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Abstract

Background: The production and use of carbon nanotubes (CNTs) is rapidly growing. With increased production, there is potential that the number of occupational exposed workers will rapidly increase. Toxicological studies on rats have shown effects in the lungs, e.g. inflammation, granuloma formation, and fibrosis after repeated inhalation exposure to some forms of multi-walled CNTs (MWCNTs). Still, when it comes to health effects, it is unknown which dose metric is most relevant. Limited exposure data for CNTs exist today and no legally enforced occupational exposure limits are yet established. The aim of this work was to quantify the occupational exposures and emissions during arc discharge production, purification, and functionalization of MWCNTs. The CNT material handled typically had a mean length <5 μm. Since most of the collected airborne CNTs did not fulfil the World Health Organization fibre dimensions (79% of the counted CNT-containing particles) and since no microscopy-based method for counting of CNTs exists, we decided to count all particle that contained CNTs. To investigate correlations between the used exposure metrics, Pearson correlation coefficient was used.

Methods: Exposure measurements were performed at a small-scale producer of MWCNTs and respirable fractions of dust concentrations, elemental carbon (EC) concentrations, and number concentrations of CNT-containing particles were measured in the workers' breathing zones with filter-based methods during work. Additionally, emission measurements near the source were carried out during different work tasks. Respirable dust was gravimetrically determined; EC was analysed with thermal–optical analysis and the number of CNT-containing particles was analysed with scanning electron microscopy.

Results: For the personal exposure measurements, respirable dust ranged between <73 and 93 μg m^{-3}, EC ranged between <0.08 and 7.4 μg C m^{-3}, and number concentration of CNT-containing particles ranged between 0.04 and 2.0 cm^{-3}. For the emission measurements, respirable dust ranged between <2800 and 6800 μg m^{-3}, EC ranged between 0.05 and 550 μg C m^{-3}, and number concentration of CNT-containing particles ranged between <0.20 and 11 cm^{-3}. **Conclusions:** The highest exposure to CNTs occurred during production of CNTs. The highest emitted number concentration of CNT-containing particles occurred in the sieving, mechanical work-up, pouring, weighing, and packaging of CNT powder during the production stage. To be able to quantify exposures and emissions of CNTs, a selective and sensitive method is needed. Limitations with measuring EC and respirable dust are that these exposure metrics do not measure CNTs specifically. Only filter-based methods with electron

microscopy analysis are, to date, selective and sensitive enough. This study showed that counting of CNT-containing particles is the method that fulfils those criteria and is therefore the method recommended for future quantification of CNT exposures. However, CNTs could be highly toxic not only because of their length but also because they could contain, for example transition metals and polycyclic aromatic hydrocarbons, or have surface defects. Lack of standardized counting criteria for CNTs to be applied at the electron microscopy analysis is a limiting factor, which makes it difficult to compare exposure data from different studies.

Introduction

The global production and use of the carbon nanotubes (CNTs) into different products and materials is rapidly growing (Dahm *et al.*, 2012; Gasser *et al.*, 2012; Ono-Ogasawara and Myojo, 2013). CNT is in the paper used as a synonym for multi-walled CNTs. CNTs were discovered in 1991 by Iijima (1991) and are a heterogeneous group of tubes at the nanometre scale consisting of pure graphene layers rolled to form cylinders with high aspect ratios. If the CNT structure consists of one cylinder, it is denoted single-walled carbon nanotube (SWCNT) and if it consists of several cylinders stacked inside each other, they are referred to as multi-walled carbon nanotube (MWCNT).

Use and commercial application

CNTs are usually manufactured by three different methods, which are chemical vapour deposition (CVD), laser ablation, and arc discharge. CVD is the most common and widely used method for CNT production while the arc discharge method is lesser used. However, since arc-discharge-produced MWCNTs with a mean length <5 µm are commercially available, occupational exposure during production with this method also need to be quantified. CNTs have desirable properties in terms of mechanical strength, chemical inertness, electrical conductivity, optical properties, and thermal properties, and these truly unique properties may make a breakthrough in many vital industries (Barkauskas *et al.*, 2010). Therefore, wide application areas are expected for CNTs in the future in industry sectors such as materials and chemistry, medicine and life science, electronics, information and communication technology, and energy (Köhler *et al.*, 2008; Barkauskas *et al.*, 2010; McIntyre, 2012). Today, CNTs are incorporated into existing materials such as plastics, rubbers, composite materials, textiles, and concrete to make them more durable (strength), lightweight, or more wear-resistant (Schneider *et al.*, 2007; Köhler *et al.*, 2008; Wohlleben *et al.*, 2011). Products on the market today containing CNTs are, e.g. sport equipments, composites for car parts, aircrafts and wind power plants, and solar cells (Hussain *et al.*, 2006; Köhler *et al.*, 2008; Thomas *et al.*, 2009; Tan *et al.*, 2012). Workers exposed to CNTs may be at the highest risks while consumers are unlikely to be exposed to CNTs.

Toxicology and exposure metrics

The properties of CNTs differ depending on, e.g. number of walls, diameter, length, chiral angles, chemical functionalization, purity, stiffness, and bulk density. CNT materials consist of a complex mixture of different transition metal catalysts, e.g. iron and cobalt, inorganic

carbon impurities, and organic impurities, e.g. polycyclic aromatic hydrocarbons, which all could have a critical role in oxidative stress and the toxicology of CNTs (Plata *et al.*, 2008; Hsieh *et al.*, 2012). CNTs have nanoscaled size in two dimensions resulting in fibre-like characteristics and could be referred to as high aspect ratio nanoparticles (Donaldson *et al.*, 2011). The fibre shapes and the small dimensions result in very high surface to mass ratios. The structures of MWCNTs are stiffer compared with the SWCNTs. Membrane piercing of cells is mainly described for long and stiff CNTs with a length >15–20 μm (Nagai *et al.*, 2011; Gasser *et al.*, 2012). Since CNTs are fibre-like in their characteristics, there are structural similarity between them and asbestos fibres. Thus, concern has been raised if some forms of CNTs could induce similar adverse biological effects as asbestos, e.g. mesothelioma (Poland *et al.*, 2008; Donaldson and Poland, 2009; Donaldson *et al.*, 2011; Palomäki *et al.*, 2011). Animal studies have shown serious effects in the lungs, i.e. inflammation, granuloma formation, and fibrosis, after repeated inhalation exposure to MWCNTs (Ma-Hock *et al.*, 2009; Ryman-Rasmussen *et al.*, 2009; Pauluhn 2010; Porter *et al.*, 2013), even at realistic exposures and doses. Studies exposing the abdominal cavity in animals to MWCNTs indicated a certain carcinogenic potential (Poland *et al.*, 2008; Takagi *et al.*, 2008). Furthermore, recent studies clearly demonstrated threshold effects of the fibre length. Silver nanofibres with a length >4 μm were pathogenic and caused acute inflammation when the nanofibres were injected into the pleura (Schinwald *et al.*, 2012b). But if the silver nanofibres instead were administrated by pharyngeal aspiration, the threshold fibre length for acute pulmonary inflammation was between 10 and 14 μm (Schinwald *et al.*,2012a). Shorter CNTs entangle and coil and are preferentially enclosed by the cells (Nagai *et al.*, 2011). But shorter MWCNTs, for example with a median length of 3.9 μm, have in several studies shown to both penetrate alveolar macrophages, the alveolar wall, and visceral pleura (Mercer *et al.*, 2010) and cause pulmonary inflammatory effects and fibrosis (Mercer *et al.*, 2011; Porter *et al.*, 2013). Also, repeated exposure to very short MWCNTs (0.2–0.3 μm) has in rats shown to cause bronchoalveolar inflammation and thickening of the alveolus septum indicative of interstitial fibrosis (Pauluhn, 2010). In the future, measurements of biological oxidative damage might be used as a biomarker for CNT exposure (Hsieh *et al.*, 2012). To date, no toxicological data for humans exist. Thus, exposure to all types of CNTs must be avoided as long as the adverse biological effects are not fully understood. Until the relevant dose metrics of CNTs are known, exposure to CNTs should be measured with multiple exposure metrics, for example mass concentration, elemental carbon (EC) mass concentration, and particle

number concentration of CNT-containing particles (Brouwer *et al.*, 2012; Dahm *et al.*, 2012; Hedmer *et al.*, 2013).

Methods for measuring CNTs

How to collect and count CNTs on filters with electron microscopy is not obvious today due to a lack of standardized protocols. Based on the similarities between CNTs and asbestos, the method for standard fibre counting from World Health Organization (WHO,1997) has been applied in a few previous studies of workplace exposure of CNTs (Bello *et al.*, 2009; Lee *et al.*, 2010). According to the WHO method, a fibre is counted if it has a minimum length of 5 μm, a width <3 μm, and length:width ratio >3:1 (WHO, 1997; OH Learning, 2010). Furthermore, if the fibre is attached to a non-CNT carrier particle, the carrier particle is neglected and the fibre is counted if the visible part of the fibre meets the above definition. Also, split fibres, fibre bundles, and ends of fibres partially within imaged area are counted. If >1/8th of the imaged area is covered with dust or particles, the area is rejected for counting and another area is chosen. The workplace studies that follow this method quantified no or few CNTs (Bello *et al.*, 2009; Lee *et al.*, 2010). Most airborne CNTs do not have these typical fibre dimensions due to agglomeration (Schulte *et al.*, 2012). Therefore, we decided to not apply the WHO standard fibre counting criteria and instead we counted every CNT-containing particle regardless of length. Furthermore, it is not clarified what will happen with the agglomerated CNTs that are deposited in the surfactant lining fluid in the lungs. Workplace exposure Since the use of CNTs is increasing and is predicted to do so even more strongly in the future, occupational exposure to CNTs can occur during the whole life cycle: production, purification, functionalization, incorporation in different materials/products, use, repair, disposal, and end of life. Both the occupational exposure in terms of number of exposed workers and airborne concentrations of CNTs may increase if market expands and goes from small-scale production to mass production. Exposure through inhalation has been identified to be the dominating exposure route and potentially entailing the highest risk (Ma-Hock *et al.*, 2009; Pauluhn 2010; Gustavsson *et al.*, 2011; Porter *et al.*, 2013; Hedmer *et al.*, 2013). Thus, airborne exposures of CNTs need to be quantified and controlled, especially in open and manual handling of CNT powder. Up to now, a limited number of studies have been carried out on workplace exposure to CNTs during production (Maynard *et al.*, 2004; Bello *et al.*, 2008; Han *et al.*, 2008; Lee *et al.*, 2010; Dahm *et al.*, 2012) and even fewer during specific steps in laboratory work such as purification and functionalization (Dahm *et al.*, 2012). Moreover, there are also very limited exposure data on machining of CNT composites

(Bello *et al.*, 2009, 2010). To our knowledge, to date, no exposure data for arc-discharge-produced CNTs exist. Thus, the exposure data for airborne CNTs are still limited. In some studies, personal exposure measurements were performed during specific work tasks, e.g. during CVD production of CNTs, harvesting of CNTs, or weighing of CNT powder, and the sampling times were therefore short (Maynard *et al.*, 2004; Bello *et al.*, 2008; Dahm *et al.*, 2012).

