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Chapter

Risk Assessment and Health, Safety, and Environmental Management of Carbon Nanomaterials

Guilherme Lenz e Silva, Camila Viana, Danieli Domingues and Fernanda Vieira

Abstract

The management of health, safety, and environmental (HSE) aspects during production, manipulation, storage, incorporation, and disposal of carbon nanomaterials is the key factor for the development of a safe-by-design work based on nanotechnology. The almost endless possibility of functionalization, chemical interaction, and addition of nanomaterials into new products implies a new management approach of HSE. Low amount of reliable toxicity and ecotoxicity data of nanomaterials and nanomaterial composites is available. As complete exposure/release assessments are a challenging task, recommendation for control measurements is still based on the precautionary point of view. There is an incomplete understanding of environmental fate- and time-related exposure, and of consumer- and worker-related risks and hazards. Control banding and risk evaluation matrix tools can be used to mitigate labor and environment impacts of carbon nanomaterials. This chapter presents new tools and methodologies for exposure assessment and risk evaluation of hazards used on HSE management system of carbon nanomaterials.

Keywords: risk assessment, risk analysis, risk evaluation, nanocarbons, nanotechnology, HSE

1. Introduction

Looking into the last 20 years—since the classical publications from the Royal Society, ETC Group, OECD/Allianz, European Commission, Swiss Reinsurance, and studies and think tanks related to risks and uncertainties of nanotechnology [1–7]—without any doubt, we are now in a better position concerning risks (assessment, analysis, evaluation, management, communication, policies, monitoring, and treatment) and benefits of nanotechnologies. However, new nanomaterials and new nanoproducts are achieving several markets, and the global changes on the business environment—including, fast, small and short-term life enterprises, start-ups and spin-offs based on new technologies—underline the need of special attention from the society regarding safety and environmental issues. Sometimes,

in the nanotechnology business endeavor, low capital and poor-trained people without enough knowledge and guidance about safety, health and environmental regulations, standards and protocols could expose, unnecessarily, workers, consumers and the environment.

From public and private investments, thousands of publications, research efforts, and scientific projects (money, time, and minds) have been done and much more should be done to follow the rapid technological and scientific development of nanoscience and its applications.

The knowledge of bio and physicochemical interactions between nanomaterials and living organisms, the understanding of life cycle analysis (LCA) of nanomaterials on environment, and the time-related effects of chronic dose-response toxicity are key points that should be taken in account during the debate and to improve the safety approach of nanotechnological development.

Risk assessment and management of health, safety, and environmental (HSE) nanotechnology are very important aspects to mitigate risks and improve the benefits and transform opportunities into technological development on medical applications (cancer treatment, tissue engineering, diagnosis of diseases, DNA manipulation, etc.), flexible and communication devices, portable energy, food conservation, agriculture productivity and pest control, and countless new applications and uses.

Carbon is one of the most important elements on Earth. Carbon nanomaterials are changing the technology of XXI century, and its fundamental electronic and hybridization states transform it into one of the most remarkable chemical elements with applications from regenerative medicine to rocket capsules and flexible electronic devices.

2. Carbon nanomaterials

Carbon hybridization states with sp^3 and sp^2 bonding system ally with the allotropy of carbon materials that produces soft, hard, light, and dense materials.

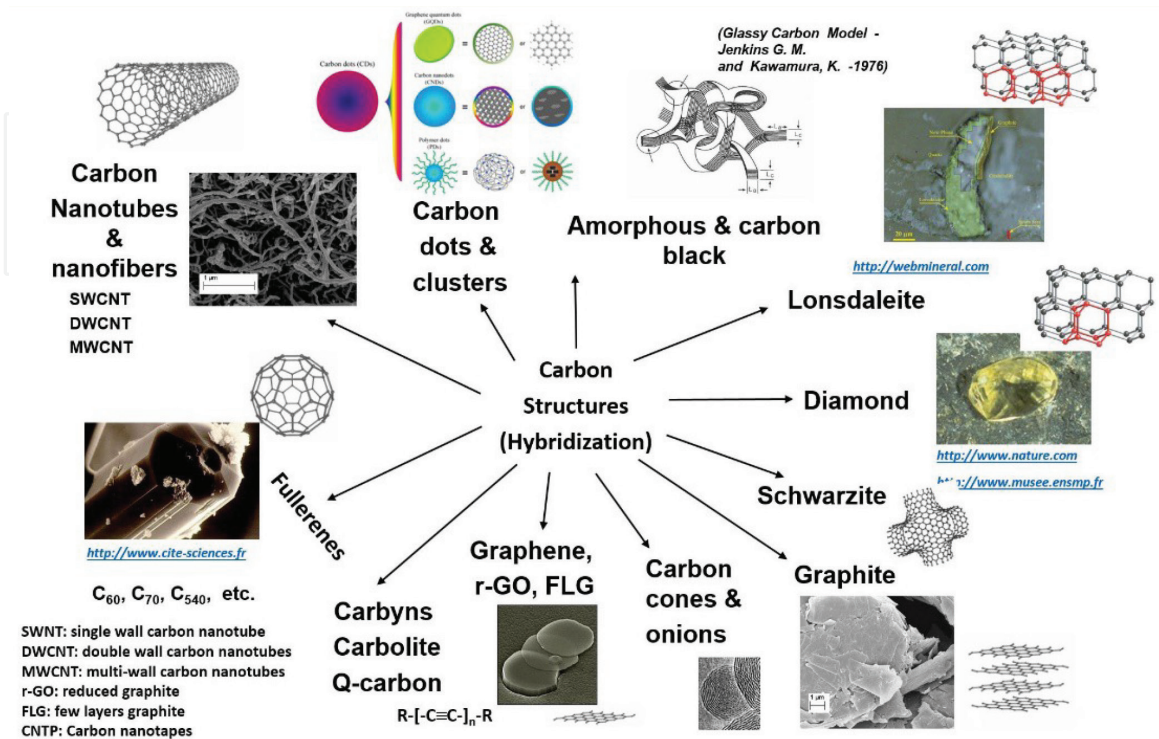


Figure 1. Carbon allotropes family (adapted from Ref. [12]).

The carbon use and applications came from charcoal for heating, passed by nuclear reactors to carbon-carbon composites used on new aircrafts or space capsules. However, after the discovery of fullerenes from Curt et al. [9, 10] and discovery of graphene by Geim and Novoselov [11], the research of carbon nanomaterials has been expanding in an unimaginable way [8–11]. **Figure 1** shows the carbon allotropes with special attention on nanoforms.

