PRELIMINARY HEALTH RISK ASSESSMENT OF OCCUPATIONAL EXPOSURE TO NANOPARTICLES IN ELECTRONIC WASTE PROCESSING

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Abstract

Engineered nanomaterials (ENMs) are applied in a wide range of products worldwide. The use of ENMs results in generation of increasing amounts of waste containing nanomaterials. Waste of electronic and electrical equipment (e-waste) is one of the main waste streams recycled in municipal and industrial waste. There are limited studies that assess the potential exposure to nanomaterials during the recycling processes. The main way how e-waste is prepared for the following recycling is the reduction of its size.

The aim of the study was to carry out the preliminary risk assessment of nanomaterials generated within e-waste processing. Occupational exposure was measured in a worker's breathing zone at the recycling site by Condensation Particle Counter (CPC 3007). Workplace air samples were collected on glass microscope slides using the Nano-ID Select Wide Range Aerosol Sampler (NANO-ID Select 005) and analysed by Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDS). The qualitative risk assessment has been carried out in CB Nanotool v 2.0. The highest concentrations of nanoparticles were detected for the following elements: chromium, copper, zinc, and tin. The average aerosol number concentration (size range of 10 - 1000 nm) in workplace atmosphere was 65792 particles/cm^3 (SD ±6292 particles/cm^3) for all particles. The level of risk (RL, the risk level based management system) obtained from CB tool was equal to RL2 (Periodic review of the tasks, procedures, and controls by OSHH disciplines is necessary), and RL3 (Tasks require a standardized one-page permit as a higher level of control documentation in justifying the implemented controls will reduce risks relative to operative OELs). Local exhaust ventilation was proposed, based on the assessed risk level, to ensure occupational health and safety.

This field study has been conducted as a case study for the subsequent detailed risk assessment and management.

Keywords: Nanoparticles, e-waste, occupational exposure, qualitative risk assessment

1. INTRODUCTION

Engineered nanomaterials (ENMs) are used today in a wide range of nanoproducts and applications [1]. Over time, the manufacturing and use of nanomaterials will result in the generation of increasing amounts of ENM-containing waste [2] as well as waste from the production processes themselves [1]. Solid waste containing ENMs cannot be identified as such, and currently, waste containing ENMs is not processed separately but is collected and treated together with regular waste. ENMs release into the environment may take place during all steps in a waste management system (e.g. collection, recycling, incineration and landfilling) [1]. ENMs could be emitted during shredding, milling, sorting and thermal processing, resulting in possible direct exposure in the working environment [1]. Only a few experimental studies on ENM fate during End of Life (EoL) are available. There are no studies that assess the flows of nanomaterials during the recycling processes, which may be the most likely EoL fate for nanoproducts, at least for some developed economies [3]. Recycling of waste is one element in strategies of waste minimisation or waste prevention [4]. Effective solid waste management is a cooperative effort involving state, regional, and local entities [5]. Waste of electronic and electrical equipment is one of the main waste streams recycled in municipal and industrial waste [5].

Information about the fate of nanomaterials in recycling processes is only beginning to emerge. Mostly, exposure scenarios are based on modelling, and not on direct evidence [5]. Improved understanding of the flows and fates of ENMs within the waste management system is therefore required [1].

This paper aims at providing information about the waste management of waste containing ENMs. The goal of the current work is to carry out the preliminary risk assessment of nanomaterials generated within e-waste processing.

2. METHODOLOGY

2.1. Process description

The field study has been carried out in the pre-recycling technology of e-waste processing (collecting of waste, dismantling, sorting by hand, shredding and separation of the fractions - non-magnetic metals, iron, glass, plastics, etc.). The handled e-waste comprises wash-machines, TVs, cookers, and computers. The dismantled material is separated based on the waste catalogue and collected for recycling. The work shift takes 7 hours (from 6 AM to 1 PM) with a half hour break.

The technology is situated in the hall of size 39.5 x 29.5 x 6 m. The whole process consists of following work operations (W):

- W1: line waste rough sorting/gross pre-screening;
- W2: manual separation of impropriate material - hand sorting;
- W3: line transport of e-waste to magnetic shredding;
- W4a: separation of e-waste containing iron (or metal waste);
- W4b: separation of e-waste based on the customer request.

