

# **CHEMICAL INCIDENT INVOLVING A SPRAY APPLICATION OF A WATER-BASED NANO-SIZED WATERPROOFING AGENT**

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# Case report

1. Case description
2. Medical treatment
3. Product properties
4. Reconstruction

## The application

Tue-March-24 2010 ~ 17:00

Approximately 1 liter of a waterproofing product was used in a spray gun at an air pressure of 2 atm to coat two table tops in a wood workshop of 260 m<sup>2</sup> without forced ventilation and without respiratory protection.

The label said the product is water-based and should be applied by rubbing on the surface with a cloth



## Primary exposure

Person	Role	Age (y)	Gender	Smoker	Time after start of application	During (min)	Health complaints
A	Applicator	47	Male	No	00:00	> 60	No
B	By-stander	40	Female	No	01:15	15	No
C	By-stander	43	Male	5-20/day	02:30	25	Yes

At 19:30 person C spent about 10 minutes in the room where the tables had been treated. He did not notice any spray mist or smell. Around 20:30 he spent another 15 min in the workshop to do some repairs on a milling machine. Later, he worked in the office and did not return to the workshop any more. At 23:15 he was not feeling well, experiencing serious dyspnea and asphyxiation (perceived as if 'drowning') and reported to the emergency room of the local hospital.

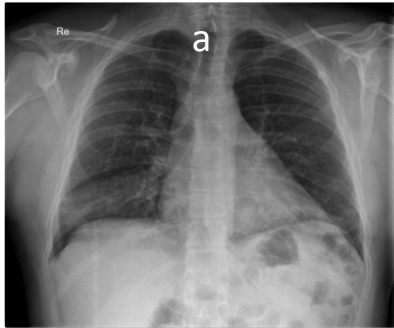
# Medical anamnesis upon hospital admission

Aspect	Description
Medical history	No (recorded) history of respiratory disease
Respiratory complaints	Dyspnea, cough, producing blank sputum
Neurological	Impaired vision, shaking hands and tingling sensation in extremities
Other complaints	Feeling cold

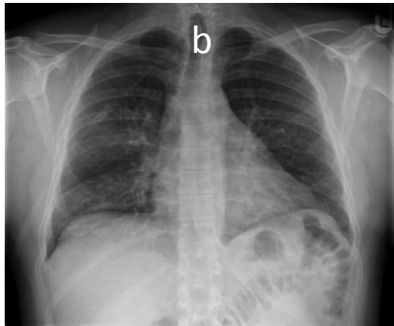
# Physical exam at emergency unit

Parameter	Person C	Normal for male adult
Blood pressure (systolic/diastolic mm Hg)	125/61	120/80
Pulse rate (min <sup>-1</sup> )	105	60-100
Body temperature (°C)	39	36.1-37.2
Oxygen saturation without respiratory support (%)	60	>95
Oxygen saturation when using non-rebreathing oxygen mask at setting of 15 L/min (%)	96	>95
Leukocytosis	19.1 x 10 <sup>9</sup>	4.0 - 10 x 10 <sup>9</sup>
C-reactive protein (mg/L)	57	< 10

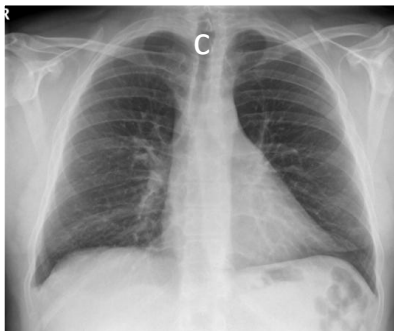
# Chest X-ray



a. On the day of hospital admission

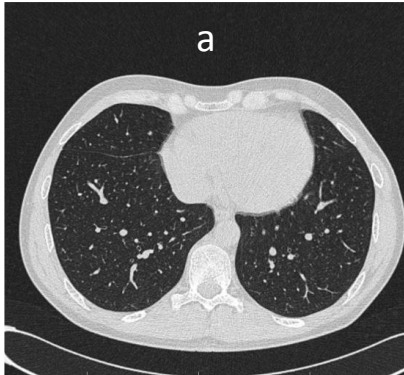


b. Infiltrative impairments and pronounced bronchovascular markings on the basal lung fields on both sides

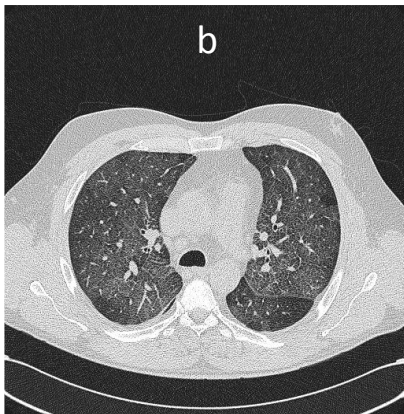


c. Complete normalization after two weeks

# HRCT-scan



- a. Extended crazy paving of all pulmonary lobes but most pronounced in the central pulmonary region, matching pneumonitis on the second day of hospitalization

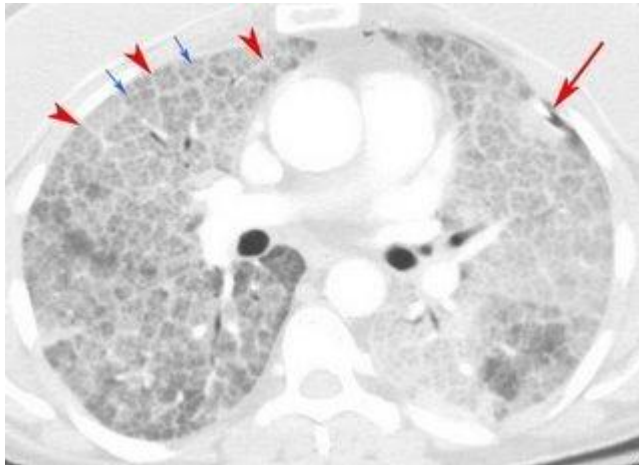


- b. Normal HRCT of the chest is shown for comparison

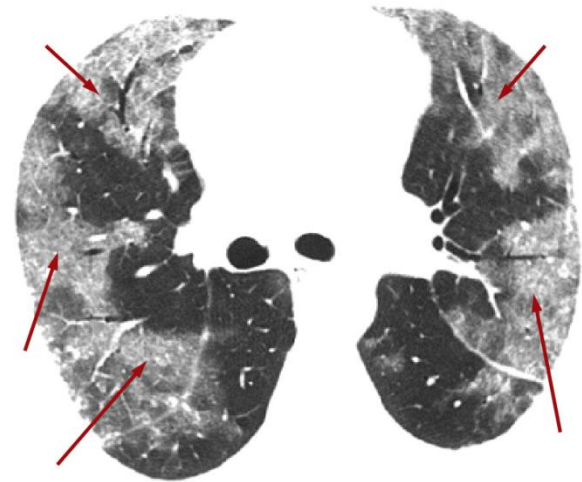


# Interpretation of CT-scan

- Crazy paving of lung lobes with 'ground glass'
- This is consistent with a severe chemical pneumonitis
- This pattern is not consistent with extrinsieke allergische alveolitis