The hybridization states of carbons allow then to assume different geometries in the space from 0D dimension (fullerenes, carbon dots) to 1D fiber type materials with high aspect ratio, passing by 2D flat material (graphene) to high complex 3D material such graphite, diamond, or schwarzite materials.

3. Health, safety, and environmental (HSE) management of nanomaterials

Why we should think differently about health, safety, and environment when dealing with nanomaterials or nanoobjects? Nanotechnology has defined areas of science that take place at nanoscale (1–100 nm) [13, 14]. Many specific and fundamental aspects are related to HSE, including surface energy, functionality, and size. **Figure 2** shows the main nanoparticle properties and how they are related regarding toxicological and risk assessment of nanomaterials. Those properties and the relation between them can be considered main aspects that should be considered to assess specific nanoparticle's risks.

Size (distribution), shape, surface area, chemical composition/crystalline structure, and solubility are very important properties regarding the risk assessment of carbon nanomaterials [15].

These properties can be assessed using different analytical tools. **Table 1** shows the nanomaterial properties, the main characterization techniques, and also the degree of importance on the knowledge of such property for a risk assessment point of view.

It is noticed that the concentration of nanomaterial could be described using different metrics such as mass/volume or number of particulates (or fibers)/volume.

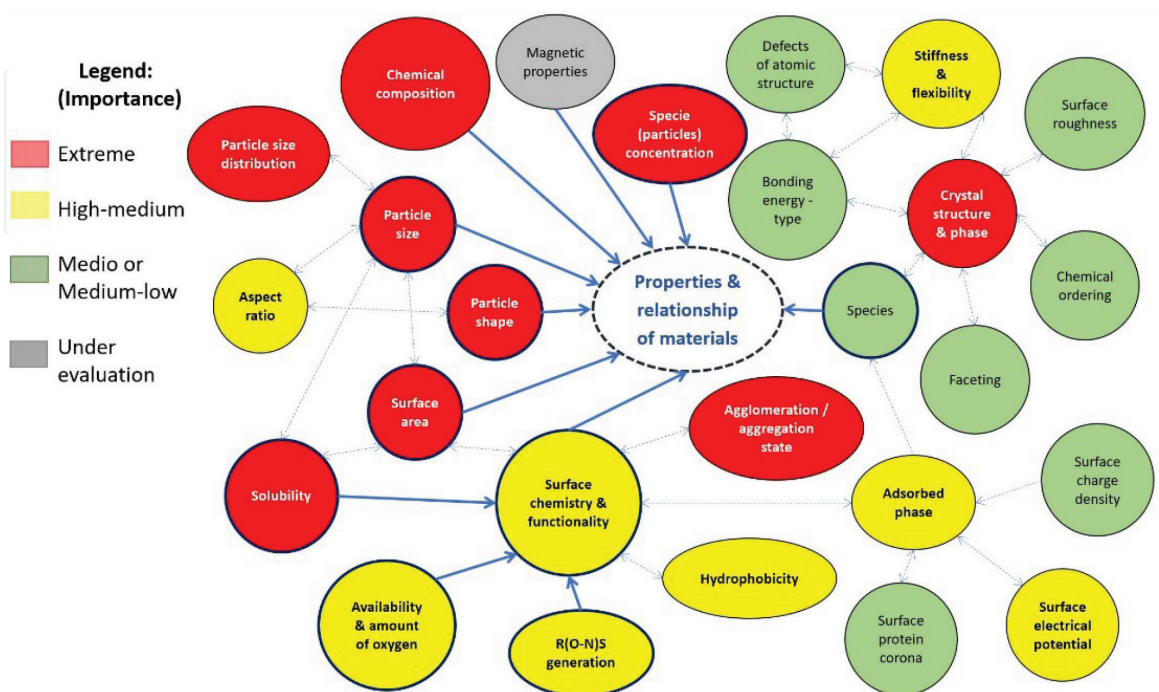


Figure 2. Major relationships between properties and risk/toxicological interactions (adapted from Ref. [15]).

Nanomaterial properties	Importance	Main analytical characterization techniques
Chemical composition, structure and crystalline phase	Extreme	XRD, XRF, ICP-AES, AAS, HPLC, SIMS, MALD-TOF, EDS
Specific surface area (density, porosity, and reactivity: flammability and explosivity)	Extreme	Multimolecular gas adsorption (BET/adsorption isotherm method), gas (He) pycnometer, mercury intrusion porosimetry (MIP)
Shape dimensionality/morphology (0D, 1D, 2D, or 3D), number of layers	Extreme	TEM, XRD, SEM, Raman
Stiffness (rigid and flexibility, aspect ratio)	High-medium	Microscopy (SEM, TEM, ...), XRD
Solubility (dissolution and toxicant species release)	Extreme	Tables of solubility, Hildebrand and Hasen parameters
Surface species: R(O-N)S: reactive (oxygen and nitrogen) species, C/O atomic ration, etc.	High-medium	XPS, FTIR, NBT test, ESR, EPR
Surface chemistry (functionality, hydrophobicity and hydrophilicity, and adsorbed compounds and groups)	High-medium	Oxygen singlet analysis, XPS, FTIR, pH, contact angle microscopy, AES, EELS, DTA
Size and size distribution (aerodynamic, hydrodynamic)	Extreme	SEM, DLS, FCS, XRD
Solid bonding energy and type	Medium-low	DSC-TGA, simulation (first principles)
Surface charge density	Medium	SPM, PCM, SPR
Surface speciation	Medium-low	XPS, FTIR, NMR
Agglomeration and aggregation state	High-medium	XRD, SEM
Surface nanoparticle-protein corona	Medium	Simulation, electrophoresis
Bio-(persistence, accumulation, degradation and digestibility), endotoxin content	High-medium	Specific corrosion, digestibility, chemical analysis, LAL, TET, TNF, etc.
Structural atomic defects, ordering, and faceting	Medium-low	Microscopy (TEM, SEM), XRD, Raman
Quantum, electric and magnetic properties	Under evaluation	Induced magnetization, Currie balance
Concentration (mass, number of particles/fibers): property of area: environment, workplace, office, etc.	Extreme	OPC, CPC, light-scattering photometer, gravimetric analysis, etc.

