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Nano Risk Evaluation in Laboratory Environment by a Customized Layer of Protection Analysis Approach

Erika Lunghi[a], Andrea P. Reverberi[b], Laura Pastorino[c], Bruno Fabiano[a,*]

[a]Civil, Chemical and Environmental Engineering Department DICCA, Polytechnic School, Genoa University, via Opera Pia 15, 16145 Genoa, Italy.
[b]Chemistry and Industrial Chemistry Dept. DCCI, Genoa University, via Dodecaneso 31, 16146 Genoa, Italy.
[c]Informatics, Bioengineering, Robotics and System Engineering Dept., via Opera Pia 13, 16145 Genoa, Italy.
brown@unige.it

Nanotechnologies are widely used in various industrial settings and by the year 2020, it is expected that nearly 20 % of all products manufactured in the world will take a certain amount of nanotechnology. However, there is a substantial imbalance of knowledge between application of nanotechnology and its impact on health and environment, also considering that nanoparticle synthesis by chemical methods assumed a key role for economic, industrial and scale-up issues. The information currently available on nanomaterial risk assessment within the workplace are limited: systematic methods for assessing exposure are not known yet and the number of workers exposed is hardly estimated. This knowledge gap imposes to the scientific community the need to join efforts to provide a shared opinion on safety, health and welfare of workers who use, manipulate, or produce nanomaterials, adopting as well preventive and protective measures proportionated to the risk according to the precautionary principle. We develop a novel framework for Nano Risk Assessment within the laboratory context, by combining LOPA and HazId techniques, assigning credit factors to specific operative procedures and safety training, suitable to mitigate risk exposure and avoid over-conservative evaluations. Conclusions are drawn on applicative results and possible direction for further implementation of the approach, in view of sustainable, healthy and safe production at research and industrial level.

1. Introduction

Nowadays, the role of nanotechnology in global industries and, more generally, in the scientific research community is growing in importance and extent of use. Many nanomaterials are used as ingredients in cosmetics, food products, pharmaceutical nanocapsules for the delivery and controlled release of drugs in the human body. Because of their physico-chemical properties, nanoparticles (NPs) are suitable in a wide range of applications, e.g.: CO_2 capture by nanoporous silica modified with amine groups (Gonzàlez-Barriuso et al., 2016); degradation of recalcitrant organic pollutants by nanostructured anodic porous titania (APT), (Shayganpour et al., 2016); catalyst selectivity and conversion improvement, e.g., ethylene oxidation process, (Fabiano et al.,2015); cancer diagnostic and therapy by gold nanoparticles (Giljohann et al., 2014); antibacterial activity of silver nanoparticles against Staphylococcus Aureus and Escherichia Coli (Shahverdi et al., 2007); NPs encapsulation in multi-walled carbon nanotubes for Claus plant possibly with oxygen-enriched process enhancing S recovery but posing additional hazards (Palazzi et al., 2014). The first three applications reveal the up-to-date tendency of coupling the precepts of green chemistry with nanoparticles research field, in order to extend the concept of sustainability (Murphy, 2008). In this context, nanotechnology is regarded as a promising method to enhance non-conventional hydrogen production for fuel cell applications (Palazzi et al., 2002), increasing as well photocatalitic conversion of pollutants such as hydrogen sulphide (Reverberi et al., 2016a). A wide range of nano-materials poses a potential threat to human health and environment, being by definition: “natural, incidental or manufactured material containing particles in an unbound state, or as an aggregate, or as an agglomerate and where, for 50 % or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm – 100 nm” (SCENHIR, 2010). They cause a demand for new approaches in process safety, as many standard test methods can no longer be used for these materials, either because

