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Consumer exposures to laser printer-emitted engineered nanoparticles: A case study of life-cycle implications from nano-enabled products

Sandra V. Pirela¹, Georgios A. Sotiriou¹, Dhimiter Bello^{1,2}, Martin Shafer³, Kristin Lee Bunker⁵, Vincent Castranova⁶, Treye Thomas⁷, and Philip Demokritou^{1,*}

¹Department of Environmental Health, Center for Nanotechnology and Nanotoxicology, School of Public Health, Harvard University, 665 Huntington Ave., Boston, MA, USA

²Department of Work Environment, College of Health Sciences, and Center for High Rate Nanomanufacturing, University of Massachusetts, Lowell, MA, USA

³Wisconsin State Laboratory of Hygiene, 2601 Agriculture Drive, Madison, WI, USA

⁵R. J. Lee Group, Inc., Monroeville, PA, USA

⁶Department of Basic Pharmaceutical Sciences, West Virginia University, Morgantown, WV, USA

⁷U.S. Consumer Product Safety Commission, Office of Hazard Identification and Reduction, Rockville, MD, USA

Abstract

It is well established that printers emit nanoparticles during their operation. To-date, however, the physicochemical and toxicological characterization of “real world” printer-emitted nanoparticles (PEPs) remains incomplete, hampering proper risk assessment efforts. Here, we investigate our earlier hypothesis that engineered nanomaterials (ENMs) are used in toners and ENMs are released during printing (consumer use). Furthermore, we conduct a detailed physicochemical and morphological characterization of PEPs in support of ongoing toxicological assessment. A comprehensive suite of state of the art analytical methods and tools was employed for the physicochemical and morphological characterization of 11 toners widely utilized in printers from major printer manufacturers and their PEPs. We confirmed that a number of ENMs incorporated into toner formulations (*e.g.*, silica, alumina, titania, iron oxide, zinc oxide, copper oxide, cerium oxide, carbon black among others) and released into the air during printing. All evaluated toners contained large amounts of organic carbon (OC, 42–89%), metals/metal oxides (1–33%), and some elemental carbon (EC, 0.33–12%). The PEPs possess a composition similar to that of toner

*Corresponding author: Phone number: (617) 432-3481. pdemokri@hsph.harvard.edu.

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and contained 50–90% OC, 0.001–0.5% EC and 1–3% metals. While the chemistry of the PEPs generally reflected that of their toners, considerable differences are documented indicative of potential transformations taking place during consumer use (printing). We conclude that: (i) Routine incorporation of ENMs in toners classifies them as nano-enabled products (NEPs); (ii) These ENMs become airborne during printing; (iii) The chemistry of PEPs is complex and it reflects that of the toner and paper. This work highlights the importance of understanding life-cycle (LC) nano-EHS implications of NEPs and assessing real world exposures and associated toxicological properties rather than focusing on “raw” materials used in the synthesis of an NEP.

Keywords

printer emitted nanoparticles; toner; engineered nanoparticles; nano-EHS; nano-enabled products

INTRODUCTION

The market for NEPs is estimated to have had an annual growth rate of approximately 50% since 2009 (Limited, 2011), rendering the possible consumer exposure to ENMs inevitable. The current “*modus operandi*” used in the nanoparticle risk assessment paradigm which focuses only on the pristine (raw) ENMs is not often appropriate to address possible adverse health effects associated with NEPs during a product’s LC. Even though such information is crucial for risk assessment of occupational exposures during the manufacturing of NEPs, consumers typically do not get exposed to the pristine ENMs used in the synthesis of NEPs, but rather, to the nanoparticles released during use of a product. Such emissions may have potentially altered physicochemical and (possibly) toxicological properties that are different from those of the “raw” ENMs. This important knowledge gap has been emphasized recently in both the National Research Council report, as well as in the National Nanotechnology Initiative’s strategy on nano-environmental health and safety (nano-EHS) (NNI, 2011, NRC, 2012). If these nano-EHS uncertainties surrounding the LC implications of NEPs remain unaddressed, a proper public health risk assessment will not be possible and the sustainable development of the nanotechnology industry as a whole will be affected at the societal and economic levels.

Thus, new methodological approaches are urgently needed to address LC implications of NEPs (NNI, 2011, NRC, 2012). Here, such an integrated methodology for exposure assessment of NEPs during consumer use is presented for nano-enabled toners used in laser printers. This case study demonstrates the importance of studying the release of ENMs from NEPs during consumer use and characterizing their physicochemical, morphological and, subsequently, toxicological properties.