Legend: XPS: X-ray photoelectron spectroscopy, XRD: X-ray diffraction, XRF: X-ray fluorescence, OPC: optical particle counter, CPC: condensation particle counter, FTIR: Fourier-transform infrared spectroscopy, NMR: nuclear magnetic resonance, ICP: inductively coupled plasma, AA: atomic absorption spectroscopy, HPLC: high-performance liquid chromatography, ESR: electron spin resonance, DLS: dynamic light scatter, EDS: X-ray energy dispersive spectroscopy, AES: Auger electron spectroscopy, TGA: thermogravimetric analysis, LAL: Limulus amoebocyte lysate, FCS: fluorescence correlation spectroscopy, EPR: electron paramagnetic resonance, TEM: transmission electron microscopy, SEM: scanning electron microscopy, BET: Brunauer-Emmett-Teller, pH: hydrogen-ion activity, OES: optical emission spectroscopy, SPM: single potentiometric method, PCM: potentiometric conductometric method, SPR: surface plasmon resonance, FP: first principles, MIP: mercury intrusion porosimetry, NBT: nitroblue tetrazolium test, MALD-TOF: matrix-assisted laser, desorption/ionization-time of flight, EELS: electron energy loss spectroscopy, and TET: TNF- α expression test (where: TNF is tumor necrosis factor).

Table 1.

Nanomaterial evaluation: main relevant properties related to risk assessment and usual material characterization techniques [16–20].

Concentration, type/chemical, and physical state, in general, are the most important technical aspects related to HSE management of workplace under evaluation.

A careful analysis on nanomaterial's processes such as handling, storage, manipulation, production, and incorporation are essential to determine exposure routes

and to identify possible emission procedures or other safety aspects. **Figure 3** details the possible relations between biokinetics and pathways for nanoparticles exposure route and translocation.

The interaction between nanoparticles and cells is important to determine health surveillance (target organs and excretory pathways) and the possible damage mechanics and effects related to nanotoxicity such as physical damage of lysosomes, lipid peroxidation in vesicles, DNA damage of cellular nucleus, mitochondrial damage of cell mitochondria, protein misfolding on Golgi apparatus, and cellular membrane damage from oxidative stress, surfactant interaction, membrane damage by ions, and disruption of cell membranes [22]. Then, new properties from nano-sized effects (high area and energy, specific functionalization and quantum effects) provide different biological, physical, and/or ecological effects, turning risk assessment and evaluation more complex, sometimes more specific and time-consuming.

3.1 Occupational nanoparticle exposure routes and controls

Occupational exposure routes are intimately related to physical state of nanoparticles from processing methods (synthesis), processing equipment, workplace design, pollution-control equipment, handling steps, and operational procedures. Mainly, dispersion and inhalation are the main exposure contamination route. HEPA class filter are very efficient to control the number of nanoparticles disperse on air (>99.97%), while ULPA class filters have at least 99.995% of efficiency [22]. Use of a proper project design of air filtration is one of most important stages to avoid personal and environmental contamination. **Table 2** shows the typical HEPA and ULPA filter specifications based on ISO 1822:2009 (*) and the principal four primary mechanisms of filter particle collection [23]. The use of clean rooms or lamellar flow chamber or environmental/gas-controlled glove box could be applied to contain particulates during the handling of nanomaterials [24]. Personal protective equipment (PPE) also uses HEPA filtration on mask or coupled filtration devices. Main aspects of contamination and failure to prevent contamination regarding filtration masks came from poor personal training to fix and use

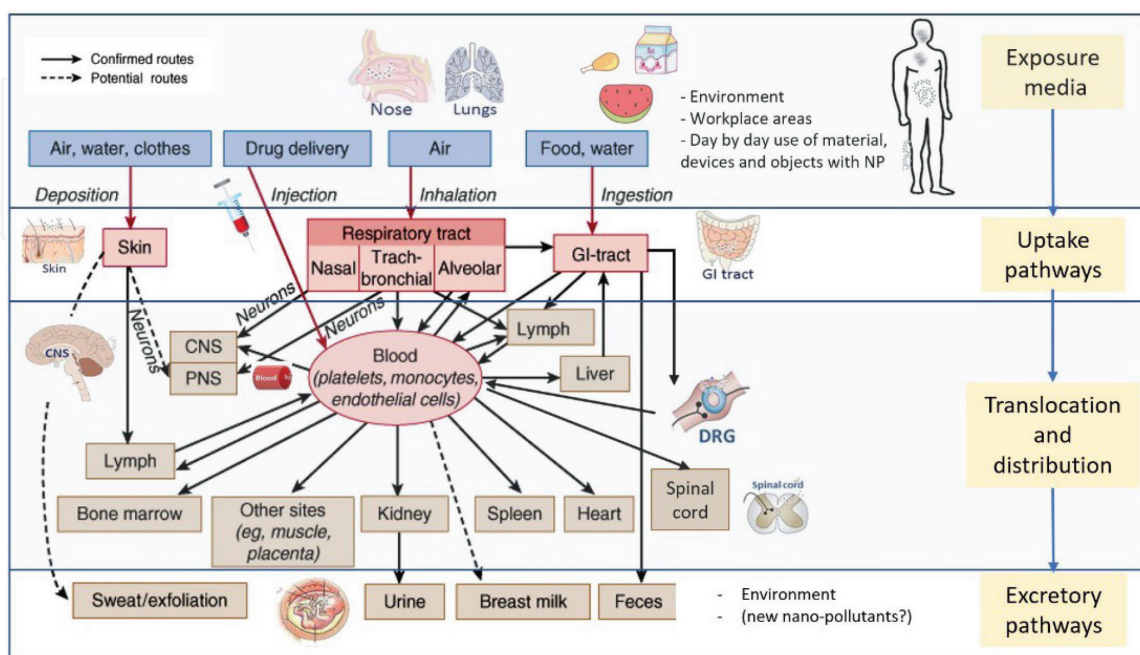


Figure 3. Biokinetics of nanoparticles related to exposure routes, uptake pathways, translocation/distribution and excretory pathways of NP (adapted from Ref. [21]).

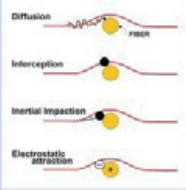
HEPA/ULPA Class	Retention (total %)	Filtration Mechanisms	Main Capture Sizes (µm)
H13	> 99.95		- Diffusion: < 0.1 microns - Interception: ~0.4 microns - Inertial impaction: ~0.4 microns - Electrostatic attraction: depend on size, charge and distance between particles and filter treated fibers.
H14	> 99.995		
U15	> 99.9995		
U16	> 99.99995		
U17	> 99.999995		
HEPA: High Efficiency Particulate Air ULPA: Ultra Low Particulate Air			
Retention efficiency based on MPPS (Most Penetrating Particle Size) test using 300 nm size particles.			

Table 2.
HEPA and ULPA filters' retention characteristics.

masks and the incorrect size and face matches (respiration facepiece and face). A chartered safety and health practitioner's evaluation based on work activities, operational procedures, workplace environment, nanoparticulate type/chemical concentration, and respirator fit factor should be applied according to occupational standards and guides [25–27].

