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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

* 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

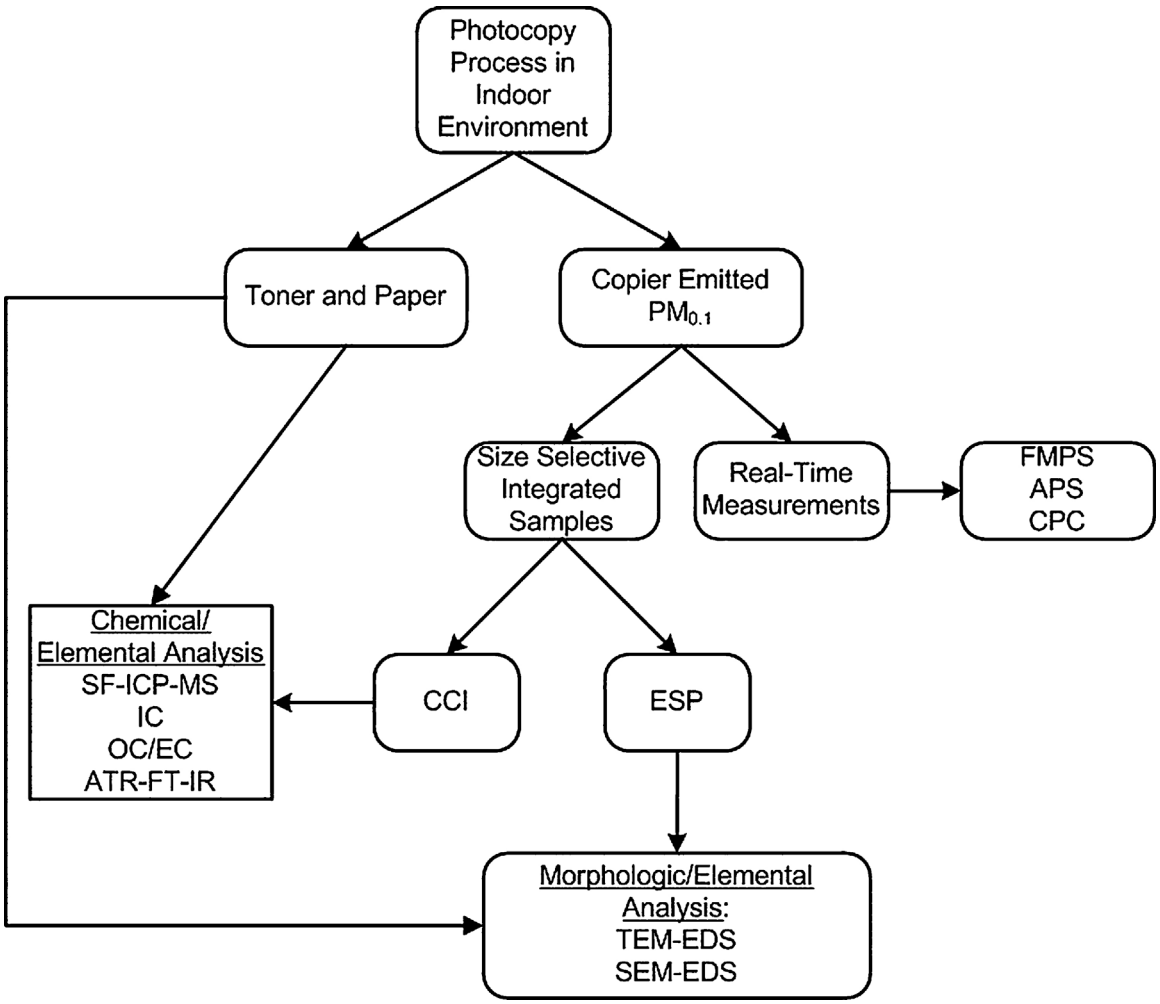

Fig. 1. General schematic of study design. FMPS, Fast Mobility Particle Sizer; APS, Aerodynamic Particle Sizer; CPC, Condensation Particle Counter; SF-ICP-MS, Sector Field Inducitvely Coupled Plasma Mass Spectroscopy; IC, Ion Chromatography; OC/EC, Organic carbon/elemental carbon; ATR-FTIR, Attenuated Total Reflectance Fourier Transform Infra-Red Spectroscopy; CCI, Compact Cascade Impactor; ESP, Electro-Static Precipitator; TEM-EDS, Transmission Electron Microscopy-Energy Dispersive X-Ray Spectroscopy; SEM-EDS, Scanning Electron Microscopy-Energy Dispersive X-Ray Spectroscopy.

Windows (SPSS, Chicago, IL) for analysis. After examining histograms and probability plots, real-time data were found to be lognormal and all statistical analyses were conducted on log-transformed data. Further, all real-time data were evaluated for autocorrelation bias using SAS PROC AUTOREG (Supplementary information). We report summary statistics, uncorrected for autocorrelation; geometric mean (GM), geometric standard deviation (GSD) and maximum (max) for real-time particle measurements.