Evaluating consumer risk of nanoparticle exposure from the use of nano-enabled toners during printing has become a necessity, since the market for this office technology has increased substantially. The laser printer market has shown positive year-over-year growth, with halftone and color laser devices accounting for 82.3% and 60%, respectively, of the total laser market in 2013 (IDC, 2014). With the wider use of the hardcopy printing

technology comes the increased likelihood of consumer exposure to PEPs emanating from toner cartridges.

Prior studies on the emission of particulate matter (PM) from laser printer equipment have focused on the particle size distribution and concentration of the emitted aerosol and factors that influence these emissions (*e.g.*, printer operational parameters, printer manufacturer, age) (Barthel et al., 2011, Tang et al., 2012, Castellano et al., 2012, Wang et al., 2012, Kagi et al., 2007, Wensing M, 2006, Brown, 1999). Recently, it was shown that laser-based printing equipment can produce up to 1.3 million particles/cm³ and these PEPs have average mobility particle diameters ranging from 49 to 208 nm (Pirela et al., 2014). However, to-date there is no comprehensive data regarding the incorporation of ENMs in toners and detailed physicochemical properties of released PEPs and the relationship between PEPs and their precursors in toner powder.

In addition, published studies focusing on the toxicological properties of PEPs primarily used pristine toner particles rather than the actual released particles (Gminski et al., 2011, Mersch-Sundermann et al., 2011, Morimoto et al., 2013, Bai et al., 2010). These are both unrealistic exposure scenarios and their findings are contradictory; thus, they cannot be used towards a proper risk assessment at the consumer level. Additionally, epidemiological studies on emissions from laser printers are inconclusive since there is no clear differentiation between symptoms resulting solely from PEPs or from allergic reactions due to previous sensitization events (Ewers and Nowak, 2006). As a result, it is difficult to determine the inherent public health implications derived from this widely used NEP

Here, an exposure platform recently developed by the authors (Pirela et al., 2014) was used to generate PEPs from 11 widely used laser printers. A thorough investigation to assess the presence of nanoscale materials in the toner formulations and study the release of such ENMs in the air during printing (consumer use) was performed. A detailed physicochemical and morphological characterization on both PEPs and toner formulations was completed using state of the art analytical methods such as magnetic sector field (SF) inductively coupled plasma mass spectrometry (ICP-MS), ion chromatography, organic/elemental carbon analysis, Fourier transform infrared (FTIR) spectroscopy, and scanning and transmission electron microscopy (STEM) coupled with energy dispersive X-ray (EDX) spectroscopy. Such an integrated methodology for the risk assessment of NEPs during consumer use will not only provide detailed characterization of exposures from such a NEP product, but will also enable toxicological testing using collected real world emitted particles rather than the pristine toner particles.

METHODS

Collection of size fractionated PEPs and toner powder from commonly used laser printers

The recently developed Printer Exposure Generation System (PEGS, Supplemental Figure S1), which is suitable to generate real world exposures to PEPs, was used in this study (Pirela et al., 2014). In summary, each laser printer was placed inside an environmental chamber and set to print a single-sided monochrome document. The selected 11 printers are from the four most commercially available manufacturers (A, B, C and D) and models.

Manufacturing date varied for this particular “printer sample” to simulate that of a representative office environment. All printers here have been manufactured within the last 9 years (2004–2013), with some of them being brand new (please see Supplementary Table S1 for printer specifications including manufacturing year). It is worth noting that the effect of the wear and tear and age of the printer as a modifier of the PM emission profile was not investigated here. The reproducibility of the PM emissions from two new laser printers of the same model was verified, as well as that of the different toner cartridges used and no differences were found (data not shown). The size-fractionated PEPs were sampled using the Harvard Compact Cascade Impactor (CCI), which has a flow rate of 30 l/min (Demokritou et al., 2004) onto polyurethane foam (PUF) impaction substrates ($PM_{>2.5}$), and Teflon ($PM_{2.5}$, chemical analysis) or quartz ($PM_{2.5}$, OC/EC analysis) filters. The collection of $PM_{2.5}$ instead of two separate size fractions, $PM_{0.1}$ and $PM_{0.1-2.5}$, was done conscientiously to enable collection of sufficient mass and to keep the number of samples manageable. These were weighed pre- and post-sampling following a 48-hour stabilization process in a temperature- ($22^{\circ}\text{C} \pm 1$) and humidity- ($43\% \pm 2$) controlled environmental chamber utilizing a Mettler Toledo XPE analytical microbalance. Thus, the weight difference was used to determine the collected PEPs mass and to calculate the time averaged particle mass concentration in the chamber during the printing episode. Subsequently, the size selective fractions were analyzed for various analytes based on a previously published methodology (Bello et al., 2013, Chang et al., 2013). For each sampling episode, field blanks were also collected. Toner powder was also collected directly from each cartridge and transferred to clean scintillation vials for subsequent chemical and morphological analysis.

