PRELIMINARY RISK EVALUATION OF POTENTIALLY HAZARDOUS CARBON NANOMATERIALS

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WHY THIS WORK ?

- The need to evaluate risk for CNTs in Supercapacitor –research project
- Carbon nanotube properties are comparable to those of asbestos from a structural resemblance (Poland et al. 2008, Ali-Boucetta et al., 2012).
- Evidence data for potential adverse health effects of single-walled carbon nanotubes (SWCNT), multi-walled carbon nanotubes (MWCNT) and carbon nanofibres (CNF) from reported animal and in-vitro cellular studies. the Potential adverse health effects: pulmonary inflammation, interstitial fibrosis, fibrotic lesions in lungs and possibly genotoxicity. (NIOSH (2010) and Savolainen et al. (2010a))
- Exposure limits are very low: 7 µg/m^3 (USA and Australia), 5 mg/m^3 (EU) (8-hr-time-weighted average)
- There was not available a risk assessment tool directed to university conditions.

Risk management guides NIOSH, ECHA, Safework Australia, HSE

Risk assessment in guides: based on job&tasks assessment to determine potential for exposure

Safework Australia presents two options to manage risks: (A) detailed hazard analysis and exposure assessment, (B) Control banding

Instructions in guides:

Detailed risk evaluation procedures from Safework Australia and HSE

Instructions for PPE

Packaging&transport instructions

Emergency and cleaning procedures

Disposal procedures

NIOSH. Current intelligent bulletin 65, Occupational exposure to carbon nanotubes and nanofibers. Department of health and human services, Centers for disease control and prevention, **National institute for occupational safety and health**; 2010.

Safe work Australia. Safe handling and use of carbon nanotubes; 2012.

EU-OSHA. Tools for the management of nanomaterials in the work place and prevention measures, E-FACTS 72; 2013

ECHA. Guidance on information requirements and chemical safety assessment. Appendix R14-4 Recommendations for nanomaterials applicable to: Chapter R.14 Occupational exposure estimation. **European Chemical Agency**; 2012.

HSE. Risk management of carbon nanotubes, **Health and safety executive**. 2009.

HSE. Using nanomaterials at work including carbon nanotubes (CNTs) and other biopersistent high aspect ratio nanomaterials (HARNs), **Health and safety executive**; 2013

Nano Risk Framework. **Environmental Defense – DuPont Nano Partnership**; 2007.

OUR APPROACH TO RISK EVALUATION AT LUT

- The information aggregation concerning CNTs and CNFs from the guides by NIOSH, Safework Australia, HSE and DuPont&Environmental Defense Fund (Nano Risk Framework)

- The guides are directed to enterprises which may already have routines in other hazard material handling especially for commercialization purposes.

- Our approach to preliminary risk management is directed to universities and research institutes

- The aim is to quantify the risk and follow a control flowchart for objective decision making in follow-up actions.