Forse crazy paving: Interlobular septal thickening and intralobular lines. Source: <http://www.radrounds.com/photo/auntminnie-crazy-paving>



Ground glass opacities: Hazy areas of increased attenuation in the lung that have preservation of bronchial and vascular Markings. Source: [http://radiopaedia.org/articles/ground-glass\\_opacity](http://radiopaedia.org/articles/ground-glass_opacity)

## Secondary exposure

On the next morning at 8:30 am several employees in an adjacent mail distribution centre report persistent dry cough and sub-sternal pain upon physical exercise

No mist or smell was observed

At 11:00 am 9 persons have similar complaints.

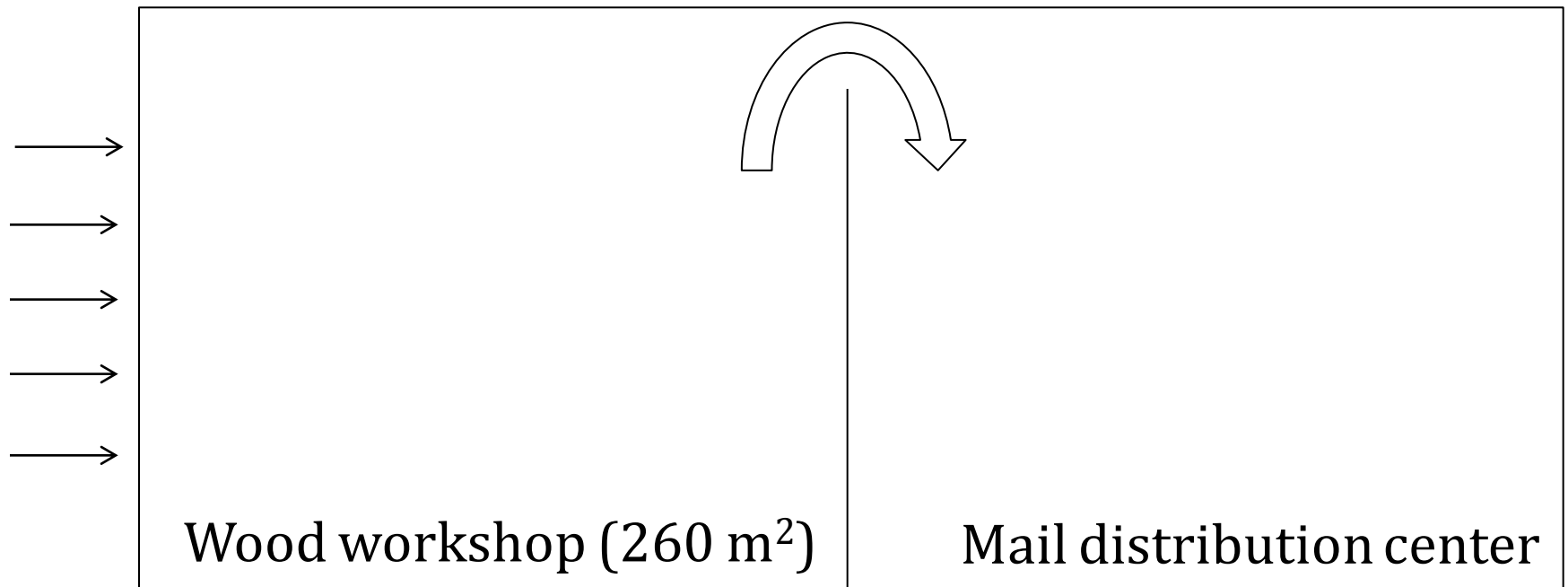
Fire brigade performs measurements

Some of the workers receive a medical exam by the occupational physician

Complaints of feeling unwell persist for one week



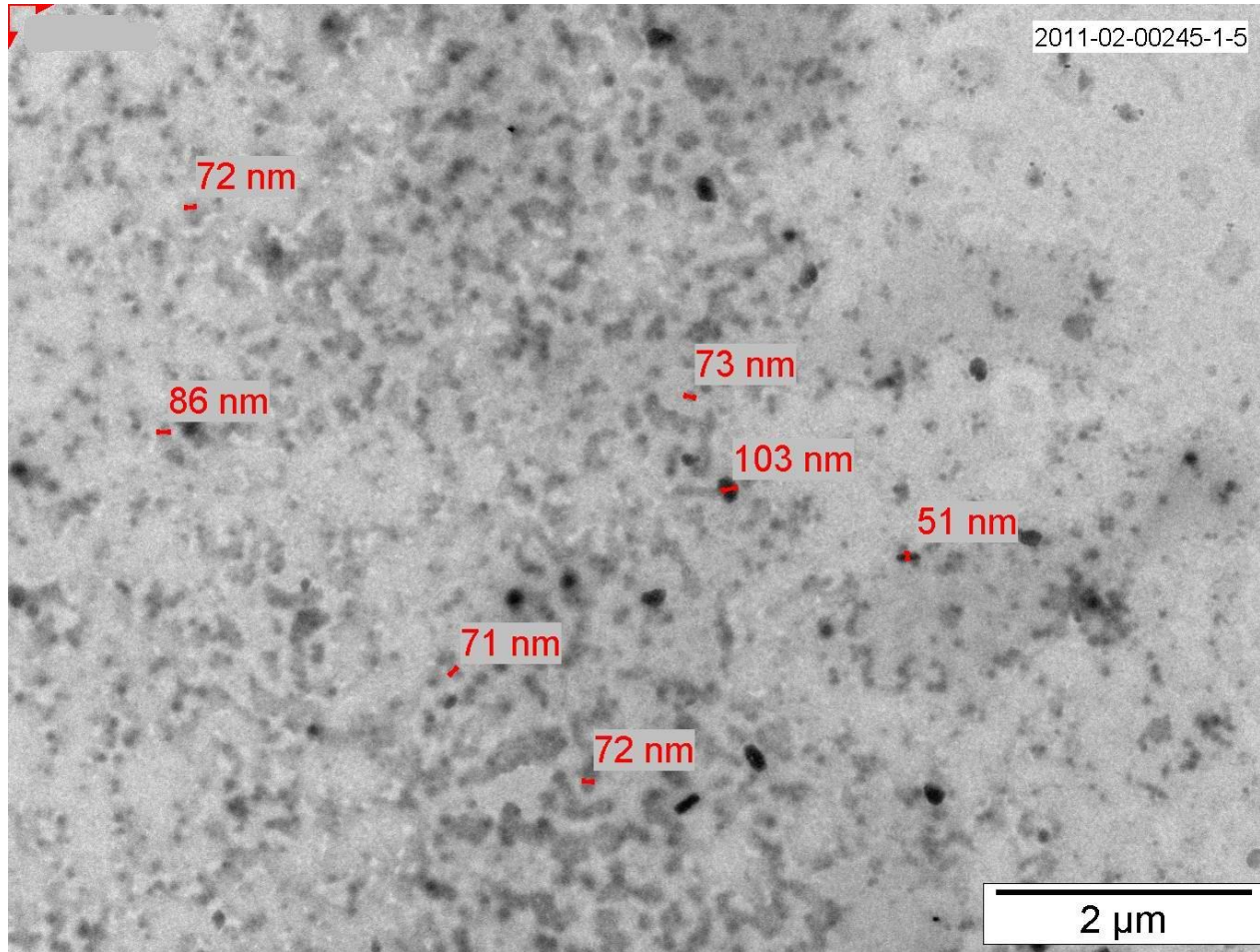