Chemical analysis of PEPs and toner powder

Detailed chemical characterization of size fractionated PEPs and toner powders, as well as the paper used during the study, included testing for total and water-soluble fraction of multiple metals (50 elements), and for organic and elemental carbon per previously published methods (Bello et al., 2013). The analyses are described briefly below for clarity:

Magnetic sector field (SF) inductively coupled plasma mass spectrometry (ICP-MS)—Evaluation of elemental composition of the collected material (airborne PM and toner powder) was performed following a protocol previously described by Herner et al. (2006). The extracted mass from the PUF substrate and the Teflon/Quartz filter was digested using an acidic solution and diluted to different volumes with high purity water (Millipore, Bedford, MA). The dilutions were then placed in low-density polyethylene bottles that were pre-cleaned using an acid solution consisting of 2.4 N hydrochloric acid for two days, then 3.2 N HNO_3 for two more days and lastly, rinsed with high purity water. The water-soluble elements in the airborne PM sample were extracted using high purity water and filtered via the use of acid-leached polypropylene syringe filters. Finally, the digested sample and extracts underwent ICP-MS analysis (Thermo-Finnigan Element 2). In addition to the collected samples, sample spikes, sample duplicates, blanks, standards, and certified reference materials (NIST 2709, NIST 1648a, NIST 2556, NIST 2702) were used in the chemical testing.

Organic carbon/elemental carbon analysis (OC-EC)—The PEPs were collected on pre-baked Quartz fiber filters. A one-cm² filter punch was used to measure OC-EC following the protocols standardized for the ACE-Asia intercomparison study. This method is adapted from the NIOSH 5040 method, which utilizes Sunset Laboratory Inc. (Forest Grove, OR) laboratory-based thermal optical analyzer. This analysis proved informative in the case of toners and PEPs because toners contain large amounts of organic carbon (in the polymer matrix), some elemental carbon (5–20%), and other metal oxide additives (Bello et al., 2013). We decided not to employ the semi-volatile organic compound (sVOC) analysis because in our earlier work we found that these species accounted for only a minor fraction of the total PEPs mass (Bello et al., 2013).

Fourier transform infrared (FTIR) spectroscopy—Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy was performed on the dry toner powders and the collected PEPs using a Perkin Elmer Spectrum One spectrometer. For the analysis of the collected PEPs, the aqueous solution containing the particles was evaporated to obtain the dried powder of the sample that was then redispersed in ultra-pure ethanol (Sigma Aldrich > 99.9%). One drop of this suspension was deposited on the ATR crystal and allowed to evaporate. The data acquisition was carried out with a resolution of 4 cm⁻¹ and the spectra were averaged at least 10 times.

Ion chromatography analysis for anions and cations—The water-soluble fraction of toners and PEPs were additionally analyzed for the following anions and cations by ion chromatography (ammonium, chloride, nitrate, and sulfate), which were extracted from the filter samples with milliQ water (15.0 mL, for 6 hours, with continuous agitation, in the dark, in pre-cleaned polypropylene tubes) and quantified using an established low-level ion chromatographic (IC) technique (Thermo Scientific Dionex, U.S.A.). QA/QC samples included sample and milliQ spikes, replicates, method and filter blanks, and primary and secondary standard checks.

Morphological analysis of PEPs and toner powder

The airborne PM from the six highest emitting printers as ranked based on real time monitoring particle number concentration data (Pirela et al., 2014) was collected onto a 100 mesh copper grid with a carbon film (EM Sciences, Hatfield, PA) using an electrostatic precipitator (ESP, Spokane Laboratories, NIOSH, WA) operating at 100 ml/min, typically for a duration of 3–10 min. The ESP flow rate was checked before sampling. Morphological analysis of PEPs collected onto the transmission electron microscopy (TEM) grids was conducted with TEM on a JEOL 2100 microscope operated at 200 kV. The toner powder was attached on carbon tape that was mounted on the scanning electron microscopy (SEM) holder imaged with a scanning and transmission electron microscope (STEM) with a Carl Zeiss Supra55 microscope. For the SEM, gun voltage ranged from 2 to 10 kV. Furthermore, energy dispersive spectroscopy (EDX) was also used to evaluate the chemical composition of both the toner powders and the PEPs (EDX, JEOL 2010).