3. Results

3.1. Characteristics of copy centers

The eight commercial photocopy centers varied with respect to their design features and copy load. In total, we observed 28 photocopiers and 37 full-time employees across the eight copy centers (Table 1). Six of eight copy centers rely on mechanical or a combination of mechanical and natural ventilation and two lacked mechanical ventilation altogether. Most copy centers visited operate 2–3 high-speed photocopiers, with at least one color model and one monochrome model and one copy center operating nine high-speed photocopiers. Daily average workloads were found to vary considerably with customer demand, and ranged from a high average of 39,035 copies per day and a low of 1994 copies per day. The highest copy load for a single day was approximately 113,000 copies. The daily average for all centers combined was 9630 copies per day, with a maximum daily average of 22,363 copies per day and a minimum daily average of 3244 copies per day.

3.2. Real-time particle measurements

Consistent with our earlier observations [16], throughout this study we did not observe a significant number of particles between 0.5 nm and 20 μm (data not shown). Therefore, we report only data as measured by FMPS. Weekly GM particle number concentration ranged between 3700 and 33,700 particles/cm^3 (Table 2). With two exceptions, the measured particle load GM during the workday was generally found to be greater than background particle loads measured overnight and off-business hours, which was found to range from 880 to 15,900 particles/cm^3 (data not shown). Process to background ratio (GM_p/GM_{bkgd}) at copy center #3 may have been influenced by settled dust in the ventilation system and subsequent stirring and emission into the indoor environment each morning when the system timer engaged about 1 h before the center opened. This is supported by observations made during working hours when at least 60 min separated print tasks where the indoor measured particle concentration was 3000 particles/cm^3 or less. Copy center #5 is located adjacent to a heavily traveled road