Exposure limits

Today, no consensus occupational exposure limits for CNTs exist. The British Standards Institute (BSI) and the Institute for Occupational Safety and Health of the German Social Accident Insurance (IFA) have proposed benchmark exposure limits for fibrous nanomaterials with high aspect ratios (>3:1 and length >5 μm) set at 0.01 fibre cm^{-3} (BSI, 2007; IFA, 2009). In Japan, a mass-based occupational exposure limit of 30 μg m^{-3} was proposed by the Japanese New Energy and Industrial Technology Department Organization (Nakanishi, 2011). The National Institute for Occupational Safety and Health (NIOSH, 2013) has recently proposed a recommended exposure limit for CNTs based on EC of 1 μg C m^{-3} as a respirable mass 8-hr-time-weighted average (TWA-8) concentration. EC is typically measured with a thermal–optical method to divide the amount of carbonaceous material in a sample into organic carbon and EC. During the EC analysis, a temperature program is used, where the carbonaceous material is oxidized in several temperature steps in the presence of a controlled amount of oxygen (e.g. 2% O_2). The amount of EC oxidized at each temperature step is then added together and reported as EC (Birch and Cary, 1996). According to Ono-Ogasawara and Myojo (2013), MWCNTs are mainly oxidized at temperatures >700°C. They also suggested that EC in the two highest temperature classes (700 and 920°C) in their study can be used as qualitative indices of MWCNTs. Furthermore, if the MWCNTs have diameters >20 nm, they were mainly measured in the highest temperature class (920°C). So far, only one study has used EC (inhalable fraction) as an exposure metric for CNTs during personal exposure measurements in production of CNTs (with CVD; Dahm *et al.*, 2012). However, the recommended exposure limit for EC proposed by NIOSH is based on the respirable mass (NIOSH, 2013). No exposure data based on single oxidation temperature classes are available today. In summary, very little information is available for occupational exposure to CNTs, and exposure and emission data from production of CNTs with the arc discharge technique are still missing.

Aim

The objective of this study was to quantify the occupational exposures and emissions to CNTs with a mean length <5 μm and therefore, personal exposure measurements in the breathing zone of workers as well as emission measurements near the expected emission source were performed during production, purification, and functionalization of arc-discharge-produced MWCNTs. Respirable fractions of dust, EC, and number concentrations of CNT-containing particles were measured to obtain multiple exposure metrics for the CNT exposure. An evaluation of the used exposure metrics was also performed by studying the correlations between the investigated metrics.

Methods

MWCNT producer

In this study, we had the opportunity to investigate occupational exposures and emissions of one of the few small-scale facilities producing MWCNTs using the arc discharge method. Also, other carbonaceous nanoparticles such as cones and discs were occasionally produced by the company. In the company, three workers were involved in the production, purification, and functionalization work of MWCNTs. Schematic drawings of the production laboratory, sieving laboratory, and purification laboratory can be seen in Fig. 1. A description of the production methods and the work tasks in the production laboratory, sieving laboratory, and purification laboratory is given below.

Production

The production of MWCNTs took place in the production laboratory and sieving laboratory. The company had an arc discharge reactor for the MWCNT production. The arc discharge method is based on application of a high-voltage field over two rods composed of high-purity graphite. The rods serve as electrodes, an anode and a cathode, and a stable arc discharge is formed between them. The MWCNTs grow on the cathode while the anode is consumed. With this production method, no metal catalysts are required and the metal impurities can therefore be very low. However, non-CNT-containing impurities (e.g. graphite and soot) are produced by this method, so purification steps are challenge when scaling up the production. According to the manufacturer, the produced MWCNTs consisted of 55 wt% CNTs and 45 wt% graphite nanoparticles and other graphitic structures. The produced MWCNTs had diameters between 2 and 50 nm and a typical length of >2 μm according to the producer. According to scanning electron microscopy (SEM) analysis on bulk material obtained from

the company during the sampling campaign, the mean length of the individual MWCNTs was 1.7 μm with a distribution ranging from 0.3 to 6.1 μm. Compared with the critical dimensions of fibres, the majority of produced MWCNTs in the studied company had a length <5 μm. The production included the following work tasks: synthesizing of MWCNTs with the enclosed arc discharge reactor, opening of reactor, and collection of reacted graphite deposit (No. 3 in Fig. 1), dry cutting of reacted graphite deposit with a band saw (No. 1 in Fig. 1), manual harvesting of produced MWCNTs (No. 2 in Fig. 1), mechanical work-up, sieving, weighing, pouring, and packaging (No. 5 in Fig. 1), lathe machining of graphite rods for the reactor (No. 6 in Fig. 1), and reactor clean out with compressed air and a vacuum cleaner with high efficiency particulate absorption (HEPA) filter (No. 4 in Fig. 1). Worker A was responsible for the above-described work tasks of which several of these included open handling of MWCNT powder.

Purification and functionalization

In the purification laboratory, the produced MWCNTs were purified to remove carbonaceous structures, e.g. graphite and soot. According to the company, the purified MWCNTs consisted of 80 wt% CNTs and 20 wt% graphite nanoparticles and other graphitic structures. Functionalization of purified MWCNTs also took place there. Workers B and C were responsible for the work tasks performed in the purification laboratory. Most work tasks were defined as laboratory work and were performed inside the two fume hoods (No. 7–11 in Fig. 1). Work tasks performed inside the fume hoods were, for example pouring of MWCNT powder, dispersion of MWCNT powder, filtration of MWCNT dispersion, grinding of CNTs (No. 11 in Fig. 1). The workers poured and weighed MWCNT powder, packed MWCNT powder into containers, and dried MWCNT powder in a furnace and these work tasks were performed outside the fume hoods.

Workplace monitoring
Strategy for air sampling
The personal exposure measurements and emission measurements of workplace air were performed in the facility during two consecutive work days, and an overview of the sampling strategy can be seen in Table 1. Three different exposure metrics (respirable fractions of mass concentration, EC, and number concentration of CNT-containing particles) were used.

Personal exposure measurements

Time-integrated sampling with filter-based methods was performed on Workers A–C. The respirable fraction of dust samples (50% cut-off at an aerodynamic equivalent particle diameter of 4 μm), EC samples, and SEM samples were collected in the breathing zone of the workers. Also, sampling with direct-reading personal aerosol monitors was carried out to be able to assess respirable mass concentrations and particle number concentrations. The direct-reading instruments and the EC sampling were used at one department per day (Table 1). Respiratory protection was used by Worker A in the production laboratory and sieving laboratory. Thus, the sampling was performed outside the half-face respirator equipped with particulate filter of Grade P3.

Emission measurements

Emission measurements of released MWCNTs at the specific work tasks previously described during production, purification, and functionalization work were conducted in the emission zone. The inlet of the sampling line of stainless steel was placed as close as possible to the expected emission source, typically at a few centimetre distance. The sampling line had a diameter of 6 mm and a total length of 1 m. The sampling line was split into three lines and these were connected to three filter cassettes for sampling of respirable dust, EC, and SEM, respectively. This we refer to as the emission station, which was moved for each work task.

Respirable dust samples

Personal samples and static emission samples of respirable dust were collected using cyclones (BGI4L, BGI Inc., Waltham, MA, USA) on 37-mm cellulose fibre filters with a pore size of 0.45 μm (SKC Inc., Eighty Four, PA, USA) mounted in plastic three-piece filter cassettes. An Escort ELF pump (MSA, Pittsburgh, PA, USA) set at 2.2 l min^{-1} provided sample flow. The air flow rate was before, during, and after the sampling regularly checked with a primary calibrator (TSI Model 4199, TSI Inc., Shoreview, MN, USA). The filters were preweighed and postweighed using an analytical balance (XP105 DeltaRange Excellence Plus, Mettler Toledo, Greifensee, Switzerland). The balance was located in a temperature- and humidity-controlled room. A 24-h equilibration period was applied before weighting. The limit of detection (LOD) of the gravimetric analysis was determined to 50 μg collected material per sample.

EC samples

Personal samples and static emission samples of respirable EC were collected according to the same procedure as described for respirable dust samples. However, preheated (at 800°C) 37-mm quartz filters (SKC Inc., Eighty Four, PA, USA) were used. Flow control and checks were carried out in the same way as described for respirable dust samples. Bulk samples of purified MWCNTs and the filters from the air sampling were analysed according to the NIOSH NMAM 5040 protocol with thermal–optical analysis (DRI Model 2001 OC/EC Carbon Analyzer from Atmoslytic Inc., Calabasas, CA, USA) (Birch and Cary, 1996). The following temperature steps were used: 680°C (EC1), 750°C (EC2), and 900°C (EC3). However, the method was modified with a prolonged oxidation time, 150 s instead of 30 s, at the highest reached temperature, 900°C, to strive for complete oxidation of all carbonaceous compounds. The carbon mass detected in each temperature step was denoted EC1–EC3 as described above. Typical thermograms for the bulk material and a filter sample are shown in Supplementary Figure S1 (available at *Annals of Occupational Hygiene* online).

Since the emitted MWCNTs mainly had diameters >20 nm and thereby could be expected to be mainly measured as EC3, we also chose to report the measured EC3 values (900°C). For the bulk samples, on average, 57% of the EC was measured as part of EC3. The LOD for EC was determined to be 0.06 µg C sample^{-1} (about 0.08 µg C m^{-3} for a 6-h sample).