The second most important exposure route of nanoparticles is from deposition or contact with skin. Usually, “perfect” skins without damages, cuts, or scratches work as barrier against nanoparticle penetration. However, the adequate gloves' and protective clothes' (made by high-density polyethylene fibers) specification should take in care several parameters such as glove material's chemical resistance compatibility [28], glove thickness, type/time of glove use (disposable/unsupported), temperature of use, type of labor activity and type, concentration, and agglomeration state of nanoparticles regarding the nanoparticle penetration behavior [29].

3.2 Nanotoxicity and information of the material safety data sheets (MSDS)

The material safety data sheets (MSDS) have essential information's and, regularly, they are used during the risk assessment and in workplaces as safe procedures

	OEDC (nano)	UN-CGH (chemicals)
Physicochemical properties	Melting point, boiling point, vapor pressure, K octanol/water, K organic/C/water*, water solubility	Appearance (physical state, color, etc.), upper/lower flammability or explosive limits, odor, vapor pressure, odor threshold vapor density, pH, relative density, melting point/freezing point, solubility(ies), initial boiling point and boiling range, flash point, evaporation rate, flammability (solid, gas), partition coefficient: n-octanol/water, auto-ignition temperature, decomposition temperature, and viscosity.
Environmental fate	Biodegradation, hydrolysis, atmospheric oxidation, bioaccumulation*	(Nonmandatory): <ul style="list-style-type: none"> • Results of tests of bioaccumulation potential, making reference to the octanol-water partition coefficient (K_{ow}), bioconcentration factor (BCF) • Other adverse effects (e.g., environmental fate, ozone layer depletion potential, photochemical ozone creation potential, endocrine disrupting potential, and/or global warming potential).
Ecological effects	Acute fish toxicity, acute Daphnia toxicity, alga toxicity, long-term aquatic toxicity, terrestrial effects	(Nonmandatory): <ul style="list-style-type: none"> • Acute or chronic aquatic toxicity data for fish, algae, crustaceans, and other plants, toxicity data on birds, bees, plants, etc.

	OEDC (nano)	UN-CGH (chemicals)
Human health effects	Acute oral toxicity, acute inhalation toxicity	Information on the likely routes of exposure (inhalation, ingestion, skin, and eye contact). The SDS should indicate if the information is unknown: description of the delayed, immediate, or chronic effects from short- and long-term exposures. The numerical measures of toxicity (e.g., acute toxicity estimates such as the LD50 (median lethal dose)) – the estimated amount [of a substance] expected to kill 50% of test animals in a single dose. Description of the symptoms. This description includes the symptoms associated with exposure to the chemical including symptoms from the lowest to the most severe exposure. Indication of whether the chemical is listed in the National Toxicology Program (NTP) Report on Carcinogens (latest edition) or has been found to be a potential carcinogen in the International Agency for Research on Cancer (IARC) Monographs (latest editions) or found to be a potential carcinogen by OSHA.
	Akin irritation/corrosion	
	Eye irritation/corrosion	
	Repeated dose	
	Genotoxicity (in vitro)	
	Genotoxicity (in vitro, nonbacterial)	
	Genotoxicity (in vivo)	
	Reproductive toxicity	
	Developmental toxicity	
	Carcinogenicity*	
	Organ toxicity (hepatotoxicity, cardiotoxicity, nephrotoxicity, etc.).	

From UN-GHS (classification and labeling of chemicals of UN-globally harmonized system).

Remark: the US National Cancer Institute published on this website several assays that have been standardized to work with a variety of nanomaterials. Information available at [38].*Non-screening information data set (SIDS) endpoints.

Table 3.
 OECD endpoint test guidelines for nanomaterials and MSDS (material safety data sheet) parameter.

for hazardous chemicals and its mixtures. The SDS enable anticipation, evaluation, recognition, and control of workplace exposures and environmental hazards [30, 31]. The major problem of SDS of nanomaterials is the lack of information and/or wrong use of “bulk material” properties instead of nano. Evaluation of nano-SDS indicated that 35% of the sheets are unreliable [32]. About this issue, American Industrial Hygiene Association (AIHA) has a program that recognizes chemical hazard communication and environmental health professionals who specializes in authoring safety data sheets and labels [33]. Recently, SECO, a Swiss State Secretariat for Economic Affairs (SECO), published a guideline and two examples of synthetic nanomaterial’s SDS [34, 35].

The knowledge of nanomaterial (quantitative) structure-activity relationships (Q)SAR is another important point of HSE evaluation during the risk assessment. Validated endpoints could explicate more clearly when a nanomaterial would be classified as “toxic” or “nontoxic” in particular exposure conditions providing more analytical, rational, and explicit data interpretation. **Table 3** shows the most common endpoints based on OECD test guidelines for nanomaterials and the UN-GHS. Notice that the UN-CGH for chemicals (including nanosized) just shows the parameter, while the OECD guideline could indicate and classify them [36, 37].

4. Risk assessment of carbon nanomaterials

Risk assessment could be defined when risk analysis and risk evaluation are carried in a joint process [39]. Health Safety Executive from the United Kingdom (HSE-UK) uses a simple five-step risk assessment based on the following topics:

- Identify the hazard.
- Decide who might be harmed and how.
- Evaluate the risks and decide on precautions.
- Record your findings and implement them.
- Review your assessment and update if necessary.

The application of this kind of assessment can be useful; however, it needs some adjustments due to uncertainties and lack of information (e.g., long-term or chronic evaluation of nanomaterials exposure), new materials without completed toxicological effects/studies or accurate dose-response database (OEL—occupational exposure limits, TLV—threshold limit values, OSHA/PEL—occupational safety and health administration-permissible exposure limits, WEEL—workplace environmental exposure level, NIOSH/PEL—National Institute for Occupational Safety and Health-recommended exposure limit, IOELV—indicative occupational exposure limit value, etc.) [40].

