



Edmund G. Brown, Jr.
Governor

QUANTIFYING POLLUTANT EMISSIONS FROM OFFICE EQUIPMENT: A CONCERN IN ENERGY-EFFICIENT BUILDINGS

PIER COLLABORATIVE REPORT



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Prepared By

R. L. Maddalena,¹ T. E. McKone,^{1,2} H. Destailats,¹
M. Russell,¹ A. T. Hodgson,¹ and C. Perino²

¹ Lawrence Berkeley National Laboratory

² University of California, School of Public Health
Berkeley, CA 94720

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Prepared For:

Public Interest Energy Research (PIER)

California Energy Commission

Guido Franco

Program Area Lead

Energy-Related Environmental Research

Marla Mueller

Contract Manager

Linda Spiegel

Office Manager

Energy Generation Research

Laurie ten Hope

Deputy Director

ENERGY RESEARCH AND DEVELOPMENT DIVISION

Robert P. Oglesby

Executive Director

and

California Air Resources Board

Ryan Johnson

Contract Manager

Research Division

Peggy Jenkins

Manager

Indoor Exposure Assessment Section
Research Division

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Preface

The California Energy Commission's Public Interest Energy Research (PIER) Program supports public interest energy research and development that will help improve the quality of life in California by bringing environmentally safe, affordable, and reliable energy services and products to the marketplace.

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Quantifying Pollutant Emissions from Office Equipment: A Concern in Energy-Efficient Buildings is the final report for California Energy Commission Contract Number 500-02-023 and California Air Resources Board Contract Number 04-302, and conducted by the University of California, Berkeley and the Lawrence Berkeley National Laboratory. The information from this project contributes to PIER's Energy-Related Environmental Research Program.

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The California Air Resources Board (ARB) carries out and funds research to reduce the health, environmental, and economic impacts of indoor and outdoor air pollution in California. This research involves four general program areas:

- Health and Welfare Effects
- Exposure Assessment
- Technology Advancement and Pollution Prevention
- Global Air Pollution

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Abstract

This study addresses emissions from office equipment with a literature review and measurements from two phases of controlled chamber experiments. Phase I experiments screened for the types of pollutants emitted from five classes of computers and printers placed in a 20 cubic meter stainless steel chamber. Phase II experiments measured volatile organic compounds, low-molecular-weight aldehydes, semi-volatile organic compounds, siloxanes, ozone, and particulate matter emissions from individual devices in a 0.395 cubic meter chamber. Thirty volatile organic compounds and semi-volatile organic compounds were identified among the chemicals emitted from operating computers, with combined emissions rates ranging between 200 to 740 micrograms per hour. Thirty-five volatile organic compounds and semi-volatile organic compounds were identified among the chemicals emitted from laser printers, with combined emissions rates ranging between 2,000 to 5,000 micrograms per hour of active printing. Laser printers had a geometric mean emission rate of 4.8×10^8 fine and ultrafine particles per second of active printing. Chemical emissions did not correlate with power use for either computers or printers, but particle emissions from printers did correlate with power use. The greatest reduction in chemical emissions from computers was achieved by aging these devices. For all equipment, machine-to-machine variability in emissions rates was greater than any emissions reduction achieved by varying operational parameters.

Keywords: Indoor emissions, pollutants, air quality, volatile organic compounds, office emissions, aldehyde, siloxane, ozone, particulate matter, emission rates

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Executive Summary

Introduction

As California moves to more energy efficient buildings many indoor environments will have reduced ventilation. Therefore it will become even more critical to control indoor sources. Office equipment is a potential significant source of indoor pollution; computers, their monitors and peripherals, and printers are found in almost every office environment and in a large number of residential environments. Both consumers and environmental health scientist are concerned with the potential impacts of office equipment emissions.

This report describes the methods and results from a study in which the primary objective was to measure emissions of organic pollutants, ozone, and particulate matter from a selected set of office equipment typically used in residential and office environments. This project was the first effort to use controlled chamber environments to systematically assess the full range of pollutant emissions from desktop computers and printers. The integration of a detailed literature review, screening measurements in a large chamber, and detailed measurements for individual units in a small chamber provided the opportunity to formulate effective and informative methods for collecting information on office equipment emissions. Although office equipment has been a focal point for governmental efforts to promote energy efficiency, little is known about the relationship between office equipment use and indoor air quality.

Purpose

This study was motivated by the widespread and growing use of office equipment by a large fraction of the population in their workplaces, homes, and schools, and the incomplete and fragmented evidence of this equipment as a source of health-relevant air pollutants. The recent literature on indoor pollution reveals that a number of potentially harmful pollutants may be emitted from office equipment such as computers with monitors and printers. Computers give off a range of volatile and semi-volatile organic compounds. Laser printers and photocopiers can generate ozone, volatile organic compounds, and fine particles in varying amounts. The volatile organic compounds are released at least in part from the toner that undergoes heating during the printing process and the particulate-matter emissions result from a number of processes within the printing device. Some of the reported emission rates of air pollutants from office equipment may be relatively low in comparison to other known sources such as building materials or cooking, which, like office machine use, are related to human activity. However, office machines can become potentially important sources of human exposure because they are typically located close to the people who use these devices.

Project Objectives

The project included a detailed literature review and two experimental phases. Phase I consisted of a series of screening-level experiments to identify and measure pollutant emissions associated with major office equipment categories. The screening experiments were carried out in a large chamber that could contain several computers, monitors, or printers during an

emissions experiment. In the Phase I experiments, emissions measurements were collected simultaneously from multiple units selected to represent a particular office equipment category (computers or printers) in a controlled chamber environment. These devices were selected to represent the current mix of products purchased in the United States. All Phase I experiments were conducted in a 20 cubic meter room-scale, stainless steel test chamber with a dedicated flow-through clean-air ventilation system. Temperature, humidity, and pressure were maintained at set levels and continuously monitored.

Five screening experiments were conducted, each focusing on different sets of equipment—laptop computers, desktop computers, inkjet printers, medium-duty laser printers, and heavy-duty laser printers. Equipment was tested under different operational phases, including periods when the devices were turned off, when they were on but not actively processing or printing, and when they were on and actively processing or printing for an experimental duration that provided the opportunity to detect the widest range of pollutants. In the Phase I experiments, the chamber air was sampled for a range of semi-volatile organic compounds, volatile organic compounds, and low molecular weight carbonyls; ozone, black carbon, elemental carbon, and particulate matter; and particle number concentrations.

In the Phase II experiments, chemical, particulate matter, and ozone emissions—as well as computer and printer operating factors (such as power consumption)—were measured for individual devices under controlled conditions. Information from the literature review and from Phase I results was used as the basis for identifying and setting priorities for Phase II procedures. All of the Phase II experiments were carried out in a continuously stirred flow-through chamber large enough to contain a single printer or computer (with monitor and peripherals) but small enough to collect and chemically analyze the full stream of air passing through the chamber.

The experimental goals for Phase II included (a) confirmation of Phase I results using single devices in smaller chambers, (b) evaluation of previously unidentified chemicals in the computer and printer emissions, (c) experiments to characterize particle emissions from laser printers, (d) energy use measurements, and (e) experiments to provide insight on efforts to mitigate emissions and potential human exposures. Substances collected and analyzed from these experiments included integrated samples targeting a subset of the volatile organic compounds and semi-volatile organic compounds collected in Phase I, as well as cyclic siloxanes. Continuous measurements of ozone and particle number concentration were also collected. Both experimental phases included the collection of duplicate samples to assess sampling error, chamber blanks to determine background concentrations, and sample blanks. Sample recovery and breakthrough experiments were also conducted.

