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ENMs IN THE BUILT ENVIRONMENT

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What are ENMs?

ENMs are engineered nanomaterials that are defined as materials having at least one external dimension in the range 1-100 nm.¹ One nanometer is one-billionth of a meter, which is like comparing the size of a marble to that of earth. ENMs differ from naturally occurring nanomaterials in that ENMs are intentionally engineered to have certain shapes and sizes to take advantages of the unique physicochemical, optical, electronic, magnetic, antibacterial, self-cleaning and other properties they offer compared to their larger bulk forms.² Because of their unique properties, ENMs are increasingly being incorporated into various industries to enable superior performance of consumer products (called nano-enabled products) compared to conventional products. Numerous nano-enabled products can be found in the built environment such as paints and coatings,³⁻⁵ thermoplastics,⁶ printer toners,^{7,8} furniture, personal care and cleaning products, packaging materials, and so on.⁹ ENMs can be either inorganic or organic substances, but the most prominent ENMs found in a built environment are mostly metal oxides, namely, titania (TiO₂), silica (SiO₂), iron oxide (Fe₂O₃), zinc oxide (ZnO), and silver (Ag).¹⁰ It has been forecasted that the global value of nano-enabled products, nano-intermediates and nanomaterials will reach US \$4.4 trillion by 2018, with a significant fraction invested in the building and construction industry to enhance material properties, conserve energy expenditure and introduce greener structural materials.^{5,11}

How are we exposed to ENMs in the built environment?

In a built environment, ENMs are typically embedded in the matrix of a consumer product such as a thermoplastic product or a wall paint and are typically not present as free-standing nanomaterials. However, as a consumer product goes through its useful lifecycle, there may be certain stresses that the product is exposed to such as thermal fluctuations, building fires, wear and tear from normal/intensive use, washing and precipitation, ultraviolet (UV) light exposure, and mechanical stresses such as cutting, drilling, grinding, friction and so on.¹² These stresses over time may cause the matrix of the nano-enabled product to start to disintegrate leading to possible release of the embedded nanomaterial, either standalone or as part of the matrix fragment. These released particulate matter over the lifecycle of the product, referred to as LCPM, may be inhaled by the consumer or building occupant, depending on the PM size. Alternatively, ENMs present in food packaging may leach into the food over time and ultimately be ingested by the consumer. ENMs present in cosmetic and personal care products may be dermally absorbed by the skin upon application. Therefore, with the increasing use of ENMs in various products, human exposures are inevitable. However, major knowledge gaps on release dynamics of ENMs from nano-enabled products in the built environment and their physicochemical transformations over the lifecycle and potential environmental health and safety (EHS) implications are still prohibiting regulators from assessing risks from such emerging materials.



A highly relevant example of exposure to ENMs in an indoor environment is the case study of laser printers performed at the Center for Nanotechnology and Nanotoxicology based at the Harvard T.H. Chan School of Public Health (www.hsph.harvard.edu/nano).^{7,8,13–15} Research found that the toner powders used in these printers were nano-enabled and the inhalable fine particulate matter emitted from the use of these printers contained the nano-sized metals used in the toner composition, resulting in potential inhalation exposure for the consumers. More recently, researchers at the HSPH Center for Nanotechnology and Nanotoxicology brought up the issue of nano-waste and the EHS implications at the end-of-life scenario of nano-enabled products, especially thermoplastics when they end up in incineration facilities.¹⁶ Certain inorganic ENMs like titania and iron oxide were observed in the released PM from thermal decomposition of these thermoplastics, raising concern about potential ENM exposures for incineration facility workers and firefighters in buildings.^{17,18}

Therefore, with the increasing use of ENMs in various products, human exposures are inevitable. However, major knowledge gaps on release dynamics of ENMs from nano-enabled products in the built environment and their physicochemical transformations over the lifecycle and potential environmental health and safety (EHS) implications are still prohibiting regulators from assessing risks from such emerging materials.

Are there health effects from exposure to ENMs?