Total volatile organic compounds (tVOC)

Although the focus of the investigation was on the PEPs, the real-time release of tVOC was also monitored using a tVOC monitor (Graywolf Sensing Solutions, Shelton, CT) equipped with a sensitive probe (parts per billion range). The instrument was factory calibrated within the past year and laboratory calibrated, as per the manufacturer's instructions, with isobutylene and zero air in the laboratory prior to the sampling. The instrument has a photoionization potential of 9.6 eV.

Mass balance calculations

Mass balance calculations were performed according to the procedure described in Bello et al. (2013). The total PM_{2.5} mass from gravimetric analysis was partitioned between organic and elemental carbon, as well as overall inorganic content (from OC/EC analysis). The inorganic fraction was then further subdivided into different elements based on the ICP-MS analysis. More prominent elements were reported individually on the pie charts (*e.g.*, Si, Fe, Al and Ti) with the remaining metals summed into a 'metals category' and the difference was expressed as 'other'. This difference, always greater than zero, includes anions (*e.g.*, chlorides, sulfates, carbonates) and cations not included in the initial list of measured elements.

It should be noted that in this study, we sampled for PM_{2.5} primarily due to cost considerations and to obtain sufficient mass for gravimetric analysis. Although the real-time data shows almost exclusively nanoparticle emissions (Pirela et al., 2014), which is consistent with published work, the total mass of PM_{2.5} is influenced disproportionately more by a few much larger particles. In separate experiments with one high emitting printer (B1), sampling was done for both PM_{0.1} and PM_{0.1–2.5}.

RESULTS

Hypothesis #1: Inclusion of nanoscale materials in toner formulations?

In this study, we examined 11 toners used in 11 laser printer models made by four different market-leading manufacturers (A, B, C and D). Based on the information provided by the toner manufacturers' Material Safety Data Sheets (MSDS), the 11 toners typically consisted of a mixture of polymers (55–85% by mass) and a small fraction of fillers, such as ferrite and silicon dioxide (<5%) and carbon black (<10%) (See Table S1 for full toner composition). No information was provided by the manufacturers in terms of the use of nanoscale materials in the toner formulation.

Figure 1 shows representative SEM images and the respective EDX spectra of dry toner powders from 3 of the eleven printers (A1, A2 and C6), which have different morphology: regular spheres (*e.g.*, Printer C6) vs. irregular spheres (*e.g.*, Printer A1, A2) of a size range of ~10–15 µm. In one printer toner (A2), we found fibers (~2–10 µm in length) on the toner particle surface, which were identified to be titania by EDX analysis. The rest of the examined toners exhibit similar morphological characteristics (Figure S4). This is in agreement with toner particles used in photocopier equipment (Bello et al., 2013).

Furthermore, the presence of nanoscale particles on the toner particle surface was clearly documented for all 11 toners examined as can be seen in the magnified SEM images in Figures 1b, 1e and 1h for three representative printers. It should be noted that nanoparticles are found not only on the surface of the toner particles, but also incorporated inside them. When the SEM operational voltage is increased from 2 kV to 10 kV, the electron beam penetrates further inside the toner particle, revealing the presence of spherical, non-agglomerated inorganic nanoparticles (Figure 1e). However, detailed imaging of nanoparticles encapsulated inside each toner particle is more challenging and requires more specialized techniques and was not performed as part of this study.

The elemental composition of toner particles was also qualitatively determined by EDX spectroscopy. Figures 1c, 1f and 1i show the EDX spectra for the corresponding toners that include signals from oxygen (O), silicon (Si), aluminum (Al) and magnesium (Mg), verifying their presence in the toner composition, most probably as metal/metal oxides. Often these surface nanoparticles are amorphous silica, as documented by closer investigation of their EDX spectra, which may be used as dispersants. The presence of other engineered nanometals and metal oxides, such as CeO₂, Al₂O₃, TiO₂ and Fe₂O₃, ZnO was also identified in the EDX analysis of some the other toners (data not shown). Of note, in one case, toner particles were covered on their surface with numerous respirable fibers (<1 to 10 µm long) made of TiO₂ (Figure 1 g,h,i).

Hypothesis #2: Are nanoparticles released during consumer use (printing) from NEP?

