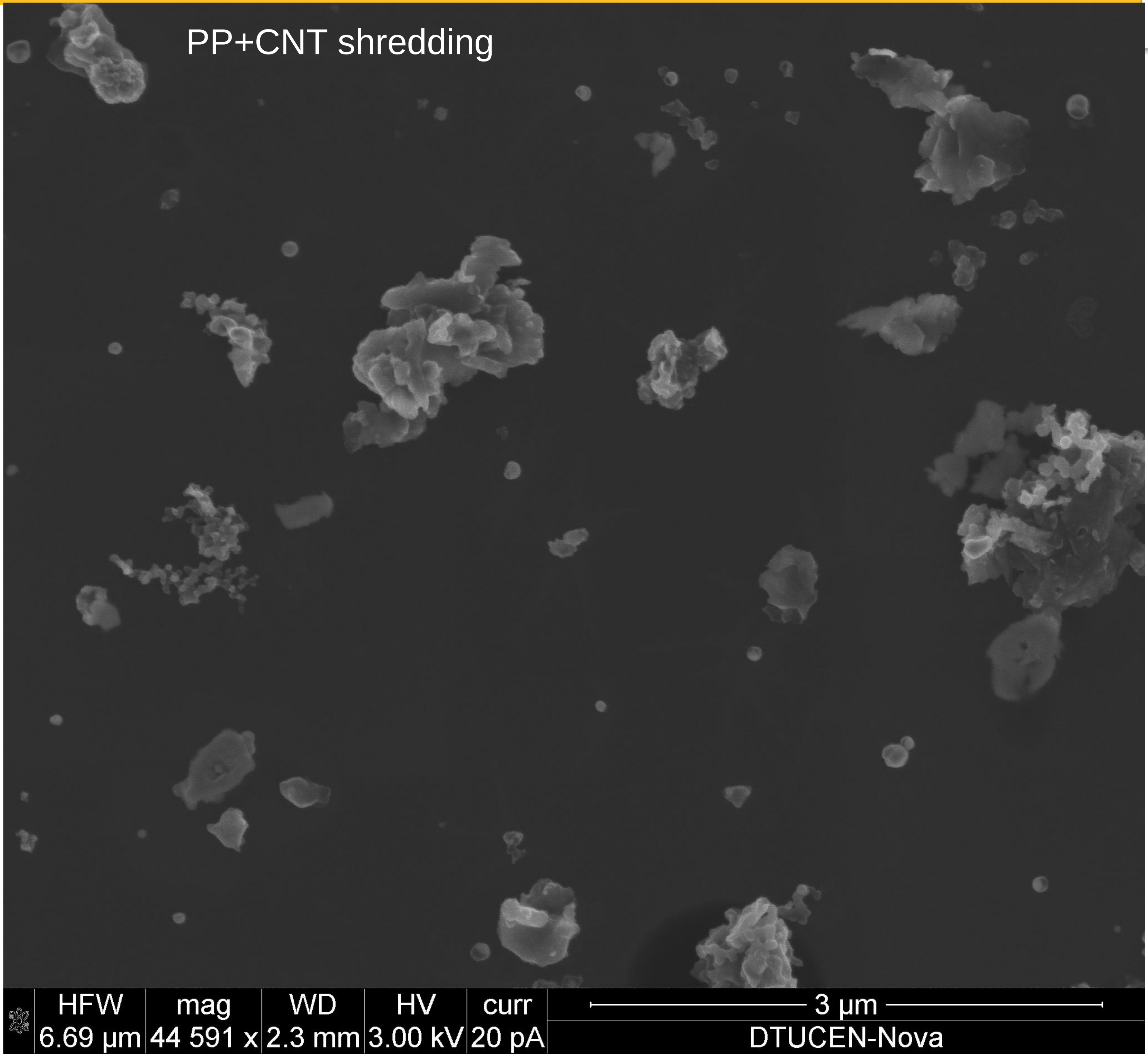
Shredding 33.39 kg of PP_{OP} bumpers. Shredder feed inlet a) total particle number concentrations and b) particle size distributions.

Shredding PP_{CNT} bumpers



Shredding 17.49 kg of PP_{CNT} bumpers. Shredder feed inlet a) total particle number concentrations and b) particle size distributions

PP+CNT shredding



SUN

A single compartment model

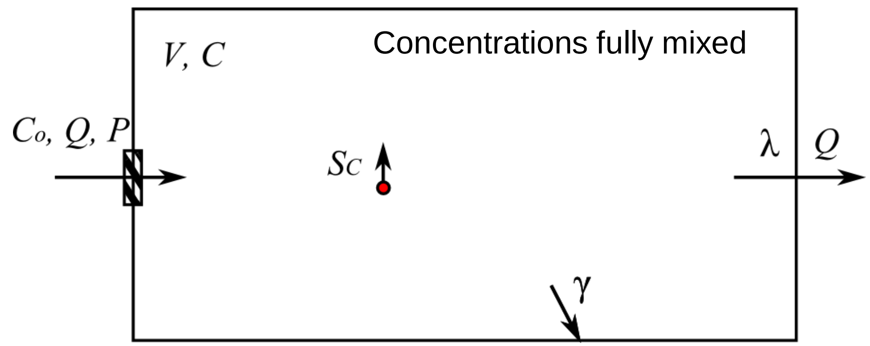
Room concentration

Emission source

$$\frac{dC(t)}{dt} = \lambda P C_0(t) + \frac{S_C(t)}{V} - (\lambda + \gamma + \omega)C(t)$$

