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Detection of multi-walled carbon nanotubes and carbon nanodiscs on workplace surfaces at a small-scale producer

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ABSTRACT

Background: The industrial use of novel manufactured nanomaterials such as carbon nanotubes and carbon nanodiscs is increasing globally. Occupational exposure can occur during production, downstream use, and disposal. The health effects of many nanomaterials are not yet fully characterised and to handle nano-objects, their aggregates and agglomerates > 100 nm (NOAA), a high degree of control measures and personal protective equipment are required. The emission of airborne NOAA during production and handling can contaminate workplace surfaces with dust, which can be resuspended resulting in secondary inhalation exposures and dermal exposures. This study surveys the presence of carbon-based nanomaterials, such as multi-walled carbon nanotubes (MWCNTs) and carbon nanodiscs, as surface contamination at a small-scale producer using a novel tape sampling method.

Methods: Eighteen different surfaces at a small-scale producer were sampled with an adhesive tape sampling method. The surfaces selected were associated with the production and handling of MWCNT powder in the near-field zone. Surfaces in the far-field zone were also sampled. In addition, tape stripping of the skin was performed on one worker. The tape samples were analysed with scanning electron microscopy to detect the carbon-based NOAA. Air sampling with a personal impactor was also performed on a worker who was producing MWCNTs the same day as the tape samples were collected.

Results: MWCNTs were detected in 50% of the collected tape samples and carbon nanodiscs in 16%. MWCNTs and carbon nanodiscs were identified in all parts of the workplace, thus, increasing the risk for secondary inhalation and dermal exposure of the workers. Both airborne MWCNTs and carbon nanodiscs were detected in the personal impactor samples. The tape-strip samples from the worker showed no presence of carbon-containing nanoparticles.

Conclusions: Tape sampling is a functional method for detecting surface contamination of carbon-based NOAA and for exposure control during production at potentially any workplace that produces or handles such manufactured nanomaterials. With the tape method it is possible to monitor if a potential for secondary inhalation exposure or dermal exposure exists through resuspension of dust deposited on workplace surfaces. By means of air sampling we could confirm that carbon nanodiscs were resuspended into the air at the workplace even though they were not handled during that particular work shift. MWCNTs were detected in the air samples, but can have been derived from either resuspension or from the work tasks with MWCNTs that were performed during the air sampling. Tape sampling is a complementary method to air sampling and together these two methods provide a better view of the hygienic situation in workplaces where NOAA can be emitted into work environments.

Keywords

carbon nanotube; dust; exposure; monitoring; carbon nanodisc; surface contamination; tape sampling; tape stripping; workplace exposure

INTRODUCTION

Several different types of carbon-based nanomaterials such as carbon nanotubes (CNTs), carbon nanofibres, carbon black, graphene nanoplatelets, carbon nanodiscs and carbon nanocones, are commercially manufactured. CNTs are mainly incorporated in composite materials for reinforcement (e.g. plastics, polymerics, ceramics, metallics, rubber, and concrete), and in fabrics, batteries and paints (Lam et al., 2006; Köhler et al., 2008; Wohlleben et al., 2011; Liu and Kumar, 2014). Carbon nanofibres are mainly used in composite materials. Carbon black has long been used in industrial applications as a colouring agent in ink, paints, resin and film, and as an electric conductive agent. Graphene nanoplatelets, carbon nanodiscs and carbon nanocones are relatively new carbon-based nanomaterials attracting substantial scientific interest. Graphene nanoplatelets may have the potential to be used as a component in, for example, composites, batteries, ultracapacitors, coatings and adhesives (Pumera, 2009; Shen et al., 2013; Kim et al., 2013). Carbon nanodiscs and carbon nanocones have the potential to be to be used as additives for making plastics electrically or thermally conductive, possibly as substrates in sensor systems or as miniature electrodes (Garberg et al., 2008).

Occupational exposure to nano-objects, and their aggregates and agglomerates >100 nm (NOAA)[1] can occur at each stage of the life cycle (ISO, 2012), such as production, downstream use (e.g. formulation, industrial use), and disposal. It is the dustiness of powders that determines the emission potential, and dustiness testing of powdered nanomaterials provides information about the propensity of a material to aerosolise during its handling. To limit the unwanted occupational exposure to airborne NOAA, it is important to avoid free airborne nanoparticles. For most work processes and handling operations, the emission of NOAA into the air in general can be controlled through different types of conventional safety

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[1] Aggregates and agglomerates <100 nm are to be considered as nano-objects.

and protection devices such as equipment for encapsulation of emission sources, enclosures, fume hoods, draw benches, process ventilation, and local exhaust ventilation (Methner et al., 2010). If the safety and protection devices are designed to fit gaseous substances, or are effective against respirable dust in general, they are also suitable and efficient enough to capture NOAA and thereby provide acceptable inhaled air quality (IFA, 2009; NIOSH, 2009). If the exposure to NOAA is not sufficiently controlled during work processes or handling operations, nanoparticles can be emitted into the workplace air and cause primary inhalation exposure to the workers. The emitted airborne NOAA can also be deposited on different surfaces in the workplace, outer clothing of the workers and on their skin contaminant layer, all of which constitute potential secondary sources of airborne NOAA (Schneider et al., 2000; Schneider and Jensen, 2009). The mechanism for contaminating surfaces vary depending on gravitational settling and Brownian and turbulent diffusion if the NOAA are in the size range <100 nm or >1 µm (Schneider et al., 2011). Surface deposition of NOAA can result in both near-field and far-field surface contamination.

Resuspension or reaerosolisation of particles deposited on different workplace surfaces will usually result in particles with sizes > 1 µm. Resuspension of NOAA from surfaces to the air can result in secondary emission sources. Resuspension to the workplace air can occur by human indoor work activities, such as walking and cleaning (Schneider et al., 1999; 2000). There are also strong suggestions that normal laboratory work can cause wind movement on workplace surfaces which could resuspend nanosized particles deposited there as dust, and thus cause secondary inhalation exposure (Tsai et al., 2008; Schneider and Jensen, 2009). It was shown, for example, that water-based cleaning of surfaces in a laboratory where manufactured nano-objects were handled greatly reduced the background concentrations of airborne particles in the size range 30-100 nm (Tsai et al., 2008).

Many NOAA, such as the carbon-based ones, have low bulk densities, which results in considerable dusting during handling (Hedmer et al., 2013). Dermal exposures from contaminated surfaces can also occur through transfer on contact.

According to Schneider and Jensen (2009) surface contamination by NOAA should be systematically studied for both production and user scenarios as it is a potential secondary source of airborne NOAA. However, to date, the documentation is still scarce of NOAA as surface contamination in workplaces and the potential for inhalation and dermal exposure. During manufacturing of CNTs, for example, it has previously been shown that CNT-containing dust was emitted into the air during different work processes and handling operations (Han et al., 2008; Lee et al., 2010; Dahm et al., 2012; Hedmer et al., 2014). A recent study has shown the presence of CNT surface contamination by means of wipe sampling during weaving (Takaya et al., 2012). Another study showed the potential for dermal exposure of single-walled CNTs during manufacturing and handling by using cotton gloves as a surrogate for the skin (Maynard et al., 2004). Knowledge of the occupational dermal exposures to other types of manufactured carbon-based nanomaterial is in general limited.

Inhalation has been identified to be the exposure route of highest concern for carbon-based nanomaterials (Schinwald et al., 2012; Donaldson et al., 2011; Ma-Hock et al., 2013; Hedmer et al., 2013). Rodents repeatedly exposed to realistic concentrations of longer (>10 µm) or shorter (<4 µm) multi-walled CNTs (MWCNTs) have been shown to have pulmonary inflammatory effects and fibrosis (Ma-Hock et al., 2009; Ryman-Rasmussen et al., 2009; Pauluhn, 2010; Mercer et al., 2011; Porter et al., 2013). Recently, it was also shown that the inhalation exposure of animals to one type of MWCNT promotes lung cancer (Sargent et al., 2014).