The availability of occupational and epidemiological data for chemicals and nanomaterials is a key aspect of risk assessment. The amount of new chemicals produced and released on the market is huge and huge means a hundred thousand per year. Based on Chemical Abstract Services (CAS) registry (a division of American Chemical Society), since 1800s, more than 145 million organic and inorganic substances were disclosed in the literature [41], while the publication 2018 TLV and BEIs from the American Conference of Governmental Industrial Hygienists (ACGIH) presents around 700 chemicals with TLV-STEL or TLV-TWA values (short-term exposure limit and time-weighted average, over the 8-hour working day). At the nanoworld, only 56 nanomanufactured materials have occupational exposure limit (OEL) proposed values [42]. **Table 4** presents some of the proposed

Types of nanocarbons	Exposure	Reference
Multiwalled carbon nanotubes (MWCNT)	No effect concentration in air $< 2.5 \mu\text{g}/\text{m}^3$	Luizi, 2009 (from Nanocyl)
Multiwalled carbon nanotubes (MWCNT)	Occupational exposure limit (OEL) $< 50 \mu\text{g}/\text{m}^3$ for 8-hour TWA during a 40-hour workweek	Pauluhn, 2010 (from Bayer)
Fullerenes (C60)	Indicative no-effect level (INEL) $< 7.4 \mu\text{g}/\text{cm}^3$	Aschberger, 2011
Multiwalled carbon nanotubes (MWCNT) 10 nm	Indicative no-effect level (INEL) $< 1.0 \mu\text{g}/\text{cm}^3$	Aschberger, 2011
Carbon nanotubes (CNTs)	Proposed nanoreference values (NRV) $< 0.01 \text{ fibers}/\text{cm}^3$	van Broekhuizen, 2012
Carbon nanotubes (CNTs)	Recommended exposure limit (REL) $< 1.0 \mu\text{g}/\text{m}^3$ for 8-hour TWA during a 40-hour workweek	NIOSH, 2013 [64]
Carbon nanofibers (CNFs)	Occupational exposure limit (OEL) $< 0.01 \text{ fibers}/\text{cm}^3$	Stockmann-Juvala, 2014
Carbon nanotube group, SWCNT, DWCNT, MWCNT	Occupational exposure limit (OEL) $< 30 \mu\text{g}/\text{m}^3$ for 8-hour TWA during a 40-hour workweek	Nakanishi, 2015

Table 4.
Proposed exposure limit values for carbon nanomaterials.

exposure limit values for carbon nanomaterials. The suggested values vary enormously, and no consensus exists between the authors.

In this scenario, the adoption of a precautionary posture should be the only option. In its strict form, the precautionary principle “requires inaction when action might pose a risk,” or in an active form, “it requires to choose the less risky alternatives when they are available, and for taking responsibility for potential risks” [43–45]. This should be adopted and carefully evaluated on control of risks (identification, evaluation, elimination, mitigation, monitoring, and communication) and on the choice of mitigation procedures when dealing with nanomaterials. The adoption of a hierarchy for health and safety controls should be mandatory.

Figure 4 shows health, safety, and environmental hierarchy controls in a schematic representation.

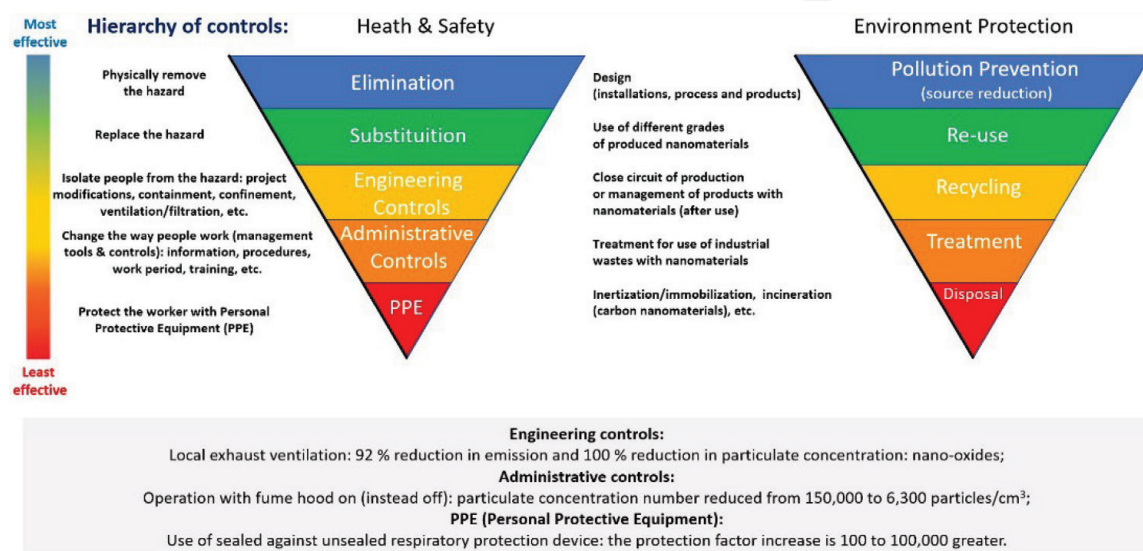


Figure 4.
 HSE hierarchy controls (adapted from Ref. [46, 47])

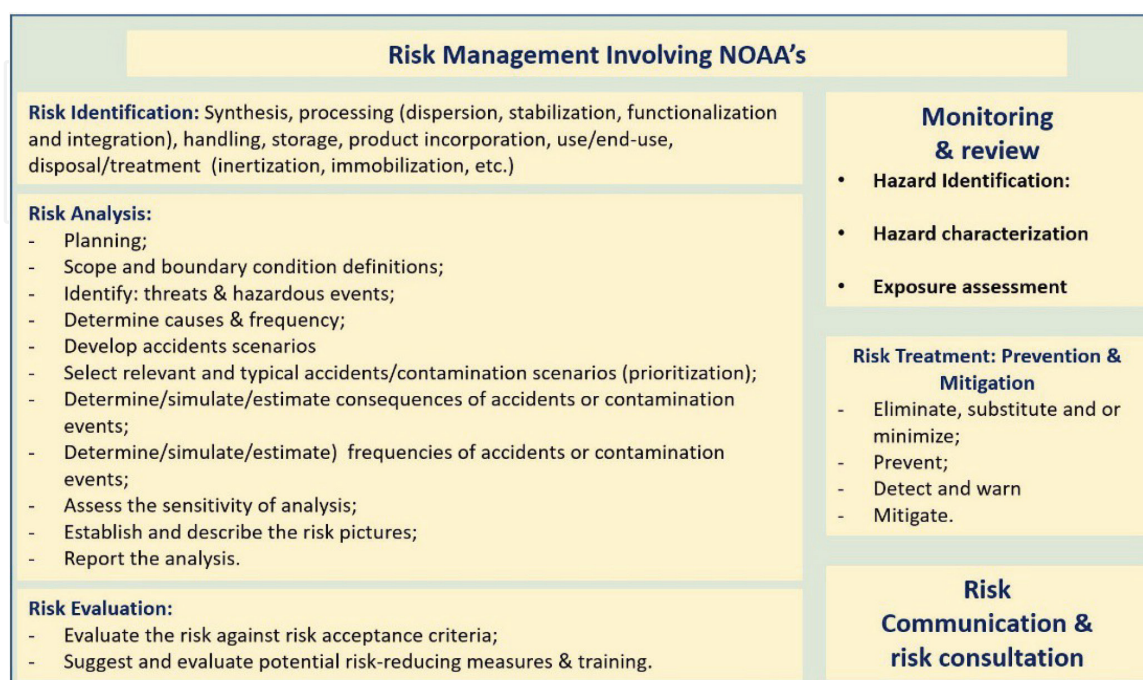


Figure 5.
 Risk management of NOAA's topics of risk identification, analysis, evaluation, treatment, and communication.