## Secondary exposure



## Product properties (source: producer)

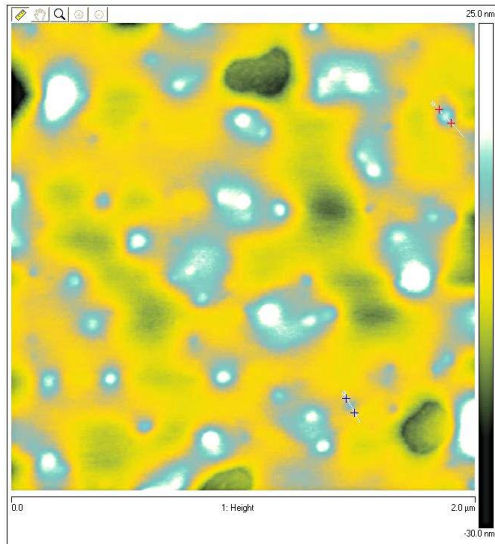
Constituent	Contribution (w %)
Water	95.3
Fluor acrylate co-polymer	1.3
Propylene glycol	1.3
Silicon surfactant	1.3
Dipropylene glycol methyl ether	0.4
Quaternary ammonium	0.4
Fatty alcohol ethoxylate	0.4
Total:	100.4

# Transmission Electron Microscopy (TEM)

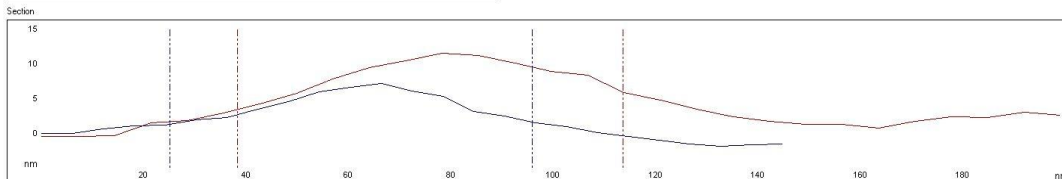




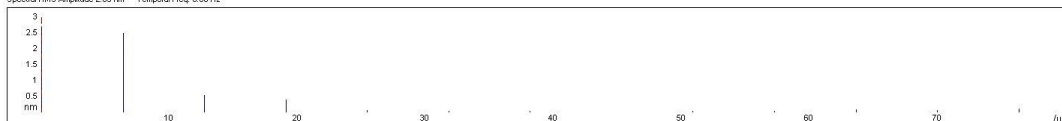
# Atomic force microscopy (AFM)



The product that was used contains 1.3 wt% nano-sized spheres with a median diameter of 71-72 nm, with strong hydrophobic properties and a slight positive charge. These particles form a stable suspension in water with a negligible tendency to form clusters.



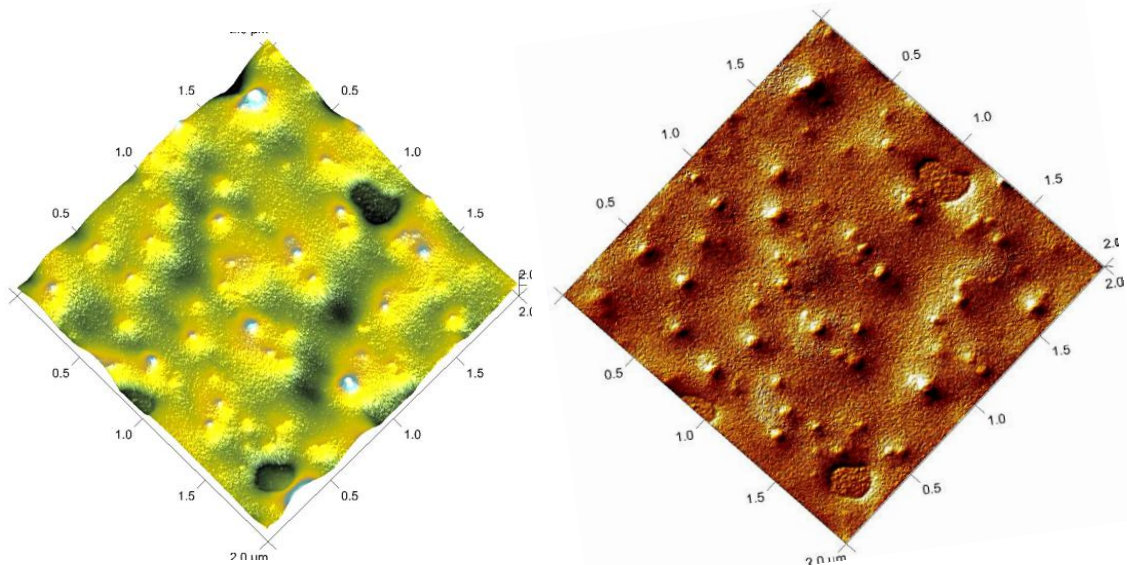
Spectral Period 0.00 μm  
Spectral RMS Amplitude 2.69 nm  
Spectral Frequency 0.00 /μm  
Temporal Freq 0.00 Hz