There are methods available to sample surface contamination originating from airborne dust, such as wipe sampling, micro-vacuuming, and adhesive tape sampling (Ness, 1994). Previously, adhesive tape sampling has been used for assessing surface contamination of fibrous dust such as asbestos (Ness, 1994) and manmade vitreous fibres (Salonen et al., 2009). Wheeler and Stancliffe (1998) tested different surface contamination sampling methods based on removal and found that the adhesive tape method was the most effective for collecting settled dust in a reproducible manner. There is also a standard practice available for sampling a surface to determine the presence of particulate contamination by tape lift (ASTM E1216). No one has previously reported surface contamination of carbon-based NOAA using tape sampling. Based on these results we decided that the adhesive tape method – an indirect method to estimate the potential for exposure – could be used to monitor deposited NOAA on different surfaces in a workplace where carbon-based nanomaterials are produced and handled. In addition, there are methods available for assessing the presence of particulate matter and fibres on human skin, such as tape stripping followed by scanning electron microscopy (SEM) analysis (van der Molen et al., 1997; Hsieh et al., 2001). Tape stripping was thus performed on one worker to assess the skin exposure to MWCNTs during production.

The objective of the study presented in this paper was to survey the presence of MWCNTs, carbon nanodiscs and nanocones as surface contamination at a small-scale producer of such carbon-based nanomaterials. Tape stripping was performed on a worker exposed to MWCNTs during their production. We wanted to assess the potential for secondary inhalation exposure and dermal exposure. Tape sampling on different surface locations in the workplace was performed to assess surface contamination of carbon-based NOAA. The collected tape samples were analysed with SEM to detect the occurrence of surface contamination of carbon-based NOAA in the workplace. Airborne particles were also collected with a personal impactor to study if resuspension of the nanoparticles to the air occurred at the workplace.

METHODS

Industrial setting

The tape samples were collected during the same sampling campaign where air sampling was being conducted at a small-scale producer of MWCNTs, carbon nanodiscs and carbon nanocones (Hedmer et al., 2014). In the facility assessed, the tape samples were collected from surfaces related to the production and purification of MWCNTs that were in the near-field zone of the exposure source. To survey how widespread the surface contamination of NOAA in the facility was, we also sampled surfaces in the far-field zone of the exposure sources. This workplace has recently been described elsewhere (Hedmer et al., 2014) but a short description will follow. In the company there were three different laboratories, and Fig. 1 presents a schematic drawing of the layout of the facility. In the production laboratory MWCNTs were synthesised with an enclosed arc discharge reactor. The reacted graphite deposit was collected and then dry cut with a band saw and manually harvested. In the sieving laboratory the as-produced MWCNTs were mechanically worked-up to pulverise the powder, which was then sieved, weighed and packaged in glass containers. The as-produced MWCNTs consisted of 55 wt% MWCNTs and 45 wt% carbonaceous impurities. In the purification laboratory the MWCNTs were purified to remove carbonaceous structures (e.g. graphite and soot) and functionalised. On average, the company produce approximately 75 g of as-produced MWCNTs per day. Three workers in the company were involved in the production, purification, and functionalisation work of MWCNTs.

The company also produced and handled another carbon-based nanomaterial consisting of ~80% graphitic nanodiscs and ~20% graphitic nanocones. However, this nanomaterial had not been produced recently but was occasionally handled in the production laboratory, for example, in the transfer of the powder from a big barrel to smaller bottles (packaging) before shipping to the customer.

The floors in the production and sieving laboratories were on average swabbed once a week and washed once a month. On the floor where the production and sieving laboratories were located, a sticky mat was placed at the base of the stairs to collect dust from the shoe soles so as not to spread it to other floors. The floor in the purification laboratory was swabbed every day. Disposable surface covers were used on most work areas in the company and the work areas were usually cleaned after the work activity. The work areas in the production laboratory and sieving laboratory were vacuum cleaned on a daily basis. The waste handling was open and waste contaminated with MWCNTs was not sealed before disposal. The waste bins were emptied on a daily basis. No other sources of carbon-based NOAA were identified in or near the factory.

Sampling strategy

Tape sampling is a useful method for assessing surface contamination of fibrous dust including asbestos (Ness, 1994). Thus, it has the potential to monitor the occurrence of carbon-based dust containing MWCNTs, nanodiscs and nanocones as surface contamination. The tape sampling method used conformed to the standardised one (ASTM E1216). On the day when the tape samplings were performed, MWCNTs were produced and handled in the workplace. According to the company management, approximately 300 g of powder containing carbon nanodiscs and nanocones were handled in the production laboratory 10 days before the sampling campaign. Packaging of powder into smaller bottles was carried out under local exhaust ventilation in the production laboratory. At the time of the sampling campaign, according to the company, carbon-based nanodiscs and nanocones were also handled in the purification laboratory to functionalise them. All tape samples were collected at the company after work had ended for the day, and thus, there were no work activities in progress in the laboratories at the time of sampling.

To obtain information of what types of airborne carbon-containing nanoparticles were present in the workplace air, a Sioutas Personal Cascade Impactor was used to conduct sampling in the personal breathing zone of the worker in the production laboratory.

Sampling of surface contamination

In total, 18 tape samples and 2 field blanks were collected from surfaces at the workplace. The sampled surfaces were made of metal, plastic, concrete, laminate and wood. The nature of the sampled surface locations are presented in Table 1 and where they are situated in the company are shown in Fig. 1. To collect a sample, ordinary transparent adhesive tape (Staples Europe B.V., Amsterdam, the Netherlands) was used with a width of 15 mm, length of ~15 cm, with ends folded. Single tape samples were collected from each surface location. The sticky surface of the tape was pressed against the workplace surface to be sampled, and rubbed lightly to assure adhesion to dust deposited on the surface. Then, the tape was pulled off with a fluent and decisive movement, and placed with the sticky side down on a new sheet of plastic film and labelled. The plastic film was placed in a new plastic cover for storage until scanning electron microscopy (SEM) analysis. A new pair of nitrile gloves was used for each collected tape sample.

Tape stripping

With tape stripping, the cell layers of the stratum corneum from the human skin were removed by use of adhesive tape (van der Molen et al., 1997). The worker in the production laboratory was assessed in advance to be the one with the highest risk of being dermally exposed to carbon-based nanomaterial in the company. The worker used a laboratory coat and protective nitrile gloves during the work activities, but no dermal protection was used in the facial region. The worker did however use a half-face respirator during the different work activities, but the respiratory protection was not used between the activities which meant that it was taken on and off frequently during the workday. This could have contributed to the blackening found on the worker's skin. Tape stripping was performed on this worker who had given informed consent to participate in the study. The tape strips were collected after a full-shift workday and were taken from the skin of his forefinger, cheek and forehead because visual traces of black dust were seen on these areas. The tape was applied to the skin, and the same procedure as described for the surfaces was followed. The tape stripping seemed to remove some of the blackening from the skin.

Sampling of airborne carbon-based NOAA

The personal size-resolved sampling was carried out with a Sioutas Personal Cascade Impactor (SKC Inc., Eighty Four, PA, USA.), with cut-off diameters of 2.5, 1.0, 0.50, and 0.25 µm. The impactor was equipped with four 25-mm polycarbonate membrane filters and one 37-mm PTFE after filter to capture particles with an aerodynamic diameter smaller than 0.25 um. To avoid bounce-off effects, the filters were sprayed with impactor grease (DS-515 Collection Substrate Spray, Dekati Ltd., Tampere, Finland). The impactor was connected to a Leland Legacy Sample Pump (SKC Inc., Eighty Four, PA, USA) that provided an air flow of 9 l min^{-1}, regularly checked before, during and after the sampling with the primary calibrator (TSI 4100 Series, USA). The same day as the tape samples were collected and the tape stripping was performed, the worker in the production laboratory carried the impactor for 403 min while working with activities such the synthesising of MWCNTs with the enclosed arc discharge reactor, opening of the reactor and collection of the reacted graphite deposit, dry cutting of the reacted graphite deposit with a band saw, manual harvesting of the MWCNTs produced, mechanically worked-up, sieving, weighing, pouring, and packaging, lathe machining of graphite rods for the reactor, and reactor clean out with compressed air and a vacuum cleaner with a high efficiency particulate absorption (HEPA) filter. The filters from one impactor sample were analysed with the SEM method described below.

