Short communication

Assessment of polyaromatic hydrocarbon emissions from laser printers

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ABSTRACT

The potential for polyaromatic hydrocarbon (PAH) emissions from laser printers has been examined using a simulated printing process and a detailed chemical analysis of printer toner. We have analysed the PAH content of both carbon black (a toner constituent) and toner before and after heating and have found measurable evaporation and subsequent condensation of PAHs. Based on our analysis we have estimated a maximum possible PAH emission rate of 82.1 $\mu g\ min^{-1}$ of printing for a 10% page coverage. Our VOC emission results agree well with those of other authors. The concentrations of individual PAHs in the emissions were relatively low, however non-trivial, especially long term.

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1. Introduction

Laser printing devices are common in workplaces, libraries and in homes. There has recently been concern over the health effects of such printers; specifically the generation of ultrafine particulate matter during the printing process. This has in turn prompted a resurgence in inkjet technology. A number of studies have measured the particle concentrations produced by laser printers (He et al., 2007; Schripp et al., 2008; Wensing et al., 2008; Morawska et al., 2009; Koivisto et al., 2010; Wang et al., 2011; Tang et al., 2012b), while others have assessed the risk of such exposures (Hänninen et al., 2010). A comprehensive study by He et al. (2007) found that a large proportion of commercial laser printers generated ultrafine particles and that around half of those that did, did so at high concentrations.

This potentially represents a health risk as there is growing evidence to suggest that the surface area of carbon nanoparticles (like those generated by heating toner in the printing process) is the most toxicologically relevant factor (Stoeger et al., 2006).

Though at this stage there is little epidemiological evidence linking printer emissions to health problems (Hänninen et al., 2010).

However, work with human lung cell cultures has found that both printer toner and printer emissions have a genotoxic effect (Gminski et al., 2011; Tang et al., 2012a; Könzcöl et al., 2013). The exact component(s) of printer toner which cause this effect are, however unclear as there are many volatile organic compounds (VOCs) and polyaromatic hydrocarbons (PAHs) present in printer toner. The presence of such compounds is an artifact of the production of carbon black (a key component in toner) via combustion in substoichiometric air. Additionally, the particles emitted during the printing process contain inorganics, such as iron, silicon and bromine (Barthel et al., 2011).

Depending on the temperature reached during the printing process, these VOCs and PAHs may be released. He et al. (2010) studied the effect of fuser roller temperature in laser printers and found that it was the most significant factor in terms of the number of particles generated.

Given that laser printers are almost exclusively used indoors, there will be a risk of exposure to printer emissions and as such consideration must be given to printer emissions when monitoring indoor air quality. Kagi et al. (2007) considered the implications of both chemical and ultrafine particles for indoor air quality. While some studies have measured and identified VOC emissions from office equipment (such as printers and photocopiers) (Lee et al.,

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2001; Lee and Hsu, 2007), as well as considering health impacts (Lee et al., 2006; Wolkoff and Nielsen, 2001), to the best of our knowledge no study has identified the compounds present in emissions from laser printers.

The presence and release of PAHs in and from toner is important as a large number of PAHs are classified as carcinogens or probable carcinogens (Straif et al., 2005). This work examines the release of PAHs from toners using a simulated printing process, to identify compounds that may be released during the printing process, as well as the PAHs that are present in toner.

2. Methods

Our "simulate" printing (or toner heating) methods emulate the evaporation–condensation processes which are likely to occur on the fuser-roller of a laser printer. We neglect the additional forces (mechanical and electrostatic) which exist in a printer. We also do not have a sorbent substance (paper) present. The heating rates in our system were necessarily slower than in a real printer, and the toner mass higher per unit area. However, we believe our system accurately replicates the evaporation of PAHs and SVOCs from toner, if not the fate once released. Our two methods (TGA and large scale) produced almost identical mass losses of toner, despite different heating rates, which supports this conclusion. Most studies of printer emissions (Morawska et al., 2009; He et al., 2007; Wang et al., 2011) have found a spike in particulate emissions at the commencement of the printing process, which rapidly diminishes after approximately 30 s. This suggests that SVOCs and PAHs may possibly deposit on the fuser roller (or other printer components), and be re-released at the start of the printing process.

Given that the release of ultrafine particles during a single printing operation is relatively low, and that PAHs only make up a small fraction of the toner constituents, identifying individual components in the emissions would be difficult. Therefore, this work has utilised a simulated printing process whereby a sample (either toner (Black MP C5503, RICOH, USA), or carbon black (Printex U, Degussa, Germany) (Bredin et al., 2011)) is heated rapidly, using a Thermogravimetric Analyser (TGA, NETZSCH Tarus TG209 F3). This allows any mass loss from the toner due to heating to be measured.

