ENVIRONMENTAL HEALTH AND SAFETY: THE ENERGY SECTOR

Exposure to chemicals in the energy sector may be quite diverse. In this report the safety evaluation will be limited to the engineered nanoparticles intentionally produced. A number of nanoparticles have been identified in the overview of commercially-available products as being used in energy products (see section on Products in Energy). These include Carbon, Copper oxide, Gold, Graphene, Multi-walled carbon nanotube (MWCNT), Nickel monoxide (nickel oxide), Strontium titanate (strontium titanium trioxide) and Titanium dioxide (titania, rutile, anatase).

A risk-banding tool called Stoffenmanager Nano[1,2] has been used to prioritise the health risks occurring as a result of respiratory exposure to nanoparticles for a broad range of worker scenarios.

The respiratory route is the main route of exposure for many occupational scenarios, while the oral route of exposure is considered minor and sufficiently covered, from a safety point of view, by good hygiene practices established in production facilities as prescribed through general welfare provisions in national health and safety legislation in EU countries (ECHA 2012)[3]. In view of the nature of the products in this sector, oral exposure of consumers is also considered to be minor.

The dermal route may be the main route of exposure for some substances or exposure situations, and cause local effects on the skin or systemic effects after absorption into the body (ECHA 2012). However, nanoparticles as such are very unlikely to penetrate the skin (Watkinson, et al. 2013), and consequently nano-specific systemic toxicity via the dermal route is improbable. Therefore, when evaluating risks from nanotechnology for the respiratory route, the most important aspects of occupational and consumer safety are covered.

Hazard assessment of nanoparticles

In Stoffenmanager Nano, the available hazard information is used to assign specific nanoparticles to one of five hazard bands, labelled A to E (A= low hazard, E= highest hazard). The table below presents an overview of selected nanoparticles of the energy sector and their hazard bands, either taken from le Feber et al. (2014)[4] or van Duuren et al. (2012), or derived in this project.

Hazard bands for the specified nanoparticles

Nanoparticles	Hazard band	Source
Carbon	Needs specification, may be carbon black, carbon nanotubes, fullerenes or graphene	
Copper oxide	E	This report
Gold	D	van Duuren et al. (2012)

1 Marquart, H., Heussen, H., Le Feber, M., Noy, D., Tielemans, E., Schinkel, J., West, J., Van Der Schaaf, D., 2008. 'Stoffenmanager', a web-based control banding tool using an exposure process model. Ann. Occup. Hyg. 52, 429-441.

2 Van Duuren-Stuurman, B., Vink, S., Verbist, K.J.M., Heussen, H.G.A., Brouwer, D., Kroese, D.E.D., Van Niftrik, M.F.J., Tielemans, E., Fransman, W., 2012. Stoffenmanager Nano version 1.0: a web-based tool for risk prioritization of airborne manufactured nano objects. Ann. Occup. Hyg. 56, 525-541.

3 ECHA, 2012. Chapter R.14: Occupational exposure estimation in: Anonymous Guidance on Information Requirements and Chemical Safety Assessment., Version: 2.1 ed. European Chemicals Agency, Helsinki, Finland.

4 Le Feber, M., Kroese, E.D., Kuper, C.F., Stockmann-Juvala, H., Hyytinen, E.R., 2014. Pre-assigned hazard bands for commonly used nanoparticles. TNO2014 R11884.

Graphene	E	This report
Multi-walled carbon nanotube (MWCNT)	E	This report
Nickel monoxide (nickel oxide)	E	This report
Strontium titanate (strontium titanium trioxide)	n/a	This report, no data
Titanium dioxide (titania, rutile, anatase)	B	le Feber et al. (2014)

Exposure assessment

Solar

Based on the provided overview of commercially available products, engineered nanomaterials are present in the products as part of a matrix (e.g. coating). No free solids or liquids containing engineered nanomaterials were listed, which can become airborne during the use-phase, were encountered. During the production of these solar products, employees can be exposed to free engineered nanomaterials.

The use of solar products results in an exposure band 1 with respect to nanomaterials (workers and consumers), whereas during the production of solar products an exposure band 4 (workers) is believed to be realistic as spraying of a nanocoating results in the highest relative exposure.