Project Outcomes

Emissions were measured and evaluated for six categories of pollutants—volatile organic compounds, low-molecular-weight carbonyls, semi-volatile organic compounds, cyclic siloxanes, ozone, and particulate matter mass or particle number concentrations for each of the substances identified, device-specific emission factors provided a way to express chemical

pollutant mass emitted per hour or particles per hour of use and, in the case of printers, particle emissions were also presented as particles per page or per print job. The total number of identified volatile organic compounds, semi-volatile organic compounds, and siloxanes emitted by new and operating computers includes some 30 compounds and amounts to 200 to 740 micrograms/hour of total chemical emissions. The total number of identified volatile organic compounds, semi-volatile organic compounds, and siloxanes emitted by actively printing laser printers includes some 35 compounds and amounts to 2,000 to 5,000 micrograms/hour of total chemical emissions.

Table ES-1 provides summary results for each of the key pollutant categories considered in this study.

Experiments to assess operational parameters that could mitigate emissions showed that the aging of computers led to a reduction in chemical emissions. For printers, only the amount of toner coverage used per page had an impact on emissions for some chemicals and for particles. User-selected factors such as print sequencing, toner selection, and paper choice had little effect on total emissions relative to the machine-to-machine variability in emissions magnitude, although both paper and toner influenced the composition of the emission stream.

Conclusions

Intermittent emissions of ultrafine particles from laser printers may be the most important and least understood impacts on the indoor environment from office equipment. These emissions can give rise to indoor particle number concentration levels that are comparable to urban and near roadway levels.

Lack of standardization makes the growing body of literature on office equipment emissions confusing and difficult to interpret—particularly for exposure and health studies. This study demonstrates the value of presenting results using a standard volume and consistent ventilation rate and converting device-specific emissions to standardized microgram per hour rates for chemicals and particles emitted for a given duty cycle or printing event.

The researchers calculated that in a small (20-cubic-meter) room with 0.2 air changes per hour, some of the substances released by computers, and many of those released by printers, would produce levels indoors that are at or above typical indoor levels from other sources. Relative to other indoor sources, computers are potential indoor sources for the following substances: dodecamethyl-cyclohexasiloxane, decamethyl-cyclopentasiloxane, and m/p-xylene. Relative to other indoor sources, printers are potential indoor sources for the following substances: ultrafine particles, tetradecane, hexanal, pentadecane, nonanal, tridecane, hexamethyl-cyclotrisiloxane, octanal, decamethyl-cyclopentasiloxane, m/p-xylene, benzaldehyde, styrene, ethylbenzene, 2-ethyl-1-hexanol, o-xylene, dodecane, acetophenone, and hexadecane.

Table ES-1. Summary table of key findings from the results

Volatile Organic Compounds
<p>Total emissions from computers (200–740 micrograms/hour) and printers (2000–5000 micrograms/hour) included ~30 to 35 identified chemical substances—most of these are volatile organic compounds.</p> <p>Computers showed an “aging” effect, where volatile organic compound emissions decreased as operating time increased, but printers did not show this effect.</p> <p>Volatile organic compound emissions were not related to power consumption for either desktop computers or printers.</p> <p>Some of the emitted compounds are on California’s Proposition 65 list of potentially harmful chemicals—estimated exposure concentrations for formaldehyde from computers and dibutylphthalate from printing may exceed Proposition 65 levels.</p> <p>Printers emitted greater overall amounts of volatile organic compounds than computers with each print sequence, and these emissions did not decrease with printer age.</p> <p>The only low-molecular-weight aldehyde emissions found in this study were formaldehyde releases from computers.</p> <p>Volatile cyclic siloxanes were added to the set of chemicals analyzed following an evaluation of “unknowns” from Phase I; they were among the largest emissions from both computers and printers and showed no apparent aging effect.</p>
Semi-volatile Organic Compounds
<p>Emissions of polycyclic aromatic hydrocarbons, brominated flame retardants, and organophosphate flame retardants were measured for computers and printers during Phase I and for computers during Phase II.</p> <p>Total polycyclic aromatic hydrocarbon Phase I emissions from computers (~70 nanograms/hour) included six identified chemicals and from printers (300–500 nanograms/hour) included eight identified chemicals (excluding naphthalene, which was included in the volatile organic compound analysis).</p> <p>Total brominated flame retardant congener Phase I emissions from computers (~60 nanograms/hour) included three identified congeners, and from printers (170–450 nanograms/hour) included seven identified congeners. No brominated aromatic hydrocarbon congeners were identified in Phase II emissions.</p> <p>Total organophosphate flame retardant emissions from computers (~660 nanograms/hour) and those from printers (1500–5000 nanograms/hour) included up to six identified chemicals.</p> <p>Computers showed an aging effect, with most semi-volatile organic compound emissions decreasing over time.</p>
Ozone
<p>Ozone emissions were not detected from either computers or inkjet printers.</p> <p>Only two of the seven laser printers tested had quantifiable ozone emissions.</p>
Ultrafine Particles
<p>Particle emissions were not detected from computers.</p> <p>Particle emissions from inkjet printers were several orders of magnitude lower than those from laser printers.</p> <p>Laser printers emitted large counts of ultrafine to fine particles (with an estimated geometric mean emission rate of 4.8×10^8 particles/second of active printing).</p> <p>Emissions were often elevated further during initial cold start prints (up to 1.8×10^{12} particles emitted from a one-page print job).</p> <p>In laser printers, the magnitude of ultrafine particle emissions increased when power consumption and toner coverage increased.</p>

Eighteen of the compounds detected in computer/printer emissions are listed in one or more national or state health-based guidelines. It should be noted that compounds without available guidelines are not necessarily safe. The concentrations from these eighteen compounds in the 20-cubic-meter room scenario described above, with an air exchange of 0.2 per hour, were compared to guideline levels. In almost all cases the modeled computer and printer concentrations were below guideline levels. But formaldehyde emissions from computers and dibutyl phthalate emissions from printers are possible exceptions where the modeled room-scale concentrations exceed California Proposition 65 levels and come close to the current California Chronic Reference Exposure Level. Particulate matter emissions from the devices tested were low, and the resulting exposure levels would not likely exceed the 24-hour National Ambient Air Quality Standard for fine particulate matter of 2.5 microns or less (PM_{2.5}). Two printers had elevated levels of ozone, but the exposure from these devices would not likely exceed the California one-hour ozone Ambient Air Quality Standard.

Recommendations

The results and experience from the current study lead to a number of recommendations listed below:

- This study tested only desktop computers with flat screen monitors and a small set of printing devices representing inkjet and laser printers. Therefore, future work should assess emissions from other office equipment such as photocopiers, or other printer functions such as the printing of pictures on photo paper or two-sided printing with and without color.
- There is a need for targeted research to explain the pattern and source of ultrafine particle emissions from printers so that effective mitigation strategies can be recommended. This work demonstrated the significance of intermittent bursts of ultrafine particle emissions from laser printers, but it did not show the mechanism by which these particles are formed within the printers. It also did not account for variations among different laser printers regarding the magnitude of this emission.
- There is a need for research focused specifically on the semi-volatile organic compound emissions from office equipment, including printers, to provide insight into the long-term low-level emissions that may accumulate indoors.
- Research tracking the changes in the emission stream is needed, primarily for semi-volatile organic compounds, as new chemicals enter the consumer products market.
- Research on activity patterns related to office equipment use is needed to relate measured emission rates to exposure concentrations and contact rates.

Benefits to California

This project provides new insight on the types of chemicals and pollutants emitted by computers and printers into the indoor environment. Both state regulators and consumers care about these emissions and their magnitude. This information can be used to identify ways to control exposures to any potentially harmful substances released from computers or printers. The California Air Resources Board and the California Energy Commission expect to use the

results of this study to compile exposure data, carry out risk assessments and other types of impact studies, and evaluate the costs and benefits of pollutant reduction efforts that are directed at improving indoor air quality while lowering energy consumption in California.

1.0 Introduction

This study was motivated by the widespread and growing use of office equipment by a large fraction of the population in their workplaces, homes, and schools and the incomplete and fragmented evidence of this equipment as a source of health-relevant air pollutants. The last few decades have seen major changes in the work environment. Fewer people spend their workdays in factories and conversely a higher proportion can be found in offices. Revolutionary developments in information technology have increased the quantity of and transformed the nature of equipment to be found in close proximity to office workers. Tabletop printers serve individual users in their workspace or clusters of users in an office suite. Fax machines and photocopiers are prevalent in office environments. It is now common for each person's workspace to contain a desktop computer, a video display unit (VDU), and often a printer.