Figure 1 E-waste processing

(1) W1 gross pre-screening; (2) W2 hand sorting; (3) W3 magnetic shredder; (4) W3 push e-waste on conveyor belt; (5) W4a separation of e-waste containing iron; (6) W4b separation of e-waste

Based on the technology of e-waste processing, it was identified which work operations could emit the nanoparticles into the working environment. The measured stations were located at W3, W4a, and W4b.

2.2. Occupational exposure measurement

Occupational exposure was measured in a worker's breathing zone at the W3, W4a and W4b. Measurements of airborne exposures were performed with a condensation particle counter TSI CPC 3007 (CPC 3007), which detects particles from 10 nm to >1 µm, and The Nano-ID Select Wide Range Aerosol Sampler (NANO-ID Select 005) that was applied for particle collection for subsequent analyses chemical composition. Samples from Nano-ID were analysed by Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDS). Given the duration of the different tasks performed during the e-waste processing, it was decided that the concentration during 10 minutes period should be measured. Before the task, the background concentration (B) of particles in the production hall was measured.

During the work operations (W3, W4a a W4b), the CPC equipment continuously collected data with a 1-s integration time for 10 minutes. Given the duration of the different tasks performed, the total duration of this phase was approximately 6 h 30 min. In the end, the outdoor background concentration (O) of particles was measured.

2.3. Control Banding - CB Nanotool version 2.0

CB Nanotool v 2.0 [7] is a pragmatic tool for risk management of chemicals with insufficient data about their toxicological effects and/or exposure. It is based on categorisation of risk as the combination of the hazard band and exposure band [6]. The method consists of determining the severity of hazard, based on the nanomaterials characteristics, and determining the probability of exposure based on the task operation to be performed [8]. The CB Nanotool v 2.0 was chosen due to the possibility of technology involved in the tool. The assessment has been conducted for the highest concentration of particles detected by SEM analysis.

3. RESULTS

3.1. Measurement results

The results obtained from CPC 3007 are presented in **Table 1**. The mean concentration of particles at W3 surpasses the background level by 28 450 particles/cm^3; if it is compared with the mean value from outdoor sampling, an 80 838 particles/cm^3 increase is found.

Table 1 Number concentration results

Number concentration (#/cm^3)					
Sample	B	W3	W4a	W4b	O
Units	#/cm^3	#/cm^3	#/cm^3	#/cm^3	#/cm^3
Mean	59 736	88 186	60 068	62 657	7 348
Min	35 793	62 978	41 416	41 658	1 435
Max	71 656	113 468	74 011	76 757	32 543
Std. Dev.	6 376	9 904	5 605	4 661	5 338

Note: B -background in production hall; W3 - workplace 3, W4a - workplace 4a; W4b - workplace 4b, O - outdoor background

The mean concentration and standard deviation of all measurements are presented graphically in **Figure 1.**