Sources and physicochemical properties of PEPs

Figure 2a shows real time representative particle number concentration profiles of the PEPs from three of the 11 tested printers (A1, B1, and C2) after 10 minutes of continuous printing. Corresponding average mobility particle size distributions over the printing duration from the same printers (A1, B1, and C2) are shown in Figure 2b and are in agreement with the literature (Pirela et al., 2014). It is also worth pointing out that detailed investigation of the real-time PM emissions of the 11 printers reveals that the number concentrations differ for each printer and reach high values within 12 minutes after initiating the print job (Pirela et al., 2014).

Figure 2 also shows STEM images (c,d,e) and the corresponding EDX spectra (f,g,h) of PEPs that were collected using an electrostatic precipitator *in situ* (inside the chamber) during the printing process. The size of these PEPs, as obtained from electron microscopy images seems to correspond well to the real-time particle size distributions represented in Figure 2a, which confirms that emitted PM is predominantly in the nanoscale. The EDX analysis (Figures 2f, 2g, and 2h) of the PEPs reveals the presence of inorganic elements, such as zinc (Zn), copper (Cu), titanium (Ti), cerium (Ce), silicon (Si), calcium (Ca), and sulfur (S), in their composition.

After confirming the presence and determining the physicochemical and morphological properties of ENMs in both the toner formulations and emitted PEPs, we aimed to investigate the sources of these emitted particles.

The chemical composition of both toner and PEPs was assessed using state of the art analytical methods such as ICP-MS for inorganic elements and EC/OC for carbonaceous compounds. ICP-MS analysis on both the toners and PEPs is illustrated in Figures 3b, 3c, and 3d and in Supplemental Material Figures S2–3. In summary, the 11 evaluated toner powders possess complex chemistries and contained large amounts of organic carbon (42% to 89%), metals/metal oxides (1% to 33%), and some elemental carbon (0.33% to 12%). Elemental carbon is almost negligible for the majority of the printers from manufacturer C (*i.e.*, C2, C4, C5, and C6). The inorganic components of the toner powders were similar across the different brands, but the amount of each element varied significantly among the manufacturers. The main elements found in all 11 toner powders were Ca, Si, S, sodium (Na), and phosphorus (P). Interestingly, only the printers from a specific manufacturer (A1 and A2) had Zn in their powder (13.5% and 2.6%, respectively). Other metals found in the chemical analysis included, but were not limited to, nickel (Ni), chromium (Cr), Cu, Ce and Mg, among others (Table S2).

Table S3 summarizes the elemental composition data of the water-soluble elemental examination PEPs from the high-emitting printers previously characterized by the authors (Pirela et al., 2014). The emitted PEPs were composed of a variety of elements that could be traced back to those found in the toner powder (*e.g.*, Si, Zn, Na, P, S). Additional chemical analysis of the PEPs indicated the presence of a variety of elements mostly identified on ICP-MS analysis, such as Cu, Ce, Cr, Ni, Fe, Ti, and Cl.

Additionally, Figures 4a and 4b show the ATR-FTIR spectra of all the 11 toner powders and the PEPs ($PM_{0.1}$, $PM_{0.1-2.5}$, $PM_{2.5}$) from the (high emitting) Printer B1. The toner and the collected emitted PM belonging to printer B1 were evaluated to determine if the same chemical fingerprint is shared by the two samples (Figure 4a). The CH_x methyl groups around 3000 cm^{-1} and the carbon and oxygen double bond at $\sim 1700\text{ cm}^{-1}$ are present in the toner, as well as the collected PEPs. Figure 4b shows the spectra for the 11 analyzed toners, which exhibit similar chemistry; this hints to a comparable toner composition (also confirmed by their reported chemistry, Table S1) despite the brand. Important to note is the presence of carbonyl reach region in the airborne PEPs. Taken together with the EDX data on both toner and PEPs, this data set provides clear evidence that there is a release of particles from the toner to the air.

Another possible source of emitted particles investigated is the paper used during printing. The paper was analyzed to obtain its chemical composition and evaluate whether particles from the paper could also be found in the emitted PM (Supporting Information, Table S4). As expected, calcium made up more than 70% of the elemental content of the paper, and can be traced back to the paper pulp (*i.e.*, calcium carbonate). Additionally, certain brightening and whitening elements, such as aluminum oxides, titanium dioxide, and silicon dioxide, were also found in the paper. By comparing the ratio of the above-mentioned signature elements on the paper, toner, and emitted PEPs, it can be postulated that paper, in addition to the toner powder, the paper itself may be another emission source of some of these airborne inorganic nanoparticles (Supporting Information, Tables S2–4).

Emission of VOC during printing

As shown in Figure 3a, the tVOC concentration increases with time during a continuous print job. Some of these VOC and sVOC can condense on the surface of solid inorganic particles surrounding them (confirmed by EDX analysis – data not shown), as shown in the inset of Figure 3a.