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they are not adequate, or because they are not acceptable in view of work place safety in the test laboratories (De Rademaeker et al., 2014). In this context, uncertainty is connected to the absence of an intelligent testing strategy (ITS) (Scott-Fordsman et al., 2014) and to the great diversity of substances and morphologies (e.g. there are currently 50,000 different types of carbon nanotubes due to different raw materials, production processes and catalysts) (Savolainen et al., 2010). All over the world, regulatory authorities developed rules also under the influence of the economic policy of the State of belonging, with difficulties in finding an equilibrium between market, economy and safety investment, a conflict that in the past caused high profile process accidents (e.g. Bhopal gas tragedy) (Palazzi et al., 2015). The two opposite poles can be represented by China and Europe the former addressing priorities to the national economy supporting technical progress much more than the worker/consumer safety; the latter increasing the requirements to assure safety, with the inevitable formation of a bottleneck in the affordability. This paper mainly focuses on the issue Occupational Health and Safety (OHS) in laboratory environment connected to the widespread issue of nanoparticle synthesis by chemical methods (Reverberi et al., 2016b), and to empirical evidence (Balas et al.,2010) that most workers do not use suitable personal protection equipment (PPE) -the ultimate layer of protection- when handling nanomaterials. Additionally, knowledge gaps between nanotoxicological research and nanomaterial safety increased the level of uncertainty (Hu et al., 2016): nanosafety, widely considered by people, contributes in evaluating nanomaterial risks, while nanotoxicity focuses on mechanisms underlying the physiology and pathology of nanomaterials. Laboratory personnel are potentially exposed to engineered nanomaterials (Johnson et al., 2010) and an easy-to-use method helpful to stakeholders in evaluating the “nano-safety” level of a laboratory may become a vanguard tool, widely used. As proper understanding and evaluating the risk of operational accidents require thoroughly analysis of the causes and of the barriers to prevent them, in this paper, we face nano risk assessment combining a customized hazard identification step and Layer of Protection Analysis (LOPA). A simple case study will be investigated, in order to provide the capability and immediacy of the method.

2. Methodology

Starting from the premise that new technologies need to be faced by new tools, or proper outfit of existing ones, in the following we present a novel semi-quantitative tool for analyzing and assessing risk, based on LOPA. Compared with classical approach, several improvements were developed, namely a specific and customized hazard identification technique, the Nano-CheckList (N-CL), to identify the main critical issues; severity evaluation by scoring criteria based upon the answers of the N-CL; the possibility of assigning credit factors to operative procedures and safety training. The Nano-LOPA tool is structured into logical steps:

- Hazard Identification (HazId) based upon the N-CL: the task is divided into two macro-categories (“ENM properties ID/Hazard Characterization”; “Lab Equipment/Procedures”).
- Evaluation of the Severity Factor (SF), depending on a scoring criterion, which relies on the “ENM properties ID/Hazard Characterization” part of N-CL.
- Evaluation of the Exposure Time/Dose Factor ETDF calculated by scoring B.01/B.02/B.03 issues of N-CL.
- Evaluation of the Independent Protection Layers Factor (IPLF) depending on scores assessed in the “Lab Equipment/Procedures” section of N-CL.

Tables 1, Table 2 and Table 3, coupled with the use of the matrix introduced in Figure 1 summarize the scoring criteria adopted in the index evaluation, as well as the actual links with the processed N-CL presented in Figures 2 and Figure 3. According to CCPS (2001), an IPL should be: effective in preventing the consequences; independent from the initiating event; auditable to be validated in some manner. Process design, Basic Process Control System, critical alarms, human intervention, physical protection and post-release protection are commonly considered the most relevant IPLs.

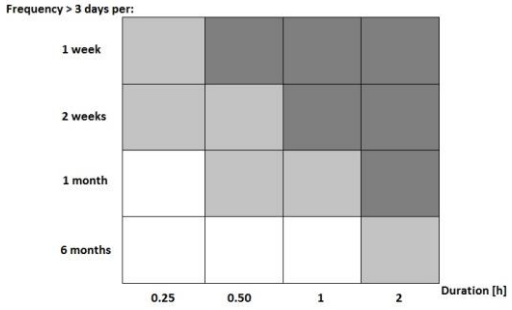

Figure 1: Semi quantitative evaluation matrix, based on actual worker exposure to Nano-hazards.