Storage

The identified products in the sub-sector storage are diverse, ranging from nanomaterials that go into final products (e.g. (parts of) batteries). SMEs account for the lion's share of producers while large private companies (PCO) only play a minor role.

Based on the provided overview of commercially available products, engineered nanomaterials present in the products may be part of a matrix or be part of free solids or liquids, which subsequently may become airborne during the use-phase.

In conclusion, the use of storage products results in an exposure band 1 (workers and consumers) if nanomaterials are in a matrix, whereas the use of solids or liquids results in an exposure band 2 (workers) due to the relatively low concentrations of engineered nanomaterials as the majority of these products are produced by SMEs.

Hydrogen

In the Hydrogen sector, only two products with nanomaterials were identified; a final product (nanomaterial unknown) and a nanomaterial (copper nanowires) that goes into a final product.

Based on the provided overview of commercially available products and the limited number of products, we are not able to draw conclusions regarding the exposure assessment for the sub-sector Hydrogen.

Alternatives

Alternative products are for a large part carbon-based nanomaterials that go into final products for the energy market. These nanomaterials include surface coatings and raw materials including graphene and carbon nanotubes.

Based on the provided overview of commercially available products, engineered nanomaterials present in the products may be part of a matrix or be free solids or liquids, containing engineered nanomaterials which subsequently can become airborne during the use-phase.

In conclusion, the use of Alternatives products results in an exposure band 1 (workers and consumers) if nanomaterials are in a matrix, whereas the use of solids or liquids results in an exposure band 2 (workers) due to the relatively low concentrations of engineered nanomaterials as the majority of these products are produced by SMEs.

OTHER

The items which were not assigned to a sub-sector include only three commercially available products whit a large range of variability, from graphene based materials to thin film coatings for windows.

Based on the provided overview of commercially available products and the limited number of products, we are not able to draw conclusions regarding the exposure assessment for the sub-sector other.

Risk assessment

The hazard and exposure bands are combined to yield so called priority bands, according to the scheme depicted in the table below. A high priority implies that it is urgent to apply exposure control measures or to assess the risks more precisely, and a low priority implies that it is not very urgent to apply exposure control measures ort to establish the risk involved with more precision. It should be emphasized that because of the scarcity of available information, the scheme is set in a conservative way (according to the precautionary principle).

Priority bands in the Stoffenmanager system

Hazard band / Exposure band	A	B	C	D	E
1	3	3	3	2	1
2	3	3	2	2	1
3	3	2	2	1	1
4	2	1	1	1	1

Key:
Hazard: A = lowest hazard and E = highest hazard;
Exposure: 1 = lowest exposure and 4 = highest exposure;
Overall result: 1 = highest priority and 3 = lowest priority (Van Duuren-Stuurman, et al. 2012).

Risks based on the hazard and exposure banding applied to the energy sector are listed the table. Due to lack of data on production and use, no risk estimates can be presented for the sub-sectors “Hydrogen” and “Others”.

Priority bands for nanotechnology energy

		Exposure band					
		Solar -production	**Solar - use**	**Alterna-tives – produc-tion**	**Alternatives - use**	**Storage – produc-tion**	**Storage - use**
Nanoparticle	**Hazard band**	**4**	**1**	**2**	**1**	**2**	**1**
Carbon	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Copper oxide	E	1	1	1	1	1	1
Gold	D	1	2	2	2	2	2
Graphene	E	1	1	1	1	1	1
Multi-walled carbon nanotube (MWCNT)	E	1	1	1	1	1	1
Nickel monoxide	E	1	1	1	1	1	1
Strontium titanate	n/a	n/a	n/a	n/a	n/a	n/a	n/a
Titanium dioxide (titania, rutile, anatase)	B	1	3	3	3	3	3
Zirconium dioxide	A	2	3	3	3	3	3

The high hazard materials are towards the E end of the ranking while the high exposure materials are towards the 4 end of that ranking. Thus the materials with the lowest risk will have hazard A and exposure 1 and those with the highest risk will have hazard E and exposure 4. There are, however, materials of moderate risk and low exposure that are less risk potentially that lower risk materials with high exposure.