Pair	Horizontal Distance	Vertical Distance	Surface Distance	Angle	Rmax	Rz	Rz Count	Rms	Ra (Frequency Cutoff)	Frequency Cutoff	Radius	Radius Sigma	Length	Spectral Period	Spectral Frequency
0	0.073 (μm)	0.336 (nm)	0.074 (μm)	0.265 (°)	6.905 (nm)	0.000 (nm)	0.000	2.641 (nm)	2.316 (nm)	0.000 (μm)	0.110 (μm)	0.756 (nm)	0.073 (μm)	0.000 (μm)	0.000 (1/μm)
1	0.078 (μm)	2.939 (nm)	0.080 (μm)	2.147 (°)	8.793 (nm)	0.000 (nm)	0.000	4.390 (nm)	3.916 (nm)	0.000 (μm)	0.115 (μm)	0.540 (nm)	0.078 (μm)	0.000 (μm)	0.000 (1/μm)
2	0.070 (μm)	2.939 (nm)	0.080 (μm)	2.147 (°)	8.793 (nm)	0.000 (nm)	0.000	4.390 (nm)	3.916 (nm)	0.000 (μm)	0.115 (μm)	0.540 (nm)	0.078 (μm)	0.000 (μm)	0.000 (1/μm)

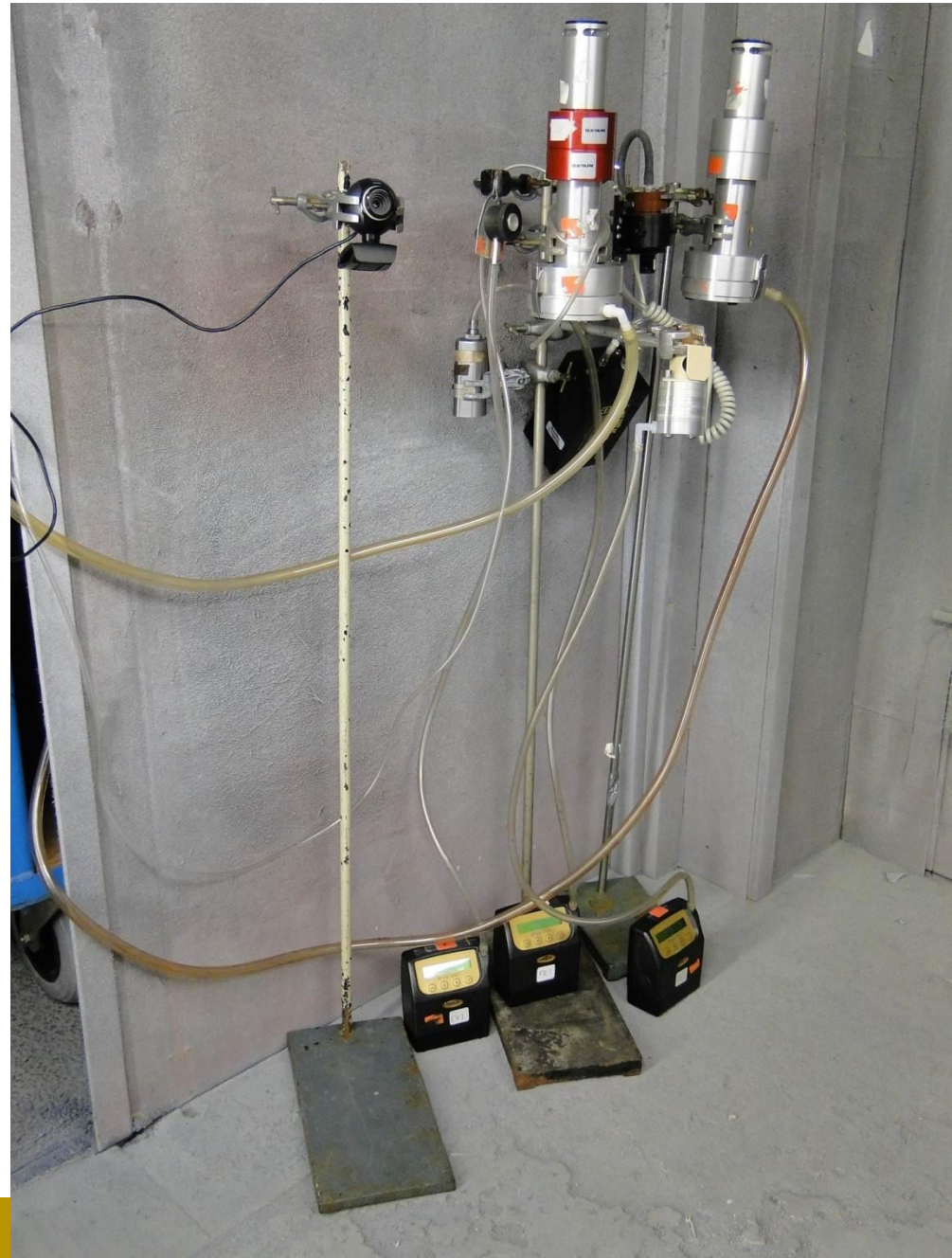
# Atomic force microscopy (AFM)

The particles were chemically characterized as water-free solid organic silica cores, with a soft shell consisting of fluorinated aliphatic hydrocarbons characterized as tri-block-copolymers containing both polyethylene oxide and polypropylene oxide, presumably end-capped with ethylene oxide.