Classical LOPA does not consider as IPLs training and certification, the procedures and the communications, while the customized tool considers these last items as relevant protection layers. The Nano-Index (NI) can be evaluated according to Eq(1):

$$NI = SF - ETDF - IPLF \quad (1) \qquad SF = log\ (SFi) \quad (2)$$

where Eqs (2), (3) and (4) provide the adopted quantitative correlations between factors and indexes.

$$ETDF = ETDFi \quad (3) \qquad IPLF = log(IPLFi) \quad (4)$$

The choice of attenuating the first and third term of the right-hand side of Eq(1) is justified by the principles of conventional LOPA technique (CCPS, 2001). It should be remarked that SF evaluation is mainly linked to the intrinsic hazardous properties of the reference substance, while the amount and the exposure time can be modulated and ETDF plays a pivotal role. Nano risk is considered broadly acceptable if by applying Eq(1) it results NI ≤ 0.5; whether NI exceeds the value 0.5, further independent protection layers should be added.

Table 1: Scoring criteria for the Severity Factor index (reference is made to the worked example in Figure 2).

#	Score	#	Score
A.01	No score.	A.17	If answer: “5”: 4pt; “4”: 3pt; “3”: 3pt; “2”: 2pt; “1””: 1pt.
A.02	Size range [1;10]:4pt [11;40]:3pt [41;70]:2pt [71;100]:1pt [100;…]:not nano	A.18	If answer: “1”: 4pt; “2”: 3pt; “3”: 3pt; “4”:2pt; “5”: 1pt
A.03	If ☐:1pt; if ☑:see next question	A.19	If ☑ : 2pt
A.04	If ☑: 2pt	A.20	No score.
A.05	If ☑: 3pt	A.21	If ☑: 3pt
A.06	If ☑: 3pt	A.22	If ☑: 4pt
A.07	If ☑: 3pt	A.23	If ☑: 3pt
A.08	If ☑: 4pt	A.24	If ☑: 3pt
A.09	If ☑: 4pt	A.25	No score.
A.10	Repeat the same scoring criteria of A.03-A.09	A.26	1 pt for each ☑
A.11	If ☑ AND A.02 ϵ [1;10]: 4pt; If ☑ AND A.02 NOT ϵ [1;10]: 2pt;	A.27	1 pt for each ☑
A.12	Repeat the same scoring criteria of A.11	A.28	If ☑: 3 pt
A.13	If ☑: 4pt	A.29	If answer: “5”: 4pt; “4”: 3pt; “3”: 3pt; “2”: 2pt; “1””: 1pt.
A.14	If isotope: “Graphene”:4pt; “Fullerene”: 2pt; “Nanodiamond”:1pt; “C black”: 1pt	A.30	If ☑: 4pt
A.15	If ☑: 3pt	A.31	If ☑: 2pt
A.16	If ☑: 2pt	A.32	If ☑: 1 pt

Table 2: Scoring criteria for the Exposure Time/Dose Factor index (matrix evaluation according to Figure 1).

#	Score

B.01	If A.04 ☑ THEN If quantity ϵ [40 mg ; 400 mg] THEN
	If duration/frequency (case D.GREY: 1pt; case L.GREY: 2pt; case WHITE: 3pt) [see Figure 1]
	If quantity > 400 mg THEN
	If duration/frequency (case RED: 0pt; case L.GREY: 1pt; case WHITE: 2pt) [see Figure 1]

B.02	If A.05 OR A.06 OR A.07 ☑ THEN If quantity is in the range [20 mg ; 200 mg] THEN
	If duration/frequency (case D.GREY: 1pt; case L.GREY: 2pt; case WHITE: 3pt) [see Figure 1]
	If quantity > 200 mg THEN
	If duration/frequency (case D.GREY: 0pt; case L.GREY: 1pt; case WHITE: 2pt) [see Figure 1]

B.03	If A.08 OR A.09 ☑ THEN: 0pt in any case.