The materials copper oxide, graphene, MWCNTs and nickel monoxide have a high priority (1), indicating the need to apply exposure control methods or to assess the risks more precisely. Gold is of medium priority (except in solar energy production) while titanium dioxide and zirconium dioxide showed the lowest priority profiles of the materials considered, being in the lowest priority category (3) for all life cycle stages examined except for the production phase in the solar energy subsector).

EHS References

Abderrazak, A., Syrovets, T., Couchie, D., El Hadri, K., Friguet, B., Simmet, T., Rouis, M., 2015. NLRP3 inflammasome: From a danger signal sensor to a regulatory node of oxidative stress and inflammatory diseases. Redox Biology 4, 296-307.

Agarwal, K., Sharma, A., Talukder, G., 1990. Clastogenic effects of copper sulphate on the bone marrow chromosomes of mice in vivo. Mutation Research Letters 243, 1-6.

Alarifi, S., Ali, D., Verma, A., Alakhtani, S., Ali, B.A., 2013. Cytotoxicity and genotoxicity of copper oxide nanoparticles in human skin keratinocytes cells. Int. J. Toxicol. 32, 296-307.

Aufderheide, M., Halter, B., Möhle, N., Hochrainer, D., 2013. The CULTEX RFS: A comprehensive technical approach for the in vitro exposure of airway epithelial cells to the particulate matter at the air-liquid interface. BioMed Research International 2013.

Bhunya, S.P., Jena, G.B., 1996. Clastogenic effects of copper sulphate in chick in vivo test system. Mutation Research - Genetic Toxicology 367, 57-63.

Bondarenko, O., Juganson, K., Ivask, A., Kasemets, K., Mortimer, M., Kahru, A., 2013. Toxicity of Ag, CuO and ZnO nanoparticles to selected environmentally relevant test organisms and mammalian cells in vitro: A critical review. Arch. Toxicol. 87, 1181-1200.

Cho, W., Duffn, R., Poland, C.A., Howie, S.E.M., Macnee, W., Bradley, M., Megson, I.L., Donaldson, K., 2010. Metal oxide nanoparticles induce unique infammatory footprints in the lung: Important implications for nanoparticle testing. Environ. Health Perspect. 118, 1699-1706.

Cohen, D., Soroka, Y., Ma'or, Z., Oron, M., Portugal-Cohen, M., Brégégère, F.M., Berhanu, D., Valsami-Jones, E., Hai, N., Milner, Y., 2013. Evaluation of topically applied copper(II) oxide nanoparticle cytotoxicity in human skin organ culture. Toxicology in vitro : an international journal published in association with BIBRA 27, 292-298.

Donaldson, K., Schinwald, A., Murphy, F., Cho, W.-., Duffin, R., Tran, L., Poland, C., 2013. The biologically effective dose in inhalation nanotoxicology. Acc. Chem. Res. 46, 723-732.

Duch, M.C., Budinger, G.R.S., Liang, Y.T., Soberanes, S., Urich, D., Chiarella, S.E., Campochiaro, L.A., Gonzalez, A., Chandel, N.S., Hersam, M.C., Mutlu, G.M., 2011. Minimizing oxidation and stable nanoscale dispersion improves the biocompatibility of graphene in the lung. Nano Letters 11, 5201-5207.

ECHA, 2012. Chapter R.14: Occupational exposure estimation., in: Anonymous Guidance on Information Requirements and Chemical Safety Assessment., Version: 2.1 ed. European Chemicals Agency, Helsinki, Finland.

El-Ansary, A., Al-Daihan, S., Bacha, A.B., Kotb, M., 2013. Toxicity of novel nanosized formulations used in medicine. Methods in Molecular Biology 1028, 47-74.

Fahmy, B., Cormier, S.A., 2009. Copper oxide nanoparticles induce oxidative stress and cytotoxicity in airway epithelial cells. Toxicology in Vitro 23, 1365-1371.

Fahmy, M.A., 2000. Potential genotoxicity in copper sulphate treated mice. Cytologia 65, 235-242.

Fujita, K., Morimoto, Y., Ogami, A., Myojyo, T., Tanaka, I., Shimada, M., Wang, W.-., Endoh, S., Uchida, K., Nakazato, T., Yamamoto, K., Fukui, H., Horie, M., Yoshida, Y., Iwahashi, H., Nakanishi, J., 2009. Gene expression profiles in rat lung after inhalation exposure to C60 fullerene particles. Toxicology 258, 47-55.