SEM analysis of tape samples

The tape samples were prepared for SEM analysis by removing the plastic film and mounting a piece of the tape (~ 1 cm in size) on a silicon wafer. The nonconductive tape was then coated with a thin layer of platinum on the glue side to avoid charging artefacts in the electron microscope image. The tape samples were qualitatively analysed by SEM (FEI Nova Nanolab 600, FEI Company, USA) at a magnification of 5000x. Each sample was manually investigated for roughly 2 h giving a level of detection of 70 NOAA cm^{-2}. In all tape samples except one, we assessed the occurrence of NOAA to be low, in the order of 1 out of 100 total collected particles.

If the SEM analysis showed – based on size, shape and elemental composition – particle characteristics of an MWCNT (fibrous nature) or of a nanodisc, a closer investigation was performed at a higher magnification to verify the detection. No MWCNTs or nanodiscs or other surface contaminants were detected in the analysis of the field blank tape samples. A recent SEM analysis of bulk material of MWCNTs from the company showed that the MWCNTs on average had a length of 1.7 µm (range 0.3-6.1 µm) (Hedmer et al., 2014). The elemental composition of the carbon nanodiscs in the field samples was analysed using an energy dispersive X-ray analysis (EDX; SDDXEDS, Oxford Instruments, Oxfordshire, UK).

SEM analysis of the personal impactor samples

A piece corresponding to approximately a quarter of the filter from all the collected impactor samples was mounted on a silicon wafer and coated with platinum. The SEM analysis was performed according to a procedure recently described by Hedmer et al. (2014).

RESULTS

Surface contamination

The results from the SEM analysis of the tape samples are presented in Table 1. Carbon-based nanoparticles were detected in 9 of the 18 tape samples collected on different surface locations at the workplace. MWCNTs were detected in 50% of the tape samples (N=9). MWCNT contamination was found on 4 of the 5 sampled surfaces in the production laboratory, on both sampled surfaces in the sieving laboratory, on 2 of the 3 sampled surfaces in the purification laboratory, and on 1 of the 4 sampled surfaces in the office of the production worker. The SEM analysis showed that the MWCNTs present on the workplace surfaces were larger heterogeneous agglomerates with an average length and width of 15-100 µm. The agglomerates were also built up of other carbonaceous compounds such as soot and graphite. Carbon nanodiscs were detected in 16% of the tape samples (N=3) and were also found on surfaces in all three laboratories in the company. These 3 tape samples also contained MWCNTs and were all collected from surfaces assessed to be seldom cleaned in the “other surfaces” sampling location. The detected nanodiscs had on average a diameter of 1.5±0.5 µm and a thickness of 60±14 nm. Elemental analysis showed that the nanodiscs in the field samples consisted of 95-98% carbon and a few percentage of oxygen. No carbon nanocones could be identified on the tape samples. Typical SEM images of the detected surface contamination of MWCNTs and carbon nanodiscs in the workplace can be seen in Fig. 2a-d. Soot aggregates present in the MWCNT powder as an impurity can also be seen in the SEM images. We assessed the occurrence of nanoparticles to be low in all tape samples except one: in sample no. 15 there were numerous carbon nanodiscs present (Fig. 2a), but in the same sample only a few MWCNTs were found (Fig. 2b).

Dermal contamination

The tape strips collected from the worker's skin showed no presence of MWCNTs, carbon nanodiscs, nanocones, other carbon dust, or any other non-carbon particles. The SEM analysis indicated that only skin cells appeared to be collected on the tape strips. Thus, the collected skin cell layer may have obscured the view of possible skin contaminants.

Airborne carbon-based NOAA

The analysis showed that both MWCNTs and carbon nanodiscs were present in the workplace air. Analysis of the different personal impactor stages showed that the airborne MWCNT-containing particles collected consisted most of heterogeneous agglomerates (Fig. 3a-e) but also of individual MWCNTs.

Airborne carbon nanodiscs were detected in the impactor sample: in stage A collecting particles > 2.5 µm, in stage C collecting particles between 1.0-0.50 µm (Fig. 3c), in stage D collecting particles between 0.50-0.25 µm (Fig. 3d), and on the after filter, that is, the stage collecting particles < 0.25 µm (Fig. 3e). Numerous of carbon nanodiscs were collected in stage C.

DISCUSSION

To our knowledge this is the first published study showing the occurrence of carbon-based nanomaterials as surface contamination in a workplace by means of adhesive tape sampling. With this method, it is possible to detect if carbon-based NOAA are present as surface contamination in work environments. MWCNTs were produced on the sampling occasion, and thus it was expected that only MWCNT contamination would be detected on the surfaces in the company. The tape samples, however, also showed the presence of carbon nanodiscs, a nanomaterial that the company occasionally handled. According to the company management, carbon nanodiscs were handled in the purification laboratory in the facility at the time of the tape sampling. Tape samples were collected from both frequently cleaned surfaces (e.g. work areas and floors) and seldom cleaned surfaces (e.g. band saw, cable channels and computer mouse). The surface contamination of MWCNTs and carbon nanodiscs was widely spread and found in all parts of the facility: production laboratory, sieving laboratory, purification laboratory and office. Surface contamination of MWCNTs was found on both frequently and seldom cleaned surfaces. However, carbon nanodiscs were only found on surfaces that were seldom cleaned. The tape sampling also showed that carbonaceous nanoparticle contamination was not widely spread to surfaces located outside the laboratories in the company (e.g. floor in corridor, stairs, handles, desks).

The handling of MWCNT materials in the company during the production, purification and functionalisation was open, and air sampling performed during the different work tasks in the emission zone showed emission of MWCNTs into the air (Hedmer et al., 2014). Since MWCNTs and carbon nanodiscs were detected on 50% of the sampled surfaces in the workplace, this indicates that the NOAA were not sufficiently controlled during the work processes and handling operations. Furthermore, it is of importance that workplace surfaces are cleaned at regular intervals to prevent them from becoming secondary sources of NOAA (Schneider and Jensen, 2009).

In the SEM analysis of the filters from the personal impactor sampling, both MWCNTs and carbon nanodiscs were detected. The airborne MWCNTs could have originated from either work-related emissions during the sampling or from resuspension of MWCNT-containing dust on surfaces. But the collected airborne carbon nanodiscs could only have originated from resuspension of the carbon nanodisc dust deposited on workplace surfaces, since this nanomaterial was not handled in the production and sieving laboratories during the sampling campaign. At the time of the sampling campaign, carbon nanodiscs were being handled in the purification laboratory, but we did not detect any airborne carbon nanodiscs in the personal and stationary air samples collected in this laboratory (Hedmer et al., 2014).

Heterogeneous MWCNT-containing particles were for example collected at all stages of the personal impactor. Larger agglomerated MWCNT-containing particles collected in the impactor in the stage > 2.5 µm (Fig. 3a) were found to a much greater extent compared to the filter samples (respirable fractions). This is most likely due to aerodynamic equivalent particle diameters larger than 4 µm, which was the cut-off for the cyclones used (recently published by Hedmer et al., 2014). Particles with aerodynamic diameters larger than 4 um have a low probability reach and deposit in the alveolar region of the lung.

Many MWCNT-containing particles collected in the impactor stages < 2.5 µm were in the size range of ~tens of µm. One explanation is that these particles had aerodynamic diameters much smaller than their geometric size, which is expected for porous particles with complex shapes. Another possible explanation could be particle bounce, where particles bounce from one stage to the next. If larger agglomerated MWCNT-containing particles bounced-off and re-entered the airstream, although use of impactor grease, and were collected on later stages they potentially contaminated the analysis. Long sampling time combined with high air concentration of MWCNT might have contributed to the particle bounce. However, from the impactor sampling we received knowledge about MWCNT-containing particles also existed in other size ranges not included in the respirable fraction sampling.