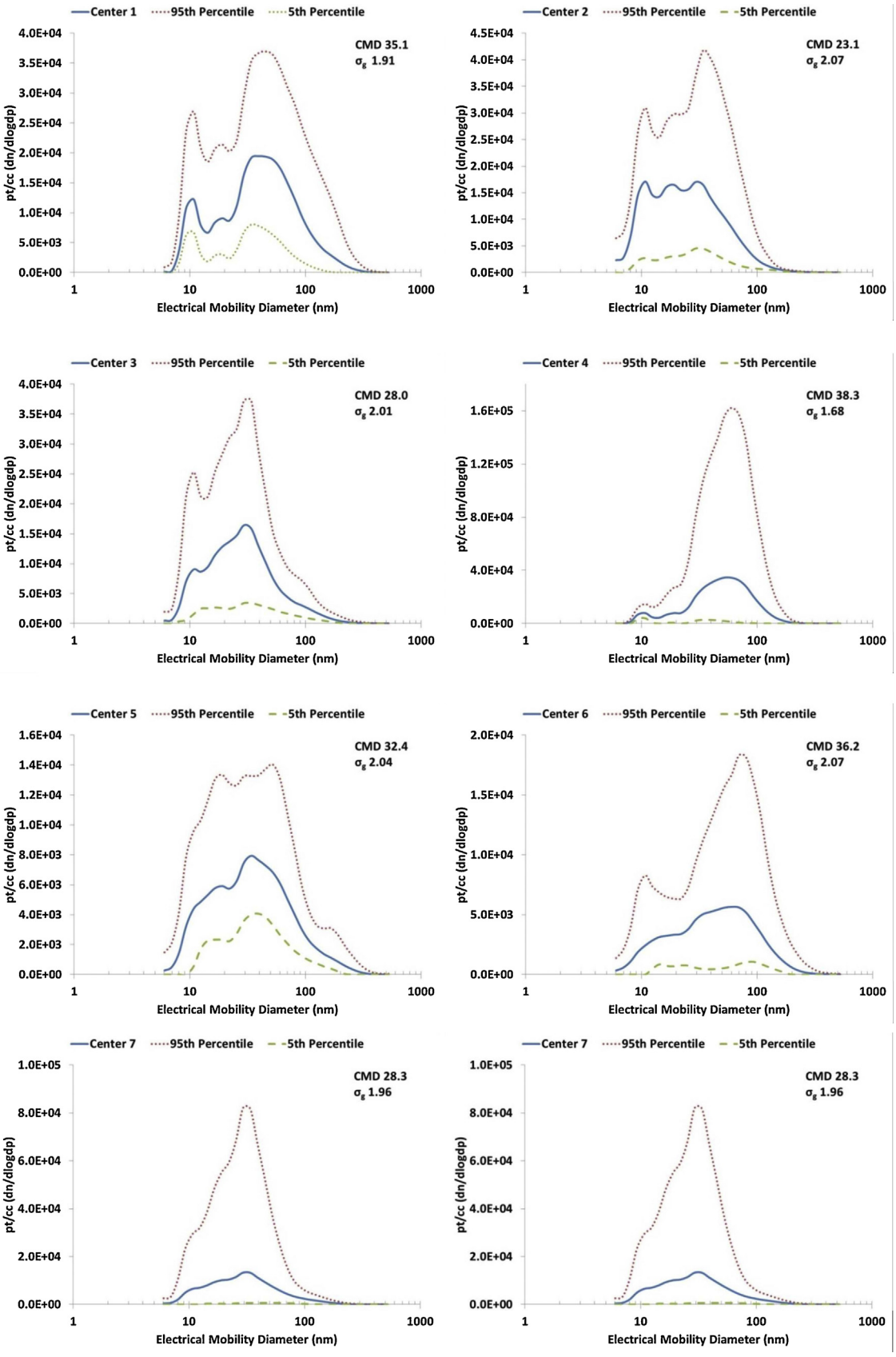

Fig. 2. Average weekly size distributions (5th and 95th%) of emissions measured at commercial photocopy shops in the Greater Boston Area. CMD, count median diameter; σ_g, geometric standard deviation.

Table 1
Physical characteristics, manufacturer and number of photocopiers, full-time employees (FTE) and copy loads of each high-volume photocopy center studied. Each copy center was given a numeric identification 1 through 8and each copier manufacturer was assigned an alpha identification A through D.

ID	Manufacturer	Number of copiers	FTE	m^2	Volume (m^3)	Ventilation	Building level	Windows	Average copies/day	Range of daily copies	
1	A	2	3	94	286	Natural	2nd floor	4	14,373	5,670	21,674
2	A	2	2	36	109	Mechanical	Basement	3	4498	1,053	12,060
3	B	3	3	92	280	Mechanical	Basement	0	5258	2,094	8,313
4	A	3	3	105	319	Mechanical	Ground	11	3461	1,969	4,747
5	A, D	1, 2	2	158	722	Mechanical	Ground	4	4546	2,086	7,435
6	A, D	2, 1	3	59	181	Mechanical	Ground	2	3874	260	8,908
7	A, D	1, 2	6	161	528	Mechanical	Ground	3	1194	1,081	3,022
8	C	9	15	74	317	Natural	Ground	0	39,035	11,625	112,741

Table 2
Summary statistics of the total number concentration of airborne nanoparticles at eight high volume commercial photocopy centers in the Greater Boston Area. GM_p/GM_{bkgd}, geometric mean of process measurements/geometric mean of background measurements.

Center ID	Weekly GM(particles/cm^3)	GSD	Max (particles/cm^3)	Range of daily GMs (cm^3)	$PM_{0.1}$ mass conc. ($\mu g/m^3$)	GM_p/GM_{bkgd}
1	13,633	1.7	46,000	8,859–23,612	4.5	12.1
2	12,966	1.7	62,600	4,274–15,264	2.2	1.7
3	9,486	1.8	283,000	7,550–23,658	1.9	0.6
4	11,435	2.9	143,000	4,895–30,795	2.2	3.5
5	6,278	1.4	52,500	5,722–6,501	3.6	0.8
6	3,670	2.2	1,400,000	2,192–11,533	4.6	1.1
7	4,376	2.8	280,000	3,182–6,462	1.8	4.9
8	33,743	3.3	836,000	23,649–51,829	6.4	6.2

and approximately 15 m from a major intersection. The possibility of particle intrusion from this intersection, combined with a lower than normal workload for the week may have contributed to the process/background ratio <1 for this week. Weekly PM size distributions from each copy center show, in most cases, subtle differences with count median diameters (CMDs) ranging from 28 to 38 nm and corresponding GSDs of 1.75–2.07 (Fig. 2). Day to day exposures varied with each copy center, driven primarily by variable workloads and design features of the center (natural or mechanical ventilation, size, *etc.*). For example, daily GM particle concentration in copy center #1 ranged from 8859 to 23,611 particles/cm^3 with corresponding GSDs of 1.27–1.41. Similarly, daily GM particle concentration for copy center #8 ranged from 23,650 to 51,829 particles/cm^3, with GSD's ranging from 3.09 to 4.52.

Weekly average $PM_{0.1}$ mass concentration at each copy center ranged from 1.8 to 6.4 $\mu g/m^3$ (Table 2). We also measured, for comparison purposes, the $PM_{2.5}$ mass concentration, which ranged from 0.8 to 10.0 $\mu g/m^3$ (data not shown).

3.3. Lung deposition model

The estimated total particle deposition in the lungs was based on the Multiple Particle Path Dosimetry Model software (MPPD v.2.1), and varied from 28% to approximately 40%, with increasing gradient of deposition from the head to the alveolar region (Table S1). This information is important and relevant for equivalent dose calculations for *in-vitro* and *in-vivo* human nanotoxicology [12,17–20].

