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Occupational exposure to nanoparticles at commercial photocopy centers

John Martin[a], Dhimiter Bello[a,b,*], Kristin Bunker[c], Martin Shafer[d], David Christiani[b], Susan Woskie[a], Philip Demokritou[b]

[a] *Department of Work Environment, University of Massachusetts, Lowell, MA, USA*
[b] *Department of Environmental Health, Center for Nanotechnology and Nanotoxicology, Harvard School of Public Health, Boston, MA, USA*
[c] *R J Lee Group, Inc., Monroeville, PA, USA*
[d] *Wisconsin State of Hygiene Laboratory, 2601 Agriculture Drive, Madison, WI, USA*

HIGHLIGHTS

- Copiers emit very high levels of nanoparticles; with bursts up to 700X background.
- Complex chemistry includes several airborne engineered nanoparticles.
- This occupational and public exposure hazard warrants equipment controls/redesign.

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ABSTRACT

Photocopiers emit high levels of nanoparticles ($PM_{0.1}$). To-date little is known of physicochemical composition of $PM_{0.1}$ in real workplace settings. Here we perform a comprehensive physicochemical and morphological characterization of $PM_{0.1}$ and raw materials (toners and paper) at eight commercial photocopy centers that use color and monochrome photocopiers over the course of a full week. We document high $PM_{0.1}$ exposures with complex composition and several ENM in toners and $PM_{0.1}$. Daily geometric mean $PM_{0.1}$ concentrations ranged from 3700 to 34000 particles/cubic-centimeter (particles/cm^3) (GSD 1.4–3.3), up to 12 times greater than background, with transient peaks >1.4 million particles/cm^3. $PM_{0.1}$ contained 6–63% organic carbon, <1% elemental carbon, and 2–8% metals, including iron, zinc, titania, chromium, nickel and manganese, typically in the <0.01–1% range, and in agreement with toner composition. These findings document widespread ENM in toner formulations and high nanoparticle exposures are an industry-wide phenomenon. It further calls attention to the need to substantially redesign the interface of this technology with workers and consumers.

1. Introduction

Many businesses rely upon the commercial printing industry to handle large, repetitive printing tasks, which are often completed using digital presses that rely on dry toner. A search of Standardized Industrial Classification (SIC) codes for 2759 “commercial printing, not otherwise specified” and 7339 “photocopying & duplicating services” reveals approximately 21,000 commercial copy and duplicating businesses in operation in the United States today. This may account for up to 160,000 workers and an unknown number of full-time permanent and part-time student employees working in copying and duplicating centers at any of the approximately 6500 colleges and universities in the United States. This does not account for the unknown number of patrons using photocopiers employed in nearly every business office in commercial businesses, hospitals, K-12 schools, municipal buildings and other public service locations. It is estimated that approximately 400,000,000 pounds of toner is consumed annually in the United States alone [1].

It is well documented that laser printers emit nanoparticles <100 nm in diameter ($PM_{0.1}$), with some models emitting transient particle bursts up to 1 million particles/cm^3 [2–4]. Compared to laser printers, there is a notable paucity of exposure data for photocopier emissions, and even less is known of conditions at working high-volume photocopy centers that often feature multiple copiers

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[*] Corresponding author at: Department of Work Environment, KI 200, University of Massachusetts, One University Ave., Lowell, MA 01854, USA.
E-mail address: Dhimiter_Bello@uml.edu (D. Bello).

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operating concurrently in small work spaces, often with minimum or no ventilation. One report suggests total average particle number concentrations double to over 10^7 particles/cm^3 during copying operations [5].

Since 2004 studies of photocopy employees have reported increased biomarkers of oxidative stress and genotoxicity measured in different biological media (*e.g.*, lymphocytes, buccal cells) relative to controls [6–11]. A recent study conducted by our group documented upper airway inflammation and systemic oxidative stress in human volunteers at realistic exposure levels [7], which were substantiated with a series of *in-vitro* studies in human primary cell lines [12,13] and instillation studies in mice [14]. In these studies, $PM_{0.1}$ were comparable in potency to welding fumes and several times more potent than copper oxide nanoparticles [12,14]. Chronic inflammation in humans was recently documented [15]. Thus, evidence to-date suggests $PM_{0.1}$ from photocopiers are potentially toxic, and additional research is needed to assess the chemical and toxicological properties of $PM_{0.1}$ across a full range of manufacturer toner formulations, equipment and usage, and realistic workplaces and practices. In a recent exploratory paper focusing on one photocopy center, we documented the presence of engineered nanoparticles (ENP) in two toners and $PM_{0.1}$. We hypothesized that engineered nanoparticles may have penetrated significantly the toner market. We recommended larger-scale exposure assessment studies should be conducted to investigate chemical composition of $PM_{0.1}$ emissions in photocopy centers, especially with regards to the presence of engineered nanoparticles and compositional variability between various manufacturers [16]. This large scale nanoparticle exposure characterization work is the first and most comprehensive characterization of its kind in the photocopying industry, proves our initial hypotheses and establishes that our earlier findings of high $PM_{0.1}$ exposures containing ENM are an industry-wide phenomenon.