3. Applicative case-study

Cobalt nanoparticles are widely applied in the catalysis and in the medical fields and are chosen to discover the outcomes of the method and fill in the section A of the Nano-CheckList (see Figure 2). In the given context, Co-NPs are synthesized by chemical decomposition of $Co_2(CO)_8$ at high temperatures, obtaining spherical

nanoparticles with low size distribution (Soares Zola et al., 2014). According to recent scientific literature, it is assumed that Co-NPs are characterized by: effects of genotoxicity, immunotoxicity, ocular-skin-liver toxicity and pulmonary inflammations (Magaye et al., 2012); moderate/negligible neurotoxicity effects (Catalani et al.,2012); persistence, with neither mutagenicity or bio-accumulation characteristics (Wang et al., 2013); capability of crossing internal barriers by a mechanism involving transmission of purine nucleotides and intercellular signaling within the barrier (Bhabra et al., 2009). The compilation of the section B of the N-CL shown in Figure 3 is delegated to the relevant laboratory expert. Results of the example provide NI = -1, thus indicating that no additional technical, organizational, or personal LOPs are required for the given process.

Table 3: Scoring criteria for the Independent Protection Layers Factor index (based upon Figure 3).

#	Score
B.04	If I) ☑: 3 pt; If II) ☑: 2 pt; If III) ☑: 1pt.
B.05 to B.26	1 pt for each ☑
B.27	If answer: "5": 5pt; "4": 4pt; "3": 3pt; "2": 2pt; "1"": 1pt

NANO-CHECKLIST A) ENM Properties ID / Hazard Characterization

Code	Question	Reply	Notes
A.01	Enter the name of the ENM.	COBALT	
A.02	Enter the size [nm] of the ENM.	28	Range: 2 to 60 nm
A.03	ENM is classified by the competent Authority.	☑	
A.04	The hazard level of the ENM is characterized by at least one among the Hazard Statements: H302; H312; H315; H317; H319; H332; H335; H336.	☑	
A.05	The hazard level of the ENM is characterized by at least one among the following Hazard Statements: H301; H311; H331.	☐	
A.06	The hazard level of the ENM is characterized by at least one among the following Hazard Statements: H305; H341; H351; H361; H362; H371; H373.	☑	
A.07	The hazard level of the ENM is characterized by at least one among the following Hazard Statements: H314; H318.	☐	
A.08	The hazard level of the ENM is characterized by at least one among the following Hazard Statements: H300; H310; H330.	☐	
A.09	The hazard level of the ENM is characterized by at least one among the following Hazard Statements: H304; H334; H340; H350; H360; H370; H372.	☑	
A.10	Answer questions A.03-A.09 with reference to the bulk.	☑	The same as for nano
A.11	ENM is a pure metal.	☑	
A.12	ENM is an alloy.	☐	
A.13	ENM is a nanotube/nanofibre.	☐	
A.14	ENM is pure C (specify the isotope).	☐	
A.15	ENM is soluble into water.	☐	
A.16	ENM is crystalline.	☑	
A.17	On a scale 1-5, specify the ENM surface reactivity (1: low degree of reactivity; 5: high degree of reactivity).	5	
A.18	On a scale 1-5, specify the ENM tendency to aggregate (1: low aggregation; 5: high aggregation).	3	
A.19	ENM has characteristics of persistence.	☑	
A.20	Enter the dose-responses for critical target organs.		No target organs
A.21	ENM has the potential to react with constituents of cells (i.e. proteins, lipids, etc.).	☑	
A.22	ENM has the capability to cross internal barriers (blood-placental barrier, blood-brain barrier, etc.), or produce the same damage with other type of mechanism.	☑	
A.23	ENM may bio-accumulate.	☐	
A.24	ENM may generate pulmonary inflammation.	☑	
A.25	The most dangerous path for humans is represented by: inhalation; skin contact; ingestion.		Inhalation
A.26	ENM in vitro tests reveal: genotoxicity; immunotoxicity; neurotoxicity; ocular toxicity; skin toxicity; liver toxicity.	☑	All except neurotoxicity
A.27	ENM in vivo tests reveal: reproductive toxicity; organ toxicity; immunotoxicity; genotoxicity.	☑	
A.28	ENM has characteristics of mutagenicity.	☐	
A.29	Enter the roundness characteristics of the ENM on a scale 1-5 (1: very irregular shape; 5: circular shape).	3	
A.30	The process comes in open milieu.	☐	
A.31	The process comes in closed milieu.	☑	
A.32	ENM is handled in powder form.	☑	

Figure 2: Nano-CheckList – Section A. Engineering Nano-Materials Properties ID/Hazard Characterization.