3.4. Chemical analysis

3.4.1. Toner

3.4.1.1. Organic and elemental carbon. OC content in toner from Manufacturer A ranged from 58 to 91%, toners from Manufacturer B ranged from 54 to 89%, toners from Manufacturer C ranged from 52 to 80% and for black toner from Manufacturer D it was approximately 41%. EC content in toners from Manufacturer A ranged from 0.3 to 1.4%, 0.13 to 0.17% in Manufacturer B, 0.2 to 2.0% in Manufacturer Cand 0.7% in black toner from Manufacturer D (Table S2). OC/EC percentages for each toner are illustrated in supplemental Fig. S1 through S4.

3.4.1.2. Elemental analysis. SF-ICP-MS analysis on toner particles are summarized in Supplementary Table S3 and illustrated in Supplementary Figs. S1–S4. There are some notable similarities and differences between manufacturers. Iron (Fe) is the most abundant element consistently found in all toners that ranged from 0.9 to 4.2% across the toner manufacturers, followed by titanium (Ti) that ranged from 0.05 to 0.09%. Other elements commonly found in all toners were sulfur (S) (0.01–0.07%), manganese (Mn) (0.01–0.12%), zinc (Zn) (0.02–0.04%) and copper (Cu) (01–0.09 %). Other elements, such as chromium (Cr), nickel (Ni), niobium (Nb) and cerium (Ce) were all found in trace amounts (<0.001%).

There were elemental (*e.g.*, copper (Cu), molybdenum (Mo) and phosphorous (P)) differences found across the color formulations. Cyan formulations contained 3330 and 5150 $\mu g/g$ copper in Manufacturer's C and A, respectively, compared to yellow formulations with 1.15 and 5.48 $\mu g/g$ Cu. In magenta toners, the concentration of P was found to be 8.7 $\mu g/g$, 40.1 $\mu g/g$ and 143 $\mu g/g$ in Manufacturers C, A and B, respectively. The P concentration in all formulations analyzed were <3.0 $\mu g/g$, with the exception of yellow, black and cyan formulations from Manufacturer A. Results reported here are in general agreement with manufacturer's SDS's, but go beyond the sparse details of SDS's to confirm the complex elemental makeup of toner formulations. These data represent the first independent elemental analysis reported on multiple color toner formulations stretching across major manufacturers, and show differences in elemental composition from manufacturer to manufacturer, and from color to color.

3.4.2. Paper

3.4.2.1. Elemental analysis. The elemental composition of the most commonly used paper (20 pound, 92 bright, various manufacturers) as determined by SF-ICP-MS for all analyzed papers (Supplementary information, Table S4) was generally similar between manufacturers, with calcium (Ca), magnesium (Mg), aluminum (Al) and S representing the most abundant elements.