Organization (acronym)/country and website
IRSST (Canada), Institut de recherche Robert-Sauve en sante et en securite du travail/www.irsst.qc.ca
ILO/ONU (International Labour Office-Swiss)/www.ilo.org
CDC-NIOSH and OSHA (USA), Centers for Disease Control and Prevention—The National Institute for Occupational Safety and Health/https://www.cdc.gov/niosh/topics/nanotech/pubs.html Occupational Safety and Health Administration/https://www.osha.gov/dsg/nanotechnology/nanotech_standards.html
Cordis (Europe), Community Research and Development Information Service/www.cordis.europa.eu/nanotechnology
SWA (Australia), Safe Work Australia/http://www.safeworkaustralia.gov.au/https://www.worksafe.qld.gov.au
ISO (Switzerland), International Organization for Standardization/www.iso.org
HSE (UK), Health and Safety Executive/www.hse.gov.uk, www.safenano.org
BAuA (Germany), German Federal Institute for Occupational Safety and Health/www.baua.de
DTU (Denmark), Danish Ecological Council and Danish Consumer Council/http://nanodb.dk/en/nanoriskcat/
ANSES (France), Agence Nationale de Securite Sanitaire de l'alimentation/www.anses.fr
AIST (Japan), National Institute of Advanced Industrial Science and Technology/https://www.aist.go.jp/index_en.html
OECD (France), The Organization for Economic Co-operation and Development/www.oecd.org/http://www.oecd.org/science/nanosafety/
RIVM (Holland), Dutch National Institute for Public Health and the Environment/https://www.rivm.nl/en/nanotechnology
ABDI (Brazil), Brazilian Agency for Industrial Development/www.abdi.com.br/http://livroaberto.ibict.br/handle/1/624
EUON (Europe), European Union Observatory for Nanomaterials/https://euon.echa.europa.eu/

Table 5.

Major protocols, standards, and guidelines on the safe handling of nanomaterials and the risks associated with nanoparticles available from different organizations [52].

Tool	Web address	Country
CB Nanotool	https://controlbanding.llnl.gov/	USA
IVAM Guidance	http://www.industox.nl/Guidance%20on%20safe%20handling%20nanomats&products.pdf	Holland
Swiss Precautionary Matrix	http://www12.esdc.gc.ca/sgpe-pmps/servlet/sgpp-pmps-pub?lang=eng&curjsp=p.5bd.2t.1.3ls@-eng.jsp&curactn=dwnld&pid=61345&did=5245	Swiss
Stoffenmanager Nano	https://nano.stoffenmanager.com/	Nederland
ANSES CB Tool	https://www.anses.fr/en/system/files/AP2008sa0407RaEN.pdf	France
NanoSafer CB	http://nanosafer.i-bar.dk/Default.aspx	Denmark
NCBRA—Nanomaterial Control Banding Risk Assessment	https://www.worksafe.qld.gov.au/data/assets/pdf_file/0005/110975/nanotechnology-control-banding-tool.pdf	Australia
CBG—Control Banding Guideline	http://www12.esdc.gc.ca/sgpe-pmps/servlet/sgpp-pmps-pub?lang=eng&curjsp=p.5bd.2t.1.3ls@-eng.jsp&curactn=dwnld&pid=61345&did=5245	Canada

Table 6.

Major risk assessment tools based on control banding and risk matrices ([53] and Google searching tool).

The most effective control is the elimination of the hazard, and the less effective is the use of protective equipment. The viability to apply each type should be analyzed, case-by-case, considering the identified risks and its classification.

The risk management of nanomaterials nano-objects, aggregates and agglomerates (NOAA) could be based on international standards like ISO 31000 [48] and should be incorporated in the quality, health, safety, and environmental system management. Adaptations for the correct use of risk assessment tools to deal with specificities and specific properties of nanomaterials are necessary [49, 50]. **Figure 5** shows the core points of risk management and several tools that could be used to facilitate the understanding and the day-by-day procedures.

The applying of safety aspects in early stage of projects involving nanomaterials is fundamental to mitigate risks and improve the quality (robustness) of HSE system. The CDC/NIOSH guide from Nanotechnology Research Center (NTRC): “Controlling Health Hazards When Working with Nanomaterials: Questions to Ask Before You Start” is a very good starting point to deal with nanomaterials in a safe manner [51]. **Table 5** shows major protocols, standards, and guidance on the safe manipulation of NOAAs.

4.1 Risk analysis and evaluation

Due to lack of exposure limits and lack of information concerning toxicological effects of nanomaterials (in general and carbon nanomaterials specifically), the use of risk assessment based on control banding has been widely applied. Several tools based on this concept are available as shown in **Table 6**.

5. Environmental risk management

Along with all carbon nanomaterial developmental stages—from laboratory to industrial scale operations—different routes can lead to environmental emissions. Decision making related to waste disposal and control actions to avoid (or allow) air and water emissions should be taken in the early stages, prior to the enhancement of production scales. These types of decision will also be needed after the use phase of the nano-enabled products. Naturally, through several possible paths, different environment compartments will interact (or better, are interacting) with carbon nanoparticles.

5.1 Air

Depending on the scale, type of synthesis route, and activity, carbon nanoparticle emissions to the atmosphere can occur in larger or smaller amounts. As mentioned, exposition via inhalation is the main concern in the field since several authors have reported possible effects and damage to the respiratory system [18, 54]. In this sense, important precautionary actions comprise the establishment of emission control strategies and exposure monitoring.

5.1.1 Emission control strategies

Nanoparticles in the air were traditionally referred to ultrafine particles [55]. Main processes can occur with these particles in the air: photochemical reactions, agglomeration, and deposition. The deposition depends on the gravitational settling velocity, which is proportional to the diameter of the particle—smaller nanoparticles in the air will deposit at a much slower rate than larger particles [56, 57].

It is possible to assume that the particle diffusion in the atmosphere is governed by Brownian motion, being the diffusion rate inversely proportional to the particle diameter. In that sense, it is possible to assume that “aerosolized” nanoparticles in an agglomerate form, even at a low mass concentration, will be deposited at a faster rate than larger particles [56–58].