# Reconstruction

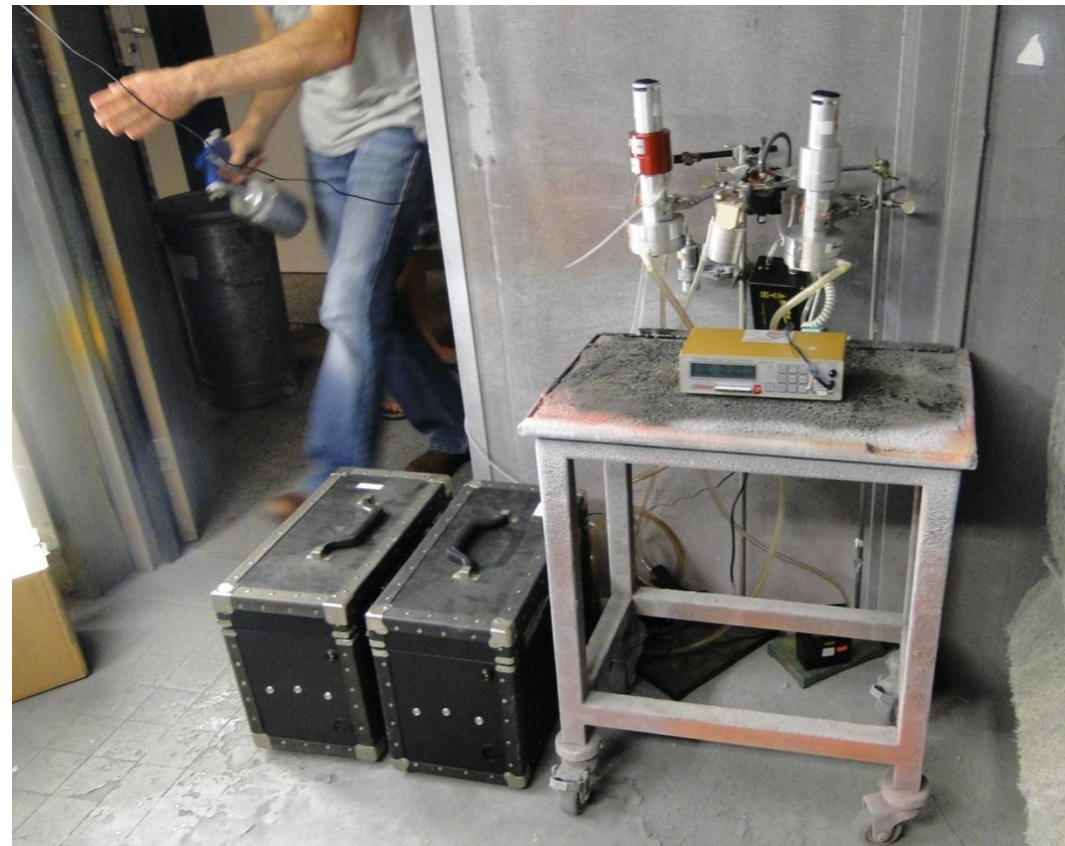
- Application of 700 ml on wood surface of 4 m<sup>2</sup>
- Eminent type E31 EHT M01 spray gun
- Approx. 2 atm air pressure
- Duration ca. 10 minutes
- Spray booth
- PPE: P3 mask and gloves



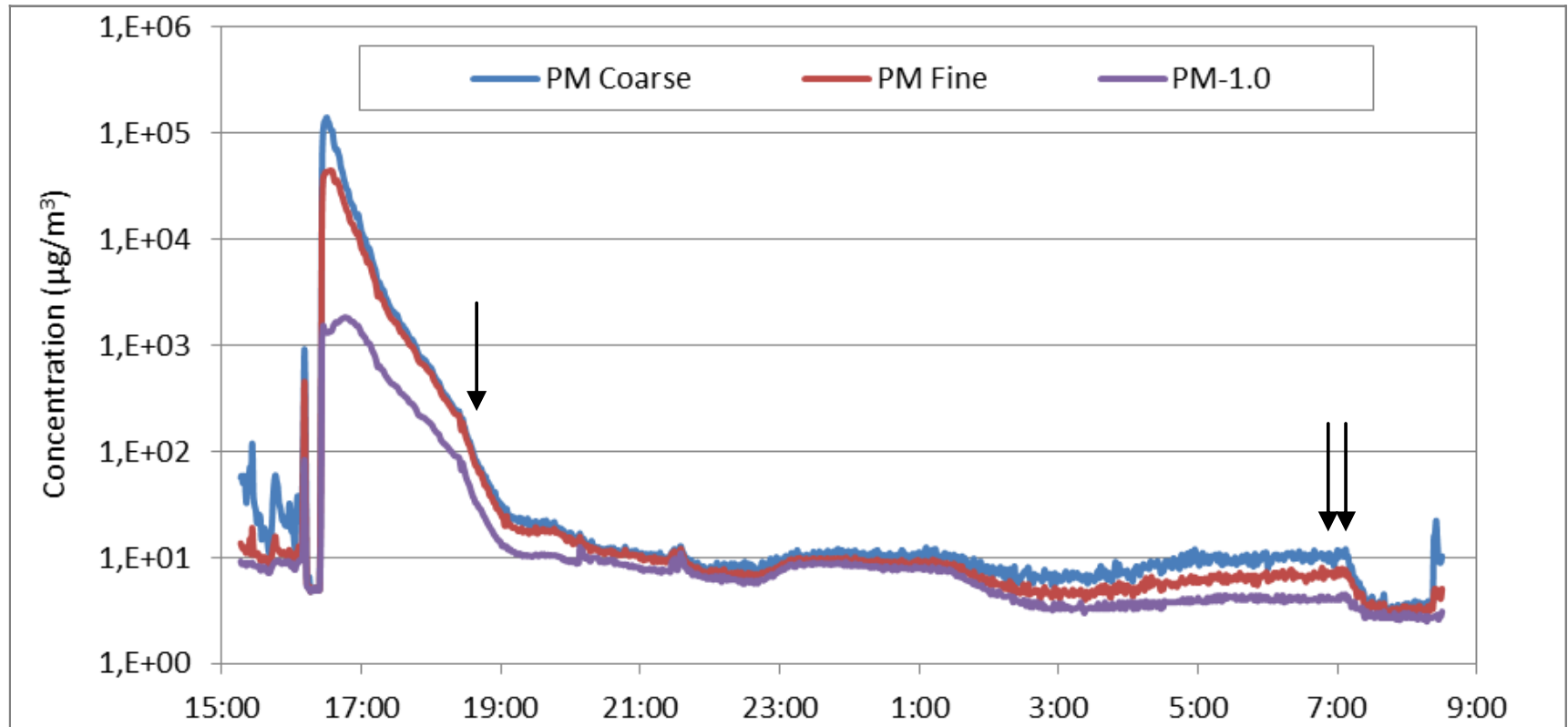


# Reconstructie

- Filter samples:  
Inhaleerbaar, thoracic (PM-10), respirabele (PM4) and PM-2.5
- Cascade impactor:  
8 stages
- Light scattering:  
Grimm 1.109 (0.25-35  $\mu\text{m}$ )  
OSIRIS  
Hazdust (PM-10)