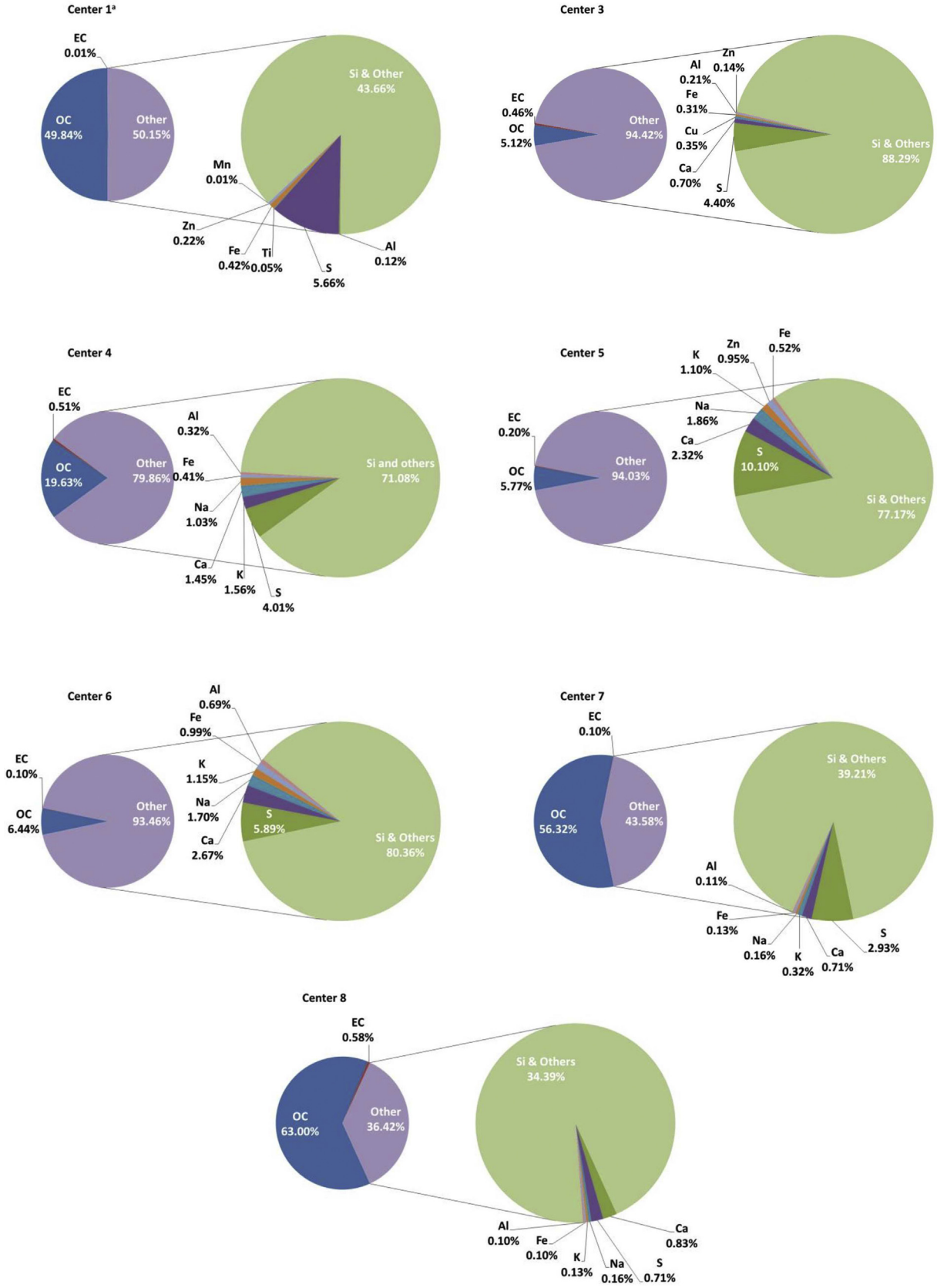

Fig. 3. Elemental composition of $PM_{0.1}$ collected at high-volume commercial copy centers in the Greater Boston Area. Center one, seven and eight primarily operated black and white copiers and copy centers four, five and six primarily operated color copiers during the days(s) of the study. [a]Reproduced with permission from Bello et al. [16].

3.4.3. $PM_{0.1}$

It is worth noting the PM $_{0.1}$ fraction for SF-ICP-MS analysis of center #2 was unfortunately lost during chemical analysis. As a result, it is not possible to calculate mass balance for center #2. However, it is reasonable to assume that the chemistry of aerosols in center #2 are similar (if not identical) to those of center #1 based on the notion that the photocopier models and toner formulations are identical for both centers.

3.4.3.1. Organic and elemental carbon. The GM OC concentration in $PM_{0.1}$ calculated throughout the centers was 2.72 μg/m^3, with a corresponding GSD of 1.12. Similarly, the EC GM calculated across the centers was 0.03 μg/m^3, with a resulting GSD of 3.74. OC content of $PM_{0.1}$ ranged from ~6% (centers 5 and 6) to 63% (center 8) (Fig. 3). Corresponding EC content ranged from 0.01% (center 1) to 0.6% (center 8) and most commonly being around 0.1%.

3.4.3.2. Elemental analysis. SF-ICP-MS results of $PM_{0.1}$ are summarized in Table 3. Much like results of toner analysis, considerable variation in elemental concentration and percent water-soluble result can be seen from center to center. S was the most abundant element in $PM_{0.1}$, followed by Ca, sodium (Na), Fe, potassium (K) and Zn. Iron was found in $PM_{0.1}$ ranging from 1030 to 9950 μg/g and corresponding percent water-soluble fraction ranged from 3.4 to 9.3%; copper was found ranging from 370 to 8930 μg/g with a corresponding water-soluble fraction ranging from 2.5 to 45%. Similarly, Mn was found ranging from 6.5 to 604 μg/g with a corresponding percent water-soluble ranging from 1.3 to 34.6%. Ni was found ranging from 1.8 to 390 μg/g, with its percent water-soluble fraction ranging from 7.8 to 100%. Inorganic components of collected $PM_{0.1}$ varied considerably from center to center, from 36% in center 8 to 94% in center 5 (Fig. 3). Silicon (Si) was not quantified during this analysis. However, its presence in $PM_{0.1}$ was confirmed in our earlier work using targeted reanalysis, single particle analysisand other imaging. The inorganic anions and cations (chloride (Cl^-), nitrate (NO_3^-), sulfate (SO_4^-), ammonium (NH_4^-) and potassium (K^+) explained only a small fraction of this mass balance in center #1, which is consistent with recent findings from Pirela et al. on emissions from printers inside a chamber [3]. These anions and cations explain only 10.7% of the $PM_{0.1}$ mass in center #1. SO_4^- accounted for 6.9% and NH_4^- accounted for 2.9% while all others account for <0.7% collectively (Supplementary information, Table S5). While the exact composition of this remaining fraction is unknown, the oxygen in oxides and other anions are likely to be a major constituent of the mass balance equation.