DISCUSSION

ENMs in toner formulations

As illustrated in Figure 1, toner powder particles have a size of approximately 10 μm and their morphology depends on the formulation technique that is utilized during their production (Xerox, 2013). For example, mechanical milling leads to toner particles with irregular shape (Figures 1a, 1b), while particles made by emulsion aggregation have a rather spherical shape (Figures 1d, 1e). In addition, it was clearly demonstrated here that a variety of nanoscale particles have been incorporated into toner formulations in order to improve the functional properties of the toner, such as charging and heat-resistance and enhance the sharpness of the image and text quality (Xerox, 2013). Both electron microscopy and EDX analysis provided confirmation that toners contain a variety of ENMs and constitute broadly a NEP. The ENMs found in toners included ceria, silica, titania, alumina, zinc oxide, iron oxide, magnesium oxide, and carbon black. These findings are consistent with our recently published work which provided evidence of the incorporation of several types of ENMs (silica, alumina, titania and iron oxide among others) in toners from photocopiers (Bello et al., 2013). This previous study gathered sufficient evidence to postulate that the copier toner manufacturing industry has shifted towards using nano-enabled toners and called for an industry-wide investigation on the chemical and possible toxicological outcomes of ENMs released from laser-based printing equipment in general. Our findings here establish that toner manufacturing in general has shifted mainstream to nanotechnology.

Laser printers release ENMs into the air

It has been well established in the literature that laser printers emit airborne nanoparticles during printing (Schripp et al., 2008, Morawska et al., 2009, Pirela et al., 2014). Here, it is demonstrated that that PM peak emissions were brand-independent and varied between 3000 to 1.3 million particles/ cm^3 with modal diameters ranging from 49 to 208 nm, with the majority of the PEPs in the nanoscale (<100 nm). Of note, size of the PEPs observed in the STEM analysis is in agreement with the real time aerosol data shown in Figure 2, and presented in greater detail in our recently published companion paper (Pirela et al., 2014).

It is worth noting that the highest emitting laser printers A1 and B1 (Figure 2), emitted over one million particles/ cm^3 , a substantially high particle number concentration compared to the approximate value of 2000 particles/ cm^3 typically found in an urban indoor environment (Quang et al., 2012). In fact, such high particle exposure levels are similar to those of highly polluted highways (Padro-Martinez et al., 2012), for which a range of human health effects, from increased morbidity to stroke attacks to low birth weight and changes in global gene expression patterns of human bronchial epithelial cells (Ding et al., 2014, Vinikoor-Imler et al., 2014, Yu et al., 2014), has been documented. It is not only the potentially high exposure

levels encountered during printing but also the chemistry of such emissions that require more thorough toxicological and epidemiological investigations. As Khatri et al. (2013) showed, a few hours of exposure to 20,000 to 30,000 copier-emitted particles/cm³ is sufficient to induce clear inflammatory responses in healthy human volunteers.

The composition of inorganic constituents in airborne PEPs and especially the presence of ENMs in them, are an emerging area of research. Here, we establish that such a NEP (toner) releases particles including nanoscale particles used in its synthesis. An important contribution of this study is, therefore, not only the incorporation of nanoscale materials in the toner formulation and their release to the air during consumer use, but also the detailed physicochemical and morphological characterization of both toner and released particles. More importantly, it was demonstrated that realistic exposure properties should be used in the toxicological characterization studies rather than the currently use of toner particles

Sources of airborne PM emitted by laser printers: toner powder and paper

It is evident based on the EDX spectra of Printers A1, B1, and C2 that emitted ENMs during consumer use (printing) (Figure 2f, 2g, and 2h) are of metal origin. Specifically, the presence of these exact elements was also identified by ICP-MS in the respective toner powder used by the printers (Tables S1 and S2). The nearly identical chemical fingerprinting of the toner and PEPs serves as evidence that the ENMs currently being incorporated into the toner powder are indeed making their way into the emitted PM during printing. These findings are in agreement with a published analysis performed by the authors on photocopier-emitted particles, which found Cr, Fe and Ni in the chemical composition of the copier toner and the copier-emitted PM (Bello et al., 2013). Even though elemental carbon occupies a rather large fraction of up to 12% in the toner formulations presumably as pigment, it is present only in minor quantities of less than 0.5% by mass in the PEPs. Of note, the total inorganic fraction in the airborne PEPs was printer dependent and varied from ~50% for Printer A to less than 2% for Printer C1. This remarkable variation in the chemistry of airborne PEPs supports our earlier recommendation for an industry wide assessment of the chemistry of such exposures. New in the chemical characterization is analysis of anions and cations (Table S4). Of the species analyzed, the more abundant ions were chlorides, sulfates, and sodium, which originated primarily from the paper. These species account for only a small fraction of the total PEPs mass, from 0.2% to 1.4% (and 0.4% to 7% in toners and 5% to 10% in the paper). Therefore, only a negligible mass of the 'other' component in the pie charts could be accounted for these ions.