The detected airborne carbon nanodiscs in the production and sieving laboratories could have originated from surfaces in both laboratories, since the door between theses was normally open. Only one worker was working in the production and sieving laboratories and he moved around in all parts of the two laboratories during a normal workday. The detected airborne carbon nanodiscs could have been emitted from the sampled surfaces where carbon nanodiscs were found as contaminants. However, the detected airborne carbon nanodiscs could also have originated from other contaminated surfaces in the production and sieving laboratories not included in the tape sampling survey. The purification laboratory was located on a different floor than the production and sieving laboratories and the distance between was >25 m including a closed door. Thus, it not realistic to believe that the inhalation exposure had drifted in from elsewhere in the facility.

Smaller particles (< 1 µm) deposited on surfaces are held by strong forces. The forces responsible for the particles' adhesion to a surface are also the same forces responsible for the particles' adhesion to each other (Ziskind et al., 1995; Ostiguy et al., 2006). The smaller the particles, the more difficult it will be for them to detach from the surface and resuspend into the air. In general, resuspension seems only relevant for particle sizes >1 µm, and the resuspension rate increases for particles increasing in size from 1 µm to >10 µm (Qian and Ferro, 2008; Schneider and Jensen, 2009). The detected surface contamination of MWCNT agglomerates in sizes between 15-100 µm found on surface locations in this study can thus be considered to have the potential for resuspension. The carbon nanodiscs found on some surface locations also could be resuspended because their sizes were > 1 µm.

The characteristics of the surface also play an important role. For example, surface roughness can greatly reduce the force of adhesion of a particle, which can contribute to increased resuspension (Ziskind et al., 1995). From the results presented in Table 1 almost half of the samples surfaces, 44% (8 out of 18), were assessed to be rough. Carbon-based nanomaterial was detected on 50% of these types of surfaces (4/8). Based on the results, it is difficult to draw any conclusions. However, it is obvious that surfaces closer to the emission sources (near-field surfaces) were contaminated to a higher extent than surfaces at a farther distance (far-field surfaces). To avoid the risk for resuspension of NOAA, the removal of dust deposited on the floors and work surfaces must be performed regularly (e.g. cleaning) (Ostiguy et al., 2006).

Thus, our findings in the study confirm that surface dust containing carbon-based nanoparticles can resuspend into the workplace air. Our findings can be explained by inadequate routines for cleaning in combination with a lack of adequate engineering controls of the airborne exposure to MWCNTs and carbon nanodiscs during the different work processes, or handling operations. This has recently been described elsewhere (Hedmer et al., 2014).

Since dust containing both MWCNTs and carbon nanodiscs was present on surfaces in the workplace, there was a potential for the workers to be exposed to uncontrolled secondary inhalation of MWCNTs or carbon nanodiscs via resuspension. This exposure could occur anytime, not only during the work activities per se. A half-face respirator with particulate filter of grade P3 was used by the worker in the production and sieving laboratories during the different work tasks, but not between the work tasks. However, the two workers in the purification laboratory did not use any respiratory protection at all. There is reason for concern as toxicological studies have shown that inhalation of MWCNTs with lengths similar to those found on the tape samples (< 4 µm) cause adverse effects, such as pulmonary inflammation and fibrosis in animal studies (Pauluhn, 2010; Mercer et al., 2010, 2011; Porter et al., 2013).

The morphology of the detected carbon nanodiscs resembles that of graphene nanoplatelets, which in general have nanoscaled thickness (Donaldson et al., 2013). It has recently been shown that nanoplatelets with a diameter < 30 µm were respirable due to their aerodynamic properties, which allows them to deposit in the lower respiratory tract. We found carbon nanodiscs in almost all stages of the personal cascade impactor including the after filter; thus their aerodynamic equivalent diameter could be < 0.25 um. This means that they have a very high probability to penetrate down into the alveolar region of the respiratory tract. Platelets deposited in the pleura space can cause frustrated phagocytosis, inflammation and have further adverse effects (Schinwald et al., 2012; Donaldson et al., 2013). With similar size and shape, there is potential for carbon nanodiscs with a diameter > 4 µm to be respirable and affect the lungs. However, the nanodiscs in this study were very thin (thickness around ~ 60 nm) and had an average diameter of 1.5 µm, thus allowing for complete phagocytosis by alveolar macrophages in the pulmonary alveoli. The risk for adverse health effects seems to be less if the nanodiscs are < 15 µm, similar to what Schinwald et al. (2012) suggested for nanoplatelets to minimise human adverse health effects.

MWCNT was found on one of the tape samples collected from the floor of the office next to the sieving laboratory. MWCNT was also detected on the floors in the sieving laboratory and production laboratory (Fig. 1). Since the laboratories in the company where carbon-based nanomaterials were produced and handled were not separated from the rest of the facility, and since no shoe protection was used in the workplace and the same shoes were used in the whole facility, we expected to find MWCNT dust on the floor in the office next to the sieving laboratory. Our air sampling showed that the work activities performed in the sieving laboratory emitted higher concentrations of MWCNTs to the air than any of the other work activities (Hedmer et al., 2014). Thus, the floor in the sieving laboratory may have been one of the most contaminated surfaces in the workplace.

MWCNT was also found on the computer mouse in the production laboratory, indicating the potential of dermal exposure in the workplace. However, protective gloves made of nitrile and laboratory coats were used to reduce dermal exposure. As there are no data on skin penetration and health effects following dermal deposition of MWCNTs, the precautionary principle must be applied and efficient skin protection is needed to prevent and minimise the dermal exposure to MWCNTs. Coveralls, hoods, and shoe protection must be used to more efficiently protect the workers in the company from dermal exposure to carbon-based nanomaterials.

An advantage with the adhesive tape sampling method is that it is inexpensive and easy to use and can be set up rapidly in the field. The collection of a representative number of tape samples in a workplace is rather quickly carried out. Another advantage is that the tape samples can be analysed by SEM without any complicated sample preparation. According to Holopainen et al. (2002), the tape method is useful in places where the dust lies loosely on the surface and where the amount of dust is fairly small. Disadvantages with this tape sampling method are that only qualitative data are obtained, and that the SEM analysis is expensive and time consuming.

The efficiency of any method for sampling dust particles is an important factor. The tape sampling method used in this study, however, has not been validated and as a result, we have no data about its removal efficiency on different types of surfaces. Tape sampling of very rough surfaces could result in false negative values because the tape does not always adhere to NOAA deposited on such surfaces. In our sampling, though, carbon-based NOAA were detected on 50% of the surfaces assessed to be rough. This indicates that the surface sampling in this study seemed to work. Of course, one should in the first case choose to sample surfaces with a smooth finish to avoid problems with the removal efficiency. In addition, tape sampling has been used successfully for other types of particulate contamination (Salonen et al., 2009), and should also work for agglomerates and aggregates of nanoparticles with sizes > 1 µm. Even though the method used was only indicative, it has still been very informative and useful. Further developments of this method should include validation as well as refinement and standardisation for quantitative assessments.

Tape stripping is a technique that removes deposited particles and also some of the stratum corneum cells (Lundgren et al., 2006). However, the tape strips did not confirm the presence of carbon-based NOAA contamination on the skin of the worker. In other studies, the method used showed the presence of, for example, singular glass fibres and particles of TiO_2 on human skin (van der Molen et al., 1997; Hsieh et al., 2001). A possible explanation why we were unable to image any carbon-based NOAA could be due to poor visibility among the many dermal cells that were involuntarily collected on the tape strips. We were only able to analyse the tape strips with the sticky side up because with the other side up, the electron beam could not penetrate the tape due to its thickness. Future developments should also address this issue.