3.4.4. Single particle analysis

A common feature shared by all toners in the study is the visible presence of engineered nanoparticles (ENP) on their surface. Depending on the toner, one to several types of ENM were clearly visible (Supplementary information, Figure S5). In multiple formulations, we observed nanoparticles shedding off (detaching) from the toner surface, as depicted in Supplementary Fig. S6. EDS on toner particles yielded silica (Si), Ti, Cu, Cr, Mg and Fe.

Single particle analysis of $PM_{0.1}$ revealed Fe, Mg, Si, Cr, Ni, Cu, tin (Sn) and Ti. All elements detected by single particle EDS analysis of $PM_{0.1}$ were also present in corresponding dry toner formulations, and these findings are in agreement with our previous work in one copy center and the chamber study [3,16], establishing beyond any doubt that photocopying emits inorganic nanoparticles, which contain several transition metal oxides.

3.4.5. FT-IR

FT-IR spectra of three submicron fractions (250–500 nm from stage 7 of the Nano-ID) and single particle analysis on the nanoscale fraction share three prominent absorbance frequencies consistent with toners from which the particles originate (Fig. S7). In the fingerprint region (1500–500 cm^{-1}), spectra from Manufacturer A reveal similarities at approximately 1400 cm^{-1} and 1100 cm^{-1}, which suggests oxygenated functional groups, also present in the parent toner (Supplementary information, Fig. S8, signals consistent with the vibrational frequency of alcohols, carbonyls, aromatic rings, esters, ethers and alkanes). Aerosol from center #3, which exclusively used toners from Manufacturer C shows similar spectra, with the addition of a pronounced absorbance at approximately 800 cm^{-1}, which suggests the presence of an aromatic ring and is not present in FT-IR spectra obtained from aerosols where the printing process relied exclusively on Manufacturer A. This supports our hypothesis that emissions from different formulations will result in different chemical and elemental composition of $PM_{0.1}$.

4. Discussion

In this work we performed extensive physicochemical characterization of $PM_{0.1}$ exposures in eight photocopy centers and the raw materials used in them, with particular focus on toners as nano-enabled products, presence of ENM in $PM_{0.1}$, and variation in chemical composition of raw materials (toners-black or colored, and paper).

4.1. Toners are nano-enabled products

The number of consumer products that now claim to incorporate ENMs is rapidly growing. In 2008, there were a few hundred products, two years later there were over 1000 products and now there are over 1600 in 2014 [21]. It is not surprising that ENM have made their way into dry toner for photocopy and laser printers. While references to individual ENM such as silica and iron oxide in toners have been made in the past [22], the extent of ENM incorporation in toners was documented recently [3,16]. Eight different types of ENM were found in toners used in printers, including amorphous silica, titania, alumina, ceria, iron(III) oxide, magnesium(IV) oxide, zinc(II) oxide and carbon black. Our findings here agree with observations of Pirela et al. in that we find widespread incorporation of these types of ENM in toners across various manufacturers. Moreover, Pirela found other transition metal oxides, including copper oxide, manganese oxide, zinc oxide and titanium dioxide, which is consistent with our findings. The overall conclusion of this analysis is that industrial toner formulations have shifted to nano-enabled toners and there seems to be no systematic differences between toners used in consumer laser printers and commercial photocopiers. Consumer printing and commercial photocopying rely on similar processes to produce an image, seem to use similar (if not identical) raw materials and generate similar $PM_{0.1}$ chemistries. Therefore, similarities between the two technologies far outweigh any differences and it is appropriate to refer to them as the same technology: hard copy devices.

The exact composition of toners is proprietary and information provided on their Safety Data Sheets (SDS) is limited. The common reported components of toner are resin, wax, iron(III) oxide, carbon black and pigments. The SDS's do not report that several of these additives are engineered nanomaterials, in part because there are no regulatory requirements to distinguish ENM from their macro counterparts on SDS's [22–24]. The presence of several toxic transition metals in raw materials, at significant concentrations, is particularly concerning. This includes oxides of Mn, Ni, Cr and Ti. We found that certain developers (*e.g.*, manufacturer C) contain 10–30% manganese oxide and several toners from A and C contained up to 9100 μg/g Mn. Metallic Mn is a well-established neurotoxin [25,26]. While direct worker/operator contact with toners is arguably limited, we have witnessed cases of explosive

Table 3
Sector field inductively coupled plasma mass spectrometry results of $PM_{0.1}$ samples collected from each participating copy center. Elemental analysis included 50 elements, of which the most abundant are tabulated.