Horie, M., Fujita, K., 2011. Toxicity of Metal Oxides Nanoparticles. Advances in Molecular Toxicology 5, 145-178.

Horie, M., Fukui, H., Nishio, K., Endoh, S., Kato, H., Fujita, K., Miyauchi, A., Nakamura, A., Shichiri, M., Ishida, N., Kinugasa, S., Morimoto, Y., Niki, E., Yoshida, Y., Iwahashi, H., 2011. Evaluation of acute oxidative stress induced by NiO nanoparticles in vivo and in vitro. Journal of Occupational Health 53, 64-74.

Horie, M., Nishio, K., Fujita, K., Kato, H., Nakamura, A., Kinugasa, S., Endoh, S., Miyauchi, A., Yamamoto, K., Murayama, H., Niki, E., Iwahashi, H., Yoshida, Y., Nakanishi, J., 2009. Ultrafine NiO particles induce cytotoxicity in vitro by cellular uptake and subsequent Ni(II) release. Chem. Res. Toxicol. 22, 1415-26.

Karlsson, H.L., Cronholm, P., Gustafsson, J., MÃ¶ller, L., 2008. Copper oxide nanoparticles are highly toxic: a comparison between metal oxide nanoparticles and carbon nanotubes. Chem. Res. Toxicol. 21, 1726-32.

Lanone, S., Rogerieux, F., Geys, J., Dupont, A., Maillot-Marechal, E., Boczkowski, J., Lacroix, G., Hoet, P., 2009. Comparative toxicity of 24 manufactured nanoparticles in human alveolar epithelial and macrophage cell lines. Particle and Fibre Toxicology 6.

Le Feber, M., Kroese, E.D., Kuper, C.F., Stockmann-Juvala, H., Hyytinen, E.R., 2014. Pre-assigned hazard bands for commonly used nanoparticles. TNO2014 R11884.

Lohcharoenkal, W., Wang, L., Stueckle, T.A., Dinu, C.Z., Castranova, V., Liu, Y., Rojanasakul, Y., 2013. Chronic exposure to carbon nanotubes induces invasion of human mesothelial cells through matrix metalloproteinase-2. ACS Nano 7, 7711-7723.

Marquart, H., Heussen, H., Le Feber, M., Noy, D., Tielemans, E., Schinkel, J., West, J., Van Der Schaaf, D., 2008. 'Stoffenmanager', a web-based control banding tool using an exposure process model. Ann. Occup. Hyg. 52, 429-441.

Midander, K., Cronholm, P., Karlsson, H.L., Elihn, K., Möller, L., Leygraf, C., Wallinder, I.O., 2009. Surface characteristics, copper release, and toxicity of nano- and micrometer-sized copper and copper(II) oxide particles: A cross-disciplinary study. Small 5, 389-399.

Morimoto, Y., Hirohashi, M., Ogami, A., Oyabu, T., Myojo, T., Hashiba, M., Mizuguchi, Y., Kambara, T., Lee, B.W., Kuroda, E., Tanaka, I., 2011. Pulmonary toxicity following an intratracheal instillation of nickel oxide nanoparticle agglomerates. Journal of Occupational Health 53, 293-295.

Morimoto, Y., Hirohashi, M., Ogami, A., Oyabu, T., Myojo, T., Nishi, K.-., Kadoya, C., Todoroki, M., Yamamoto, M., Murakami, M., Shimada, M., Wang, W.-., Yamamoto, K., Fujita, K., Endoh,

S., Uchida, K., Shinohara, N., Nakanishi, J., Tanaka, I., 2010. Inflammogenic effect of well-characterized fullerenes in inhalation and intratracheal instillation studies. Particle and Fibre Toxicology 7.

Nezakati, T., Cousins, B.G., Seifalian, A.M., 2014. Toxicology of chemically modified graphene-based materials for medical application. Arch. Toxicol. 88, 1987-2012.

NIOSH, 2013. Current Intelligence 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, Washington DC, USA.