Electron microscopy samples

Personal samples and static emission samples of respirable dust were collected on 37-mm non-fibrous polycarbonate membrane filters with a pore size of 0.4 µm (SKC Inc., Eighty Four, PA, USA) mounted in plastic three-piece filter cassettes. The same sampling procedure as described above was used. Analysis was performed with SEM (FEI Nova Nanolab 600, FEI Company, Hillsboro, OR, USA). With the used SEM method, a piece corresponding to approximately a quarter of the polycarbonate filter was mounted on a silicon wafer and coated with platinum. The visible LOD was >35 nm (1 pixel) but during the SEM analysis, it was possible to see particles with sizes >10 nm if a higher magnification was used, and this will be discussed further on. The SEM analysis was done at images with a standard resolution of 3584×3301 pixels. At least five but up to 29 areas per filter were randomly chosen for image acquisition. Each imaged area was 9050 µm^2. The standard deviation of the derived concentrations of CNT-containing particles varied between ±10 and ±50% for the reported samples. All CNT-containing particles imaged by the SEM were manually counted and defined as any particle with visible CNT content. In comparison with SEM analysis of

asbestos according to the WHO method, we counted both fibres that fulfilled the asbestos counting criteria (length of >5 μm, width <3 μm, and length:width ratio >3:1) and those which did not (WHO, 1997). If several fibres were attached to a particle, it was counted as one CNT-containing particle. This differs to how asbestos is counted; if the asbestos fibre is attached to a particle, it is then assessed as if the particle does not exist and is counted if the visible part of the fibre meet the above definition (OH Learning, 2010). Based on the sampled air volume, the number of CNT-containing particle cm^{-3} could be calculated. Analysis of blank filters as well as of field blanks showed that the used polycarbonate filters did not contribute with matrix particles/fibres. The calculation of the 95% confidence limits was based on ISO 10312 (1995). The elemental composition of the CNTs was analysed using a transmission electron microscopy with energy dispersive X-ray analyser (TEM/EDX; Jeol 3000F, Tokyo, Japan, and SDD XEDS, Oxford Instruments, Oxfordshire, UK).

Direct-reading instruments

Two direct-reading instruments commonly used in occupational hygiene were used for personal monitoring in the workers' breathing zone. A Nanotracer (Philips Aerasense, Eindhoven, The Netherlands) that was based on detection of electrical charges carried by particles, which have passed a unipolar corona charger in the device was used to monitor particle number concentrations. From this, the particle number concentration (10–300 nm) and mean particle (mobility) diameters were derived. The sampling flow rate was 0.24 l min^{-1}. A 0.51-m tubing was applied to be able to place the inlet of the Nanotracer in the breathing zone. Data were logged every 16 s. Additionally, a Photometer (model SidePak Model AM510, TSI Inc., Shoreview, MN, USA) equipped with a 0.91-m tubing connected to a 10-mm Dorr-Oliver cyclone (50% cutoff of 4 μm) was used to assess the respirable mass concentration by illuminating a particle containing space and detect the light scattered against the particles. The SidePak used in the study was calibrated by the manufacturer using the respirable size fraction of Arizona test dust. Thus, the mass concentrations from measurements of non-spherical particles with unknown refractory index should be considered as indicative only. The air flow rate was set to 1.7 l min^{-1} with a primary calibrator (Model 4199, TSI Inc., Shoreview, MN, USA) and the instrument was set to log data every 1 s. Moreover, a condensation particle counter (Model CPC 3022, TSI Inc., Shoreview, MN, USA) also simultaneously monitored the particle number concentration in the size range 0.01 and >3 μm in the emission zone (<10 cm from the source).

Statistics

The correlation between the different exposure metrics was evaluated. The correlations were described with the Pearson correlation coefficient, r. Values below the LOD were given the value of half the LOD. The correlation between direct-reading instruments in the breathing zone (Nanotracer) and in the emission zone (CPC) was investigated. The sampling line residence time, which is not the same for the two instruments, was corrected for, and averages were calculated for the CPC data (data sampled every 1 s) to match the sampling time of the Nanotracer (every 16 s). Pearson correlation coefficients between the two data sets were calculated on log-transformed data as:

$$r = \frac{1}{n-1} \sum_{i=1}^{n} \left(\frac{X_i - \bar{X}}{s_X} \right) \left(\frac{Y_i - \bar{Y}}{s_Y} \right)$$

where X and Y are the data set from the Nanotracer and CPC, respectively, n is the number of data points in one set, $\bar{X}$ and $\bar{Y}$ are the sample means, and s_X and s_Y are the sample standard deviations.

Results

Personal exposure measurements

Personal exposure measurements during production and laboratory work with MWCNTs were conducted, and the mean sampling time was 5.7 h (range 5.2–6.7 h). The measured concentrations of respirable dust, respirable EC, and number concentrations of CNT-containing particles (respirable fractions) are presented in Table 2. Arithmetic means of the respirable dust concentrations during the production of MWCNTs were 86 µg m^{-3} (range 93 and 79 µg m^{-3}) and <73 µg m^{-3} during purification and functionalization work, respectively. Respirable EC was measured during one of the two sampling days and EC was only quantified during work in the production and sieving laboratory (7.4 µg C m^{-3}). The personal exposure measurements showed that both workers in the production laboratory and sieving laboratory as well as in the purification laboratory were exposed to MWCNTs. The worker in production was exposed to the highest number concentration of CNT containing particles, in mean 1.3 cm^{-3} CNT-containing particles (range 0.6–2.0). The workers in the purification laboratory work had a mean exposure of 0.07 cm^{-3} CNT-containing particles (range 0.04–0.1). Thus, the MWCNT exposure during production was about an order of magnitude higher in comparison with the laboratory work. In Fig. 2, two types of common airborne CNT-containing particles are shown. The highest personal respirable dust concentration (93 µg m^{-3})

was not measured during the same day as the highest number concentration of CNT-containing particles. Thus, emission sources releasing other types of particles than CNTs contribute with particle mass. SEM analysis of the polycarbonate filters showed that airborne particles other than CNT-containing ones dominated by number in the respirable size range. The sampled particles consisted of pure soot agglomerates, raw production materials (graphite), particles from the sieve (containing CNTs), and a large amount of small particles (<0.3 μm) that may be partly infiltrated from ambient air. Unfortunately, no EC sample was collected parallel to this SEM sample. EDX analysis of the CNT material in this study showed that the material did not contained any transition metal catalysts. A summary of the respirable mass concentrations, particle number concentration, and mean particle size obtained from the personal exposure measurements with the direct-reading instruments can be seen in Table 3. A time series from the measurement of assessed respirable mass concentration in the production laboratory is shown in Fig. 3. The direct-reading instrument (Sidepak) showed the highest peak exposure during the reactor clean out Part I. However, the filter-based SEM sample collected during this specific work task showed no presence of CNT-containing particles, indicating that the emitted particles from the clean out consisted of other carbonaceous particles, such as soot and graphite. The direct-reading instrument used for personal exposure measurements of particle number concentration (Nanotracer) measured the highest peak concentration during lathe machining of graphite rods, up to 34 000 particles cm^{-3} (Fig. 4a). The mean diameter of the particles released during lathe machining was small, ~30–40 nm. Sampling in the purification laboratory during Day 2 showed a much higher background concentration, on average 11 000 particles cm^{-3} a.m., compared with the average concentrations between 1800 and 2500 particles cm^{-3} in the production laboratory and sieving laboratory (Table 3). It is possible that thermal sources such as a furnace that was continuously forming non-CNT-containing particles from, for example heating of insulation etc. contributes to the high background in the purification laboratory. The highest release of nanometre-sized particles in the purification laboratory was measured during weighing of MWCNTs followed by opening of the furnace (Fig. 4b). The arithmetic mean diameter of these particles was ~20–30 nm. The measured particle number concentration from the personal exposure sampling (Nanotracer) was compared with emission data from a stationary CPC in the emission zone and the Pearson correlation coefficient was $r = 0.30$ for the measurements performed in the production laboratory and sieving laboratory (Fig. 4a). The corresponding value in the purification laboratory was 0.84 (Fig. 4b). The correlation of the real-time data from the Nanotracer (breathing zone) and CPC (emission zone) can be seen in

Fig. 4c. With increased particle number concentrations, a stronger correlation between the instruments can be seen. A personal instrument (Nanotracer) could be used if the expected particle number concentrations in the work environment are not too low. But particle number concentrations measured by the CPC in the emission zone could also work as a proxy for the personal exposure.

Emission measurements

Emission measurements were performed at 12 different work tasks during production, purification, and functionalization work in the facility (Table 4). The sampling time ranged between 4 and 70 min. By sampling close to the emission source during different work tasks, important information of the emitted concentrations of each work task was obtained. In only one out of 12 emission samples from the emission zone could the respirable dust concentration be quantified above LOD. This was during a 4-min clean out of the arc discharge reactor with compressed air and vacuum cleaning (use of a vacuum cleaner equipped with HEPA filter) and a dust concentration of 6800 μg m^{-3} was measured. Also, the highest concentration of EC was measured during the clean out of the reactor. However, the SEM analysis showed no emission of CNT-containing particles during this work task. Most likely, the emitted particles consisted of other carbonaceous materials such as soot and amorphous carbon. The EC concentration measured at different work tasks ranged between 0.05 and 550 μg C m^{-3}. The number concentration of CNT-containing particles released during production ranged between 0 and 11 CNT-containing particles cm^{-3}. The highest emission concentrations of CNT-containing particles occurred during sieving, mechanical workup, weighing, pouring, and packaging. These were the work steps where MWCNT powder was openly handled. For example, MWCNT powder was poured from a container into the sieve or from a beaker into a small glass container with plastic lid. On the contrary only, a low concentration of EC and EC3 could be measured during the work tasks in the purification laboratory (0.05 μg C m^{-3}). The correlation between respirable EC and number concentration of CNT-containing particles had a Pearson correlation coefficient of 0.088 (Fig. 5). The correlation between respirable EC3 and number concentration of CNT-containing particles had a Pearson correlation coefficient of 0.33 (Fig. 6).