Conclusions

This study has demonstrated that tape sampling is a useful method for the detection of surface contamination of carbon-based NOAA at workplaces and for assessing if the NOAA exposure at a workplace is sufficiently controlled. With the tape method it is possible to monitor the potential for secondary inhalation and dermal exposures. Combined with the air sampling data, we could confirm that carbon-based nanomaterial was resuspended into the air in the workplace, allowing for secondary inhalation exposure to the workers. Thus, this study showed that there was potential for both secondary inhalation exposure and dermal exposure due to the presence of MWCNTs and carbon nanodiscs on different surfaces throughout the workplace. We suggest tape sampling as a complementary method to air sampling. These two methods combined could, with advantage, provide a better overview of the hygienic situation in workplaces where carbon-based NOAA are emitted into work environments.

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TABLES

Table 1. An overview of the 18 tape sampled surface locations and the presence of MWCNTs and carbon nanodiscs on different surfaces in the company producing and handling different carbon-based nanomaterials.

Sampling location		Unit	Description of the sampled surfaces/Distance to the expected exposure source	Cleaning rate	Surface characteristics		No. of tape sampling location in Fig. 1	SEM analysis	
					Material	Approx. indication of surface roughness		Detection of carbonaceous nanomaterial (Yes/No)	Type of carbon-based nanomaterial
Work areas	Table	Purification laboratory	Close to the balance where MWCNT powder was openly weighed/In the near-field zone	Regularly[a]	Laminate	Smooth	1	Yes	MWCNTs
	Desk	Office located next to the sieving laboratory	Belonging to the production worker/ In the far-field zone	Seldom[b]	Coated wood	Smooth	2	No	-[c]
Floors	Next to the arc discharge reactor	Production laboratory	Close to the reactor/ In the near-field zone	Regularly	Concrete	Rough	3	Yes	MWCNTs
	Between the saw and the table	Production laboratory	Close to two MWCNT sources: dry cutting and manual harvesting/ In the near-field	Regularly	Concrete	Rough	4	Yes	MWCNTs
	Top step on the stairs down to the production laboratory	Production laboratory	-/In the far-field zone	Regularly	Stone	Rough	5	No	-
	Sieve shaker	Sieving laboratory	Sieving of as-produced MWCNT powder/In the near-	Regularly	Concrete	Rough	6	Yes	MWCNTs

			field zone						
	Next to the fume hood	Purification laboratory	Close to the fume hood where MWCNT powder was handled/In the near-field zone	Regularly	Plastic flooring	Rough	7	No	-
	Next to the table	Office for the production worker	Located next to the sieving laboratory /In the far-field zone	Regularly	Concrete	Rough	8	Yes	MWCNTs
	Next to the door	Office for the production worker	Located next to the sieving laboratory /In the far-field zone	Regularly	Concrete	Rough	9	No	-
	Corridor	Located next to the production laboratory	-/In the far-field zone	Regularly	Plastic flooring	Rough	10	No	-
Handles	Door handle 1	Door between purification laboratory and corridor	Corridor side/In the far-field zone	Seldom	Metal	Smooth	11	No	-
	Door handle 2	Door between purification laboratory and corridor	Purification laboratory side/ In the far-field zone	Seldom	Metal	Smooth	12	No	-
	Door handle	Door between sieving laboratory and office for the production worker	Sieving laboratory side/In the far-field	Seldom	Metal	Smooth	13	No	-
Other surfaces	Sieve shaker	Sieving laboratory	On the sieve shaker/In the near-field zone	Regularly	Metal	Smooth	14	Yes	MWCNTs, nanodiscs
	Band saw	Production laboratory	On the saw/In the near-field zone	Regularly	Metal	Smooth	15	Yes	MWCNTs, nanodiscs
	Computer mouse next to the arc discharge	Production laboratory	On the computer mouse/In the near-field zone	Seldom	Plastic	Almost smooth	16	Yes	MWCNTs

	reactor								
	Computer mouse	Office for the production worker	On the computer mouse/In the far-field zone	Seldom	Plastic	Almost smooth	17	No	-
	Cable channel	Purification laboratory	Close to the balance where MWCNT powder was openly weighed/In the near-field zone	Seldom	Metal	Smooth	18	Yes	MWCNTs, nanodiscs

[a] Regular cleaning (e.g. daily or weekly)