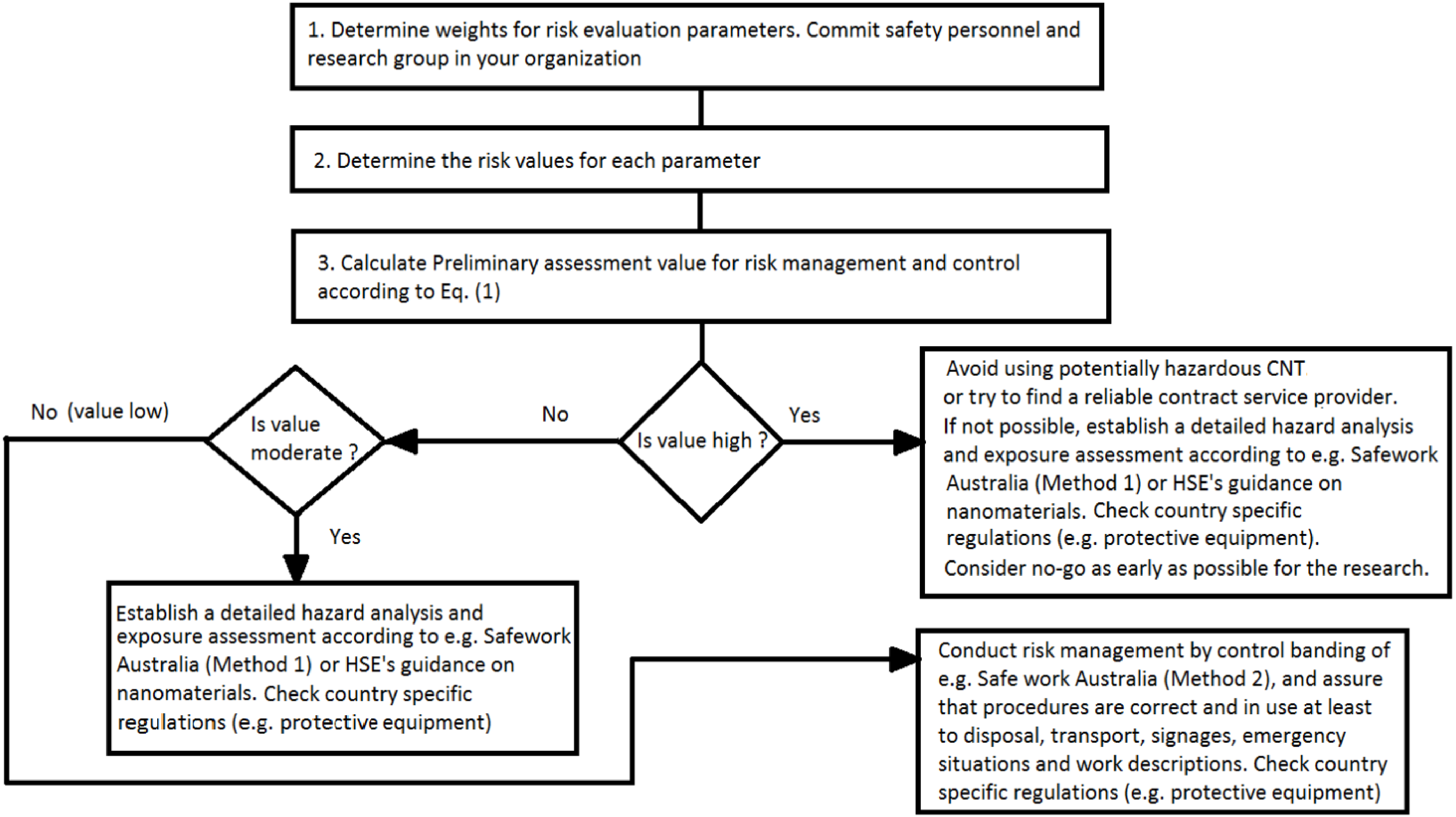
INFORMATION AGGREGATION CONCERNING CNTS AND CNFS IDENTIFICATION OF RISK EVALUATION PARAMETERS

EVALUATION PARAMETER DESCRIPTION	REASONING	SOURCES WHERE ADAPTED FROM
Material risk (very hazardous, less hazardous forms)	Different forms of nanocarbons are available	NIOSH, HSE, Safe work Australia
Quantity risk (over 1 kg ; 100 g -1 kg ; 10 g-100 g ; 1 mg - 10 g)	The amount correlates to potential exposure	Safe work Australia, DuPont&Environmental defense
Handling risk (dry/wet/degrading matrix/ non-degrading matrix)	Nanocarbons in attached media is less potential for exposures	Safework Australia, NIOSH, HSE
Processing risk (weighing dry material/milling/ grinding/scraping/no mechanical treatment)	Processing correlates to potential exposure	NIOSH, HSE, Safe work Australia, DuPont&Environmental defense
Human exposure risk (organizational competence for engineering controls)	Engineering control facilities and preparedness to engineering controls essentially influences human exposures	Risk management methods do not regard safety baseline of organizations.
Personnel risk (students / professional persons)	Experienced and trained professionals in research work provide good capabilities for handling nanocarbons	In principle, risk management methods suppose professional personnel involvement
Work environment risk (flammable compounds, reactive compounds or electric systems present, heat, pressure etc. / no flammable or reactive systems, ambient conditions)	Other potential hazards raises the level of risk	HSE, Safe work Australia, DuPont&Environmental defense