NANO-CHECKLIST B) Lab Equipment / Procedures			
Code	**Question**	**Reply**	**Notes**
B.01	If A.04 ☑: enter the quantity [mg] and the duration /frequency of use.		100 to 150 mg, 2h/d, 5d/w
B.02	If A.05 or A.06 or A.07 ☑: enter the quantity [mg] and the duration /frequency of use.		60 to 80 mg, 2h/d, 5d/w
B.03	If A.08 or A.09 ☑: enter the quantity [mg] and the duration /frequency of use.		20 to 40 mg, 1h/d, 5d/w
B.04	The air is renewed: very often; often; rarely.		Often
B.05	Filters are regularly checked.	☐	
B.06	A low pressure level is maintained in the room.	☑	
B.07	The manipulation under fume hood is compulsory.	☑	
B.08	The staff uses safety glasses.	☑	
B.09	The staff uses FFP3 masks or masks with assisted ventilation (if handling duration > ... h).	☑	
B.10	The staff uses hands protections.	☑	
B.11	Concerning body protection, the staff uses overshoes and overall.	☐	
B.12	Just laboratory personnel is allowed in cleaning procedures.	☐	
B.13	Just authorized persons can access the area.	☑	
B.14	Just nano activities are allowed in the area.	☐	
B.15	It is compulsory to separate city/lab clothes.	☑	
B.16	A basic training is foreseen.	☑	
B.17	A continuous training about nano manipulation is foreseen.	☐	
B.18	There are written working procedures.	☑	
B.19	Concerning the transport of ENM: double bag for toxic waste is foreseen, with storage of bags in sealed container.	☐	
B.20	Concerning the elimination of ENM substances: package for solid / package for liquid are foreseen.	☑	
B.21	Concerning the storage: there is a ventilated storage room.	☑	
B.22	A special work authorization is needed for pregnant women.	☐	
B.23	The entire process is in confined environment.	☑	
B.24	The laboratory devices are subjected to regular maintenance.	☐	
B.25	Sensors are properly installed.	☑	
B.26	Alarms are properly installed.	☑	
B.27	On a scale 1-5, define the degree of awareness of the personnel concerning the procedures.	4	

Figure 3: Nano-CheckList – Section B referred to Laboratory Equipment and Procedures.

4. Conclusions

In a scientific community where the field of nanotechnologies is becoming increasingly dominant, safety issue in the workplace is located halfway in the dichotomy created by the concept of sustainability applied to the sector. Indeed, as evidenced by the most recent studies, from one side sustainable production methods are investigated (Liu et al., 2013) and sustainable energy sources, as well as environmental remediation are increasingly considered as end-goals of nanotechnology field (Reverberi et al., 2016c). From the other side, these trends towards environmental sustainability imply that a huge number of workers is exposed to nanoparticles hazards, as the synthesis by chemical methods assumed a key role for economic, industrial and scale-up issues. Because of the novelty of the field, which unavoidably means poor standardization of regulations and poor awareness on novel hazard exposure, risk analysts should develop new tools, or new outfits for existent tools. The methodology proposed in this paper fits in a context of lack of literature and would begin to bridge the gap: a novel framework for a Nano-LOPA tool has been elaborated, by developing a scoring criterion referred to a specific Nano-Check List. The last one takes into proper account both the intrinsic hazards of the involved substance and the adopted process, relevant operative conditions, as well as the laboratory or the context where the given process is actually performed. The outcomes of the illustrative example indicate that adequate risk mitigation layers at the strategic, technical and organizational levels are enforced in the given research work environment, under confined conditions. The tool my help in defining human-centric procedures and control measures to be combined with appropriate training programs based on the procedures and contributing to sustainability, quality, and improved productivity. In the awareness that this paper is just a starting point, needing further multidisciplinary refinement and experimental validation, authors wish that a simple stone might become the cornerstone.

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