Discussion

This study investigated the feasibility and relative performance of three exposure metrics for exposure and emission to short CNTs (<5 μm) during arc discharge production, purification,

and functionalization of MWCNTs. Parallel measurements of respirable dust, respirable EC, and number concentration of CNTcontaining particles were performed during both personal exposure measurements and emission measurements for each work task. Thus, we have valuable exposure data and can thereby assess the occupational exposure as well as evaluate the used exposure metrics. Based on the exposure data in this study, we consider the exposure metric number concentration of CNT-containing particles to be the best marker for occupational exposure to CNTs since it was the only exposure metric that was selective and could specifically quantify the exposure to CNTs. Analysis of CNT-containing particles with SEM To date, there is no standardized method for sampling of airborne CNT-containing particles. In this study, we collected MWCNTs on polycarbonate membrane filters in combination with SEM analysis, and particles with a size >35 nm were visible and thus counted. Similar methods were utilized by Ogura *et al.* (2011) and Takaya *et al.* (2012). But other studies have instead used methods developed for asbestos for sampling of CNTs, where CNTs were collected on cellulose fibre filters in combination with TEM analysis (Bello *et al.*, 2008, 2009, 2010; Han *et al.*, 2008; Lee *et al.*, 2010; Dahm *et al.*, 2012). However, it is not only the sampling methods that contribute to difficulties to quantify CNT exposures, but it is also the absence of counting rules for CNTs at the electron microscopy analysis. So far, no standardized electron microscopy–based method for counting CNTs has been developed. Thus, to date, it is not clear how CNTs on filter samples should be counted (Brouwer *et al.*, 2012; Schulte *et al.*, 2012). A harmonization of the counting of CNTs in electron microscopy analysis will make it possible to compare exposure data for different workplace measurements. According to the standard fibre counting criteria by the WHO (1986, 1997), a particle is defined as a fibre if it has a length of >5 µm, a width <3 µm, and >3:1 aspect ratio. These criteria are applied, for example in asbestos exposure quantification. Airborne CNTs appear to be heterogeneous in their shapes and structures as well as they more often are agglomerated compared with asbestos. Since CNTs often not have the typical fibre dimensions, the standard fibre counting criteria cannot be applied (Schulte *et al.*, 2012). Our collected CNT-containing particles had often not the fibre dimensions and the length of the particles was commonly <5 µm. If we had followed the standard fibre counting criteria by WHO during the CNT counting, very few CNTs would then have been counted. Thus, the standard fibre counting criteria could not be followed, and instead, we chose to count every CNT-containing particle that was imaged with SEM. This is in accordance with how Dahm *et al.* (2012) counted CNTs who also found that their airborne CNT-containing particles were heterogeneous in their shapes and structures ranging from single CNTs to large

agglomerates. Most of the counted CNT-containing particles in our study did not consist of individual tubes (79%). The CNTs were instead entangled or embedded in impurities and were thus larger in size compared with the individual tubes (Fig. 2b) but were nevertheless in the respirable size range. Thus, the detected airborne CNT-containing particles could be classified into different particle types. There is very limited knowledge of how the different types of CNT-containing particles will act after deposition in the lungs. For example, de-agglomeration of fibre bundles or fibres and carrier particles may take place (Wong *et al.*, 2009). Thus, we find it is important to report all detected airborne CNT-containing particles. With the SEM method, distinction was made between CNT structures and other types of particles, e.g. impurities and background particles. One limitation with SEM analysis is a potential high particle load on the filter if the exposure concentration is high when personal exposure measurements are conducted over extended time (for example full shift measurements). Overlap of deposited particles complicates the manual counting of CNT-containing particles with SEM. Furthermore, it was not straight forward to automatize the counting of particles with SEM due to interference of the pores in the membrane filters, and thereby the SEM analysis was time consuming and expensive. In one study, CNT clusters > ~3 and 0.3 μm were counted at the 1000 and 10 000 magnification, respectively (Ogura *et al.*, 2011). With our SEM method, we could identify and measure individual and small bundles of CNTs down to the nanometre size range (Fig. 2a,b). We also noted that particles with diameters <35 nm were present in our samples. During the SEM analysis, it was possible to use higher magnification and thus, smaller particles down to ~10 nm could be identified and it could be investigated if these particles contained CNTs or not. However, this was only performed on a small number of particles with diameters <35 nm. Toxicological effects of CNTs have mainly been discussed for CNTs with a length 10–20 μm due to frustrated phagocytosis (Brown *et al.*, 2007; Donaldson *et al.*, 2010; Murphy *et al.*, 2012). However, CNTs with <5 μm have also shown to have effects *in vivo* (Pauluhn, 2010). It is not clarified how small bundles of CNTs or CNT-containing particles as shown in Fig. 2b will act when deposited in the surfactant lining fluid in the lungs. For example, the worst-case scenario for shorter CNTs (<5 μm) would be if the CNTs attached to particles dissolved and detached from the particles and became free individual CNTs inside cells in the respiratory tract. Shorter CNTs will not behave like longer CNTs (>14 μm) *in vivo* and cause frustrated phagocytosis. Shorter CNTs have in animal studies shown to cause adverse effects such as pulmonary inflammation and fibrosis (Mercer *et al.*, 2010, 2011; Pauluhn, 2010; Porter *et al.*, 2013). Based on the fact that longer CNTs could cause frustrated phagocytosis, the

nanotechnology industry may design safer materials by using shorter CNTs to avoid critical human effects, and the production of CNTs might then change towards production of shorter CNTs. Thus, it is very important to know how to best measure occupational exposures and emissions of shorter CNTs.

Respirable dust

From the exposure data in Tables 2 and 4, it is obvious that respirable dust is not suitable as an exposure metric for CNT exposure. For the majority of the measurements of respirable dust, the mass concentrations were below the detection limit, while SEM analysis detected a significant number of airborne CNT-containing particles. Similar results have also been reported previously (Johnson *et al.*, 2010; Methner *et al.*, 2012). Also the opposite result was obtained when the respirable dust measurement indicated a high mass concentration during reactor clean out Part II, and the SEM analysis showed no exposure to airborne CNT-containing particles. Thus, the exposure metric respirable dust had low sensitivity and specificity to measure and quantify exposures to CNTs. With this method, no distinction could be made between CNT structures and other types of particles, e.g. impurities and background particles.

Elemental carbon

EC is a selective exposure metric for carbonaceous compounds including CNTs, amorphous carbon, graphite, and soot, but it does not specifically measure CNT exposure. NIOSH has recommended that occupational exposures to all types of CNTs should be monitored by a mass-based airborne concentration until additional data are available to determine if other exposure metrics or techniques would be more effective in protecting workers health (NIOSH, 2010). Furthermore, exposure measurements of CNT exposure should according to NIOSH include measurements of EC and a recommended exposure limit of 1 μg m^{-3} has been proposed (NIOSH, 2013). From the parallel measurements in this study, it was shown that EC does not correlate with the number concentration of CNT-containing particles (Fig. 5). The correlation between EC3 and number concentration of CNT-containing particles was higher but still low. A correlation between EC and number concentration of CNT structures counted by TEM was shown by Dahm *et al.* (2012). The correlation coefficient was reported to be 0.44, which corresponds to a R2 of 0.19. This means that only 19% of the variability in the CNT exposure could be explained by the EC measurements. Also, some of the EC values in that study showed no or very low mass concentrations, while a significant number of CNT

structures were counted by TEM analysis, thus indicating false negative values and that EC had low sensitivity for CNT exposures. Furthermore, from the parallel personal exposure measurements of the workers in the purification laboratory, EC was not detected while a TWA of 0.04–0.1 CNT-containing particles cm^{-3} could be measured. Thus, it was clearly shown that also purification laboratory work with CNTs causes occupational exposure. We considered the exposure metric EC to be both too insensitive and unspecific to be used as a generic exposure metric for CNT exposures during arc discharge production. SEM analysis is time consuming, expensive, and not at all as commercially available as EC analysis, but it is very important that the analytical method used to quantify exposures to CNTs has high selectivity and sensitivity to CNTs. In this study, the emission measurements were performed for work tasks handling carbonaceous material with different CNT content. If measurements were performed repeatedly for the same work task, it would probably give high correlation between CNT and EC given that the same type of CNT material was used. With material dependence, EC could be used as a proxy for CNTs for the specific work task if the correlation is known. However, the correlation between EC or EC3 and CNTs would differ significantly between different tasks due to variations in the CNT matrix composition. This assumption is based on a specific CNT material's ability to agglomerate as well as the purity of the material, and the correlation is expected to be better between the same manufacturer of MWCNT as opposed to a different manufacturer of MWCNT. Finally, it should be pointed out that manufacturing of CNTs with the arc discharge method may represent a worst case scenario as large amounts of non-CNT carbonaceous by-products may be emitted, a substantial fraction of which is classified as EC with the thermal–optical method. According to Ono-Ogasawara and Myojo (2013), EC3 (carbon mass oxidized at 920°C) could be a more selective exposure metric to CNT exposure than EC since the MWCNTs thereby could be separated from other carbonaceous substances with smaller geometrical dimensions that oxidize at lower temperatures in the EC method. From the parallel samples collected during reactor clean out Part II, no CNT structures were detected but the highest EC concentration was measured indicating release of other carbonaceous compounds than CNTs. EC analysis showed that the EC3 fraction of total EC was only 35% for this task, while it was up to 96% of total EC for work tasks where the emitted concentrations of CNTs were high. This indicates that oxidation of other carbonaceous compounds than CNTs preferentially occurs at lower temperatures. The correlation between EC3 and the number concentration of CNT-containing particles was low and only 6% of the

variability in CNT exposure could be explained by the EC3 measure. Thus, our limited data do to some extent support the results presented by Ono-Ogasawara and Myojo (2013), but the explained part of the variability by the EC3 measurement is still very small.

The EC method does not distinguish between CNT structures and other types of carbonaceous particles, e.g. impurities and background particles. One limitation with the EC measurements was that we used 37-mm filters instead of 25-mm filters, which caused a slightly higher LOD. Another limitation in the EC sampling in our study was the lack of sampling outdoors to be able to assess the extent of anthropogenic sources of infiltrated EC contamination inside the facility. However, in the nearby rural background site 65 km to the east of the location of the company, the 1-week average concentration of EC was $0.32 \pm 0.03 \ \mu g \ C \ m^{-3}$ at the time of the exposure measurements. Further, three out of the eight analysed EC samples were below the detection limit; this suggests that infiltrated EC from ambient air was only very weakly affecting our results. Another more general problem with EC analysis is that there are several different EC protocols available (with large variations in oxidation temperatures used, oxidation time at each step, different strategies to correct for positive or negative artefacts from organic carbon etc.). So, there is a need for a standardized and specific 'CNT protocol' for EC analysis of CNT material to be set up as soon as possible. A harmonization of the EC analysis of CNTs will make it possible to compare exposure data for different workplace measurements. Based on our data, it is clear that the CNT-specific protocol needs to include temperatures with prolonged oxidation time up to at least 900°C, as CNTs may require higher oxidation temperatures compared with most other carbonaceous materials.