[b] No regular cleaning

[c] No manufactured nanomaterial was detected

FIGURES

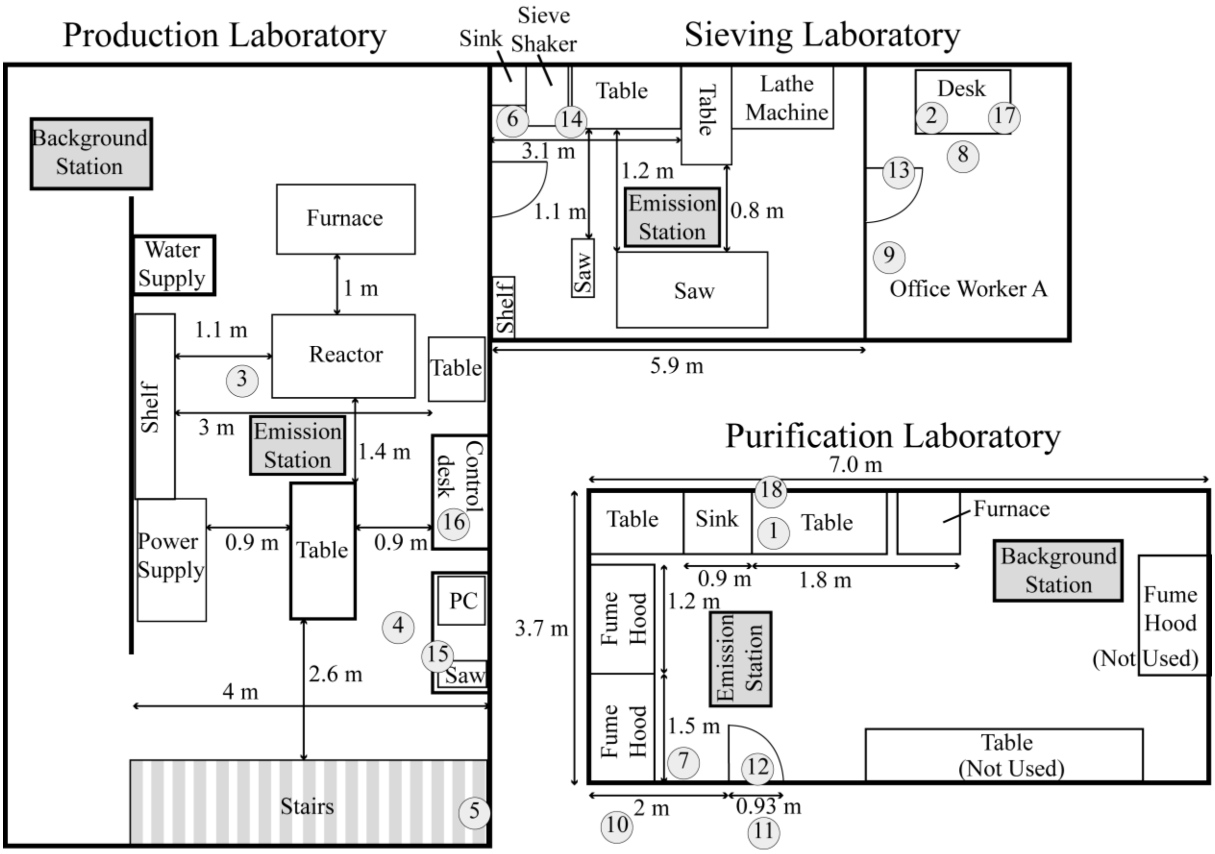
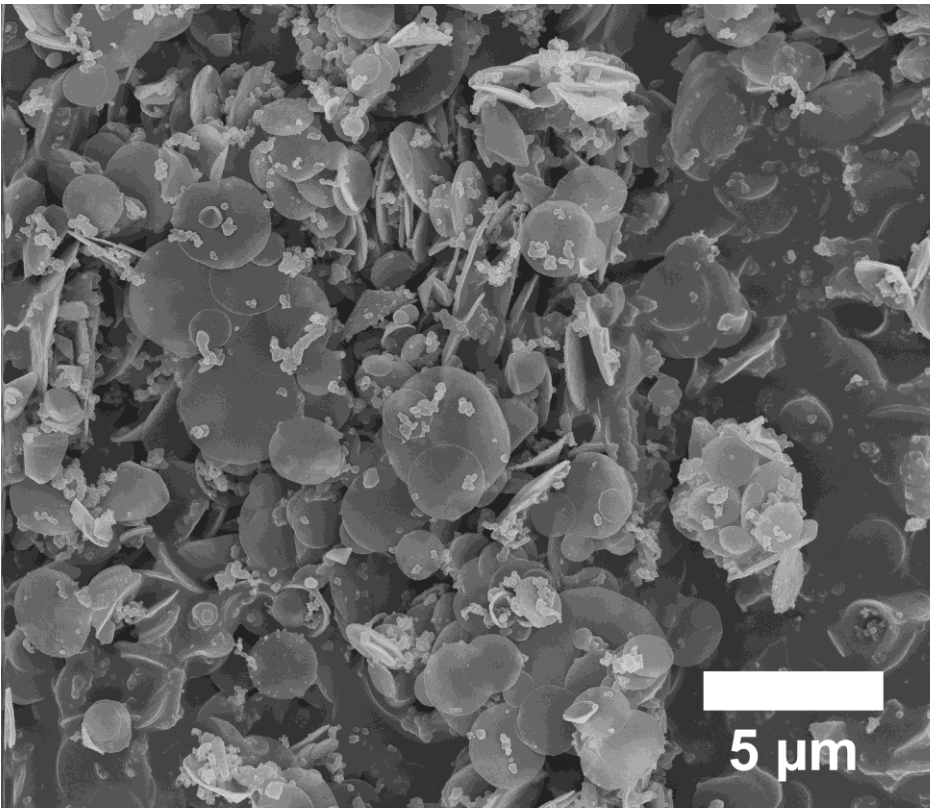
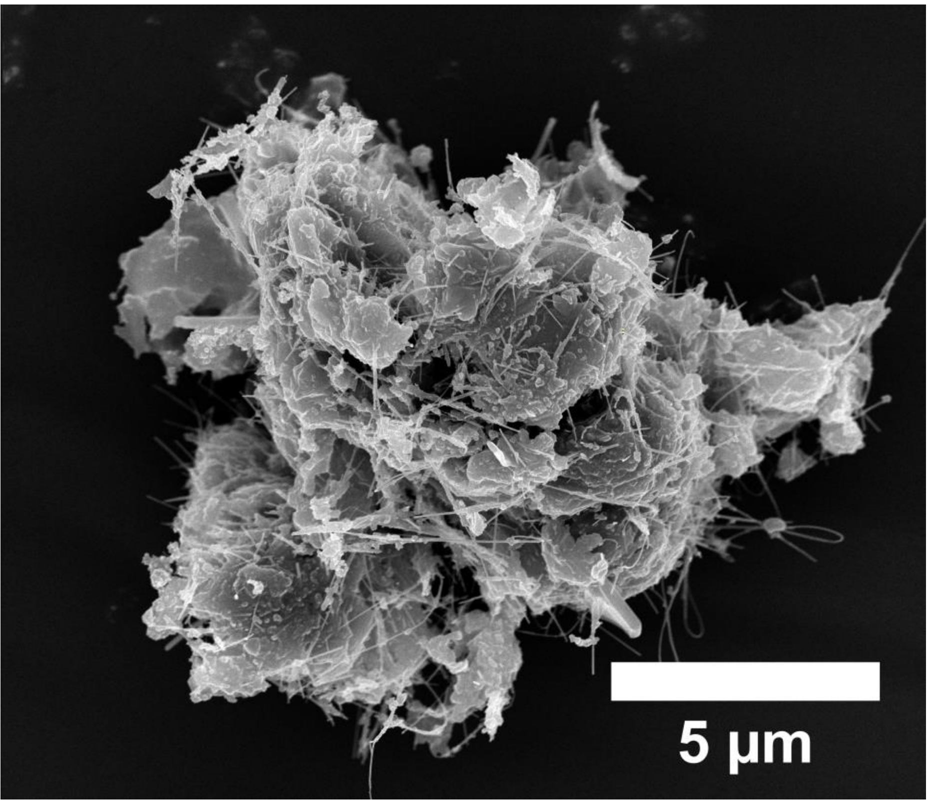


Fig. 1. Schematic drawing of the small-scale production facility. The numbers in grey circles correspond to the 18 surface locations that were tape sampled. The production and sieving laboratories were located on a different floor than the purification laboratory, and the distance between was approximately 25 m. There was also a closed door between the floors.



(a)