ENMs, because of their extremely small size and large surface-to-volume ratio, tend to be more biologically active than their larger counterparts and have been implicated in various adverse biological effects in numerous nanotoxicological studies.¹⁹ Although no specific human disease resulting from ENM exposure has been documented, many in-vitro and in-vivo studies have demonstrated adverse systemic effects like cytotoxicity, DNA damage, lung inflammation and fibrosis and carcinogenicity.^{14,20–26} ENMs have the potential to translocate across biological barriers reaching pulmonary connective tissues, lymphatics, or even the circulating blood and thus gain access to other critical organs.^{27,28}

Although nanotoxicological research has expanded over the past decade or so, the underlying mechanisms of toxicity are not very well-known. In addition, there is much debate surrounding the selection of environmentally relevant doses of ENMs in these studies because of a lack of release estimates and exposure data of ENMs in various environmental compartments. Most of the toxicological studies so far have focused primarily on pristine or raw ENMs and do not consider the potential fate and transformation of the ENM properties over the lifecycle of the nano-enabled product, that might affect their toxicological profiles. For example, it has been recently shown by the authors that ENMs such as metal oxides (e.g., titania) are not only released into the aerosolized PM but can potentially catalyze formation and hence release of complex mixtures of toxic gaseous byproducts such as polycyclic aromatic hydrocarbons when a nano-enabled thermoplastic undergoes certain lifecycle scenarios such as incineration or thermal decomposition.²⁹

Are there regulations to prevent exposure to ENMs?

There is no federal or state legislation specific to ENMs in the US, however, they are currently managed under the regulatory framework for chemicals by the US Environmental Protection Agency (EPA) under the Toxic Substances Control Act (TSCA). EPA requires premanufacture notifications for new nanomaterials and has the authority to collect information on exposure, release and environmental health and safety of nanomaterials from companies that produce them in order to assess their risk.³⁰

With regards to the workplace environment where exposures to pristine ENMs are more likely, the US National Institute of Occupational Safety and Health (NIOSH) has published recommended exposure limits (RELs) for the following ENMs to protect worker safety and health although not legally enforceable: titanium dioxide (TiO₂), carbon nanotubes (CNTs), and carbon nanofibers (CNFs).³¹

Under current US law, there are no labelling requirements for ENMs on consumer products – be it food, cosmetics or other useful products.

**What can I do to stay safe?**

Persons working with ENMs in workplaces and laboratory settings must use a combination of engineering controls, administrative controls, safe work practices and personal protective equipment as established by their organization's environmental health and safety (EHS) office to minimize potential exposures and ensure a safe working environment. Consumers should use products only for their intended use, duration and under the manufacturer recommended conditions to prevent degradation of the product and hence potential exposure to ENMs in the product. For instance, while using laser printers at home or office, consumers should minimize their exposure to the released PM by placing the printer in a well-ventilated location, not spending excessive time close to the printer and replacing the old with new and more efficient printers.