ID		Fe	Zn	Cu	Mn	Sn	Cr	Al	Mo	Ca	Mg	Ti	Ni	P	Sr	S	Ba	V	Co
1	Total (μg/g)	4390	2310	287	99.4	146	39.7	1370	38.3	2610	678	570	101	559	15.2	59100	246	154	4.92
	SD	101	56	7.91	2.73	1.24	1.22	32.2	0.771	117	16.5	11.3	2.61	21.4	0.384	1290	2.25	2.9	0.0781
	% WS	9.32	97.9	44.8	49.1	2.91	20.5	8.1	57	92.8	58.3	0.137	50.6	98.9	67.4	102	45.7	71.8	48.8
2[a]	Identical chemistry with center 1 (samples not analyzed)																		
3	Total (μg/g)	8080	3760	9220	244	253	85.8	5590	41.5	18300	1770	475	390	892	54.3	115000	185	471	12.3
	SD	34.1	13.2	49	1.23	1.31	1.06	43.1	0.439	142	24.6	3.33	2.93	10.8	0.662	425	0.0907	2.62	0.114
	% WS	1.55	15.6	26.3	5.04	2.14	2.77	0.364	7.08	12.7	7.19	0.197	7.77	46.3	9.93	9.94	6.59	5.02	5.69
4	Total (μg/g)	4100	1810	778	132	243	110	3240	27	14500	1960	548	88.7	1200	31.6	40100	162	24.5	2.46
	SD	18.4	12.7	2.64	0.738	1.7	0.872	21.6	0.365	92.7	9.39	6.34	1.13	10.1	0.452	289	10.6	0.297	0.0475
	% WS	3.4	64.6	7.76	56.4	5.84	4.6	17.3	28	73.7	44.4	16.5	75.7	97.7	116	62.6	30.1	22.6	8.17
5	Total (μg/g)	4870	8930	435	104	107	103	2120	144	21800	1580	777	74.4	4290	243	94700	168	33.1	5.4
	SD	2.35	7.84	0.339	0.234	0.0811	0.0438	2.98	0.157	32.6	9.68	0.393	2.74	4.94	0.192	75.5	2.2	0.0566	0.032
	% WS	6.73	55.8	24.5	59	35.7	10.2	26.3	24.2	89.4	158	0.47	79.1	57.3	22.4	53.7	18.8	27	37.8
6	Total (μg/g)	9950	1840	604	316	172	1190	6940	43.4	26700	5620	1580	272	945	543	58900	178	38.1	7.39
	SD	27.8	7.79	1.78	0.889	1.27	2.72	25.2	0.237	97.2	18.8	7.7	1.72	5.93	1.93	201	6.72	0.221	0.067
	% WS	2.99	56.1	13.5	33.1	11.3	0.967	12.6	28.4	50.6	7.52	1.23	245	145	11.7	57.8	18.2	16.5	25.4
7	Total (μg/g)	1300	370	177	6.49	134	540	1120	8.92	7120	726	358	103	189	11.9	29300	29.7	59.7	1.67
	SD	8.1	2.24	0.863	0.389	1.26	1.11	10.8	0.0981	53	3.42	1.92	0.618	2.09	0.435	99.3	0.786	0.24	0.015
	% WS	6.78	10.9	2.45	127	2.07	0.218	9.96	44	17	66.4	2.68	100	87.2	57.4	8.4	138	3.62	61
8	Total (μg/g)	1030	790	575	23.3	78.8	550	962	11.1	8330	263	121	86	801	7.21	7120	28.4	27.8	70
	SD	10.7	9.63	3.28	0.438	1.46	3.32	14.2	0.259	98.1	4.87	3.23	1.13	9.46	0.427	71.4	3.13	0.298	0.511
	% WS	7.25	63	6.21	120	43.7	20.1	32.3	47.6	51.6	52.5	1.43	83.4	120	181	136	43.1	24	68.5

cartridge failure that coated copy center surfaces and operators with toner dust. Therefore, high acute human exposure scenarios do occur and toner waste is being generated.

4.2. Photocopier emissions are chemically complex

Emissions from photocopiers are chemically complex and variable, and consistently contained Fe, Zn, Al, Mn, Sn, Cu, Ni and Ti. While their total content was not large, their presence in a mixture with carbonyl-rich organics is of particular interest. The organic carbon results in $PM_{0.1}$ ranged from 5.8% to approximately 63%, although elemental carbon content was very low (0.01–0.5%). Such mixtures may engage in synergistic interactions that eventually lead to enhanced reactive oxygen species generation and toxicity [27,28]. The majority of elements of toxicological interest had water-solubility in the 0.1–10% range (Supplementary information, Table S2). Water-solubility is important as some metal ions (*e.g.*, Zn^{2+}) impart toxicity via ion leaching and may play a role in the initiation of oxidative DNA damage and reactive oxygen species (ROS) formation [29,30]. Our findings are in good agreement with the chamber study of Pirela et al., and others [31–33].