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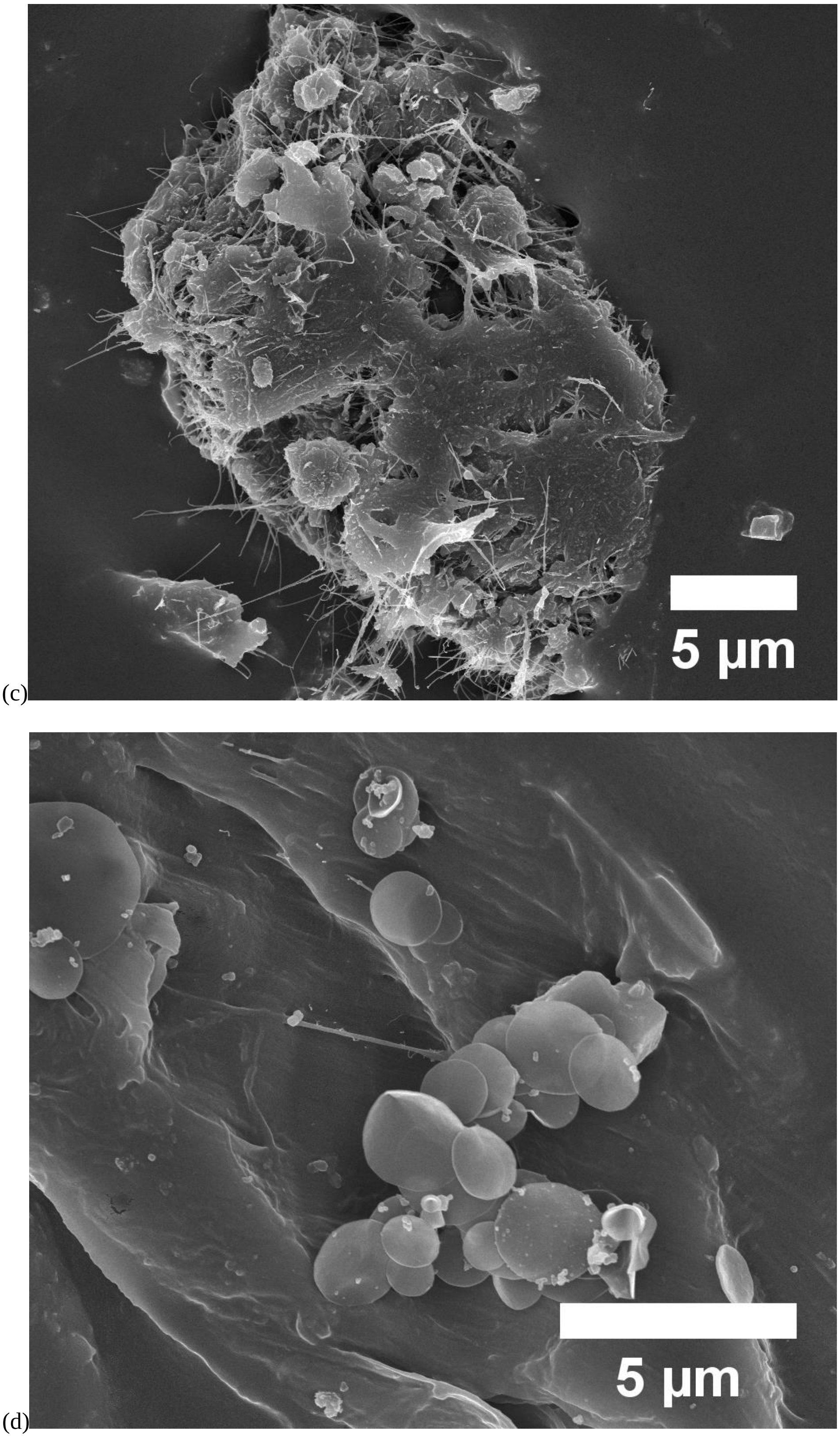
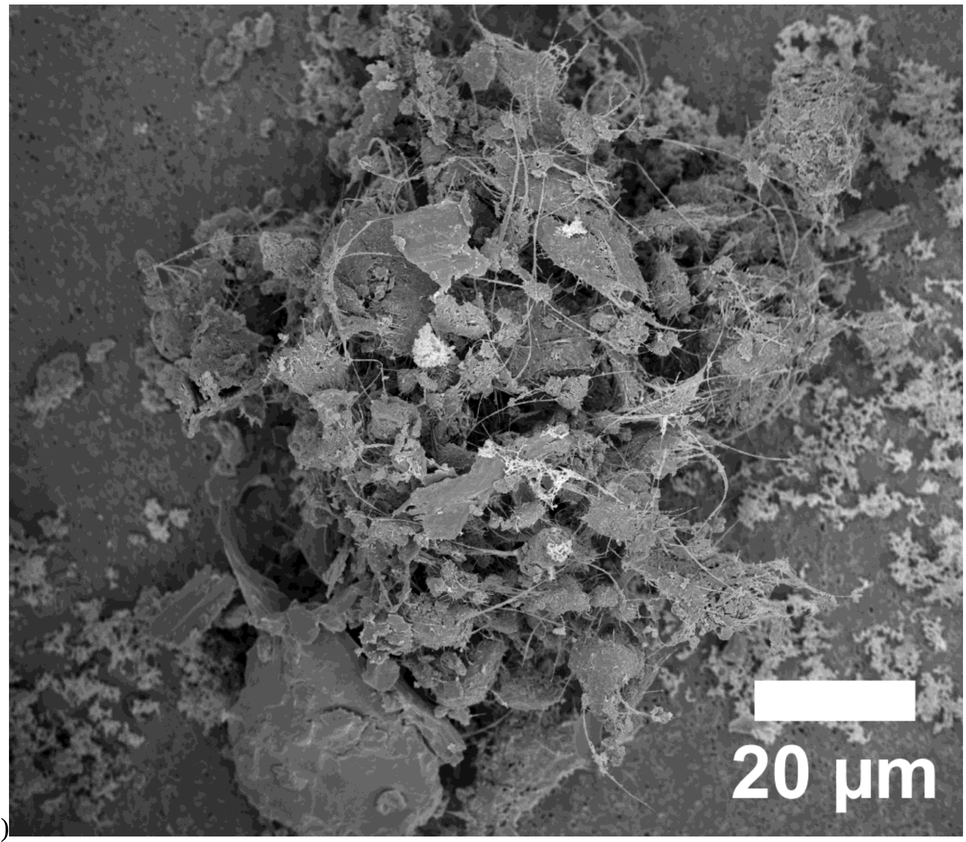
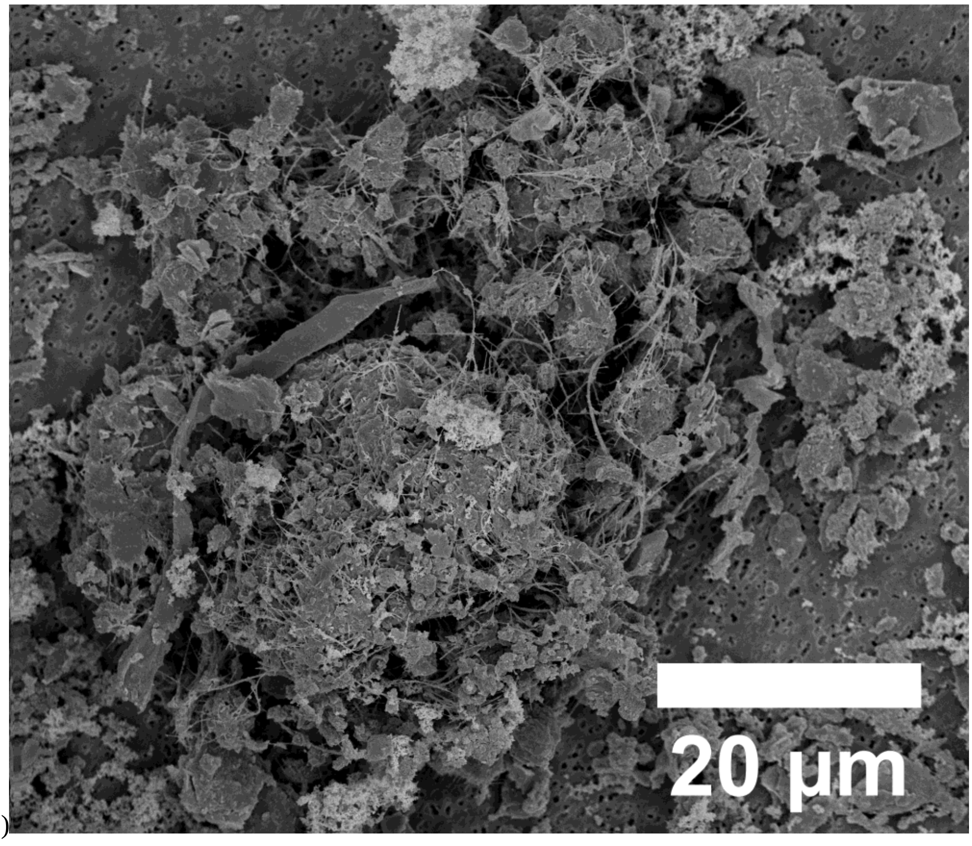


Fig. 2. SEM images of surface contamination of carbon-based nanomaterials. a) Carbon nanodiscs in a tape sample by the band saw in the production laboratory. b) MWCNT agglomerates detected near the band saw in the production laboratory. c) An agglomerated MWCNT particle detected on the sieve shaker in the sieving laboratory. d) Carbon nanodiscs found on the sieve shaker.



(a)