A significant portion of the PEPs from all evaluated printers is organic in nature. Yet their chemistry is not well characterized. Using ATR-FTIR to analyze the toners and PEPs, similar fingerprint features were identified (Figure 4A). In particular, the toner powder exhibits the distinctive spectrum for a polyester resin mixture (Merrill et al., 2003), as also stated in the corresponding MSDS. Additionally, there were CH_x methyl groups (3000 cm⁻¹) and carbon and oxygen double bonds (1700 cm⁻¹) in both the toner and the collected PM. At lower frequencies, however, there are some differences in the spectra. Significantly, the peak that is present in the toner powder corresponding to the aromatic ring (1600 cm⁻¹) is absent in the PEPs. This is in agreement with a previous study characterizing resin and

epoxy resin composites, the main components of toner powder (Liao et al., 2012). The current data indicate that the organic composition of the PEPs is similar to the original toner powder to a certain extent, possibly explained by the chemical transformation the toner undergoes, due to the high temperatures (~225°C) and pressures required to melt and fuse the toner to the paper during printing. Furthermore, additional research is needed to better characterize this substantial organic fraction of airborne PEPs.

Another important finding in this study is the fact that the data obtained via ICP-MS (Table S2) and the general information reported in the Material Safety Data Sheets (MSDS, Table S1) for the toner powders are generally in good agreement with results from various chemical analyses (OC-EC, ICP-MS, the EDX and FTIR spectra), especially as it relates to its main ingredients: the polymer content (assessed via OC analysis), elemental carbon (EC analysis), individual elements (via ICP-MS), and ENM (via morphological TEM/EDX analysis and limited XRD analysis not presented herein). For example, Manufacturer A toner cartridges were composed of polyester resin, iron oxide, carbon black, polymer wax, titanium dioxide and blue pigment. Manufacturer B toners composition contained styrene acrylate copolymer, carbon black, fatty acid ester, silica, PMMA and polyester resin. Manufacturer C toner cartridges included styrene acrylate copolymer, iron oxide, wax, carbon black, amorphous silica, titanium dioxide and zinc. Lastly, manufacturer D toner cartridges list styrene acrylate copolymer, iron oxide and wax as their main components. However, it is also worth mentioning that the MSDS sheets do not provide any information about the size of its ingredients, which highlights the importance of a nano labeling system for NEPs (Kessler, 2011), or presence of large amounts of metals of up to 34% by mass (*e.g.*, toners of Printers C2, C4-6, D1), of which appreciable amounts of transition metals of toxicological relevance, such as Mn, Cr, Co, and Ni (Table S2), or the presence of respirable TiO₂ fibers on one toner.

Consumer exposure to PEPs: possible health implications?

The presence of metal/metal oxide nanoparticles in the PEPs and the complex chemistry of PM, even at minute concentrations, is concerning because metals/metal oxides have the potential to trigger a toxic response in the lungs and translocate to other organs (Bondarenko et al., 2013, Kumar and Nagesha, 2013, Moschini et al., 2013, Demokritou et al., 2013, Cohen et al., 2014, Zhou et al., 2014). Specifically, metal oxides, such as silica, ceria, iron oxide and zinc oxide have been shown to produce DNA damage to cells exposed at doses as low as 5 µg/ml for 4 hours (Watson et al., 2014). Moreover, an integrative study by Sotiriou et al. (2012) and Demokritou et al. (2013) using the Harvard VENGENES showed significant toxicity (*e.g.*, lung injury and inflammation, decreased cell viability) by exposure to nanoscale iron oxide and ceria using both an *in vitro* and *in vivo* experimental design. Other recently published studies assessing the toxicological potential of ceria, titania, zinc oxide, copper oxide and iron oxide have confirmed increased inflammation, reactive oxygen species generation, neutrophilia, and neurotoxicity in exposed rodents and human cell lines (Shrivastava et al., 2013, Kumar and Nagesha, 2013, Landsiedel et al., 2014). It is also worth noting that particle size- and dose-dependent pulmonary effects were found in mice instilled with two size fractions of copier-emitted PM (PM_{0.1} and PM_{0.1-2.5}) (Pirela et al., 2013). These copier emissions have a similar chemical fingerprint as those from PEPs; thus,

it may possible that this complex chemical makeup may render the PEPs deleterious to the lung to those who are exposed to them.