Occupational exposure to CNTs

The personal exposure measurements were performed during both production and laboratory work. The highest exposure was measured during production work with sieving, mechanical work-up, pouring, weighing, and packaging of CNT powder in the sieving laboratory; unfortunately, we could not with the used sampling strategy estimate the different emissions for these different tasks because they were integrated with each other and the sampling time would otherwise have been too short. However, Worker A in the production laboratory and sieving laboratory used a negative-pressure half-face respirator with particulate filter of Class P3 at the different work tasks, but Worker A did not use the half-face respirator between the work tasks. For practical reasons, the personal exposure measurements were performed outside the half-face respirator. However, Workers B and C in the purification laboratory

were also exposed to CNTs and they did not use any respiratory personal protective equipment (PPE). Their exposures were 6–50 times lower in comparison with the worker in production. The proposed benchmark exposure limits for fibrous nanomaterials with high aspect ratios (>3:1 and length >5 µm) of 0.01 fibre cm^{-3} (BSI, 2007; IFA, 2009) cannot be used for CNT exposures as described here due to the heterogeneous structures of CNTs, their agglomeration and CNTs not having the typical fibre dimensions (aspect ratio). Thus, it is difficult to compare our number concentrations from the SEM analysis with other studies due to differences in how the CNTs were counted. For example, two previous studies followed the WHO counting criteria for asbestos in combination with analysis with phase contrast microscopy (NIOSH Method 7400, 1994) with a visible LOD >250 nm and reported no or few CNT fibres (Bello *et al.*, 2009; Lee *et al.*, 2010). In the study by Dahm *et al.* (2012), a method for asbestos was used for quantification (NIOSH Method 7402) but the method was modified and the steps required for asbestos identification were eliminated. The personal exposure measurements ($N = 7$) in that study performed at different work tasks during CNT production and laboratory work, ranged from 0.003 to 0.4 CNT structures cm^{-3} and ND-1.6 CNT structures cm^{-3}, respectively (Dahm *et al.*, 2012). Furthermore, one of our two personal exposure measurements exceeded the proposed recommended exposure limit of EC (1 µg C m^{-3}). Dahm *et al.* (2012) also measured levels of EC (0.68–5.25 µg C m^{-3}) at different work tasks during CNT production exceeding the recommended exposure limit for EC. Thus, the measured number and EC concentrations in our study are in the same order as reported by Dahm *et al.* (2012). The exposure sources differ in the studies. We measured exposure to arc-discharge-produced MWCNTs while Dahm *et al.* (2012) measured exposure to both SWCNTs and MWCNTs mainly from the CVD method. Both types of production methods produce CNTs that can have a high content of carbonaceous impurities, 40–45% (Popov 2004; Köhler *et al.*, 2008). Thus, production of MWCNTs with arc discharge and CVD seems to cause occupational exposure within the same range, but of course, other parameters in the workplaces, e.g. protective measures also have influence on the exposure. During the arc discharge production in the studied facility, no metal catalysts were used. Thus, surrogates for CNT exposure based on metal content cannot be used in this case. Metal surrogates such as Fe and Ni have been reported for CNT production with CVD and laser ablation (Maynard *et al.*, 2004). In this study, the measured personal respirable dust concentrations were up to almost 100 µg m^{-3}. Thus, it is in the same concentration range as reported by Ma-Hock *et al.* (2009) to cause mild granulomatous inflammation in the lung and in lung-associated lymph nodes in rats. It is therefore possible that unprotected work during production could cause

similar adverse health effects to the worker. However, the properties of the CNT materials differ, for example in terms of tube length and purity, and as previously discussed, total dust is not at all a specific exposure metric for CNTs. In the fields of occupational hygiene, direct-reading instruments to measure, e.g. mass concentration or particle number concentration are often used to monitor exposure. This type of direct-reading instrument is often pre-calibrated against a specific type of particles by the manufacturer and thus, the measured concentrations should only be used as indicative. To the Nanotracer monitor, we applied 0.51-m tubing and the measured average particle sizes ranged between ~50 and 65 nm. We calculated the diffusion losses in the tubing with the used flow rate of 0.24 l min^{-1}, and for 50-nm-sized particles, 99.8% of the sampled particles reached the instrument and the corresponding value for 100-nm-sized particles was 99.9%. Thus, diffusion losses in the tubing during the samplings were very low. As long as the particles are not too small in size (e.g. <10 nm), the deposition in the tubing can be neglected in relation to the accuracy of the instrument (Asbach *et al.*, 2012). In this study, it was shown that the usefulness of the direct-reading instruments was limited because they were too unspecific to measure exposures to CNTs, which is in accordance with what Dahm *et al.* (2013) also reported. For CNT exposures, selective and sensitive methods must be used to quantify exposures. The results from more sophisticated stationary direct reading instruments and the comparison of size distributions determined by these devices (for example an Aerodynamic Particle Sizer) and the size distribution of both CNT containing and 'total' concentration of particles detected by SEM will be presented elsewhere. A comparison between personal sampling (Nanotracer) and sampling in the emission zone (CPC) of particle number concentrations showed a correlation in the purification laboratory although that the measurement points had different distance to the emission source ($r = 0.84$). The particle number concentration data from the two direct-reading approaches in the production laboratory and sieving laboratory did not correlate that well, which might be due to that the worker was more mobile in his work than the workers in the purification laboratory ($r = 0.30$). Clearly, a direct-reading instrument that shows a reasonable degree of specificity for CNTs would be highly desirable to use in the future, particularly in research oriented emission studies of CNTs. This would complement the SEM analysis that is per default offline and has limited time resolution. Highly time-resolved instruments give strongly superior possibilities both to identify sources and effectively mitigate emissions. Candidates to be investigated include filter-based direct-reading instruments such as Aethalometers or Particle Soot Absorption Photometers that measure black carbon based on the wavelength-dependent light-absorption properties and more

sophisticated direct-reading aerosol mass spectrometers (Onasch *et al.*, 2012, Nilsson *et al.*, 2013). It is noteworthy that some non-authority institutions have proposed mass-based occupational exposure limits for CNTs, for example NIOSH and Bayer, but up to now, no country has adopted occupational exposure limits for CNTs. This study gives support to the complexity authorities are facing when discussing occupational exposure limits for CNTs.

PPE and engineering controls

The used PPE and engineering controls in the facility can be seen in Table 4. The worker in the production laboratory and sieving laboratory used a half-face respirator with particulate filter of Grade P3 as PPE during the different work tasks. The workers in the purification laboratory did not use any respiratory protection at all. To protect the workers from dermal exposure to CNTs, protection gloves made of nitrile and laboratory coats were used. The handling of CNTs in the facility was open both during work in the production laboratory and sieving laboratory as well as in the purification laboratory. The open handling of CNT powder contributed to increased airborne exposure but also to dermal exposure due to surface contamination with dust on different surfaces in the workplace. For CNT exposures, the precautionary principle must be applied until the toxicological effects of CNT exposure have been evaluated. In practice, this means closed handling in combination with a high level of control measures and a high degree of use of PPE. Thus, the workers in the facility were assessed to have higher exposure than necessary due to lack in the PPE as well as in the engineering controls. Dry CNT powder should not be openly handled in the facility without any engineering controls, e.g. ventilated enclosures (Schulte *et al.*, 2012). During all open handling of CNTs in the facility, respiratory protection must be used. To protect the workers more efficiently, PPEs such as coveralls, hoods, and shoe protection were needed especially in the production laboratory to prevent dermal exposure and to inhibit the CNT dust to be spread in the workplace. Furthermore, the enough for controlling the CNT exposure. For example, the production laboratory was not located in a closed area since it was part of a larger room that was used for other purposes such as storing; see Fig. 1 for the layout of the facility. The production laboratory was connected via stairs to other rooms in the building without any airtight sluice. This means that airborne CNT-containing particles could be present in other rooms in the building and thereby cause exposure to other unprotected workers. Also, the office used by production workers was located next to the sieving

laboratory, and since the same shoes were used in both the production laboratory and sieving laboratory as in the office, there might be a high risk that the floor in the office was contaminated with CNT dust.

Conclusions

The occupational exposures as well as the emissions during specific work tasks, performed in a small-scale factory producing MWCNTs by arc discharge, have been quantified. The highest exposure to CNTs occurred during work with producing CNTs. The highest measured concentration in the emission zone, 11 CNT-containing particles cm^{-3}, was measured at open handling of CNT powder during work tasks as sieving, mechanical work-up, pouring, weighing, and packaging. To be able to quantify exposures and emissions of shorter as well as longer CNTs, a selective and sensitive method is needed. To date, only filter-based methods in combination with SEM/TEM analysis can be selective and sensitive enough. Furthermore, a standardized protocol for counting criteria of CNTs must be set up as soon as possible. A harmonization of the electron microscopy analysis will make it possible to compare exposure data for different workplace measurements.