Office equipment is also prevalent in home environments. By 2000 more than half of U.S. households had at least one computer (Newburger 2001). In addition, the use of laptop computers spanning both work and non-work environments is on the rise. These issues provide compelling arguments for a systematic study of pollutant emissions from office equipment. But setting up such a study is a challenge, due to the diversity of the available equipment, the rapid evolution and turnover of product lines, and the variability in equipment operating conditions.

The recent literature on indoor pollution reveals that a number of potentially harmful pollutants may be emitted from office equipment. Laser printers and photocopiers can generate ozone (O₃) and fine particles. Toner and paper dust from printing devices can become airborne, respirable particles. Printers and photocopiers also are sources of volatile organic compounds (VOCs), which derive at least in part from the toner that undergoes heating during the printing process. Volatile organic compounds identified in the emissions from printing devices include toxic air contaminants (TACs) such as benzene, toluene, ethylbenzene, xylenes, styrene, formaldehyde, and acetaldehyde. Electronic devices, including office equipment, contain and may emit a number of flame retardants such as the polybrominated diphenyl ethers (brominated flame retardants, or BFRs) and organophosphorus compounds. Among the semi-volatile organic compounds (SVOCs) emitted from computers are triphenylphosphate and other organophosphate esters from plastic covers of VDUs and various flame retardants from printed circuit boards.

Some of the reported emission rates of air pollutants from office equipment may be relatively low in comparison to other known sources such as building materials. However, office machines are potentially important sources of human exposure due to their very close proximity to people who use the devices both at home and in offices. Ozone and particulate matter have been associated with occupational symptoms such as eye, nose, or throat irritation; headache; and fatigue (Mendell et al. 2002; Wolkoff et al. 2006).

To address the need for a systematic study of pollutant emissions from office equipment, this project deployed a two-phase experimental effort informed by a detailed review and analysis of the current literature on the emissions of air pollutants from office equipment. Phase I included screening-level experiments to broadly identify and measure pollutant emissions associated

with major classes of office equipment. Phase II built on the screening-level experiments to focus on important chemicals and to measure emissions and energy use with individual devices, under controlled conditions and using defined protocols. The details of Phase II experiments were developed with input from the California Air Resources Board (ARB) only after the synthesis of information from the literature review and from results of the Phase I experiments.

1.1. Project Overview and Objectives

This report provides results and findings from a research project in which the primary objective was to measure emissions of organic pollutants, ozone, and particulate matter from a selected set of office equipment typically used in residential and office environments. The primary objectives of this research were to: (1) Identify and quantify levels of specific VOCs, SVOCs, ozone, and particulate matter emitted by major categories of office equipment in a controlled chamber environment, (2) quantify emissions of pollutants from individual machines within each of the major office equipment categories in a controlled chamber environment, (3) characterize the effects of aging on emissions for individual machines spanning several categories, (4) evaluate the importance of operational factors that can be manipulated to reduce pollutant emissions from office machines, and (5) explore the potential relationship between energy consumption and pollutant emissions for machines performing equivalent tasks.

The project included a detailed literature review and evaluation and two experimental phases. The Phase I experimental work consisted of a series of screening-level experiments to identify and measure pollutant concentrations associated with major office-equipment categories. The screening measurements were collected simultaneously from multiple units (computers or printers) in a controlled chamber environment. In the Phase II experimental work, emissions and other factors were measured for individual devices under controlled conditions. Information from the literature review and the screening measurements in Phase I was used as the basis for identifying and ordering of priorities for Phase II efforts. The research was conducted with attention to energy use in office equipment. In particular, this entailed measuring energy use by the equipment during emissions experiments (or under comparable conditions). Phase II experiments considered how emissions vary when equipment is operated at different energy levels such as standby, low-power consumption, and high-power consumption, and how emissions vary for different units having different power demands but performing the same operation.

1.1.1. Literature Review and Evaluation

Task 1 of this project was a comprehensive review and analysis of published literature and other available information on the emissions of air pollutants from office equipment. This review focused on summarizing experimental methods that have been used to characterize emissions and on identifying critical research needs in this field. The office equipment evaluated in this review included computers (desktops and notebooks), printers (laser, ink-jet, and all-in-one machines), and photocopy machines. Pollutant categories considered in the literature review included VOCs, ozone, particulate matter, and several SVOCs. Also considered were studies reporting airborne concentrations in indoor environments (offices,

residences, schools, electronics recycling plants) where office equipment is present and deemed to be a significant contributor to the total pollutant burden. The literature review helped established the research objectives for the current project—to provide a systematic process to measure the contribution of office equipment to the indoor concentrations and exposures for a number of important pollutants. In particular, because indoor VOCs, ozone, polycyclic aromatic hydrocarbons (PAHs), phthalate esters, and fine particulate matter can originate from a variety of sources, the use of a two-phased approach to assess emissions for these pollutants is a significant contribution of the present study and was formulated during the literature review.

1.1.2. Phase I Experimental Effort

The Phase I experimental effort included screening experiments to identify and quantify pollutants emitted by recently purchased (less than three months old) desktop computer systems with liquid crystal display (LCD) monitors and peripherals and several different types of printers. An additional experiment was included with current-generation laptop computers to provide preliminary information about the test chamber performance and experimental conditions. The first comprehensive experiment to characterize emissions was carried out with multiple desktop computers. Three additional experiments were conducted with major categories of printers including: (1) printers and multipurpose devices using inkjet technology, (2) low- to medium-output printers and multipurpose devices employing laser technology, and (3) high-output laser printers. The screening experiments were conducted with printers that had been used for approximately 12 to 24 months, the premise being that emissions may increase as the machines age and wear.

A wide range of pollutants were assessed during the screening experiments. The focus for computer systems was on VOCs, low molecular weight carbonyl compounds (aldehydes and acetone), SVOCs, ozone, and particulate matter as both particulate matter (PM) and particle number concentration (PNC). There was particular emphasis on criteria pollutants for which health-based ambient concentration limits have been set (specifically ozone and PM_{2.5}) and compounds appearing on California's list of toxic air contaminants (TACs), including PAHs, brominated and organophosphorus flame retardants, and other organophosphorus compounds. Pollutants measured during experiments with printers included ozone; PM, PNC, black carbon (BC), organic carbon (OC), and elemental carbon (EC), along with the speciated VOCs including carbonyls; and SVOCs. Metals were included in the original research plan but particle levels were too low to facilitate determination of specific metal concentrations.

The Phase I effort concluded with the preparation of an interim report summarizing the literature review, describing methods and results from Phase I experiments, and providing guidance about specific pollutants of interest and the experimental matrix recommended for Phase II experiments. In September 2006, the interim report was provided to ARB and California Energy Commission (Energy Commission) staff, who reviewed the report and prepared comments. These comments were addressed, and a final version of the interim report was issued in December 2006. It is summarized in Sections 2 and 3 of this report, and the final Phase 1 report is provided as Appendix A.

1.1.3. Phase II Experimental Efforts

During Phase II, the research team measured pollutant emissions and energy use for individual representative units within each equipment category, both to confirm results from Phase I and to gain additional insight on the factors that impact the magnitude of pollutant emissions. This second experimental phase extended the broad characterization of specific pollutants identified in Phase I to specific equipment and operation protocols. Phase II included three experimental tasks. First was the measurement of VOC and SVOC emissions and energy use for individual computer systems and their components, to confirm results from Phase I and to further evaluate factors influencing emissions. The next task was to measure VOC, ultrafine particle, and ozone emissions along with energy use for individual printing devices. The duration of the emission phase for printers was limited by several factors, such as the need to refill paper and the buildup of humidity in the chamber during printing. As a result, long-term integrated SVOC measurements were not collected for printers. Based on Phase I results and recommendations, the research team developed and used protocols for measuring the effect of aging on emissions for a subset of the individual units. The third task was an investigation of variables other than age that affect device energy use and emissions, such as the use of non-OEM (original equipment manufacturer) printing supplies, selection of paper, varied duty cycles and types of operation, and the effects of heavy use and/or extended aging. This task focused on an improved understanding of the factors leading to particulate emissions from printers but also considered VOC and ozone emissions.