2. Methods

2.1. Selection criteria

Eight commercial photocopy centers were recruited by telephone survey from the greater Boston area. Consideration for admission to the study was dependent on three selection criteria: (1) the copy center must employ at least one full-time employee (FTE); (2) must exceed 1000 copies per day; and, (3) employ photocopiers from one of the commonly found manufacturers in the area. A general schematic of the study design is presented in Fig. 1.

Participating copy centers were visited on a randomly selected week, during which detailed environmental information of each facility (size, layout, ventilation type), as well as production information (toner, machine model, workload and paper) were collected.

2.2. Real-time measurements

Particle number concentration as a function of particle size diameter (5.6 nm–20 μm) were measured for three to five consecutive days during business and non-business hours using three complimentary real-time instruments. A Fast Mobility Particle Sizer (FMPS, 3091) measures particle diameter from 5.6 to 560 nm, an Aerodynamic Particle Sizer (APS, 3321) was used to measure particles from 560 nm to 20 μm, and, a Condensation Particle Counter (CPC, 3007) was used to measure total number concentration from 20 nm to 20 μm (all from TSI, Inc., Shoreview, MN). Real-time instruments were factory calibrated and passed a field "zero" calibration test, and the onboard time clock synchronized to the attached laptop PC. Instrument inlets were positioned at breathing zone height approximately in the center of the room, close to the nearest photocopier, so as not to interfere with the operators' activities. Data logging was enabled for each instrument at a 1 s averaging interval.

2.3. Elemental analysis

$PM_{0.1}$ samples were collected with the Harvard Compact Cascade Impactor (CCI) and Nano-ID (Particle Measuring Systems), and sample mass determined by gravimetric analysis (Supplementary information). Elemental composition of $PM_{0.1}$ was determined by magnetic-sector field inductively coupled plasma mass spectroscopy (SF-ICP-MS) as described by Bello et al. [16]. Briefly, Teflon filters were dissolved in a mixture of high purity acids (1.0 mL 16N nitric acid, 0.1 mL 28N hydrofluoric acid, and 0.25 mL hydrochloric acid) in Teflon bombs with a programmable microwave digestion unit (ETHOS, Milestone). Digestates were diluted to 15 mL with high-purity water (18 MΩ cm^{-1}) and stored in pre-cleaned polyethylene bottles for 48 h. The digestates were analyzed for 50 elements by SF-ICP-MS (Thermo-Finnigan 2). Additional elemental analysis by energy dispersive X-ray spectroscopy (EDS) was performed on single toner and $PM_{0.1}$ particles by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), respectively (Supplementary information).

2.4. Organic and elemental carbon

$PM_{0.1}$ for OC/EC were analyzed using a modified NIOSH 5040 method, which uses a a Sunset Laboratory Inc., laboratory-based thermal-optical analyzer (Forest Grove, OR) as described by Bello et al. [16].

2.5. FT-IR

Qualitative FTIR analysis was performed on several toners (yellow, magenta, cyan and black) from two manufacturers covering three different formulations, and three $PM_{0.1}$ samples collected at three separate copy centers. The FTIR analysis was performed on a Bruker Tensor 27 using transmission IR (KBr pellet method). Toner pellets were made by mixing approximately 10 mg of toner into approximately 300 mg of KBr, placing this mixture into a pellet die and applying approximately 20,000 pounds per square inch (psi) pressure under a vacuum for 60 s. Similarly, micro pellets were made by mixing approximately 0.1 mg $PM_{0.1}$ into approximately 20 mg of KBr and applying approximately 20,000 pounds psi under a vacuum for approximately 60 s (5 mm diameter pellet). Spectra were collected at a resolution of 4 cm^{-1} averaged over 32 scans.

2.6. Lung deposition model

Multiple Particle Path Dosimetry Modeling Software (MPPD v.2.1) was used to estimate total particle deposition in the lung airway from the head to the alveolar region. Using real-time particle measurement data, the count median diameter (CMD) and GSD was calculated as described in Hinds (1999), and used in the input parameters for the model. Additional software specific parameters input were: Functional Residual Capacity, 3300 mL; Head Volume, 50 mL; Breathing Route, Nasal; Title Volume, 625 mL; Breathing Frequency, 12 breaths/min; Inspiratory Fraction, 0.5 (unitless); Pause Fraction, 0.0 (unitless).

2.7. Data analysis

All real-time data were downloaded to a laptop PC, and transferred to SAS v. 9.3 (SAS Institute, Cary, NC) and SPSS 17 for