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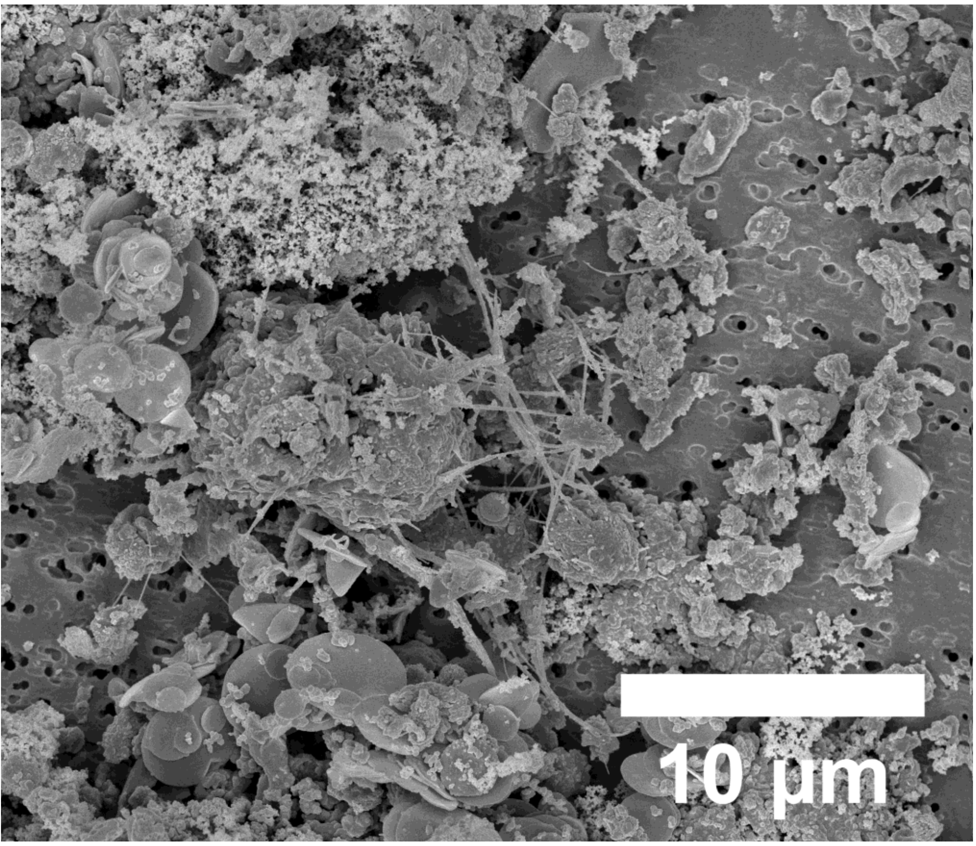
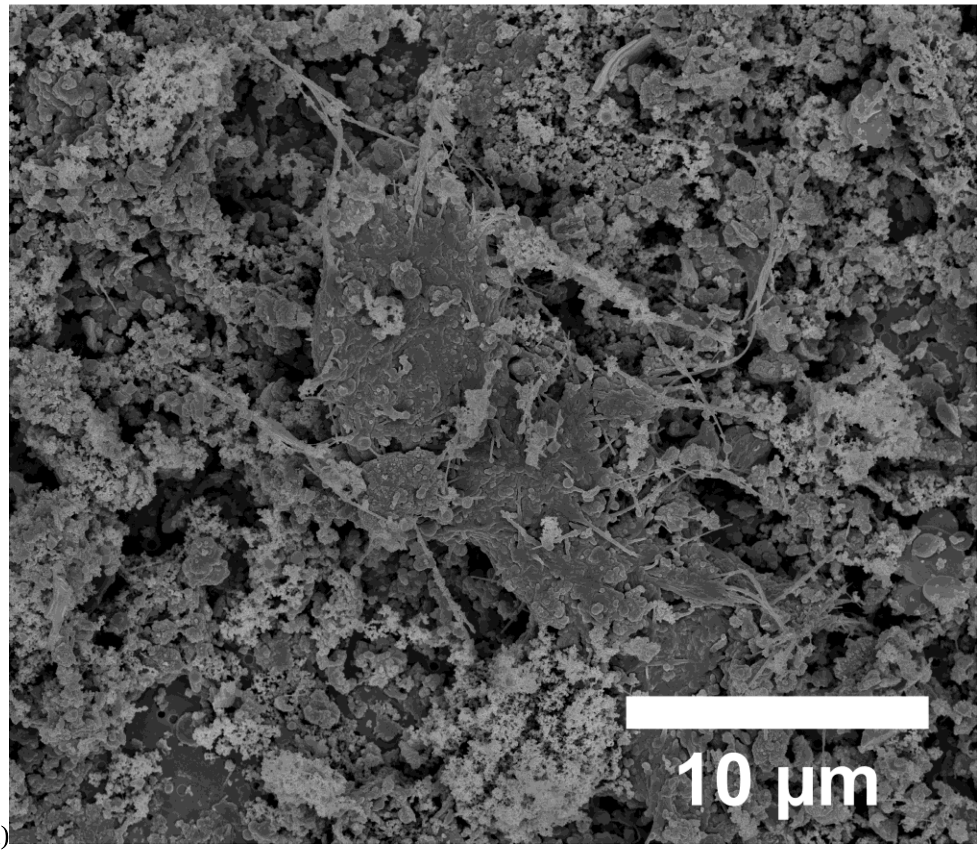


(c)



(d)

(e)

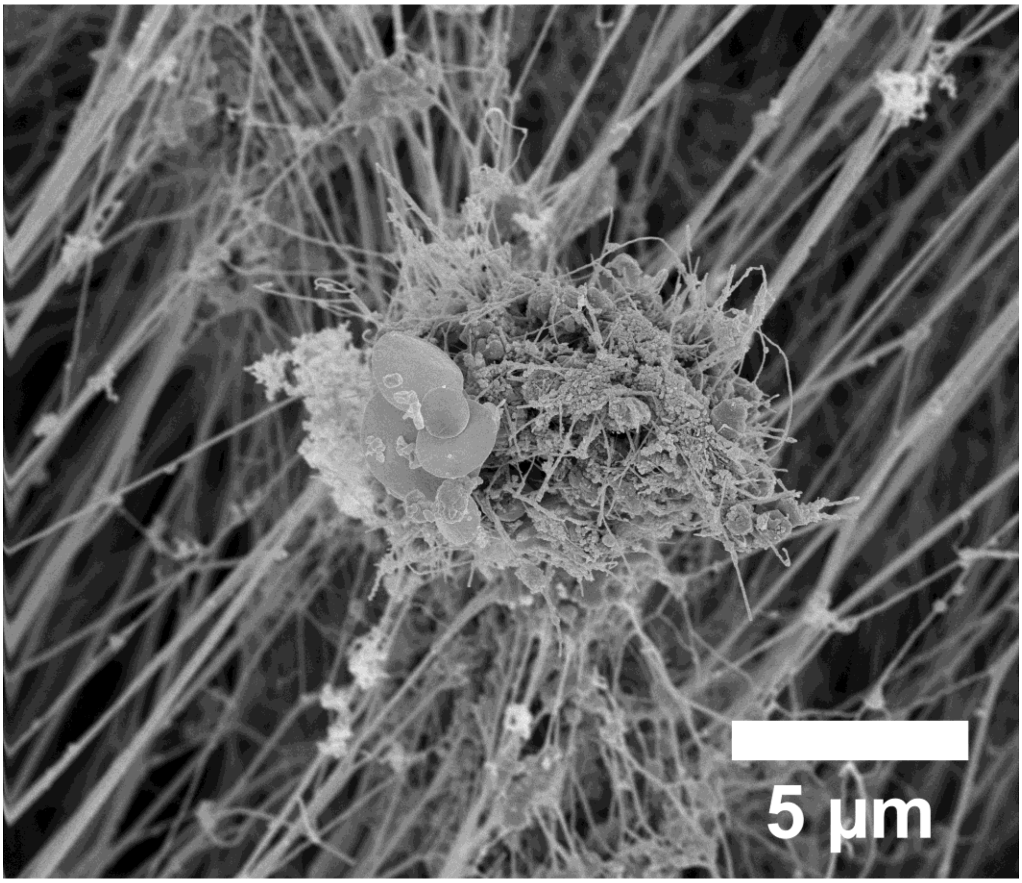


Fig. 3. SEM images of airborne agglomerates of MWCNTs collected in the breathing zone of the worker in the production laboratory with a Sioutas Personal Cascade Impactor. Typical particles from the different stages are presented. Soot aggregates present in the MWCNT powder as an impurity can also be seen in the SEM images. a) MWCNT-containing particles collected at the stage > 2.5 µm. b) MWCNT-containing particles collected at the stage 2.5-1.0 µm. c) MWCNT-containing particles and carbon nanodiscs collected at the stage 1.0-0.50 µm. d) MWCNT-containing particles and carbon nanodiscs collected at the stage 0.50-0.25 µm. e) Carbon nanodiscs collected on the after filter (< 0.25 µm) made of polytetrafluoroethylene (PTFE, Teflon). An airborne agglomerated MWCNT particle is also visible in the image.