1.2. Project Organization

This project was a collaboration among scientists at the University of California, Berkeley (UCB) School of Public Health and the Lawrence Berkeley National Laboratory (LBNL) Indoor Environmental Department. The University of California, Berkeley, was the lead institution. The overall research team structure was one in which the Principal Investigator (PI), Thomas McKone, served as the lead contact between UCB, ARB, the Energy Commission, and the Project Advisory Committee (PAC) and had overall project management responsibility as well as responsibility for project synthesis and for all interim and final reports. First Al Hodgson then Randy Maddalena served as Co-Investigator in charge of all work conducted at LBNL, including both experiments and laboratory analyses of fine particles, ozone, VOCs, and sample collection and extraction for SVOCs in Phase I and part of the SVOC chemical analysis performed during Phase II. Professor S. Katherine Hammond served as Co-Investigator in charge of SVOC analysis at UCB during Phase I and part of Phase II, and she supervised the work in her laboratory. Randy Maddalena and Hugo Destailats had primary responsibility for designing and supervising the implementation of experimental LBNL protocols.

Day to day research activities for each task were carried out by research teams, each of which were composed of a co-investigator, one or more scientists, and one graduate student and/or technician. The team members changed as the focus of the project changed but were generally comprised of the PI or Co-PI, a scientist, and one or more technician(s) or student(s).

2.0 Literature Review and Evaluation

The literature review (Destailats et al. 2008) and evaluation (Task 1 of the work plan) addresses both the types of experimental methods used to measure emissions from office equipment and the types of substances that have been measured. Also included is an evaluation of the levels of emissions found and the implications of these results for the experimental work.

Characterizing emissions from office equipment can be difficult, due to the diversity of available equipment, the rapid evolution and turnover of product lines, and the variability in environmental and operating conditions. Studies designed to investigate emissions of office equipment are therefore limited by necessity to a narrow spectrum of equipment, pollutants, and operational conditions. This limitation often results in a large variability in reported emission levels.

2.1. Experimental Methods Used in Emission Characterization

The following paragraphs provide a summary and evaluation of the three main elements of experiments reported in the current literature for characterizing office emissions. These include (1) the use of emission chambers, (2) the selection of office-equipment operation modes, and (3) chemical analytes and detection methods. These results are discussed in more detail in the manuscript (Destailats et al. 2008).

2.1.1. Emission Chambers

Direct determination of emissions by office equipment is typically carried out in environmental chambers. Table 1 presents an overview of chamber dimensions, materials, and operation conditions that have been employed by researchers in the current literature. In most cases, emissions from computers or printers are measured in glass or stainless steel chambers in the size range 1–35 cubic meters (m^3), operating at room temperature (21°C – 23°C , or 70°F – 73°F), and with intermediate humidity conditions (45%–55% relative humidity, or RH). To improve the comparability of results from emissions studies for electronic equipment, the European Computer Manufacturers Association (ECMA International) developed detailed test procedures to measure VOCs, ozone, and particulate matter, along with algorithms to relate the measurements to emission rates (ECMA 2006).

Standard chamber methods designed for measuring VOCs, ozone, and particulate matter may not be appropriate for SVOCs. Compounds with low vapor pressures will partition between air and surfaces in a chamber with potentially large fractions of mass transferred to surfaces. Evidence of this sink effect for BFRs has been described by Kemmlein et al. (2003a) in a study where chamber concentrations of tri-, tetra- and penta-congeners emitted by a printed circuit board held at 60°C (140°F) increased with time over a period of 50 or more days. In another experiment, these researchers found that heating the chamber following removal of the test specimen resulted in the release of a significant mass of sorbed BFRs. Hoshino et al. (2003) used this procedure to quantitatively recover sorbed SVOCs, thus overcoming chamber surface effects.

Uhde et al. (2001) employed a cooled plate (fogging chamber) to collect and quantify the phthalate SVOCs that condensed on the chamber walls. Both Uhde et al. (2001) and Clausen et al. (2004) have found that with this procedure about half of the SVOC emissions to the chamber are deposited on the chamber surfaces. Clausen et al. (2004) also reported dust uptake of diethylhexalpthalate that was equivalent to four times the gas phase levels.

Chamber modifications such as using Teflon surfaces, decreasing chamber surface-to-volume ratios, and decreasing contact times by increasing air change rates may result in improved accuracy in measurements of SVOC emission rates. However, it is likely that the losses of some compounds to chamber surfaces still will be substantial. Another approach is to quantify sorption rates and equilibrium partitioning for SVOCs interacting with chamber surfaces. Mass balance models can then be applied to the observed temporal concentration patterns in the chambers to more accurately estimate device emission rates. This general technique has been demonstrated by Maddalena et al. (2002). Alternative methods to determine SVOCs emission from surfaces using passive flux samplers have been implemented for a variety of plastic materials (Fujii et al. 2003).

2.1.2. Office Equipment Operation Modes

Experimental conditions typically used during emissions studies employ multiple equipment modes, including off, idle, operating, and sometimes power-saving modes. For printing devices, the “typical” operating mode includes a printing cycle representative of a normal duty cycle for the unit being tested and for a specified period that is often limited by the paper capacity (when it is necessary to complete the test without opening the test chamber) or by the buildup of moisture within the chamber. For computers, the operating mode is poorly defined. In many reported experiments, the unit is simply turned on (Nakagawa et al. 2003) or a series of keystrokes are used to simulate use (ECMA 2006). These approaches do not necessarily access all the various sub-systems in the computer in a controlled and systematic way. To date most emission studies with computers often have not taken advantage of software that can run the computer through one or more pre-defined duty cycles that engage all components of the computing system.

Table 1. Exposure chamber conditions used in published studies

Chamber dimensions (m ³)	Chamber internal surface materials	Temperature (°C)	Relative humidity (%)	Equipment analyzed	Pollutants detected	References
Not indicated	stainless steel, glass, aluminum	23 ± 2	50 ± 5	electronic equipment	VOC, ozone, PM	ECMA 2006
0.02 and 0.001	glass	23–60	50 ± 8	printed circuit boards	SVOCs	Kemmlein et al. 2003a
6.5 10 ⁻³	glass	35–200 ^a	50 ± 5	notebook computer	VOC SVOC	Hoshino et al. 2003
1	stainless steel	23 ± 1	50 ± 3	computers	SVOCs	Kemmlein et al. 2003a
1	glass	22	n.a.	computers	VOC carbonyls	Nakagawa et al. 2003
2.4	stainless steel	23 ± 2	55 ± 5	copiers, printers, all-in-one	VOCs, ozone, carbonyls, particles	Lee et al. 2001
12	stainless steel and glass	23 ± 2	50	printers	VOCs, ozone, particles	Heimann and Nies 2001; Smola et al. 2002
23	aluminum, stainless steel	26–31	30–35	copiers	VOCs, ozone, carbonyls, particles	Leovic et al. 1996; Leovic et al. 1998
26	aluminum, stainless steel, galvanized steel	26–31	30–35	copiers	VOCs, ozone, carbonyls, particles	Leovic et al. 1998
35	marlite walls & ceiling, vinyl floors	26–31	30–35	copiers	VOCs, ozone, carbonyls, particles	Leovic et al. 1998
29	stainless steel	26–31	30–35	copiers	VOCs, ozone, carbonyls, particles	Leovic et al. 1998
33	stainless steel	23 ± 0.5	50 ± 5	copiers	VOC, particles	Brown 1999

^a Temperatures correspond to different operation (ambient T) and desorption (high T) phases.