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Fig 1. Schematic drawing of the facility. The numbers in grey circles correspond to activities in Table 4. The production laboratory and sieving laboratory were located on a different floor than the purification laboratory.
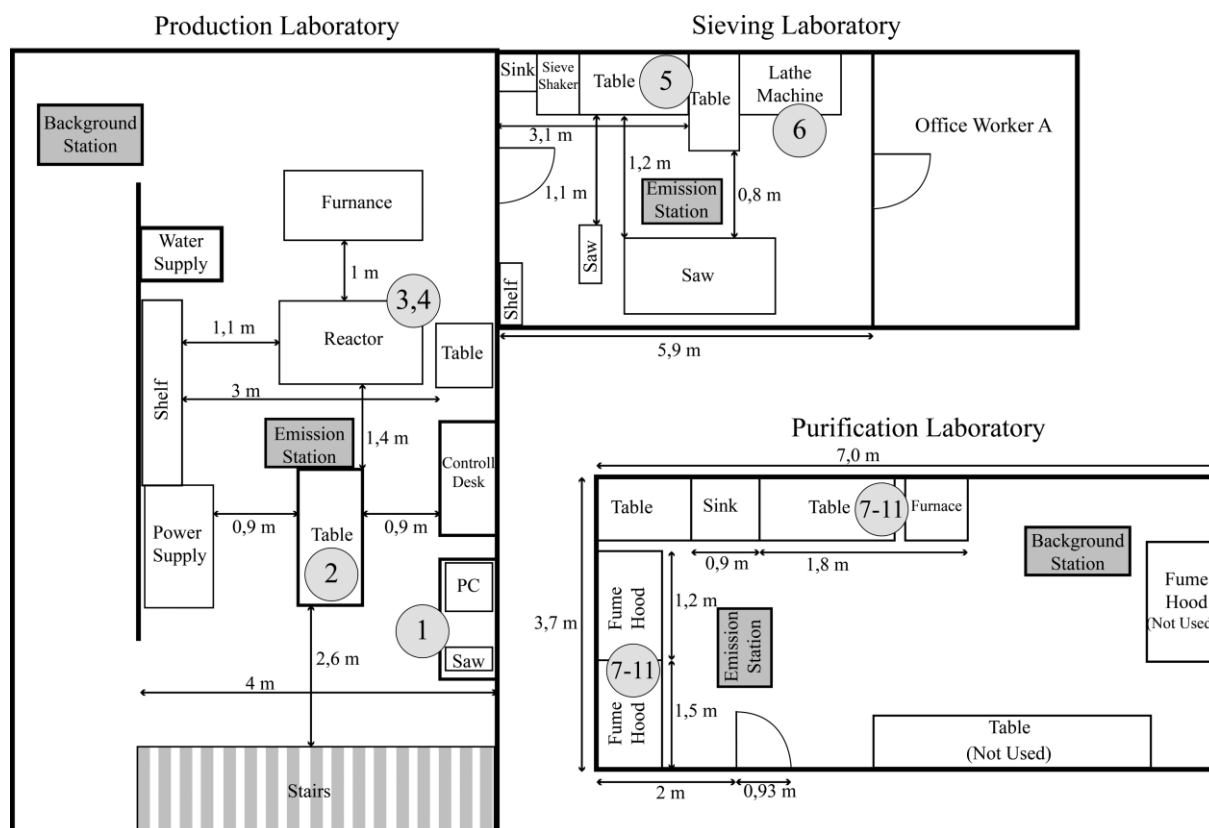
Fig 2. Two different types of airborne CNT-containing particles in the collected respirable dust fractions. (a) Individual CNTs were found in 21% of the counted particles. (b) The most frequent counted type of CNT-containing particles; large agglomerates (59%).
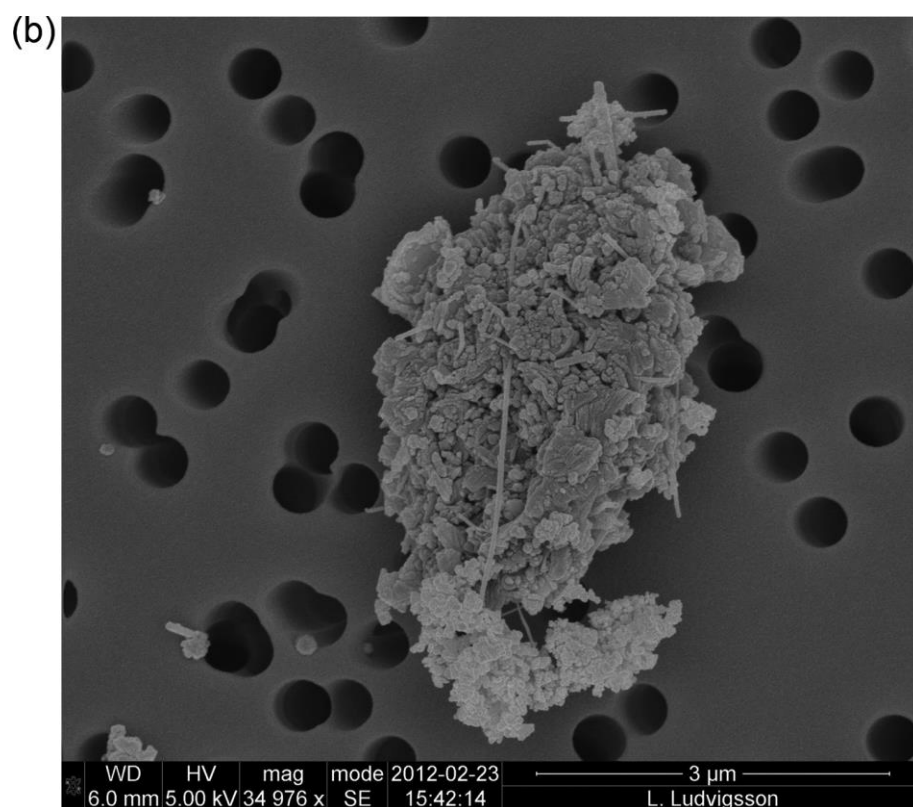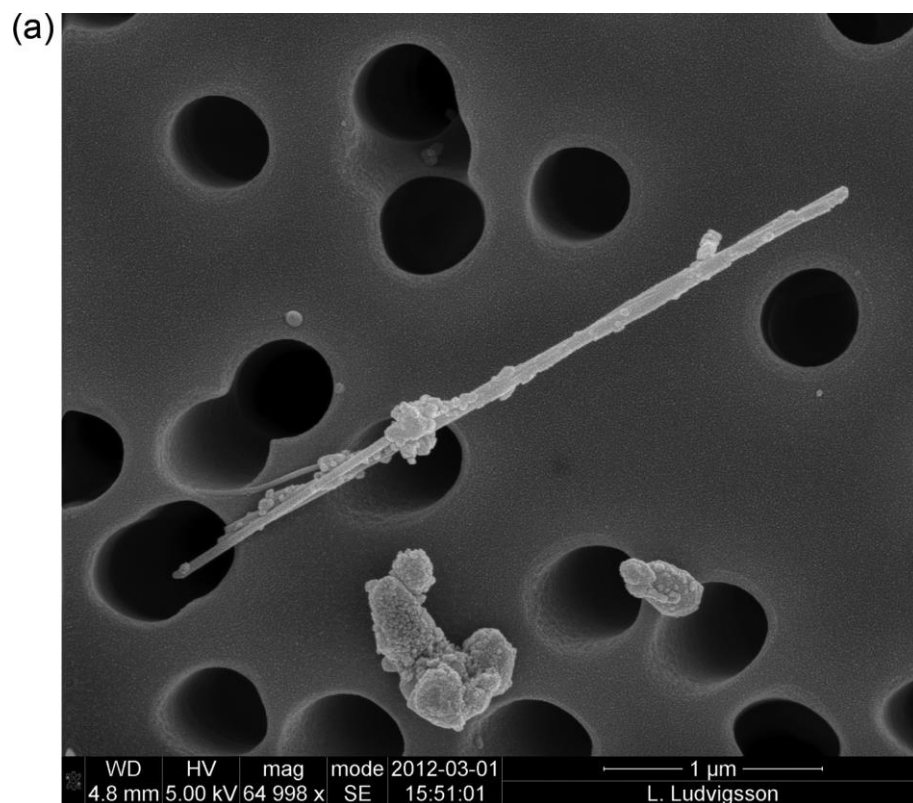
Fig. 3. Personal sampling of respirable dust with direct-reading instrument (Sidepak) on Worker A during production of MWCNTs.
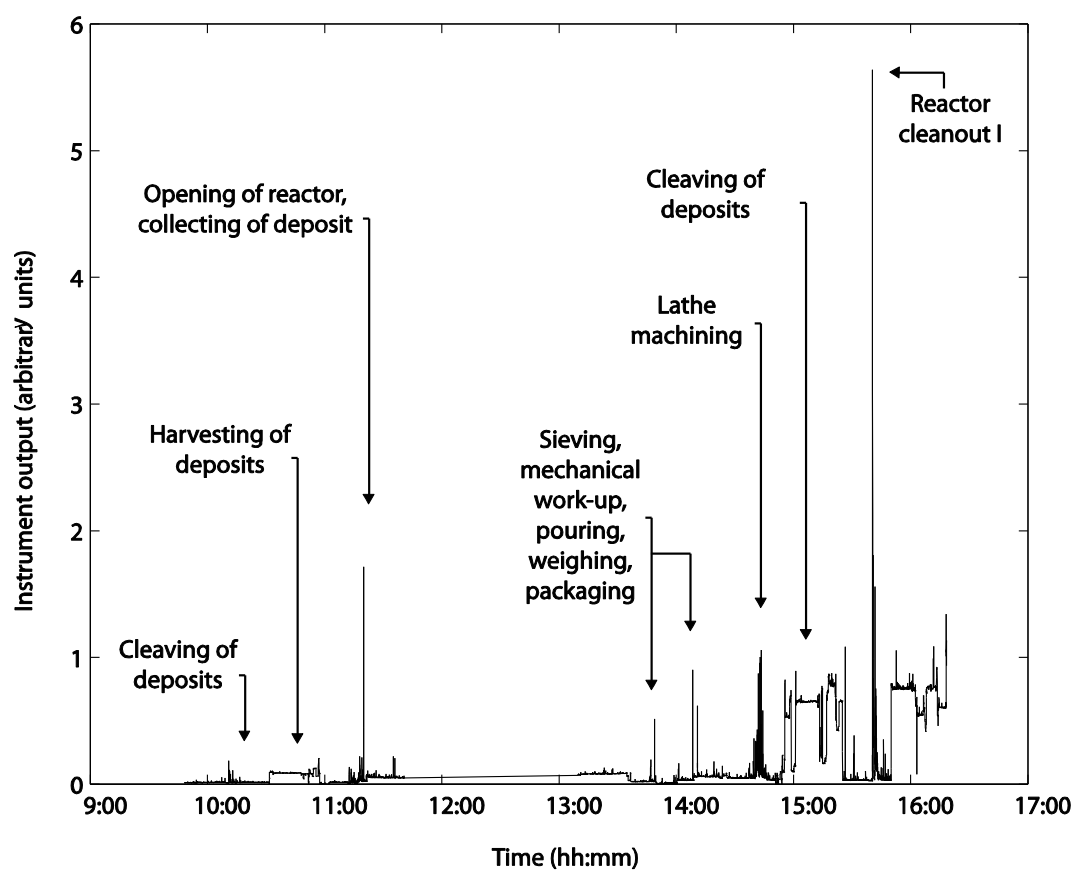
Fig. 4. Personal sampling with direct-reading instrument (Nanotracer) and emission sampling with CPC during (a) production work and (b) purification and functionalization work of MWCNTs. (c) The distribution of the real-time data from the Nanotracer and CPC (reference instrument) shows that the correlation between the two instruments is higher for higher number concentrations. Nanotracer assesses the particle number concentration using a diffusion charging technique while the CPC allows a direct counting of individual particles (up to 10 000 cm^{-3}).