Palomäki, J., Välimäki, E., Sund, J., Vippola, M., Clausen, P.A., Jensen, K.A., Savolainen, K., Matikainen, S., Alenius, H., 2011. Long, needle-like carbon nanotubes and asbestos activate the NLRP3 inflammasome through a similar mechanism. ACS Nano 5, 6861-6870.

Piret, J.-., Jacques, D., Audinot, J.-., Mejia, J., Boilan, E., Noël, F., Fransolet, M., Demazy, C., Lucas, S., Saout, C., Toussaint, O., 2012. Copper(ii) oxide nanoparticles penetrate into HepG2 cells, exert cytotoxicity via oxidative stress and induce pro-inflammatory response. Nanoscale 4, 7168-7184.

Privalova, L.I., Katsnelson, B.A., Loginova, N.V., Gurvich, V.B., Shur, V.Y., Valamina, I.E., Makeyev, O.H., Sutunkova, M.P., Minigalieva, I.A., Kireyeva, E.P., Rusakov, V.O., Tyurnina, A.E., Kozin, R.V., Meshtcheryakova, E.Y., Korotkov, A.V., Shuman, E.A., Zvereva, A.E., Kostykova, S.V., 2014. Subchronic toxicity of copper oxide nanoparticles and its attenuation with the help of a combination of bioprotectors. International Journal of Molecular Sciences 15, 12379-12406.

Rotoli, B.M., Bussolati, O., Costa, A.L., Blosi, M., Cristo, L.D., Zanello, P.P., Bianchi, M.G., Visigalli, R., Bergamaschi, E., 2012. Comparative effects of metal oxide nanoparticles on human airway epithelial cells and macrophages. Journal of Nanoparticle Research 14.

Sandhya Rani, V., Kishore Kumar, A., Kumar, C.P., Rama Narsimha Reddy, A., 2013. Pulmonary toxicity of copper oxide (CuO) nanoparticles in rats. Journal of Medical Sciences (Faisalabad) 13, 571-577.

Seabra, A.B., Paula, A.J., De Lima, R., Alves, O.L., Durán, N., 2014. Nanotoxicity of graphene and graphene oxide. Chem. Res. Toxicol. 27, 159-168.

Song, M., Li, Y., Kasai, H., Kawai, K., 2012. Metal nanoparticle-induced micronuclei and oxidative DNA damage in mice. Journal of Clinical Biochemistry and Nutrition 50, 211-216.

Sun, T., Yan, Y., Zhao, Y., Guo, F., Jiang, C., 2012. Copper oxide nanoparticles induce autophagic cell death in a549 cells. PLoS ONE 7.

USEPA, 2013. Comprehensive Environmental Assessment applied to Multiwalled Carbon Nanotube flame-retardant coatings in upholstery textiles. A case study presenting priority research gaps for future risk assessments. EPA/600/R-12/043F.

Van Duuren-Stuurman, B., Vink, S., Verbist, K.J.M., Heussen, H.G.A., Brouwer, D., Kroese, D.E.D., Van Niftrik, M.F.J., Tielemans, E., Fransman, W., 2012. Stoffenmanager Nano version 1.0: a web-based tool for risk prioritization of airborne manufactured nano objects. Ann. Occup. Hyg. 56, 525-541.

Watkinson, A.C., Bunge, A.L., Hadgraft, J., Lane, M.E., 2013. Nanoparticles do not penetrate human skin - A theoretical perspective. Pharm. Res. 30, 1943-1946.

Yang, K., Wan, J., Zhang, S., Zhang, Y., Lee, S.-., Liu, Z., 2011. In vivo pharmacokinetics, long-term biodistribution, and toxicology of pegylated graphene in mice. ACS Nano 5, 516-522.

Yildirimer, L., Thanh, N.T.K., Loizidou, M., Seifalian, A.M., 2011. Toxicological considerations of clinically applicable nanoparticles. Nano Today 6, 585-607.

Zhang, X., Yin, J., Peng, C., Hu, W., Zhu, Z., Li, W., Fan, C., Huang, Q., 2011. Distribution and biocompatibility studies of graphene oxide in mice after intravenous administration. Carbon 49, 986-995.

Zhao, J., Castranova, V., 2011. Toxicology of nanomaterials used in nanomedicine. Journal of Toxicology and Environmental Health - Part B: Critical Reviews 14, 593-632.