INFORMATION AGGREGATION CONCERNING CNTS AND CNFS IDENTIFICATION OF RISK EVALUATION PARAMETERS

EVALUATION PARAMETER DESCRIPTION	REASONING	SOURCES WHERE ADAPTED FROM
Environmental load risk (possibility to be released in environment / no possibility to be released)	Nanocarbons may be environmental risk	Safe work Australia, DuPont&Environmental defense
Organizational control preparedness (level of safety and work procedures documentation)	Established safety and work procedure documentation system provides capabilities for administrative controls	In principle, risk management methods suppose safety documentation is established during the risk management planning.
Commercial use risk (home, outdoors, work places, factories)	Evaluation of future potential exposure for users: level of safety procedures in organizations and enterprises may be higher than e.g. at homes.	DuPont&Environmental defense
Commercial product risk (CNT fraction and quantitities in product, CNT production/raw material volumes etc.)	Evaluation of future potential exposure for a product itself.	DuPont&Environmental defense

RISK EVALUATION PROCESS IN CNT HANDLING PROCESSES



- The evaluation is a combination of parameter importance and risk parameter values, scale from 1 to 4 (low/moderately low/moderately high/high). The preliminary risk assessment value Y is normed between 1.0 and 4.0:

$$Y = \frac{\sum_{i=1}^{N} X_i W_i}{N W_{av}} \qquad (1)$$

where	N	number of evaluation parameters
	W_i	Importance weight of parameter X_i value, 1-4
	W_{av}	Average of important weights of parameters X_i
	X_i	risk parameter evaluation value, 4-1

- The weight parameters can be selected by pairwise comparison analysis (Saaty, 1990) in order to determine the importance weights
- Risk assessment values are indicatively: High = 2.6 – 4.0, Moderate = 2.1 – 2.8, Low = 1.0 – 2.3. The overlapping of the values was selected to allow the evaluator judgment in borderline cases

CASES FOR EVALUATION PROCESS

- The cases presented here are related to Nationally funded Supercapacitor-project at LUT

- **Case 1.** Max. 12 g dry fibrous MWCNT (diameter 90 nm, length 5 µm, aspect ratio 56) is mixed with biodegradable polymer forming a matrix. Several sheets of polymer matrix are made to form raw material for a supercapacitor. Dry weighing and ultrasonic mixing are performed in processing.
- Personal protection equipment available but no facilities for glove boxes or isolated work areas other than fume hoods. The CNT concentration is 15 w-%-30 % in polymer matrix and 10-30 sheets could be done during one day.

- The risk assessment value was 2.7 (moderate/high), and the follow-up actions were:

1. A glove box was acquired (HEPA-filters outlet/inlet, different glove materials available, underpressure system with alarm for leaks)
2. Detailed work instructions were done
3. Hazard analysis (LUT Chem.eng.) was performed
4. Instructions for PPE
5. Emergency procedures
6. Cleaning procedures
7. Disposal procedure

- **Case 2** Supercapacitor was assembled and tested using the manufactured polymer matrix sheets. The risk assessment value was 2.1 (low/moderate), and the same follow-up actions were used as in Case 1

SUMMARY

- The presented risk evaluation method was developed for the needs in university

- The method takes into account commercialization viewpoints (Commercial use risk and commercial product risk) in the evaluation.

- Method was easily implemented in spreadsheet program (MS-Excel)

- The risk evaluation method can be used aside with Safework Australia and HSE Guides

- The decisions can be documented during the risk evaluation.

- Method can be adapted also for other hazardous particles

THANK YOU FOR YOUR ATTENTION

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