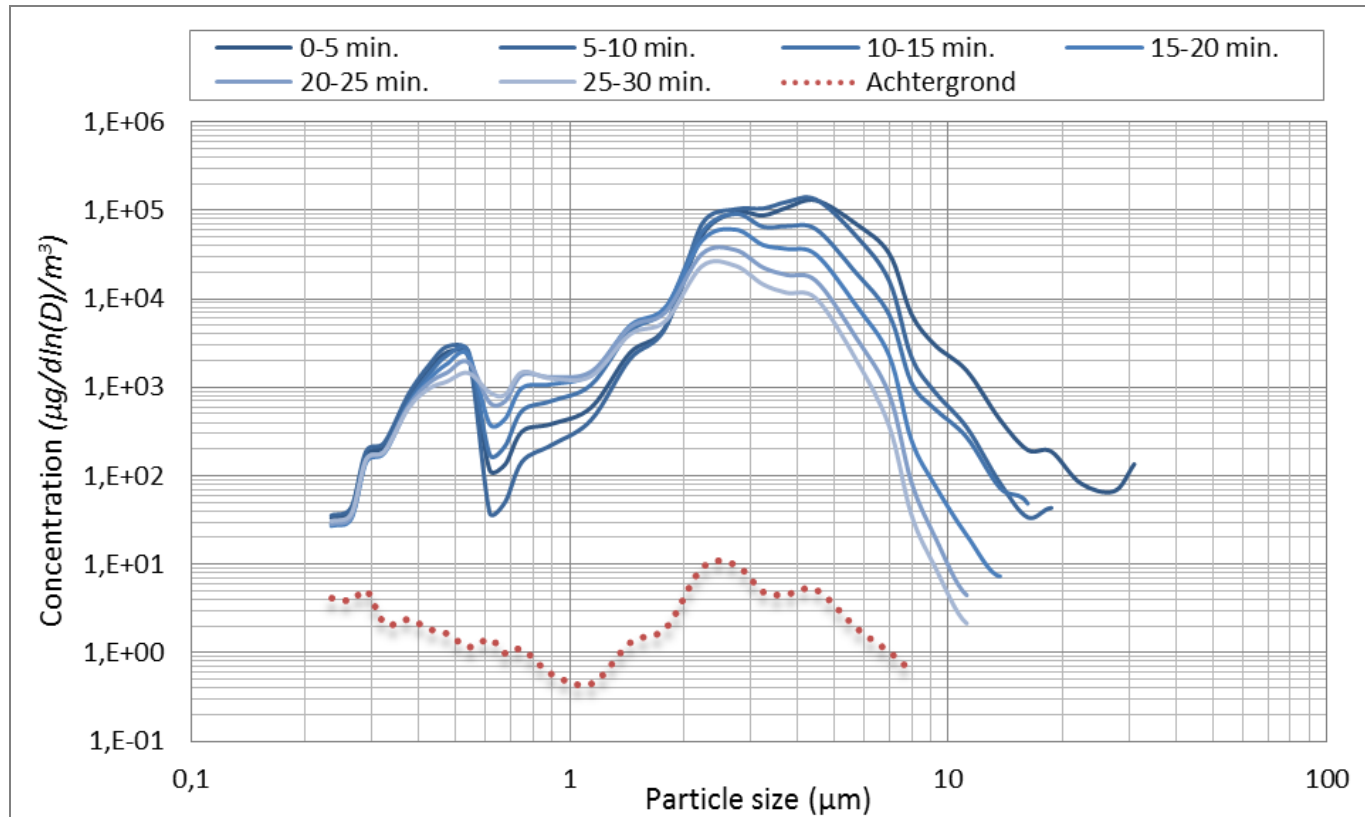


# Reconstruction



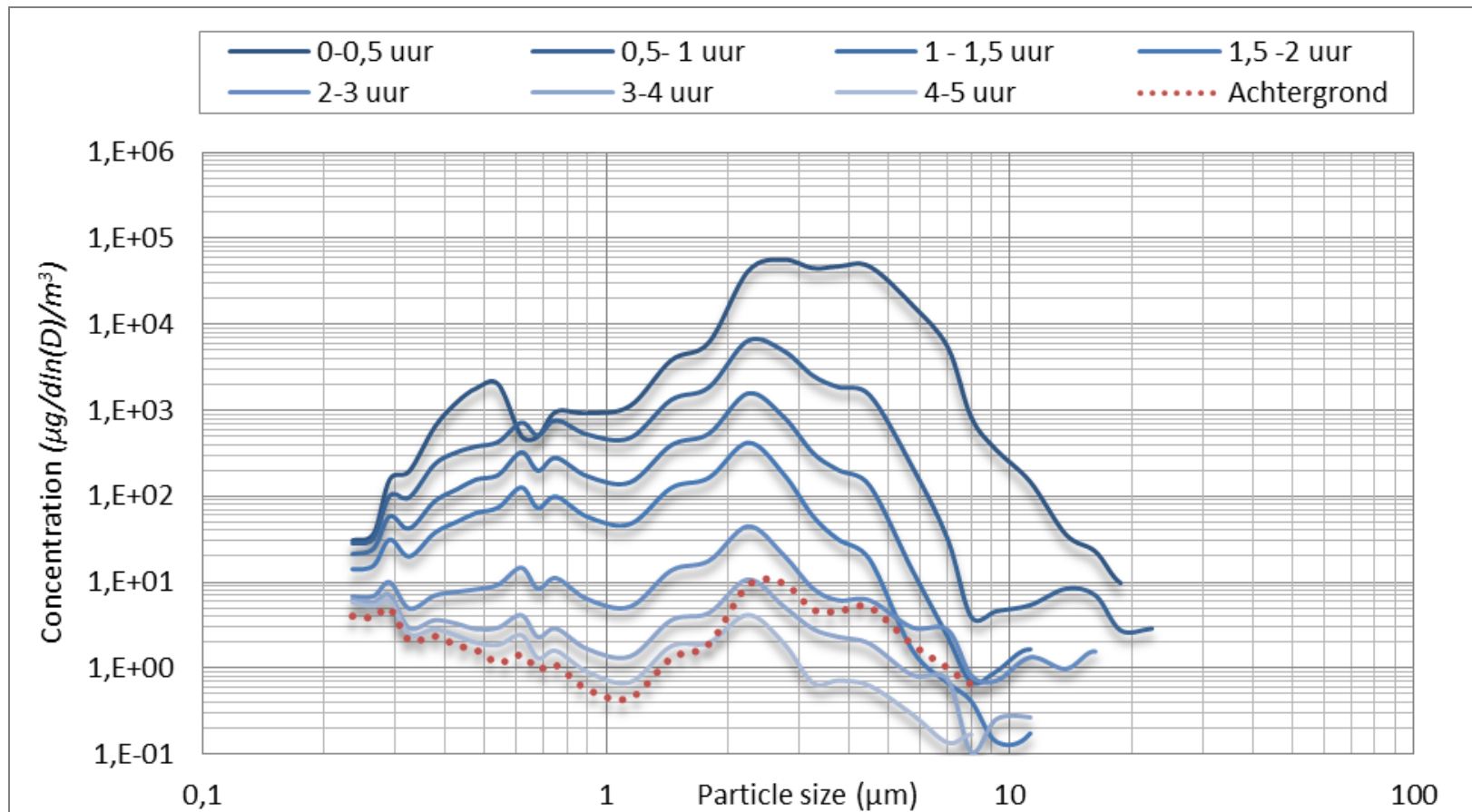
**Figure :** Trace of the Grimm spectrometer. PM Coarse corresponds to PM-10, PM Fine corresponds to PM-2.5. The drop in concentration around 8:30 pm (arrow) may have been caused by a thunderstorm passing over Nijmegen, with air velocities exceeding 100 m/s. The drop in concentration at 07:00 am (double arrow) is (presumably) caused by turning on of the ventilation system.