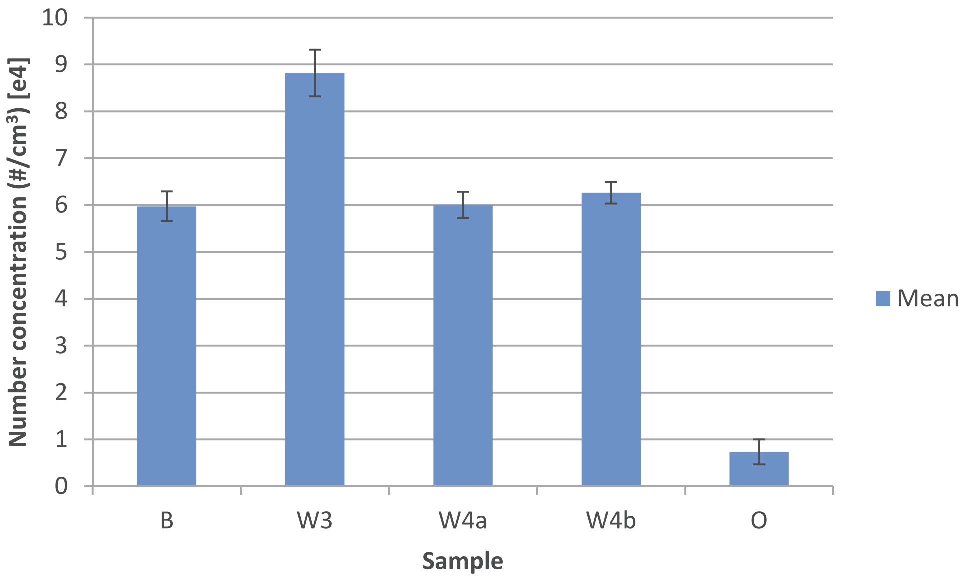
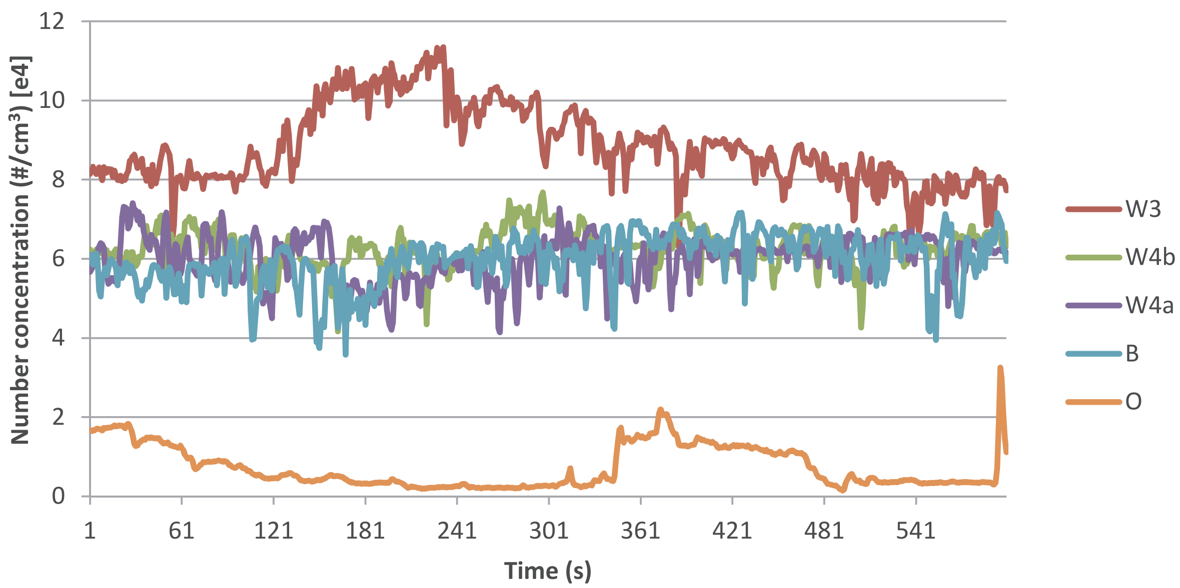


Figure 1 Graphical representation of mean value of the airborne particle concentration

Figure 2 represents the time variation of the airborne particle concentration during the e-waste processing and backgrounds. It is possible to identify periods (in W3 data) when the concentration of airborne particles increased.



Note: B -background in production hall; W3 - workplace 3, W4a - workplace 4a; W4b - workplace 4b, O - outdoor background

Figure 2 Graphical representation of the airborne particle concentration in time

The increase of the concentration of ultrafine particles was most probably caused by blockage of shredder. The shredder had to be turned off, and a worker had to get into the shredder to remove the material.

The samples of all 12 stages collected by the Nano-ID® Select were analysed for metal content by ICP-MS, THERMO XSeriesII. The results are presented in **Table 2**.