REFERENCES

1. The European Commission. *Commission Delegated Regulation (EU) No 1363/2013 amending Regulation (EU) No 1169/2011 of the European Parliament and of the Council on the provision of food information to consumers as regards the definition of "Engineered nanomaterials"*; The European Commission: Brussels, European Union, 2013.
2. Stark, W. J.; Stoessel, P. R.; Wohlleben, W.; Hafner, A. Industrial applications of nanoparticles. *Chem. Soc. Rev.* 2015, 98 (5), 2035–2044.
3. Hayashi, C.; Kashu, S.; Oda, M.; Naruse, F. The use of nanoparticles as coatings. *Mater. Sci. Eng. A* 1993, 163 (2), 157–161.
4. Kaiser, J.-P.; Diener, L.; Wick, P. Nanoparticles in paints: A new strategy to protect façades and surfaces? *J. Phys. Conf. Ser.* 2013, 429 (1), 12036.
5. Lee, J.; Mahendra, S.; Alvarez, P. J. J. Nanomaterials in the construction industry: A review of their applications and environmental health and safety considerations. *ACS Nano* 2010, 4 (7), 3580–3590.
6. Saba, N.; Tahir, P.; Jawaid, M. A Review on Potentiality of Nano Filler/Natural Fiber Filled Polymer Hybrid Composites. *Polymers (Basel)*. 2014, 6 (8), 2247–2273.
7. Pirela, S. V.; Sotiriou, G. A.; Bello, D.; Shafer, M.; Bunker, K. L.; Castranova, V.; Thomas, T.; Demokritou, P. Consumer exposures to laser printer-emitted engineered nanoparticles: A case study of life-cycle implications from nano-enabled products. *Nanotoxicology* 2015, 9 (6), 760–768.
8. Pirela, S. V.; Pyrgiotakis, G.; Bello, D.; Thomas, T.; Castranova, V.; Demokritou, P. Development and characterization of an exposure platform suitable for physico-chemical, morphological and toxicological characterization of printer-emitted particles (PEPs). *Inhal. Toxicol.* 2014, 26 (7), 400–408.
9. Weir, A.; Westerhoff, P.; Fabricius, L.; Hristovski, K.; von Goetz, N. Titanium dioxide nanoparticles in food and personal care products. *Environ. Sci. Technol.* 2012, 46 (4), 2242–2250.
10. Keller, A. A.; McFerran, S.; Lazareva, A.; Suh, S. Global life cycle releases of engineered nanomaterials. *J. Nanoparticle Res.* 2013, 15 (6), 1692.
11. Lux Research. *Nanotechnology Update: Corporations Up Their Spending as Revenues for Nano-enabled Products Increase*; 2014.
12. Duncan, T. V. Release of Engineered Nanomaterials from Polymer Nanocomposites: the Effect of Matrix Degradation. *ACS Appl. Mater. Interfaces* 2015, 7 (1), 20–39.
13. Pirela, S. V.; Lu, X.; Miousse, I.; Sisler, J. D.; Qian, Y.; Guo, N.; Koturbash, I.; Castranova, V.; Thomas, T.; Godleski, J.; et al. Effects of intratracheally instilled laser printer-emitted engineered nanoparticles in a mouse model: A case study of toxicological implications from nanomaterials released during consumer use. *NanoImpact* 2016, 1, 1–8.
14. Pirela, S. V.; Miousse, I. R.; Lu, X.; Castranova, V.; Thomas, T.; Qian, Y.; Bello, D.; Kobzik, L.; Koturbash, I.; Demokritou, P. Effects of Laser Printer-Emitted Engineered Nanoparticles on Cytotoxicity, Chemokine Expression, Reactive Oxygen Species, DNA Methylation, and DNA Damage: A Comprehensive in Vitro Analysis in Human Small Airway Epithelial Cells, Macrophages, and Lymphoblasts. *Environ. Health Perspect.* 2016, 124 (2), 210–219.
15. Pirela, S. V.; Martin, J.; Bello, D.; Demokritou, P. Nanoparticle exposures from nano-enabled toner-based printing equipment and human health: state of science and future research needs. *Crit. Rev. Toxicol.* 2017, No. May, 1–27.
16. Sotiriou, G. A.; Singh, D.; Zhang, F.; Wohlleben, W.; Chalbot, M.-C. G.; Kavouras, I. G.; Demokritou, P. An integrated methodology for the assessment of environmental health implications during thermal decomposition of nano-enabled products. *Environ. Sci. Nano* 2015, 2 (3), 262–272.
17. Sotiriou, G. A.; Singh, D.; Zhang, F.; Chalbot, M. C. G.; Spielman-Sun, E.; Hoering, L.; Kavouras, I. G.; Lowry, G. V.; Wohlleben, W.; Demokritou, P. Thermal decomposition of nano-enabled thermoplastics: Possible environmental health and safety implications. *J. Hazard. Mater.* 2016, 305, 87–95.
18. Singh, D.; Sotiriou, G. A.; Zhang, F.; Mead, J.; Bello, D.; Wohlleben, W.; Demokritou, P. End-of-life thermal decomposition of nano-enabled polymers: Effect of nanofiller-loading and polymer matrix on byproducts. *Environ. Sci. Nano* 2016, 3 (6), 1293–1305.
19. Nel, A.; Xia, T.; Mädler, L.; Li, N. Toxic potential of materials at the nanolevel. *Science* 2006, 311 (5761), 622–627.
20. Sotiriou, G. A.; Watson, C.; Murdaugh, K. M.; Darrah, T. H.; Pyrgiotakis, G.; Elder, A.; Brain, J. D.; Demokritou, P. Engineering safer-by-design, transparent, silica-coated ZnO nanorods with reduced DNA damage potential. *Environ. Sci. Nano* 2014, 1 (2), 144–153.
21. Watson-Wright, C.; Singh, D.; Demokritou, P. Toxicological implications of released particulate matter during thermal decomposition of nano-enabled thermoplastics. *NanoImpact* 2017, 5, 29–40.
22. Poland, C. A.; Duffin, R.; Kinloch, I.; Maynard, A.; Wallace, W. A. H.; Seaton, A.; Stone, V.; Brown, S.; Macnee, W.; Donaldson, K. Carbon nanotubes introduced into the abdominal cavity of mice show asbestos-like pathogenicity in a pilot study. *Nat. Nanotechnol.* 2008, 3 (7), 423–428.