Also, the specific properties of the nanomaterial such as surface charge, aspect ratio, and presence of functional groups or other molecules in the nanoparticle surface will play a significant role in the atmospheric processes, interfering in the photochemical reactions, agglomeration, and deposition. The behavior of these particles in the air is a complex and dynamic process.

Being detected the risk of a carbon nanomaterial becoming airborne, some control measures should be taken. Handling nanomaterials should be performed in a closed system, for instance, a glove box. If activities outside a closed system cannot be avoided, as during refilling or filling, dust should be extracted at the source, using exhaustion devices (like flexible air ducts). It is recommended by several agencies to use HEPA filters of class “H14” in safety cabinets or other exhaustion fume hoods at the workplace. The use of safety cabinets and microbiological safety cabinets, which recirculate air from the cabinet interiors, through a HEPA filter, back into the laboratory, can be used for small quantities of carbon nanomaterials in the absence of hazardous vapors or gases. The filter must be HEPA, and charcoal filters alone must not be used in this case. Also, suitable protective measures to avoid energetic processes that might generate airborne dusts or aerosols and the immediate sealing of bottles/vessels after use are simple and effective actions [22–26].

5.1.2 Exposure monitoring

Different methods can be used for measuring airborne nanomaterials. As illustrated in **Figure 6**, atmospheric particulate matter can be analyzed through different methods using passive or active sampling methodologies.

Online measurement methods are equipment-based measurements with low response time, giving in real time, the concentration of particles and nanoparticles in the air. Normally, it is a general measurement that cannot distinguish the type of nanomaterial (related to its composition or morphology) being analyzed. As for the carbon nanomaterials, the morphology is a differential property; the simple measurement of concentration cannot determine the presence of the nanomaterial in the air. Recently, more relevant indicators have emerged for describing nanoparticle aerosols, including particle number, surface and mass concentrations, and criteria relating to their size or optical properties (Raman-based equipment) [59, 60].

Off-line methods allow quantitative determination (by mass), and the identification of the type of nanomaterial, however, requires long-term sampling and the sampling equipment is often expensive. Since these methods comprise sample collection, the advantage is the possibility to analyze the air-collecting filters in order to determine the composition and to verify the presence of carbon nanoparticles in the filter. The complexity of these samples in terms of composition and the likely presence of other carbonaceous materials (amorphous carbon from diesel combustion, for instance) is a special challenge related to the air monitoring of carbon nanoparticles. It is important to say that quantification is another difficult task. Carbon nanoparticles are very light, and the gravimetric method gives a result related to the total particulate sampled. A recent study analyzed the use of thermogravimetric analyses in order to detect and differentiate different types of nano-carbon directly in the air-collecting filter [61]. For the off-line gravimetric method, conventional sampling regulations such as NIOSH Method 5040, NIOSH 0500, and NIOSH 0600 can be used [62, 63].

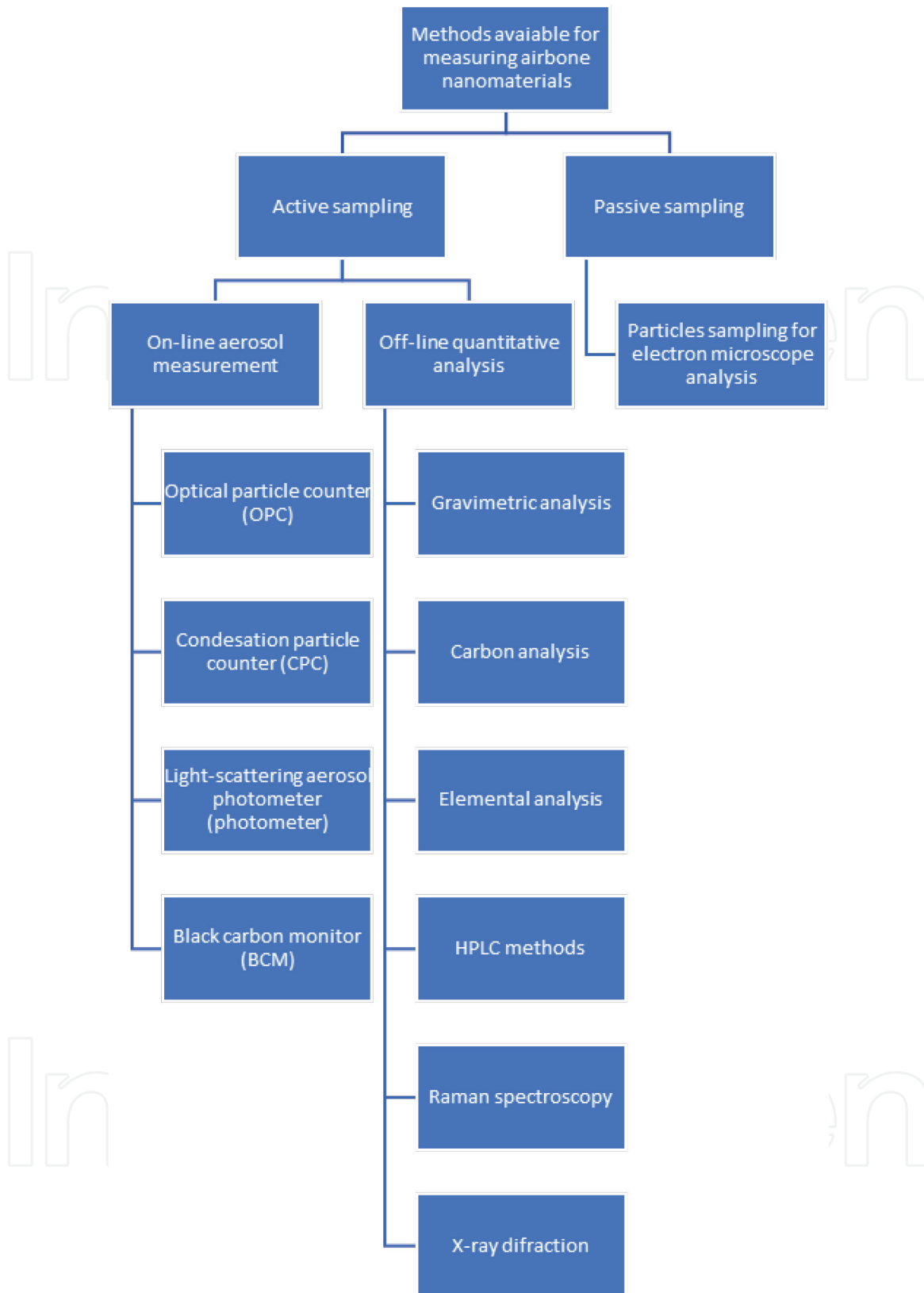


Figure 6.
Flowchart of methods for measuring airborne nanomaterials.