# Reconstruction



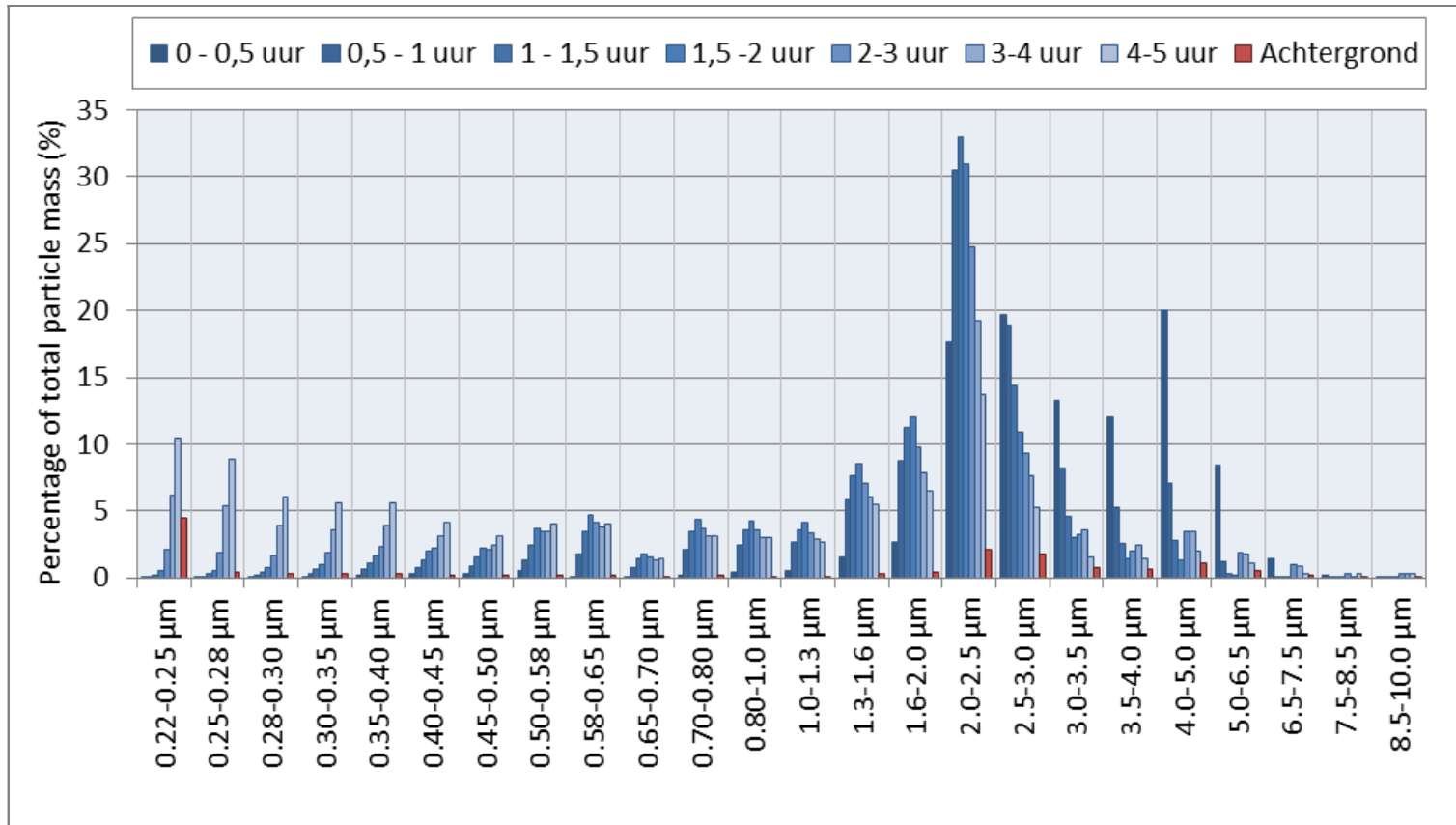
**Figure 1a:** Particle size distribution expressed by mass presented at subsequent time intervals of 5 minutes, relative to the background (estimated from  $t=-30$  to  $t=0$  min). Data from Grimm 1.109 Size selective spectrometer.

# Reconstruction



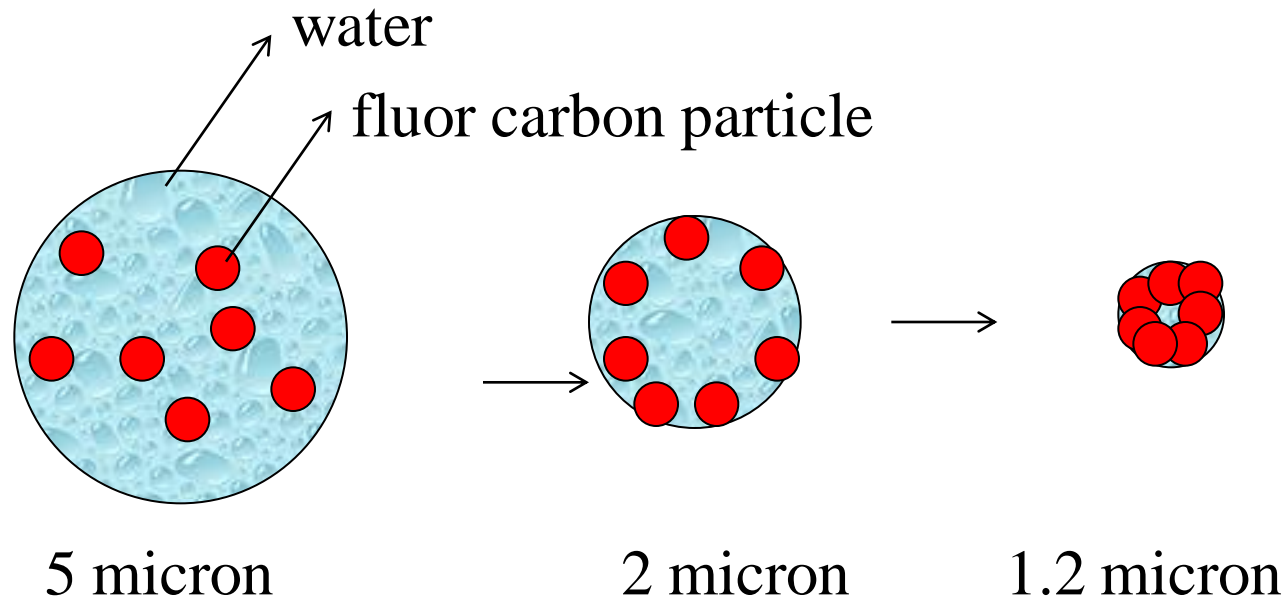
**Figure 1b:** Particle size distribution expressed by mass presented at subsequent time intervals of 30 minutes, relative to the background (estimated from  $t=-30$  to  $t=0$  min). Data from Grimm 1.109 Size selective spectrometer.