23. Lu, X.; Miousse, I. R.; Pirela, S. V.; Moore, J. K.; Melnyk, S.; Koturbash, I.; Demokritou, P. In vivo epigenetic effects induced by engineered nanomaterials: A case study of copper oxide and laser printer-emitted engineered nanoparticles. *Nanotoxicology* 2016, 10 (5), 629–639.
24. Lu, X.; Miousse, I. R.; Pirela, S. V.; Melnyk, S.; Koturbash, I.; Demokritou, P. Short-term exposure to engineered nanomaterials affects cellular epigenome. *Nanotoxicology* 2016, 10 (2), 140–150.
25. Pirela, S. V.; Lu, X.; Miousse, I.; Sisler, J. D.; Qian, Y.; Guo, N.; Koturbash, I.; Castranova, V.; Thomas, T.; Godleski, J.; et al. Effects of intratracheally instilled laser printer-emitted engineered nanoparticles in a mouse model: A case study of toxicological implications from nanomaterials released during consumer use. *NanoImpact* 2016, 1, 1–8.
26. DeLoid, G.; Casella, B.; Pirela, S.; Filoramo, R.; Pyrgiotakis, G.; Demokritou, P.; Kobzik, L. Effects of engineered nanomaterial exposure on macrophage innate immune function. *NanoImpact* 2016, 2, 70–81.
27. Konduru, N. V.; Murdaugh, K. M.; Sotiriou, G. A.; Donaghey, T. C.; Demokritou, P.; Brain, J. D.; Molina, R. M. Bioavailability, distribution and clearance of tracheally-instilled and gavaged uncoated or silica-coated zinc oxide nanoparticles. *Part. Fibre Toxicol.* 2014, 11, 44.
28. Molina, R. M.; Konduru, N. V.; Jimenez, R. J.; Pyrgiotakis, G.; Demokritou, P.; Wohlleben, W.; Brain, J. D. Bioavailability, distribution and clearance of tracheally instilled, gavaged or injected cerium dioxide nanoparticles and ionic cerium. *Environ. Sci. Nano* 2014, 1 (6), 561–573.
29. Singh, D.; Schifman, L. A.; Watson-Wright, C.; Sotiriou, G. A.; Oyanedel-Craver, V.; Wohlleben, W.; Demokritou, P. Nanofiller Presence Enhances Polycyclic Aromatic Hydrocarbon (PAH) Profile on Nanoparticles Released during Thermal Decomposition of Nano-enabled Thermoplastics: Potential Environmental Health Implications. *Environ. Sci. Technol.* 2017, 51 (9), 5222–5232.
30. EPA. Control of Nanoscale Materials under the Toxic Substances Control Act <https://www.epa.gov/reviewing-new-chemicals-under-toxic-substances-control-act-tsca/control-nanoscale-materials-under> (accessed Jun 14, 2017).
31. Brenner, S. A.; Neu-Baker, N. M.; Eastlake, A. C.; Beaucham, C. C.; Geraci, C. L. NIOSH field studies team assessment: Worker exposure to aerosolized metal oxide nanoparticles in a semiconductor fabrication facility. *J. Occup. Environ. Hyg.* 2016, 13 (11), 871–880.