The release of volatile organic compounds (VOCs) is also a concern when assessing consumer exposure to laser printer emissions. The presence of such gaseous compounds can influence the biological response to inhaled aerosols (Wang et al., 2013b, Wang et al., 2013a, Ebersviller et al., 2012). In particular, exposure to VOCs is associated with adverse changes in the pulmonary and cardiovascular system, including inflammation and heart rate variability, as well as changes in gene expression (Song et al., 2013, Weichenthal et al., 2012). Although we did not speciate tVOCs in this study, these substances have been extensively studied and summarized in past studies (Destailats et al., 2008). The presence of carbonyl compounds (*i.e.*, formaldehyde, acetaldehyde, benzaldehyde) and aromatic hydrocarbons (*e.g.*, styrene and xylenes) are of particular interest. Unfortunately, the absorption of VOCs onto the surface of inorganic nanoparticles and the interactions of the organic and the metal components of PEPs remains poorly understood in the context of this particular exposure scenario.

All of the above results point out that the recent toner formulations contain ENMs and should be categorized as NEPs. More importantly, ENMs become airborne during printer use and exposure levels can reach extremely high levels up to of 1.3 million particles/cm³. The chemistry of both toner particles and PEPs is highly complex and includes organic and elemental components, such as Mg, Al, P, S, Si, Ca, Ti, Ni, Cu, and Zn, among others. The PEPs have similar chemical composition to the toner particles and their overall nanoscale size may present health risks to consumers. These results highlight the need to perform appropriate exposure and toxicological assessments using the “real-world” emitted PM, rather than the toner particles, which were used in past efforts to assess health risks related to printing processes (Mersch-Sundermann et al., 2011, Morimoto et al., 2013, Weiss et al., 2011). In the coming companion papers, we will present evidence of the toxicological potential of PEPs from the high-emitting Printer B1 using both mono- and co-culture *in vitro* as well as an *in vivo* study designs. Results from such toxicological investigation will help assess the potential consumer risks from use such NEPs.

CONCLUSIONS

In summary, the thorough evaluation of the toner powder and PM emitted from printing equipment provided ample evidence that a variety of ENMs (at least eight different types) are embedded in current toner formulations and are released in the air during printing. The complex chemical fingerprint of the PEPs matches to a significant extent that of toner powders and paper, which identifies them as source of ENMs in PM emissions. This study will help identify potential hazards from the consumer interaction with NEPs and assist in developing future guidelines for such investigations. Furthermore, it is worth noting that a number of companion manuscripts are currently under preparation on the assessment of biological properties of PEPs and possible adverse health effects using both *in vitro* and *in vivo* approaches.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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FIGURE 1. Representative scanning electron microscopy images of three toner powders from Printer A1 (a,b), Printer C6 (d,e), Printer A2 (g,h) and their respective EDX spectrum (c,f,i). Nanoparticles on the toner surface are commonly amorphous silica, illustrated by the EDX spectra.

FIGURE 2.

Characterization of PEPs from three printers of different manufacturers: Printer A1, B1 and C2. (a) Size distribution (mean ± SE) of airborne PM emitted during the first ten minutes after printing started. (b) Peak particle number concentration achieved in the first ten minutes after printing started. (c,d,e) Transmission electron microscopy images of PEPs from three printers and their respective EDX spectrum (f,g,h). Note: Cu signal for the most part comes from the TEM grid.

FIGURE 3.

Chemistry of toners and PEPs resulting from ICP-MS, OC/EC, gravimetric, and cations and anions analysis. (a) Total VOC concentration throughout a continuous print job. Inset: electron microscopy images of PEPs from Printers A1 and B1 showing the organic layer covering the metal-rich core particle, common for airborne PEPs. (b–d) Chemical composition of toner powder and corresponding PEPs from three representative printers (printer A1, B1 and C1) tested based from magnetic sector inductively coupled plasma mass spectrometry (SF-ICP-MS) and analysis. Anions and cations can explain only 0.1–1.4% of the ‘other’ pie slice in airborne PEPs and 0.7–7% in toners.

FIGURE 4.

Fourier transform infrared (FTIR) spectroscopy results of toner powder and PEPs. (a) FTIR spectra from different size fractions of PEPs and toner powder from Printer B1 and (b) from 11 toner powders.