Background particles from ventilation air

Particle removal by ventilation, deposition, and coagulation



Terms and parameters:

$C(t)$	m^{-3}	Indoor aerosol concentration
$C_o(t)$	m^{-3}	Outdoor aerosol concentration
λ	s^{-1}	Ventilation rate
P	-	Particle filtration efficiency
$S(t)$	$\# \, s^{-1}$	Indoor particle source
V	m^3	Compartment volume
γ	s^{-1}	Particle deposition rate
ω	s^{-1}	Particle coagulation rate
Q	$m^3 \, s^{-1}$	Ventilation flow

If $C_o = 0$, and $\gamma \ll \lambda$ and $\omega \ll \lambda$:

$$\frac{dC(t)}{dt} = \frac{S_C(t)}{V} - \lambda C(t) \quad = 0$$

$$\rightarrow S_C(t) = \lambda V C(t)$$

In steady-state: $\frac{dC(t)}{dt} = 0$

Concentrations and emission rates

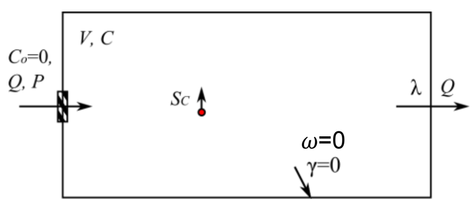
Table 1. Aerosol properties in cutting and shredding experiments.

Material	Process	Amount, [kg]	Time, t_p [mm:ss]	N, ×10^3 [cm^{-3}]	GMD, [nm]	GSD	m_{PM4}, [µg m^{-3}]	Emission of respirable mass
PP_{OP} , PP_{CNT}	Cutting	N/A	39:58	228	19.4	1.83	< 1.34	**< 0.22 µg min^{-1}**
PP_{OP}	Shredding	33.39	43:40	19.2	17	2.34	4.3	**0.41 µg kg^{-1}**
PP_{CNT}	Shredding	17.49	16:49	21	16	2.13	< 1.34	**< 0.26 µg kg^{-1}**

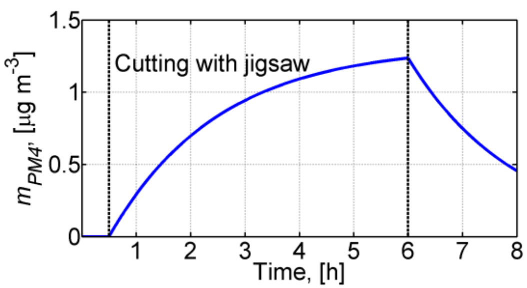
Symbols: t_p = process time, N = particle number concentration, GMD = Geometric mean diameter, GSD = Geometric standard deviation, m_{PM4} = respirable mass concentration

Example of modeled exposure in:

Cutting

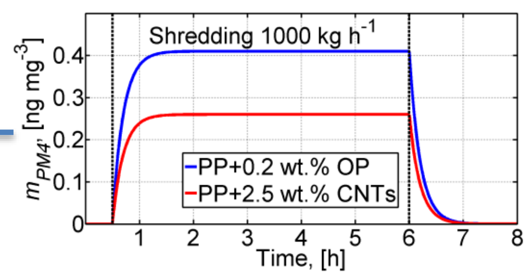


Parameterization:
V = 20 m^3
λ = 0.5 h^{-1}
S_{PM4} = < 0.22 µg min^{-1}



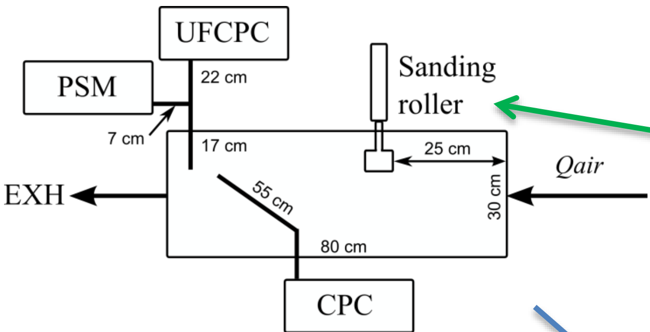
Shredding

Parameterization:
V =100 × 100 × 20 m^3 (industrial hall)
λ = 5 h^{-1}
Shredding rate: 1000 kg h^{-1}
→ S_{PM4} = 410 µg h^{-1}