Passive methods are related to the natural deposition of those particles in different substrates (TEM grids, silica, holey carbon tapes) aiming to visualize its presence using an electron microscope. Although it allows identification of the carbon nanomaterial and its morphology, it is an expensive and time-consuming method. Also, the uncertainties related to the behavior of these particles in the air make it difficult to assume the time needed for its deposition and settling in those substrates.

5.2 Water and soil

Graphene and carbon nanotube water dispersions are a market reality. Although the fact of being, originally, insoluble materials, the possibility to have water dispersions containing carbon nanomaterials is often considered, since the delivery of a product in a liquid media can allow its use for different application purposes.

Different types of liquids containing carbon nanomaterials can be generated in research and (pre) industrial facilities. The use of acids and surfactants in synthesis and functionalization routes are common and, therefore, will be components of the produced liquid waste. Besides the nanomaterial, the presence of other substances must be evaluated since the knowledge of their own risk and best disposal practice must be considered.

Carbon nanoparticles may interact with aquatic systems by sewer discharges, or indirectly, coming from soils during the solid nanomaterial (or products containing the nanomaterial) disposal in landfills.

It is unlikely that public water treatment systems will be able to remove those particles from the influent. Specific properties such as surface charge and the presence of surfactants are some of the difficulties related to the removal of these nanomaterials in a general way [65, 66]. In some cases, at higher efficiency regime, the nanomaterials are removed from the influent and adsorbed into the sludge that will be disposed in the soil [67].

While there are no specific rules that regulate the disposal of nanomaterials in the environment, it is necessary to create a precautionary strategy for the best environmental management.

A possible approach is the treatment of the liquid nanowaste, aiming the removal of the nanoparticles from the water and its possible reuse in the production process. Liquid waste treatment processes are established in the industry, making possible a similar development in the nanotechnology field. The tendency of some nanocarbons, like graphene nanosheets, to aggregate and form a precipitated agglomerated due to π - π stacking interactions, can facilitate this separation [68]. On the other hand, graphene nanosheets with attached metal nanoparticles easily aggregate in the presence of ions [66]. The treatment and recycling are strict approaches that eliminate the risk of any possible harmful effects to aquatic systems, since the nanoparticle will not reach the environment. Although it seems an interesting choice, the establishment of treatment/recycling routes will require research and development efforts, involving nontrivial issues related to characterization of nanocarbon on complex matrices and a clear understanding of key nanomaterial properties.

Besides the challenge of such approach, it has clear advantages since it adds to the nanomaterial development of a safe-by-design practice in accordance with sustainable principles, therefore creating the possibility of specific solutions for each case. A process to recover single-walled carbon nanotube anode from battery anodes [69] and the use of serpentine to treat waste graphene were already reported [70] as examples of recycling the nanocarbons used in specific applications. It is a complex subject with an urgent need for recycling and end-of-life (EOL) studies. Specifically, the generation of the nonproduct outputs in nanocarbon production process is common [71]. The industrial scale production highlights this need: the projected global annual production of carbon-based nanocarbons was in order of a few hundred tons in 2001 and estimates 58,000 tons annually to 2020 [72].

According to several recommendations [73–76], the incineration is another method to treat these types of waste. These recommendations are based on the precautionary principle, and independent of the amount, the presence of

nanomaterials in liquids that should be discarded lead to its classification as hazardous wastes. The Organization for Economic Co-operation and Development (OECD) [74], in 2013, published a document providing an overview of scientific findings on the behavior and exposure of engineered nanomaterials (ENMs) during the waste incineration process in order to identify knowledge-gaps regarding specific aspects of the disposal of waste containing nanomaterials (WCNMs). According with this document, all waste incineration plants should be equipped with a flue gas treatment system as, for instance, described in the European Union BREF document (Integrated Pollution Prevention and Control—Reference Document on the best available techniques for Waste Incineration, August 2006). Until today, there are still a large number of waste incineration plants worldwide that do not have adequate flue gas treatment systems. In addition, the treatment and disposal of solid residues from waste incineration also require further research that should include the determination of conditions that enable the efficient removal of nanocarbons from the solid waste. Each material needs to be evaluated in an individual way. Decomposition temperatures depend on the nanomaterial-specific properties: size, shape, degree of defects, and presence or not of functional groups can interfere on it.

Besides the liquids containing nanocarbons, solid wastes are also generated in research facilities and in industrial settings producing or working with carbon nanomaterials. In terms of risk management, an important question regarding the form of the nanomaterial in the solid waste: Is it bound in a matrix or free in a powder form? The classification of the types of solid and liquid wastes is a fundamental step. A careful look in the processes and the development (and clear communication) of disposal practices are essential to avoid unnecessary emissions to the atmosphere or the disposal of a solid nanomaterial, in powder form in landfill soil.

Landfill waste disposal of carbon nanomaterials leavings derived from production facilities and from nano-enabled products are relevant routes leading to the soil environment. Another possibility is the use of nanoproducts directly in the soil for agricultural and construction purposes—cement containing carbon nanotubes is a well-studied application [77].

Progress in nanowaste management also requires studies on the environmental impact of these new materials. Knowing that several parameters must be evaluated when assessing the risk—such as the amount of nanomaterial to be discarded and its singular properties—there is a preponderant factor: the complexity of the natural environment, which makes it difficult to carry out systematic studies for the identification of the risk. Studies focusing the identification of the harmful effects of these nanomaterials in realistic scenarios are rare. Works modeling the flows of engineered nanomaterials during waste handling are the important ways to support this lack of information [78, 79].

6. Conclusions and final comments

Nowadays, the amount of information of HSE of nanomaterials including the new nanocarbons is still not completed; however, the correct use of risk assessment and risk analysis tools based on a precautionary vision could mitigate risks and control the exposure at workplaces. Improving the quality and ratability information of SDS and improving the grouping of nanomaterials by risk classes based on properties and biological effects must be a continuous work. A multidisciplinary environmental assessment and use of LCA tools to nanomaterials must be continued, improving risk models and taking care of epidemiological aspects of human and environmental interaction with manmade nanoparticles.

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Author details

Guilherme Lenz e Silva^{1,2*}, Camila Viana², Danieli Domingues² and Fernanda Vieira²

1 Polytechnic School of Engineering, University of São Paulo, São Paulo, Brazil

2 MGgrafeno-CDTN/CNEN-Codemig, Belo Horizonte, Brazil

*Address all correspondence to: guilhermelenz@usp.br

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