2.1.3. Analytes and Methods

In most published studies, samples were collected during both equipment operation and idle periods. For some analytes, the sampling is continuous. For example, Brown (1999) measured ozone continuously with photometric monitors. Particles have also frequently been monitored continuously using either a PM₁₀ aerosol monitor (Brown 1999; Lee et al. 2001) or integrated by

collection on preconditioned filters (ECMA 2006). Particle counts have been collected using either optical particle counters or condensation particle counters, and size resolution has been determined with a scanning mobility particle sizer (SMPS) (Seeger et al. 2006; Wensing et al. 2006; Uhde et al. 2006; Kagi et al. 2007; He et al. 2007; Lee and Hsu 2007). Total VOCs have in some cases also been monitored continuously with a photoionization detector (Lee et al. 2001). All other reported analytes have been collected on various substrates that integrate emissions over a defined period or sampler volume. Speciation of organic analytes of interest has been carried out subsequent to collection by chromatography after sample preparation steps involving extraction and, in some cases, derivatization.

Volatile organic compounds have typically been collected on sorbent tubes filled with Tenax-TA® (Leovic et al. 1998; Nakagawa et al. 2003) or with Tenax-TA in combination with other sorbent material such as Ambersorb and charcoal (Brown 1999). Other VOC collection methods used canisters (Lee et al. 2001). In all cases, VOCs have been identified and quantified by gas chromatography-mass spectrometry (GC/MS). Volatile carbonyls have been collected in 2,4-dinitrophenylhydrazine (DNPH)-coated silica cartridges (Leovic et al. 1998; Nakagawa et al. 2003) or by direct absorption in an aqueous solution with further derivatization (Brown 1999).

Semi-volatile organic compounds have been collected on sorbent matrices. After extraction, the analytes have been identified and quantified by GC/MS for most analytes. High performance liquid chromatography (HPLC) has been used as an alternative technique for bisphenol-A-bis(diphenylphosphate) (BDP) (Kemmllein et al. 2003a). In one test where the whole chamber was heated to 200°C (392°F) after the emissions ended and the specimen was removed, SVOCs were directly collected on Tenax and analyzed by GC/MS by thermal desorption (Hoshino et al. 2003). Some studies reviewed here did not include chemical speciation of particulate phase, resulting in a likely underestimate of SVOC emissions.

2.2. Measured Emissions from Office Equipment

The sections below summarize the findings from the literature review regarding pollutant emissions from computers and printers. They summarize and discuss emissions of VOCs and SVOCs from desktop computers and emissions of VOCs, ozone, and particulate matter from printers and copiers.

2.2.1. Emissions from Desktop and Notebook Computers

Table 2 provides a summary of VOC emission rates from desktop and notebook computers that were reported in the literature. Table 2 also provides, when available, the chamber concentration data from these experiments. Emission rates are listed separately for computers operating with cathode-ray tube (CRT) monitors and with thin-film transistor (TFT) monitors. Also included, when reported in the original article, is the sum of VOC concentrations (Σ VOC). Typically, the Σ VOC emissions have been higher for computers with CRT than with TFT monitors. Reported VOC emissions include aromatic hydrocarbons, alkanes, alcohols, ketones, and volatile carbonyls, particularly formaldehyde. Reported VOC emission rates for notebook computers have been significantly lower, both for idle and operating conditions. For notebooks, the chemical composition of emissions has included alcohols, carboxylates, and ketones

(Hoshino et al. 2003). The number of Σ VOC-emissions studies is limited but generally the results indicate that Σ VOC emissions are in the range of 100 to 200 micrograms per hour ($\mu\text{g h}^{-1}$) per unit. One of the studies reported in Table 2 (Bako-Biro et al. 2004) used brand-new computers that were previously operated over a 2000-hour period (corresponding to approximately 12 months of normal office use) to avoid the strong age-dependent emission changes they observed during the initial operation of the machines.

Table 2. Summary of VOCs and ozone emitted by personal computers

Chemical	Emission rate ($\mu\text{g h}^{-1}$ per unit)	Chamber concentration ($\mu\text{g m}^{-3}$)	References
Desktop PCs in operation – CRT monitor			
Phenol	1.7		(Bakó-Biró et al. 2004)
C ₆ -C ₁₀ aromatics	45.9	1.3	
>C ₁₀ aromatics	58.3	1.6	
Bicyclic aromatics	41.0	1.1	
Toluene	47.0	1.3	
Styrene	7.6	0.2	
Xylenes	10.3	0.3	
2-Ethylhexanol	19.6	0.5	
n-Decane	11.6	0.3	
n-Undecane	7.6	0.2	
Formaldehyde	5.2	0.1	
Formaldehyde	12.8		(Nakagawa et al. 2003)
Acetaldehyde	3.6		
Propionaldehyde	0.5		
n-Butyraldehyde	1.4		
Valeraldehydye	3.1		
Hexaldehyde	4.6		
Aromatic hydrocarbons	103		
TVOC ^a	180		
Desktop PCs in operation – TFT monitor			
Formaldehyde	9.7		(Nakagawa et al. 2003)
Acetaldehyde	1.5		
Valeraldehydye	0.5		
Hexaldehyde	2.7		
Aromatic hydrocarbons	32		
TVOC	113		

Table 2. Continued

Chemical	Emission rate ($\mu\text{g h}^{-1} \text{ unit}^{-1}$)	Chamber concentration ($\mu\text{g/m}^3$)	References
Operating units –CRT and TFT monitors combined ^{b,c}			
Ethylbenzene	21–188		(Berrios et al. 2005)
m-Xylene; p-Xylene	12–237		
o-Xylene	217		
Pentadecane	20–59		
Styrene	30–82		
Toluene	17–270		
Benzaldehyde	11		
d-limonene	15–84		
Phenol	11–125		
TVOC	501–3261		
Notebook computer ^d			
Methylcarbonate	0.73 / 1.3	223 / 393	(Hoshino et al. 2003)
Toluene	0.04 / 0.15	12.5 / 45.6	
Ethylcarbonate	0.37 / 0.78	112 / 240	
Cyclohexanone	0.07 / 0.21	23 / 65	
2-Butoxyethanol	0.82 / 2.14	217 / 618	
2-Ethyl-1-hexanol	0.14 / 0.52	34 / 150	
Acetophenone	0.05 / 0.11		
Trimethyl cyclohexenone	0.13 / 0.34	18 / 86	
Cyclohexyl benzene	0.16 / 0.81	50 / 250	

^a TVOC = Total volatile organic compounds

^b The range of values is determined for three different units.

^c The article does not indicate which unit is provided with a CRT or TFT monitor.

^d Two values are reported; the first corresponds to idling conditions, and the second to operating conditions.

Table 3 provides a summary of SVOC emission rates that have been reported from studies of desktop computers in operation and chamber concentrations corresponding to the desktop studies. It also provides emission rates for a single notebook study. It is of interest that organophosphorous flame retardants have been measured during computer operation, but because they sorb to the chamber walls, brominated flame retardants have only been detected after computer operation by heating the chamber to 120°C (248°F) and collecting air samples

during the heating period. The plastic covers of VDUs have been shown to contain and emit triphenylphosphate (TPP) flame retardants by Carlsson et al. (2000). They reported time-dependent emission rates of TPP over a 193-day period with a significant reduction in air concentrations of this pollutant after the first 50 days. Printed circuit boards held at elevated temperature (60°C, or 140°F) have been shown to emit several BFRs by Kemmlein et al. (2003a). Their calculations of the emission rates for the SVOCs are in the low nanogram per hour (ng h⁻¹) per computer range.