Table 2 Chemical composition results

ID + NanoID Stage	Fe 56 (ug/sample)	Mn 55 (ug/sample)	Cr 52 (ug/sample)	Co 59 (ug/sample)	Cu 63 (ug/sample)	Zn 66 (ug/sample)	Sb 121 (ug/sample)	Pb 208 (ug/sample)	Cd 111 (ug/sample)	Sn 118 (ug/sample)
39060 stage 1	27,830	1,750	0,073	0,172	0,908	4,887	0,034	8,318	0,067	0,207
39061 stage 2	14,004	0,425	0,024	0,035	0,378	2,216	0,015	2,159	0,038	0,071
39062 stage 3	13,164	0,351	0,022	0,022	0,521	1,815	0,012	1,819	0,029	0,084
39063 stage 4	8,813	0,266	0,035	0,015	0,243	1,044	0,008	1,348	0,017	0,059
39064 stage 5	1,332	0,039	0,003	0,002	0,037	0,056	0,000	0,208	0,004	0,015
39065 stage 6	0,905	0,027	0,063	0,002	0,115	1,437	0,000	0,089	0,004	0,007
39066 stage 7	0,672	0,010	0,048	0,003	0,008	0,079	0,000	0,053	0,006	0,000
39068 stage 8	0,027	0,005	0,251	0,001	0,263	1,621	0,011	0,018	0,001	0,338
39069 stage 9	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,056
39070 stage 10	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,000	0,045
39071 stage 11	0,000	0,000	0,000	0,001	0,000	0,000	0,000	0,000	0,000	0,045
39072 stage 12	0,000	0,000	0,000	0,001	0,000	0,000	0,000	0,000	0,000	0,048

The results in **Table 2** represent the mass content of the individual size fractions. The smallest detected particles were at stage 8 measuring particles 60 nm - 250 nm. The highest concentration of elements at this stage was for chromium, copper, zinc, and tin. These elements were assessed in control banding tools, see following chapter.

3.2. Qualitative risk assessment

The qualitative risk assessment has been done for the nanoparticle elements: chromium, copper, zinc, and tin.

3.2.1. Health hazard profile of assessed elements

Chromium in the air is present as particle-bound or dissolved in droplets. Chromium(VI) trioxide (chromic acid) and soluble chromium(VI) salt aerosols may produce different health effects than insoluble particulate compounds. Exposure to chromium(VI) trioxide results in marked damage to the nasal mucosa and perforation of the nasal septum, whereas exposure to insoluble(VI) compounds results in damage to the lower respiratory tract. The products of metabolic reduction of chromium(VI) (free radicals and chromium(V) and (IV)) and the newly generated chromium(III) are thought to be, in part, primarily responsible for the genotoxic effects that may lead to carcinogenicity. Chronic inhalation of chromium(VI) compounds was carcinogenic in rats and mice, and a 2-year carcinogenicity study on oral chromium(VI) provided clear evidence of oral cancers in rats and gastrointestinal cancers in mice [9].

Copper (Cu) is one of the biogenic elements occurring in cells of all organisms. The copper can be present in the biological systems in the oxidised ($Cu2+$) or reduced state. The excessive level of copper can damage cellular components, be cytotoxic or cause the oxidative stress [10]. In a study dealing with miners in copper mines , an increased risk of deaths from lung cancer and stomach cancer was found compared with residents in the area of the studied mine [11].

Zinc is an essential element required for numerous basic functions in all living organisms. Inhalation is the main route of exposure to zinc in the occupational setting. When zinc as ore or metal and its alloys are exposed to temperatures near the metal's boiling point of 907 °C in an oxidizing atmosphere, the formation of fresh zinc oxide particles in size of approx. 0.2-1.0 µm occurs. Inhalation exposure to zinc and its compounds can cause adverse effects in gastrointestinal tract, as it was reported in a study of workers with 7-20 years of exposure in galvanizing industry. 12 out of 15 examined workers experienced frequent episodes of e.g. epigastric or abdominal pain, nausea, vomiting, ulcers, constipation [12].

Inorganic **tin** compounds usually enter and leave the human body rapidly following inhalation or oral exposure. Interestingly, tin is able to affect the metabolism of various essential minerals, such as zinc, copper, and iron. The mechanism is probably related to their absorption and retention. Airborne tin is bound to particulate matter, the highest concentrations were found to be associated with respirable particles of 1-3 µm in diameter [13]. Studies on the potential genotoxicity and carcinogenicity show conflicting results. Tin smelter workers had an increased risk of lung cancer [14]. In an earlier study [15] however, an increased incidence of lung (or other) tumours in tin mill workers was not observed (640 workers employed in the period from 1921 to 1955 [16], [17]. According to Robertson (2006) [15] different conclusions from these studies may be based on different ways of tin ore handling, its different origins and especially the possible content of carcinogens. Current exposure to various chemicals is the overriding factor complicating epidemiological studies on the toxicity of tin.

3.2.2. Inputs and result of qualitative risk assessment

The inputs for the qualitative risk assessment are mentioned in **Table 3**.