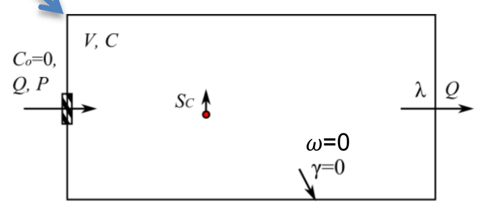
Insignificant Exposure levels

Sanding experiments in 80 L box



Bosch PRR 250 ES Sanding roller

Particle counter	D_{50}, [nm]
PSM Airmodus	1
UFCPC TSI 3776	3
CPC TSI 3007	10



Here N_{in} ~ 0 cm^{-3}, and $\gamma \ll \lambda$ and $\omega \ll \lambda$:

$$\rightarrow \frac{dN(t)}{dt} = \frac{S(t)}{V} - \lambda N(t)$$

when $S = 0\ s^{-1}$ → $N(t) = N_0 e^{-\lambda t}$ → λ = 12.7 min^{-1}

when $\frac{dN(t)}{dt} = 0$ → $S_C(t) = \lambda V N(t)$

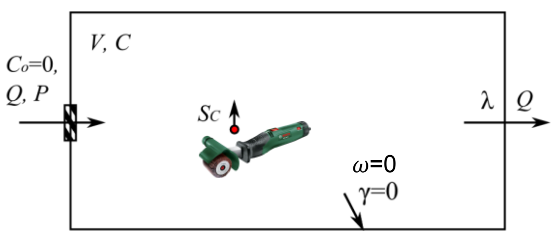
Concentrations and emission rates during sanding

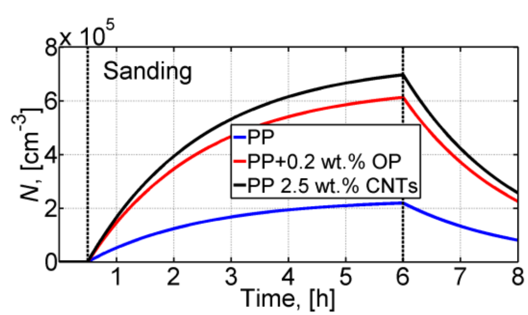
Table 2. Average particle concentrations, particle emission rates, and fractions of particles over 3 and 10 nm in diameter.

	Number concentrations *N*, $\times 10^3$ [cm^{-3}]			Particle emission rates *S*, $\times 10^{10}$ [min^{-1}]			
Material	PSM,	nCPC,	CPC	**Total**	1-3 nm	3-10 nm	>10 nm
PP_0	37.8	29.2	1.4	**3.9**	0.75	3.01	0.14
PP_{CNT}	105	42.6	3.0	**10.9**	6.15	4.43	0.32
PP_{OP}	119	60.7	4.4	**12.4**	5.62	6.32	0.46

Sanding emissions of particles > 6 nm has been shown to vary from 1×10^9 to 2×10^{12} min^{-1} (Koivisto *et al.* submitted)

Modeling example:





Parameterization:
V = 20 m^3
λ = 0.5 h^{-1}

Note: *e.g.* $\gamma\left(D_p \approx 3\ nm\right)$ = 10 to 100 h^{-1}

Conclusions

- Exposure modelings requires quantitative emissions
  → experimental concentrations are NOT enough!
- Emission rates were low in mass during cutting and shredding
- In sanding, from 30 to 60 % of emitted particles were < 3 nm in diameter
- Emissions are tool tip and material spesific
- Size resolved emission rates (see *e.g.* Hussein *et al.* 2006)

Material	Cutting, [μg min^{-1}]	Shredding, [μg kg^{-1}]	Sanding, $\times 10^{10}$ [min^{-1}]
PP	-	-	3.9
PP_{OP}	< 0.22	0.41	10.9
PP_{CNT}	< 0.22	< 0.26	12.4

Thank you!

References

Boonruksa, P. et al. Characterization of Potential Exposures to Nanoparticles and Fibers during Manufacturing and Recycling of Carbon Nanotube Reinforced Polypropylene Composites. Ann. Occup. Hyg. mev073 (2015).

Hussein, T., Glytsos, T., Ondrácek, J., Zdímal, V., Hämeri, K., Lazaridis, M., Smolik, J., Kulmala, M., 2006. Particle size characterization and emission rates during indoor activities in a house. Atmospheric Environment 40, 4285-4307.

Koivisto AJ, Kling KI, Levin M, Fransman W, Gosens I, Cassee FR, Jensen KA. (2016) First order risk assessment for nanoparticle inhalation exposure during injection molding of polypropylene composites and production of tungsten-carbide-cobalt fine powder based upon pulmonary inflammation and surface area dose. *Submitted to Nanoimpact.*

Koivisto AJ, Jensen ACØ, Kling KI, Nørgaard A, Brinch A, Christensen F, Jensen KA. (2016) Quantitative material releases from products and articles containing manufactured nanomaterials: A critical review. *Submitted to Nanoimpact.*

Sotiriou, G. A. *et al.* Thermal decomposition of nano-enabled thermoplastics: Possible environmental health and safety implications. *J. Hazard. Mater.* 305, 87–95 (2016)