Table 3. Summary of SVOCs emitted by personal computers

Chemical	Emission rate (ng h ⁻¹ per unit)	Chamber concentration (ng m ⁻³)	Equipment, experimental conditions, and citations
Hexabromo-benzene		1	Desktop PCs in operation (Kemmlein et al. 2003a; Carlsson et al. 2000 [video display units])
RDP	2	13 (100 d) ^a	
BDP	44	20 (100 d)	
TCPP	24		
TPP	25	85 (100 d) 94 (1 d) 8.6 (183 d)	
PBDE 47 (a BFR)		150	Desktop PCs after operation with chemicals extracted from chamber surfaces (Kemmlein et al. 2003a)
PBDE 100 (a BFR)		28	
PBDE 99 (a BFR)		61	
TBBPA		64 - 446	
DBP	110 / 650		Notebook computer (Hoshino et al. 2003)

^a When available, the duration of operation (days) is indicated in parenthesis next to the reported chamber concentrations

Note: RDP = Resorcinol-bis-biphenyl phosphate; BDP = Bisphenyl A bis (diphenyl phosphate); TCPP = Tris(chloropropyl) phosphate; TPP = Triphenyl phosphate; PBDE = Polybrominated diphenylethers; TBBPA = Tetrabromo bisphenol A; DBP = Di-n-butyl phthalate.

2.2.2. Emissions from Printers and Copiers

There have been a number of experiments measuring emissions from printers and copying machines. Table 4 provides reported ozone, particulate matter (PM₁₀), and VOC chamber concentrations determined during idle and operation periods for laser printers, ink-jet printers and all-in-one machines (fax, color printer, copier, and scanner). Laser printers and photocopiers are of note for several reports of their ability to produce ozone emissions in varying amounts (Smola et al. 2002; Lee et al. 2001; Leovic et al. 1996; Leovic et al. 1998; Kagi et al. 2007; Lee and Hsu 2007).

Particulate matter emissions are more specific to printing devices. For example, toner and paper dust from printing devices may become airborne, generating respirable particles that include ultrafine aerosols (Wensing et al. 2006; Lee et al. 2001; Kagi et al. 2007; He et al. 2007; Lee and Hsu. 2007). However, there is to date almost no quantitative information available for size-resolved characterization or chemical composition of particulate matter emitted by office equipment. Wensing et al. (2006) reported particle size distribution of aerosols emitted by ten different hardcopy devices (laser printers and multi-functional devices). Ultrafine particles (< 100 nanometers [nm]) predominated in every case, and their measured particle numbers were in the range 500–343,000/cubic centimeters (cc) for particles > 7 nm, but significantly lower (6–38,000/cc) for particles > 100 nm. Kagi et al. (2007) and He et al. (2007) reported the formation of ultrafine particle during operation of laser printers and Lee and Hsu (2007) have reported formation of ultrafine particles from copiers.

Printers and photocopiers have also been reported as sources of VOCs, which are derived, at least in part, from the toner that is heated during printing. Among all categories summarized in Table 4, reported levels of VOCs have been highest from laser printers and operating units had higher levels than idle units, but this difference was small. Results reported in Table 4 were measured under static conditions in a chamber containing the test unit sampled before and following a 60-page print job. The peak chamber concentrations were reported in units of parts per billion, volume (ppbv) but the results cannot be readily converted to emission rates. However, the results do indicate the relative contribution of the different chemical species in the emission stream where aromatic compounds such as toluene, ethyl-benzene, m- and p-xylene, and styrene make up the bulk of the emissions.

A relatively larger body of experimental data is available for emissions of VOCs and ozone from copier machines. This information is summarized in Table 5. In general, the VOC emission rates from photocopiers are much higher than from printers and multifunctional devices but the variability among the studies is also high, ranging over three orders of magnitude for some chemicals, such as toluene and styrene.

Table 4. Summary of VOCs, ozone, and particulate matter (PM₁₀) emitted by printers

Chemical	<i>Laser printers</i> ^{a,b} Chamber concentration (ppbv)		<i>Ink-jet printers</i> ^a Chamber concentration (ppbv)		<i>All-in-one office machines</i> ^a Chamber concentration (ppbv)	
	Idle	In operation	Idle	In operation	Idle	In operation
VOCs						
Freon 12	0.48–0.52	0.61–0.66	0.36	0.43	0.3	0.45
Methyl chloride	0.53–0.60	0.71–0.82	0.48	0.55	0.52	0.62
Freon 11	0.24–0.29	0.25–0.28	0.23	0.24	n.d.	0.27
Methylene chloride	0.38–0.42	0.46–0.58	0.57	0.61	0.69	0.74
Chloroform	0.96–1.07	1.17–1.31	0.81	0.94	0.74	0.96
Benzene	0.52–0.57	0.77–0.84	0.42	0.41	0.52	0.52
Toluene	14–15	15–16	6.22	6.43	7.9	8.2
Tetrachloroethene			0.23	0.21	0.52	0.43
Ethylbenzene	1.4–2.1	2.0–3.0	1.2	1.26	1.5	1.6
<i>m,p</i> -Xylene	1.2	1.6–1.7	0.86	0.92	0.9	0.9
Styrene	2.7–4.0	3.2–5.3	1.14	1.43	1.2	1.9
<i>o</i> -Xylene	0.9–1.0	2.0–2.3	0.69	0.68	0.58	0.58
1,4-Dichloro-benzene			0.34	0.32	0.34	0.35
1,3-Dichloro-benzene			0.34	0.32	0.34	0.35
1,2-Dichloro-benzene			0.21	0.21	0.26	0.22
1,2,4-Trichloro-benzene			0.86	0.63	0.23	0.2
Hexachloro-butadiene			0.37	0.36	0.88	0.64
ΣVOC		300–1400 (20–60 min) ^c				
Ozone						
Ozone		9–10 1–13 (20 min)		5–6		6
Aerosol particles						
PM ₁₀		65		20–38		41

^a Lee et al. 2001

^b Smola et al. 2002

^c When available, the duration of operation (in minutes) is indicated in parentheses.

Table 5. Summary of VOCs, ozone, and particulate matter emitted by photocopy machines

Chemical	Emission rate ($\mu\text{g h}^{-1}$ per unit)	Chamber concentration ($\mu\text{g}/\text{m}^3$)		Reference
		Idle	Operating	
VOCs				
Toluene	110–760 540–2000			Leovic et al. 1996, 1998
Ethylbenzene	< 50–28000 23000–29000	4.1	552–608	Leovic et al. 1996, 1998; Brown 1999
<i>m,p</i> -Xylene	100–29000 22000–29000	4.5	467–515	Leovic et al. 1996, 1998; Brown 1999
<i>o</i> -Xylene	< 50–17000 12000–15000			Leovic et al. 1996, 1998
Styrene	300–12000 6300–8400			Leovic et al. 1996, 1998
Styrene + <i>o</i> -Xylene		3.1	354–390	Brown 1999
Isopropylbenzene	150–160			Leovic et al. 1998
<i>n</i> -Propylbenzene	< 50–2100 360–460	< 0.4	7.8	Leovic et al. 1996, 1998; Brown 1999
Benzaldehyde	< 100–3800 980–1500	1.3	25–26	Leovic et al. 1996, 1998; Brown 1999
α -Methylstyrene	< 50–330 500–730	1.3	16–18	Leovic et al. 1996, 1998; Brown 1999
1,2,4-Trimethylbenzene		0.6	3.6–4.2	Brown 1999
Butylbenzene		< 0.4	14–15	Brown 1999
Acetophenone		1.6	11–13	Brown 1999
Methoxyethylbenzene		0.9	6.6	Brown 1999
C ₉ -ester		< 0.5	23	Brown 1999
Butenyl benzene		1.1	28–37	Brown 1999
<i>n</i> -Decane	< 50–450			Leovic et al. 1996
2-Ethyl-1-hexanol	130–14000			Leovic et al. 1996
Limonene	< 50–1100			Leovic et al. 1996
<i>n</i> -Nonanal	1100–3900			Leovic et al. 1996
<i>n</i> -Undecane	62–2000			Leovic et al. 1996
<i>n</i> -Dodecane	75–960			Leovic et al. 1996
Formaldehyde	< 500–2600 1900–3200			Leovic et al. 1996, 1998
Acetaldehyde	< 500–1200 510–1300			Leovic et al. 1996, 1998
Acetone	< 100–2800			Leovic et al. 1996
Propionaldehyde	< 100–260			Leovic et al. 1996
2-Butanone	< 100–380 n.d.–600			Leovic et al. 1996
Butyraldehyde	< 100–840 n.d.–410			Leovic et al. 1996, 1998
Valeraldehyde	<100–540			Leovic et al. 1996
<i>n</i> -Hexanal	100–1200 n.d.–950			Leovic et al. 1996, 1998
ΣVOC		49	1630–1900	Brown 1999
Ozone				
Ozone	1300–7900 1700–3000			Leovic et al. 1996, 1998
Aerosol particles				
PM (respirable fraction)	1420–2950	6–11	19–22	Brown 1999