A series of measurements were made using the TGA, with samples (10–30 mg) of either toner or carbon black, with one of three different temperature profiles. All measurements were preceded by a 45 min purge of the sample chamber with either air or nitrogen at 38°. The first set of measurements was conducted by heating at 50 °C min^{-1} to a temperature of 250 °C. The TGA was then held isothermal for 5 min before the temperature was returned to 38 °C as quickly as possible. The purpose of this rapid cooling is to give as close an approximation to the printing process as possible.

The second set of measurements the TGA was held isothermal at 250 °C for 1 h, before being allowed to return to the ambient temperature.

The final set of measurements considered mass loss at different maximum temperatures. In these measurements, the toner was heated to temperatures of 150, 200, 250 and 300 °C and then allowed to return to ambient temperature as quickly as possible.

In order to allow the results of the simulated printing process to be related to actual printing, we evaluated the toner consumption for a printer, by printing 100 identical pages and determining the mass loss of toner from the cartridge. For this work we used a FujiXerox DocuCentre IV C 3375, multifunction printer. These measured values, combined with measured emissions in other work were then used to calculate emission rates.

Additional experiments were also conducted using larger size toner samples (1 g) in a glass vessel. This set up involved drawing emissions from heated toner through a filter. The set-up is shown in Fig. 1.

In order to maintain an evenly distributed and stable temperature a sand and avocado oil bath was used to heat the glass vessel containing the sample (Fig. 1). The emissions from the heated toner were passed through a glass fibre filter. The oil bath was pre-heated to 230–250 °C, then the glass vessel place inside to simulate rapid heat-up during printing. After 10 min the sample vessel was removed from the oil bath and the pump left running for a further five minutes, so that any additional emissions could be drawn through the filter. The filters were weighed before and after the tests so that the collected mass of emissions could be obtained.

Each of the filters used was initially heated to either 550 °C or 250 °C and then cooled in a dessicator before use. At the conclusion of sample collection the filters were removed and returned to the dessicator before being weighed. After weighing the filter was heated to 100 °C before being returned to the dessicator and re-weighed. This process was repeated for temperatures of 150 °C and 250 °C.

In order to approximate the amount of carbon black in the toner, an elemental analysis of both toner and Printex U was performed using a Thermo Finnigan EA 1112 Series Flash Elemental Analyser.

2.1. PAH analysis

Samples of carbon black and toner were analysed for PAH content. Additional samples of carbon black were heated to 250 °C and 300 °C and then analysed to measure any loss of PAHs through evaporation, as may occur during the printing process.

Identification of the PAHs was carried out by extraction using organic solvent, followed by pre-concentration and analysis by gas chromatography–mass spectrometry (GC/MS). Control and laboratory blank samples were analysed concurrently with the toner samples.

Samples were spiked with a known amount of surrogate standard (ChemService Product CSS8250-1JM) and placed in the ASE for further extraction with 4:1 mixture of hexane and ethylacetate. The sample extracts were combined and concentrated down, a known amount of internal standard (ChemService Product PP-HC8JM) was added prior to the sample being made up to volume with equal volumes of ethylacetate and hexane. Sub-samples of the extract were analysed by GC/MS.

For the duration of this study an Agilent 6890 Gas Chromatograph (GC) coupled to a 5973 Mass Spectrometer (MS) operating in the selected ion monitoring (SIM) mode was used to carry out the analyses. The GC was fitted with a HP-5MS capillary column
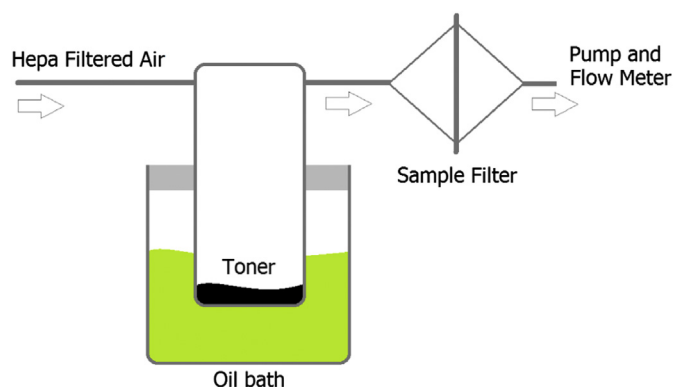

Fig. 1. A schematic of the experimental set up for the large scale experiments.