(a)
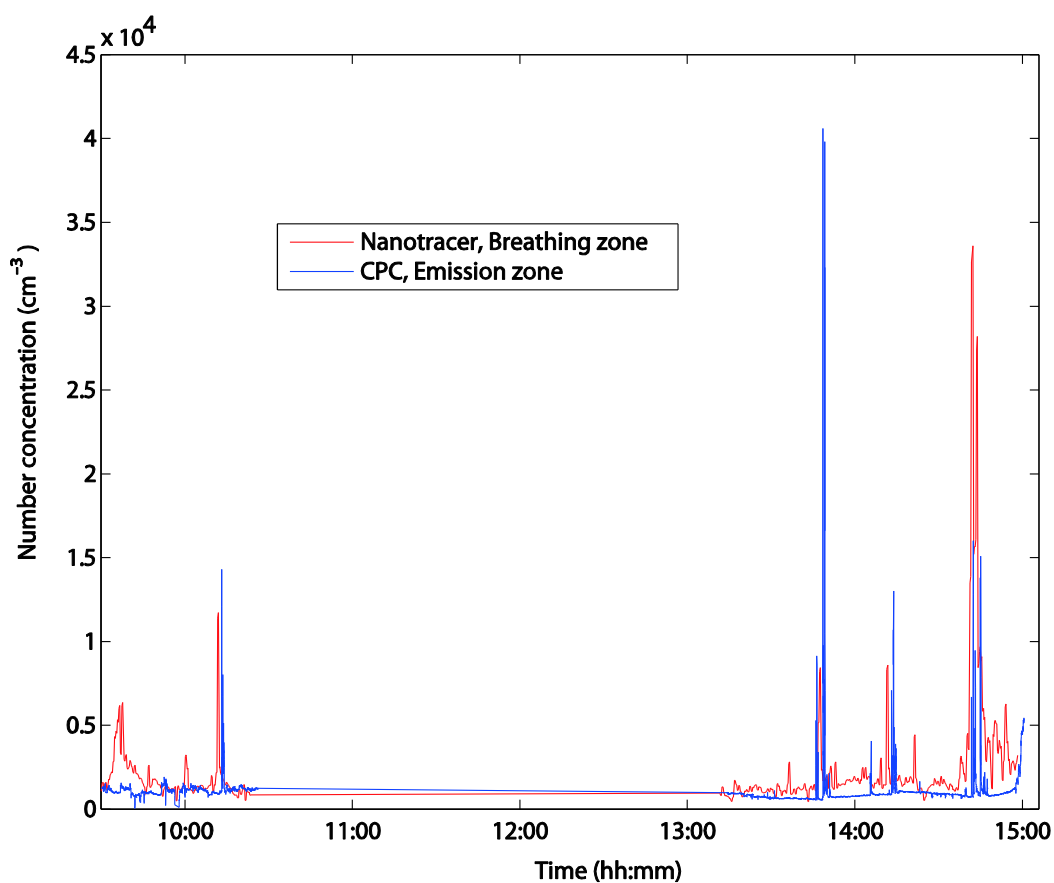
(b)
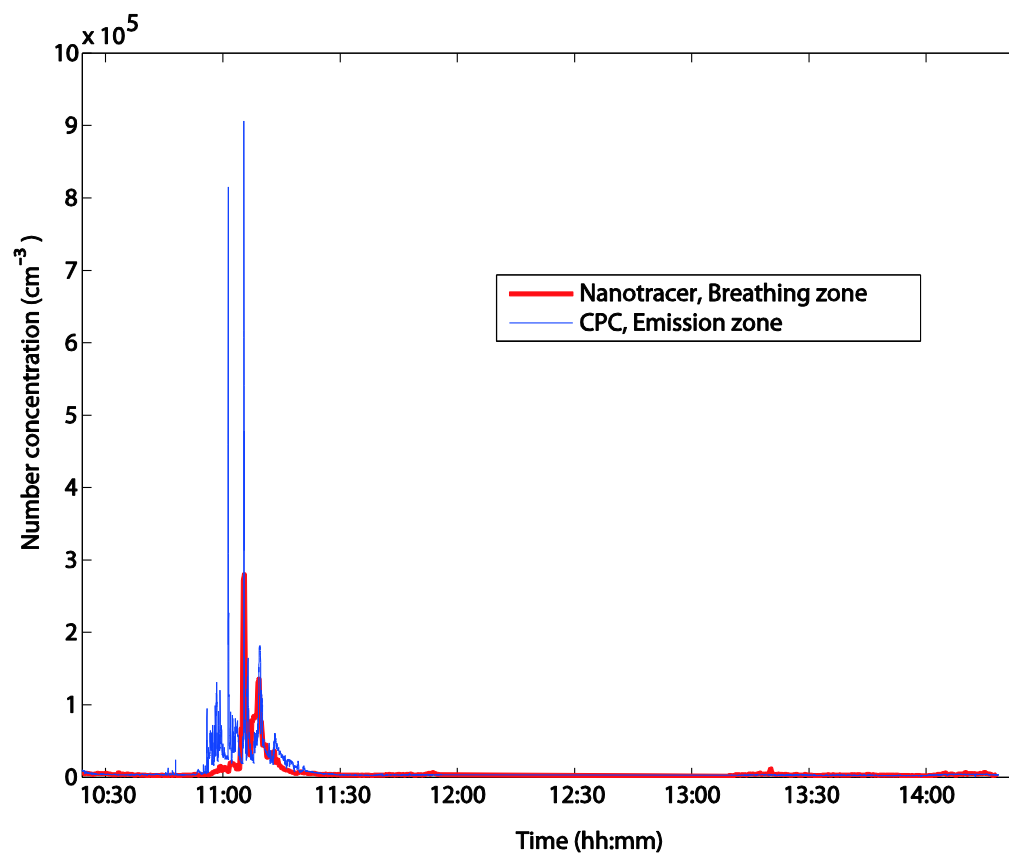
(c)