2.3. Contributions of Office Equipment to Indoor Pollution

The literature review provided an opportunity to review and evaluate all available information about when, how, and how much office equipment emissions contribute to the levels of indoor pollutants. In particular, it revealed clearly where there are information gaps and helped the research team develop experimental strategies to fill these gaps. Several studies have reported indoor measurements of pollutants that are emitted by office equipment, but have not linked these pollutants to office equipment. In many of these studies, the source of specific chemicals present in the air or in dust cannot be attributed exclusively to emissions from office equipment. The authors of these studies identify computers, printers, and/or copier machines as a likely source of the reported pollutants but do not explain how they control or account for other sources. Information on the sampling location and date may be relevant, considering that the formulation of additives such as plasticizers and flame retardants often varies from country to country and in time over the years due to different practices and regulation changes.

In the more extensive literature review provided in the Phase I report (Maddalena et al. 2006), and in a recent manuscript by Destailats et al. (2008), there are detailed compilations of indoor concentration measurements for VOCs, SVOCs, and ultrafine particles in which the source of these concentrations are qualitatively, but not quantitatively linked to office equipment as a potential source. In many of these studies there were multiple potential sources of the observed concentrations. The paragraphs below provide a summary of what Maddalena et al. (2006) and Destailats et al. (2008) report as key findings and critical information needs for defining the contribution of office equipment emissions to indoor environmental measurements.

2.3.1. Volatile Organic Compounds (VOCs)

Important sources of information for tracking VOC emissions from office equipment are a review by Wolkoff et al. (2006) of indoor concentrations of VOCs in rooms in the United States and Europe using office equipment, and a study by Stefaniak et al. (2000), who carried out VOC measurements at three photocopy centers in the United States. Stefaniak et al. (2000) observed a large variability of indoor VOC concentrations among the centers, with differences of two or three orders of magnitude in some cases. Wolkoff et al. (1993) noted that aromatic hydrocarbons, monomer residues, and toner additives (among other VOCs) may be emitted not only by the printing and copying processes, but by the paper that is used in the printer or copier, which was shown to be a significant source.

2.3.2. Semi-Volatile Organic Compounds (SVOCs)

A range of SVOCs are emitted from office equipment. Among those associated with office equipment, there have been measurements of indoor concentrations of phthalate esters, brominated flame retardants, organophosphate flame retardants, polycyclic aromatic hydrocarbons, and perfluoroalkyl compounds.

Phthalate Esters

Phthalate esters are used as plasticizers in a wide variety of plastic and polymeric materials, and therefore may be associated with office equipment emissions. Two recent studies, one in the United States (Rudel et al. 2003) and one in Germany (Fromme et al. 2004), report similar indoor

levels of the most common constituents of this class (DEP, DBP, BBP, and DEHP). However, it is difficult to apportion the contribution of office equipment to the total pollutant measured in these studies, because there are a number of other known sources for phthalates indoors. In the United States a federal regulation now applies to phthalate use.

Brominated Flame Retardants (BFRs)

Destailats et al. (2008) reviewed a number of studies that measured concentrations of polybrominated diphenyl ethers (PBDEs) and other BFRs in dust and in air from several indoor environments, including residences and settings where occupational exposure to BFRs was expected to be high. In all cases, a large variability was reported among samples included in each study. Hazrati and Harrad (2006) evaluated intra-building variability by sampling simultaneously in different rooms, but they obtained no clear and consistent evidence of statistically significant relationships between BFR levels and the presence of electronic equipment and polyurethane foam-containing furniture. However, the same study also showed that when an old computer was replaced with a newer model in one of the rooms, it resulted in an appreciable decrease of BFR levels.

Hazrati and Harrad (2006) also investigated seasonal variability and concluded that it is less significant for indoor air than for outdoor air. However, in most cases BFR levels during warm months (spring and summer) were higher than those recorded in colder months (fall and winter). Wilford et al. (2004, 2005) reported BFR levels measured in the gas phase ($n = 74$ cases) and in dust ($n = 68$ cases) in Ottawa homes. They found that indoor air concentrations of BFRs exhibited a log-normal distribution with a geometric mean of 120 picograms per cubic meter (pg m^{-3}) and a median of 100 pg m^{-3} , values that were approximately 50 times higher than those measured in outdoor air as part of the same study. Average BFR levels in dust were 2 micrograms per gram ($\mu\text{g g}^{-1}$), with a median value of $1.8 \mu\text{g g}^{-1}$, from which 42% corresponded to the deca-brominated congener (PBDE-209). These results highlight the need for better characterization of BFR sources.

Production and use of BFR formulations has been phased out in Europe, Japanese industries have voluntarily restricted their production and use (Kemmlein et al. 2003b), the California Legislature has banned two BFR products from use in the state, and several other U.S. states have begun to regulate some BFR congeners. But the use of recycled plastics containing high residual BFR levels could still incorporate these chemicals in the manufacture of new units (Morf et al. 2005).

Organophosphate Flame Retardants (OPFRs)

Destailats et al. (2008) report OPFR measurements for indoor environments from five studies. These studies include samples from residential and occupational indoor environments (including a recycling plant and an electronics store) where exposure to OPFRs is likely to be dominated by office equipment. TBP, TCEP, TPP, TBEP, and TEHP were found in most of the samples. However, some of the identified OPFRs were unique to each study, indicating a large variability of possible sources and formulations. In one study, surface wipes from a computer screen and cover showed high levels of OPFRs and clearly identified the computer as a source, but the magnitude of the release into indoor air was not reported (Marklund et al. 2003).

Polycyclic Aromatic Hydrocarbons (PAHs)

Ren et al. (2006) have measured and reported the amount of dust released during operation of computers to be between 4.0 and 6.3 mg of dust per day, suggesting a significant potential for exposure to chemicals such as PAHs that are associated with resuspended dust particles. Their study quantified PAHs in dust collected from the interior of computers at levels that were higher by a factor of three compared to those measured in outdoor air samples. In order to account for competing indoor sources, Destailats et al. (2008) compared these to PAH levels corresponding to smoking and non-smoking rooms. Some computer samples had significantly higher levels of benzo[b]fluoranthene, chrysene, fluoranthene, and phenanthrene than indoor dust. Since these compounds are present in outdoor air and can be emitted by various indoor sources, this study could not reliably quantify the contribution of computer emissions, but it is suggested that a fraction of measured PAHs might have been emitted from the heated plastic materials, chips, and other computer components. However, no study has yet quantified the contribution of office equipment emissions to indoor PAHs.

Perfluoroalkyl Compounds (PFAs)

Perfluoroalkyl sulfonamides are derived from perfluorinated surfactants that are widely used in a variety of applications that include coatings and surface treatments for electronic equipment. Two recent studies (Shoeib et al. 2004, 2005) summarize air concentrations of perfluoroalkyl sulfonamides measured in residences and laboratories. Potential health effects of these chemicals are relatively unknown, but their environmental persistence and their transformation into stable degradation products/metabolites such as perfluorooctane sulfonate (PFOS) are attracting increasing attention to this emerging class of indoor pollutants (Shoeib et al. 2004; Shoeib et al. 2005). Therefore, future studies that characterize indoor levels and specifically apportion the sources of office equipment to indoor levels are needed.