The exact chemical composition of the organic fraction is still poorly understood. In our earlier study [16], we analyzed $PM_{0.1}$ and toners for a panel of polycyclic aromatic hydrocarbons (PAHs) and over 100 SVOCs. We found no significant amounts of PAHs. Waxes, long chain hydrocarbons and hopanes accounted for only a small percentage of the total $PM_{0.1}$ mass (<2%). For this reason, we did not analyze routinely for these organics in the current study. Pirela et al. [2,3] found cations and anions accounted for only a small percentage of the total printer emitted particles (PEPs) mass (<2%). We analyzed $PM_{0.1}$ from copy center #1 (Supplementary information, Table S5) and found similar results. Overall, the exact composition of the organic fraction remains the least understood component of photocopier emissions and for this reason further structural elucidation is warranted. Similarly, we think it is important to further investigate the role of interactions between this organic fraction and inorganic metal/metal oxide constituents of photocopier emissions in their toxicological properties.

4.3. Rethinking the photocopying environment

High exposure levels to nanoparticles (daily GM up to 52,000 particles/cm^3 and peak maxima >500,000 and up to 1.4 million particles/cm^3) were measured in six of eight visited copy centers. This should not come as a surprise perhaps, since our observations suggest photocopy centers often represent retrofitted spaces (such as small spaces with limited or no ventilation and often cramped with several photocopiers) with no dedicated exposure controls.

These airborne exposures result in significant deposition of nanoparticles in the respiratory tract. Our deposition models estimate total particle deposition in the lungs range from 28% to 40%, of which ~5–7% deposit in the head airways, 7–13% in the thoracic regionand 14–20% the alveolar space. The fate and biokinetics of copier-emitted nanoparticles in human lungs are poorly understood; however, it is well known that nanoparticles in general translocate from the lungs to extra-pulmonary tissues, including the liver, spleen, brain, and heart, raising questions over long-term health effects of such exposures.

Taken together, the generally elevated exposure data, complex chemical composition, chronic nature of exposures and more recent toxicological evidence from *in-vivo* and *in-vitro* work documenting effects at comparable exposure levels, warrant consideration of exposure reduction strategies. In addition to considering redesigning commercial hard copy reproduction centers, more consideration should be given to current practices of operating such devices with no engineering controls in crowded public spaces, such as elementary and high schools, public libraries, hospitals and other environments where sensitive individuals may be exposed. This technology represents an indoor air quality issue and needs to be addressed at various levels, including developing/deploying exposure control technologies, adopting alternative printing/photocopying technologies, developing guidance on occupancy, ventilation, or others.

4.4. Study limitations

Cross-contamination from outside sources is a constant concern with real-time particle measurements and relatively uncontrolled field environments. Real-time particle measuring instruments are unable to distinguish between particles of interest and cross-contamination from other particle sources such as particle intrusion from outdoor sources (*i.e.*, automobile traffic and construction dust), which may significantly bias particle measurements toward ambient outdoor conditions. Cross-contamination from outside sources may also directly impact gravimetric and chemical analysis. We have mitigated cross-contamination issues by carefully monitoring particle concentrations during operational hours, collection of background particle measurements during non-business hours, most often during overnight periods, and collecting extensive auxiliary information about workload, activitiesand layout of these centers. The striking similarity in the overall findings between the chamber study on printer emitted particles (PEPs) and this field study on $PM_{0.1}$ is strongly suggestive that background may have influenced but not significantly distorted the results. Our data suggests contribution to the $PM_{0.1}$ from both paper and toner, and we recognize other sources may have contributed to the result observed in the $PM_{0.1}$ analysis.

5. Conclusion

We show here that high nanoparticle exposures are common in many commercial photocopy centers. As is often the case, these centers lack dedicated engineering controls for photocopier emission and have limited mechanical ventilation. Moreover, they often occupy poorly designed (or retrofitted) spaces, which are overcrowded with copier and printing equipment. We show toners universally incorporate several types of ENMs, including amorphous Si, titanium dioxide, iron(III) oxide and others, as well as considerable amounts of Mn, Fe, Cu and Zn, small amounts of which (2–8% in all) become airborne. The elemental composition of $PM_{0.1}$ is complex and, more importantly, variable across different manufacturers as well as monochrome and colored photocopiers. The data suggests that both toner and paper may be contributing to the $PM_{0.1}$ chemistry. Emissions from hardcopy devices present an indoor air problem that needs to be addressed at various levels, including developing/deploying exposure controls and promoting alternative cleaner photocopy technologies. Further characterization of the exact chemistry of the organic $PM_{0.1}$ fraction and reconsideration of design characteristics of such working environments is recommended. An investigation on long-term health effects of such exposures in photocopier operators is also warranted.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jhazmat.2015.06.021

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