# Reconstruction

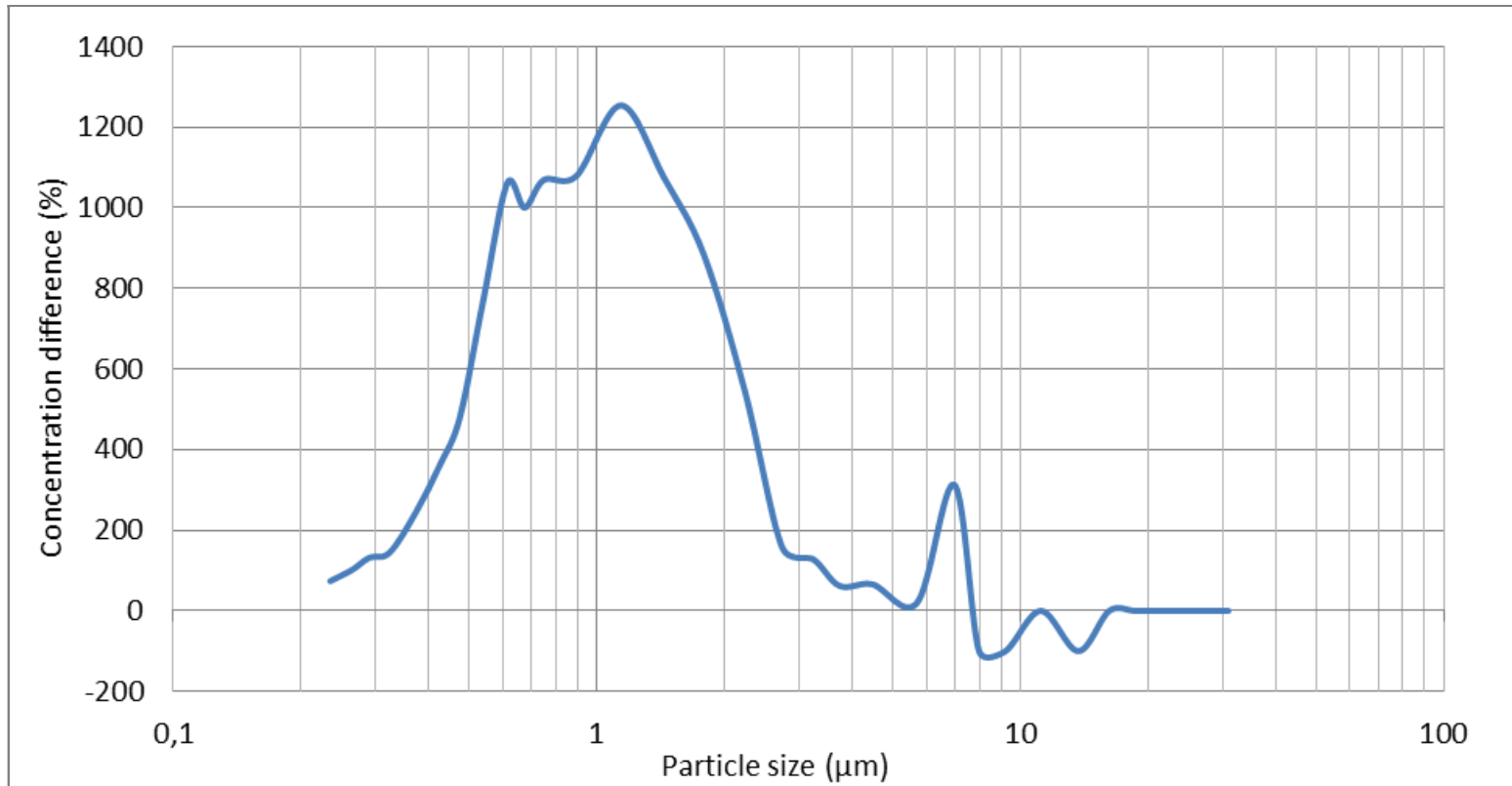


**Figure 1c:** Same data as Figure 1a (from Grimm 1.109 Size selective spectrometer) but expressed for each particle size channel separately. Again the change in time is presented for subsequent time intervals of 30 minutes.

# Hypothesis concerning aging of airborne particles



# Reconstruction



**Figure 1d:** Same data as Figure 1a (from Grimm 1.109 Size selective spectrometer) but expressed as a difference of the concentration 2,5 hours after application, relative to the background concentration for each particle size channel separately.

## Discussion

- The fire brigade did not detect any organic vapors using a photo ionization detector
- The labor inspector did not find any other chemicals
- The paramedic did not report any health symptoms in person A (applicator) and person B (by-stander)



## Discussion

- The product contains nanoparticles but what is the size of the airborne particles?
- What explains the difference in interindividual susceptibility (primary exposure)?
- What explains the persistence of the particles to remain airborne (secondary exposure)?
- How can the (presumably) extremely low concentrations of the product cause clinical symptoms on the next day (secondary exposure)?

## Discussion

- Previous incidents with waterproofing products involve fluor alkanes and alkenes
- There is no clear role of organic solvents
- This is the first report of a waterproofing incident involving a water-based product
- There is no previous report on health effects after inhalation of nanoparticles (Magic Nano was a hoax)

## Conclusions

- The application method has great influence on the health risk
- The product properties have remarkable consequences for the persistence
- The toxicity of the fluor acrylate co-polymer needs to be further characterized
- Inter-individual differences in response to the exposure requires further study