Table 3 Information input for CB Nanotool 2.0

		Name or description of nanoparticle	Zinc (Zn 66)	Copper (Cu 63)	Chromium (Cr 52)	Tin (Sn 118)
		CAS#	7440-66-6	7440-50-8		7440-31-5
		Activity classification	Machining, sanding, drilling, or other mechanical disruptions of materials containing nanoparticles			
		Current Engineering Control	Fume hood or local exhaust ventilation			
SEVERITY BAND	Parent material	Lowest OEL (mg/m3)	----	1	1	2
		Carcinogen?	No	No	Yes	No
		Reproductive hazard?	No	No	No	No
		Mutagen?	No	No	No	No
		Dermal hazard?	Yes	Yes	Yes	No
		Asthmagen?	No	No	Yes	No
	Nanoscale material	Surface reactivity	Unknown	Unknown	Unknown	Unknown
		Particle shape	Unknown	Unknown	Unknown	Unknown
		Particle diameter (nm)	> 40 nm	> 40 nm	> 40 nm	> 40 nm
		Solubility	Soluble	Insoluble	Insoluble	Insoluble
		Carcinogen?	Unknown	Unknown	Unknown	Unknown
		Reproductive hazard?	Unknown	Unknown	Unknown	Unknown
		Mutagen?	Unknown	Unknown	Unknown	Unknown
		Dermal hazard?	Unknown	Unknown	Unknown	Unknown
		Asthmagen?	Unknown	Unknown	Unknown	Unknown
PROBABILITY BAND		Estimated maximum amount of chemical used in one day (mg)	---	---	---	---
		Dustiness	Low	Low	Low	Low
		Number of Employees with Similar Exposure	1.5	1.5	1.5	1.5
		Frequency of Operation (annual)	Daily	Daily	Daily	Daily
		Operation Duration (per shift)	> 4 hr	> 4 hr	> 4 hr	> 4 hr

For the severity band, the information related to micro- and nano-elements was obtained from databases: ECHA registered substances [18], OSHA [19], and NIOSH [20]. The probability band factors were defined by the workers' task characteristics. The results of the risk assessment based on the scores are presented in **Table 4.**

Table 4 Risk assessment results using CB Nanotool 2.0

Element	Severity score	Severity band	Probability score	Probability band	Overall risk band	Upgrade Engineering control
Zinc (Zn 66)	56.5	High	27.5	Extremely Unlikely	RL2	No
Copper (Cu 63)	76	Very high	43.75	Less Likely	RL3	Yes
Chromium (Cr 52)	76	Very high	43.75	Less Likely	RL3	Yes
Tin (Sn 118)	69	High	43.75	Less Likely	RL2	No

The level of risk obtained from CB tool was equal to RL2 (periodic review of the tasks, procedures, and controls by OSHH disciplines is necessary), and RL3 (tasks require a standardized one-page permit as a higher level of control documentation in justifying the implemented controls will reduce risks relative to operative OELs). Local exhaust ventilation was proposed, based on the assessed risk level, to ensure occupational health and safety.

3.3 Conclusion

Unlike in the case of work with traditional materials, the conventional occupational hygiene measurement methods might not be fully suitable for agents in a nanomaterial form. However, it is possible to assess exposure using various direct-reading equipment and sampling media for subsequent analyses [17]. Numerous techniques were identified to measure airborne nanomaterials with respect to particle size, mass, surface area, number concentration, and composition. However, as it was confirmed in the Methner article [21] some of these techniques lack specificity and field portability, are difficult to use and expensive when applied to routine exposure assessment.

At present, there are practically no occupational exposure limits (OELs) specific to nanomaterials that have been adopted or recommended by authoritative standards and guidance organizations. Nevertheless, there are some proposals of the OEL values for a few types of nanoparticles, but these values are set up just for specific nanomaterials such as TiO_2, MWCNT [22]. Based on this, the precautionary principle was applied in case of qualitative risk assessment using CB Nanotool v 2.O. The level of risk obtained from CB tool was equal to RL2, and RL3. Local exhaust ventilation was proposed, based on the assessed risk level, to ensure occupational health and safety. This field study has been conducted as a case study for the subsequent detailed risk assessment and management.

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