Fig. 5. Correlation of number concentration of CNT-containing particles and EC (respirable fractions). The Pearson correlation coefficient was 0.088 with linear regression. Non-detect samples were given the value of half the LOD.
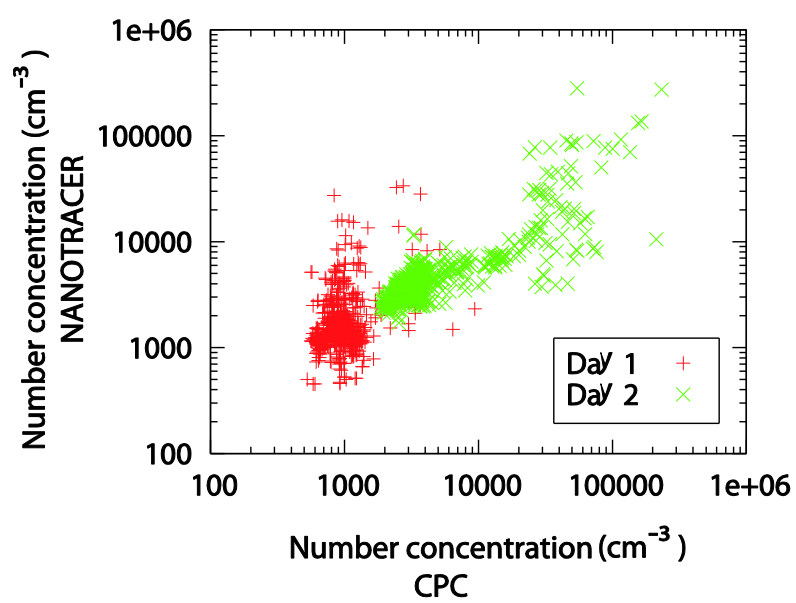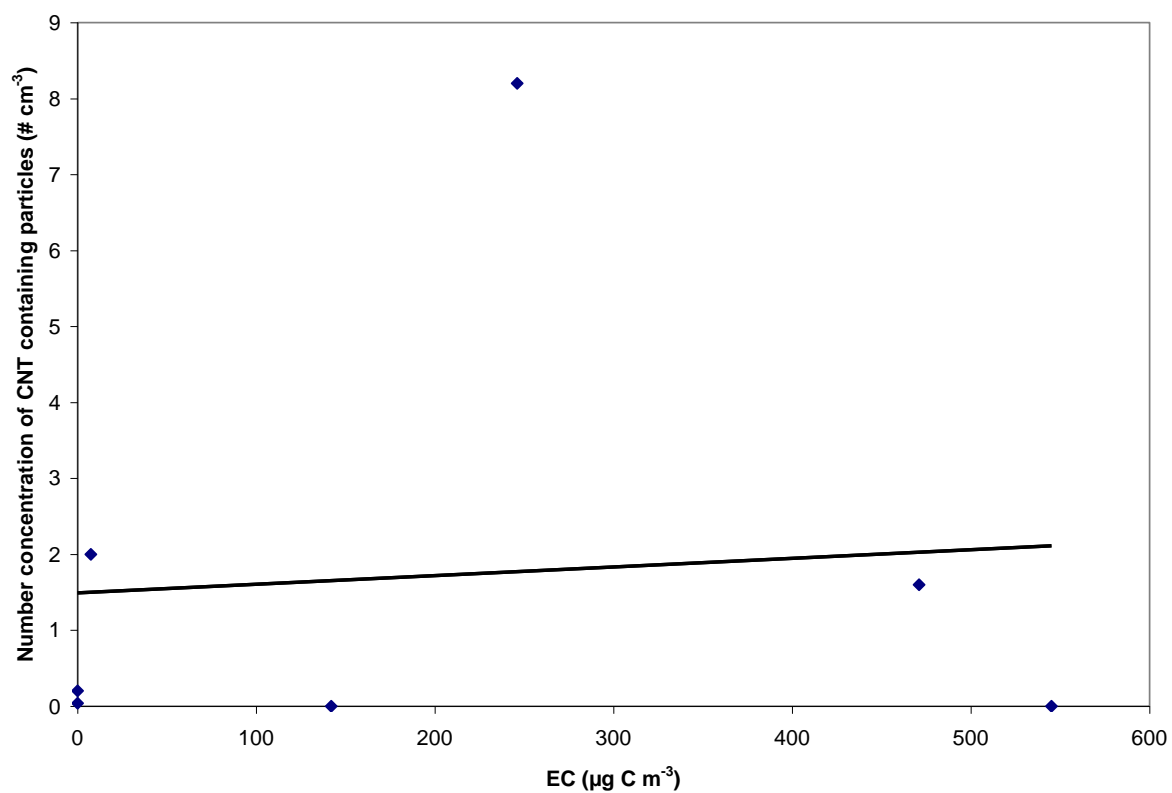
Fig. 6. Correlation of number concentration of CNT-containing particles and EC3 (respirable fractions). The Pearson correlation coefficient was 0.33 with linear regression. Non-detect samples were given the value of half the LOD.
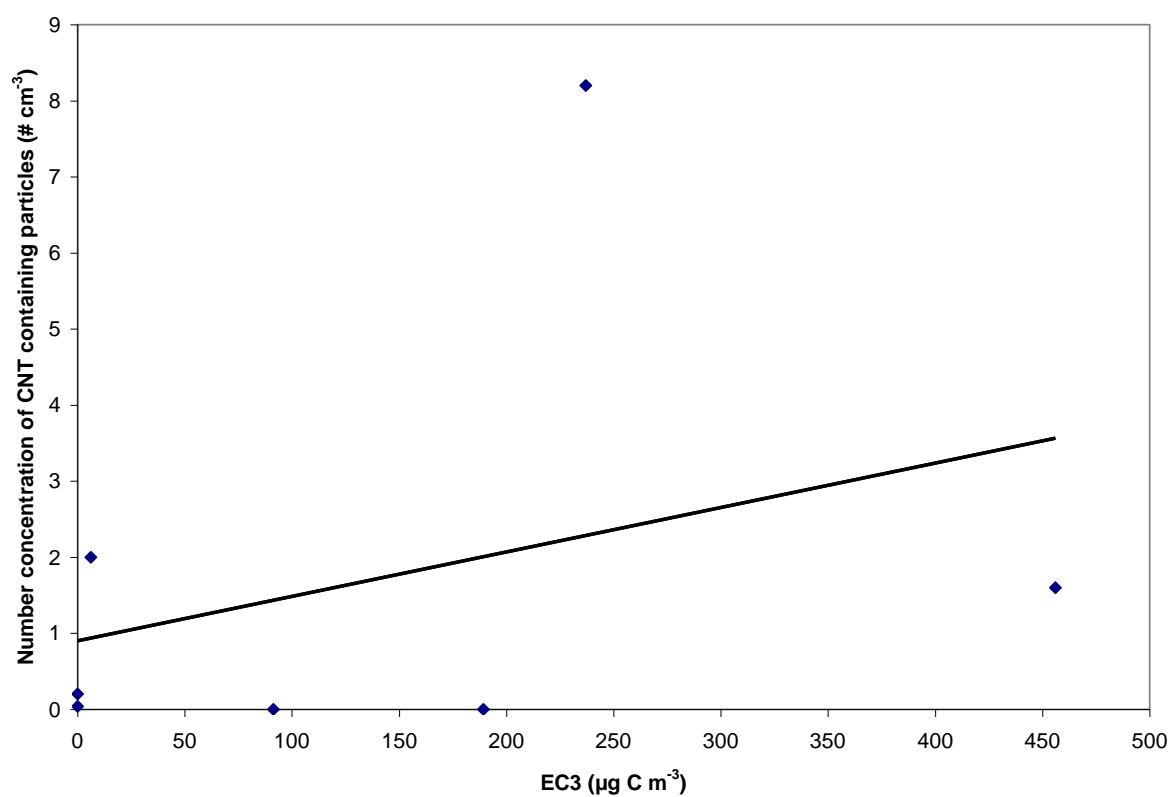
Table 1. The sampling strategy for the exposure and emission measurements at the small-scale producer of MWCNTs

Sampling day	Production laboratory and sieving laboratory		Purification laboratory	
	Personal exposure measurement during the work day	Short-term emission measurement	Personal exposure measurement during the work day	Short-term emission measurement
1	Sampling of: R1[a], R2[b], SP[c], NT[d]	Sampling of: R1, R2 for each work task; EC[e] for select work tasks	Sampling of: R1, R2, EC	-[f]
2	Sampling of: R1, R2, EC	-	Sampling of: R1, R2, SP, NT	Sampling of: R1, R2 for each work task; EC for select work tasks

[a]Respirable dust mass concentration by gravimetric analysis
[b]Respirable CNT containing particles by SEM analysis
[c]Sidepak (Photometer), assessment of respirable mass concentration
[d]Nanotracer, assessment of particle number concentration and mean size
[e]Respirable elemental carbon by thermal optical analysis
[f]Not measured

Table 2. Results from the personal sampling in the breathing zone of respirable dust, EC, and number concentration of CNT-containing particles. The sampled air volumes ranged between 680 and 890 l. EC is the actual concentration and EC3 is the amount found for the highest oxidation temperature step (900°C)

Worker	Location	Sampling day	Sampling time (min)	Respirable dust concentration (µg m^{-3})	Respirable EC concentration (µg C m^{-3})		CNT containing particles (# cm^{-3})
					EC	EC3	
A	Production laboratory and sieving laboratory	1	341	93	-[a]	-	0.6
A	Production laboratory and sieving laboratory	2	405	79	7.4	6.3	2.0
B+C[b]	Purification laboratory	1	324	<71[c]	<0.08	<0.08	0.04
B+C	Purification laboratory	2	313	<73[c]	-[a]	-	0.1

[a]Not sampled
[b]The two workers in the purification lab worked there only partly during a shift. They did only occasionally work there at the same time. Therefore, one sampler was used and swapped between worker B and C.
[c]LOD

Table 3. Summary of the personal sampling with direct-reading instruments.

Sampling day	Location	Respirable mass concentration[a] (arbitrary units)			Particle number concentration[b] (# cm^{-3})			Average particle size[b] (nm)		
		Arithmetic mean	Min	Max	Arithmetic mean	Min	Max	Arithmetic mean	Min	Max
1 (a.m.)	Production laboratory and sieving laboratory	0.04	ND[c]	1.7	1800	500	12000	59	40	86
1 (p.m.)	Production laboratory and sieving laboratory	0.23	ND	5.6	2500	500	34000	65	32	92
2 (a.m.)	Purification laboratory	0.10	ND	3.2	11000	2400	280000	50	22	70
2 (p.m.)	Purification laboratory	0.06	ND	2.8	3800	1700	3800	64	42	86

[a]Sidepak (photometer); the reported concentration is the respirable mass concentration assuming that the workplace aerosol has the same instrument response as the calibration aerosol (Arizona test dust).

[b]Nanotracer (based on unipolar electrical charging and size classification by electrical mobility, 10-300 nm)

[c]Not detected

Table 4. Results from the emission measurements of respirable fractions of dust, EC and number concentration of CNT containing particles during different work tasks. EC is the total elemental carbon concentration and EC3 is the EC concentration found at the highest oxidation temperature step (900°C).

Work tasks	Location number in Figure 1	Use of engineering controls/PPE	Respirable dust samples		Respirable EC samples			Microscopy samples		Calculated time-weighted average (# cm^{-3})
			Air volume sampled[a] (l)	Mass concentration (µg m^{-3})	Air volume sampled[a] (l)	Mass concentration (µg C m^{-3}) EC	EC3	Air volume sampled[a] (l)	CNT containing particles[b] (# cm^{-3})	
Production laboratory and sieving laboratory										
Opening of reactor, collecting the deposits	3	Local exhaust / half-face respirator[c], nitrile gloves, protecting overall	24	<2100	18	140	91	18	ND (<1.0)[d]	-[e]
Cleaving of deposits	1	None/half-face respirator, nitrile gloves, protecting overall	26	<1900	20	470	460	24	1.6	-
Harvesting of MWCNTs from deposits	2	Local exhaust/ half-face respirator, nitrile gloves, protecting overall	40	<1300	42	<1.4	<1.4	37	ND (<1.8)	-
Sieving, mechanical work-up, pouring , weighing, packaging	5	None/half-face respirator, nitrile gloves, protecting overall	117	<430	196[f]	250[f]	240[f]	117	11	8.2[f]
Lathe machining of graphite electrode	6	Local exhaust/ half-face respirator, nitrile gloves, protecting overall	29	<1700				29	1.2	
Reactor clean out - part I	4	Local exhaust/ half-face respirator, nitrile gloves, protecting overall	18	<2800				18	ND (<0.20)	
Reactor clean out - part II	4	Local exhaust/ half-face respirator, nitrile gloves, protecting overall	9	6800	9	550	190	9	ND (<2.1)	-
Purification laboratory										
Purification – part I	7	Fume hood/nitrile gloves, protecting overall	139	<360	464[g]	0.05[g]	0.05[g]	139	ND (<0.28)	0.2[g]
Purification – part II	8	Fume hood /nitrile gloves, protecting overall	154	<320				154	0.46	

Functionalization – part I	9	Fume hood /nitrile gloves, protecting overall	29	<1700		29	1.0
Functionalization –part II	10	Fume hood /nitrile gloves, protecting overall	55	<910		53	ND (<0.34)
Grinding	11	Fume hood /nitrile gloves, protecting overall	81	<620		77	ND (<0.23)

[a] The used airflow was $2.2\,l\,min^{-1}$

[b] The upper 95% one-sided confidence limits (95% CLs) of the number concentrations of CNT clusters in the air were calculated by assuming that the CNT clusters on the filter had a Poisson distribution. The confidence limit where the observed CNT cluster count was zero could be considered to be the limit of detection. The method for calculating the 95% CL was based on ISO 10312 (1995)

[c] Equipped with filter type P3

[d] Not detected

[e] Not calculated

[f] Include sieving, weighing, pouring, packaging, lathe machining and reactor clean out part I

[g] Include all purification and functionalization parts and grinding