2.3.3. Ultrafine Aerosol Particle Emissions from Printing Devices

As discussed above, recent reports have identified and measured emissions of ultrafine particle during operation of laser printers (Wensing et al. 2006; Kagi et al. 2007; He et al. 2007) and copiers (Lee and Hsu 2007). Kagi et al. (2007) also reported significant ozone levels during operation of one of the two printers they evaluated. In the presence of ozone emissions, the size distribution of particles generated during printing (in the range < 20–200 nm) showed a shift toward the lower end of the particle size range. In addition, particle number concentrations recorded in the presence of ozone were significantly higher than those measured for the printer that did not emit ozone, suggesting a possible role of ozone chemistry in the formation of ultrafine aerosol emissions from printers. Measurements performed at different distances from the printer showed a remarkable enhancement effect in the proximity of the source. By contrast, aerosol particle levels were close to background room levels at a distance of 1.5 meters (m) from the printer. Similarly, Lee and Hsu (2007) reported a correlation between ozone and ultrafine particles (< 50 nm) emitted simultaneously by copier machines. Further studies are needed to better understand particle inception and growth during the printing process, the role of ozone generated during the printing process, and the effect of microplumes at short distances from the source.

2.4. Summary Findings from the Literature Review

Office equipment has been a focal point for governmental efforts to promote energy efficiency through programs such as ENERGY STAR®. This is because energy use associated with office equipment is substantial, currently estimated at 3% of all U.S. electric power use (<http://enduse.lbl.gov/Projects/InfoTech.html>). Since distributed desktop computers and associated displays are in close proximity to people, research on pollutant emissions from office equipment logically should emphasize distributed equipment rather than large central units.

For some pollutants the link between office equipment emissions and indoor air concentrations is relatively well established, but most chemicals emitted from office equipment can also come from other sources, and their source apportionment is less straightforward. It also is important to distinguish between computers and printers when characterizing emissions from office equipment. A range of methods have been used to study emissions from office equipment, and standardized methods have recently been released (ECMA 2006).

Computers have been established as sources of VOCs and some SVOCs, but not ozone and particulate matter. Existing studies clearly show that computers emit a range of VOCs, although in most cases the relatively low emission rates suggest that these are less significant than other indoor and outdoors sources. Computers are typically not a source of ozone or particulate matter, although re-emission of ambient particles deposited in the units has been demonstrated. The existing literature provides more limited data for SVOCs. Emission factors for brominated and organophosphate flame retardants indicate levels for individual SVOC pollutants are in the nanogram per hour range. Although these numbers are significantly lower than VOCs, many of the SVOCs are found indoors, and computers are suspected as possible long-term sources. The influence of office equipment on the burden and distribution of indoor SVOCs through redistribution of particulate matter requires further investigation, as does the quantification of phthalate emissions that correct for background levels.

Printers have been characterized as an indoor source of VOCs, SVOCs, particulate matter, and ozone. Emissions of VOCs from printers (and copiers) are generally higher than for computers, particularly for styrene, toluene, xylenes, and other alkylbenzenes, but the variability between devices and between experiments is also high. Significant levels of particulate matter are generally found during operation of printers, copiers, and multifunctional devices, but better physical and chemical characterization of aerosol particle emissions during the printing process is needed, particularly for ultrafine and nanoparticles. For ozone, although the emission rates are unclear, even low levels of ozone emitted by printers might react with other VOCs, either within the machine or outside, resulting in secondary pollutants and generation of ultrafine aerosol particles (Destailats et al. 2006a, 2006b; Singer et al. 2006).

In light of the diversity of equipment, the rapid evolution and turnover of product lines, changes in manufacturing processes, and variability in operating conditions, the values summarized in the current literature represent initial estimates of emissions and their implications. The need for more detailed and systematic assessments of office equipment emissions remains strong.

3.0 Phase I Screening Experiments

As indicated in the previous section, this project was unable to develop a statistically representative sample of the current stock of office equipment in California households due to the number of vendors involved, variety of equipment offered by each vendor, the continuing rapid evolution of technology and fabrication materials, and the limited number of units that could be tested.

Rather, the goal of Phase I was to use a screening approach to identify a wide range of potentially important pollutants from new or recently purchased office equipment—including computers and printers—grouped into categories. This goal was attained by using the Phase I experiments as a “composite” approach, combining units from several different major manufacturers for each category of office equipment in a single room-scale chamber to increase coverage of different makes and models. Information on individual units was developed in Phase II of the study. The number of units that were studied in a given grouping was ultimately limited by the size of the test chamber and the need to compensate for the heat (from computers) and moisture (from printers) generated during operation.

The sections below provide details on the experimental design, sampling and analysis methods, and results for Phase I experiments. These experiments were set up to screen five categories of equipment. The first included existing laptop computers to collect preliminary emission measurements but also to test the experimental design and instrumentation. The second category included new desktop computers with monitors and peripherals. The last three categories included medium- and large-output laser printers and inkjet printers.

3.1. Phase I Methods

Methods and protocols cover both the experimental design and the chemical sampling/analysis techniques. The experimental design section provides details on the target chamber conditions and the selection and operation of office equipment. The section on sampling and analysis explains how the selected pollutants—VOCs, carbonyls (aldehydes and acetone), SVOCs, particulate matter, and ozone—were collected from the exposure chambers, extracted, and analyzed chemically along with data interpretation procedures and quality assurance measures.

3.1.1. Experimental Design

Overview of Experimental Approach

All screening experiments employed the same general approach. These experiments were conducted in a 20 m³ room-scale stainless-steel test chamber with a dedicated single pass clean-air flow-through ventilation system designed to minimize the introduction of ambient particles, VOCs, and SVOCs to the chamber air. The experiments were run in the dark. The temperatures of the inflowing air and the room housing the chamber were controlled to maintain an acceptable temperature in the chamber during different operational phases of the office equipment. Temperature, humidity, and pressure differential (inside - outside) were continuously monitored. The chamber was operated at the minimum air change rates required

to maintain the chamber temperature within an acceptable range under differing heat loads from the operating equipment.

The experiment's duration was approximately two weeks for computer runs and four days for each of the three printer runs. Equipment was tested under different operational phases, including off, on/idle, and on/active, and the duration of each phase was selected to allow the experimental system to approach steady state, providing the opportunity to detect the widest range of pollutants. The typical timelines for the room-scale computer and printer emission experiments are illustrated in Figure 1.

Pollutant concentrations were measured either continuously (such as for ozone, particle number concentration [PNC], and black carbon) or by collecting and analyzing integrated air samples (such as for VOCs, aldehydes, SVOCs, and particle mass). Duplicate samples were typically collected at each sample point indicated in Figure 1. Three different sample points were included in the active emissions phase for the computers, and at least two sampling points on two consecutive days were included for the printers.

Office Equipment Selection

An important part of the screening analysis for office equipment emissions is selection of a relevant sample of office equipment. Relevant in this context refers to equipment that is likely to be used in California residences, not necessarily a statistically representative sample of the current stock of office equipment in California households. Actual detailed survey information were recently reported by Gartner Research (Shao 2005) providing market share data by vendor revenue, unit shipment, and end-user spending, including information on brand, model, form factor, processor class, processor speed, price band, and user segment. However, this report is not publicly available. A similar report by IDC companies (Daoud and Loverde 2005) provides regional data on unit, value, and average system price, and the document can be purchased for \$4,500, but the level of detail needed in the current screening study did not justify purchase of such a detailed report.

In place of detailed (and very expensive) survey information, the office equipment selection process for this study was based on a survey of current articles in trade journals and consumer magazines, as well as information from customer satisfaction surveys—resources that are readily available to consumers. When the Phase I studies were started, the journal *PC World* had just summarized the Gartner and IDC reports on global personal computer (PC) sales (Krazit 2005). The top four manufactures in terms of U.S. sales for 2005 were listed. These results actually represent the top six computer vendors because some of the manufacturers had merged but still produced the name brands. Information on non-name brand computer systems, sometimes referred to as “white-box” computers, is not readily available but likely makes up a small fraction of sales relative to the name-brand units. The American Customer Satisfaction Index (ACSI) lists five manufacturers plus an “All Others” category.¹

¹ American Customer Satisfaction Index (ACSI) website: www.theacsi.org/. Last checked 02/11/08.

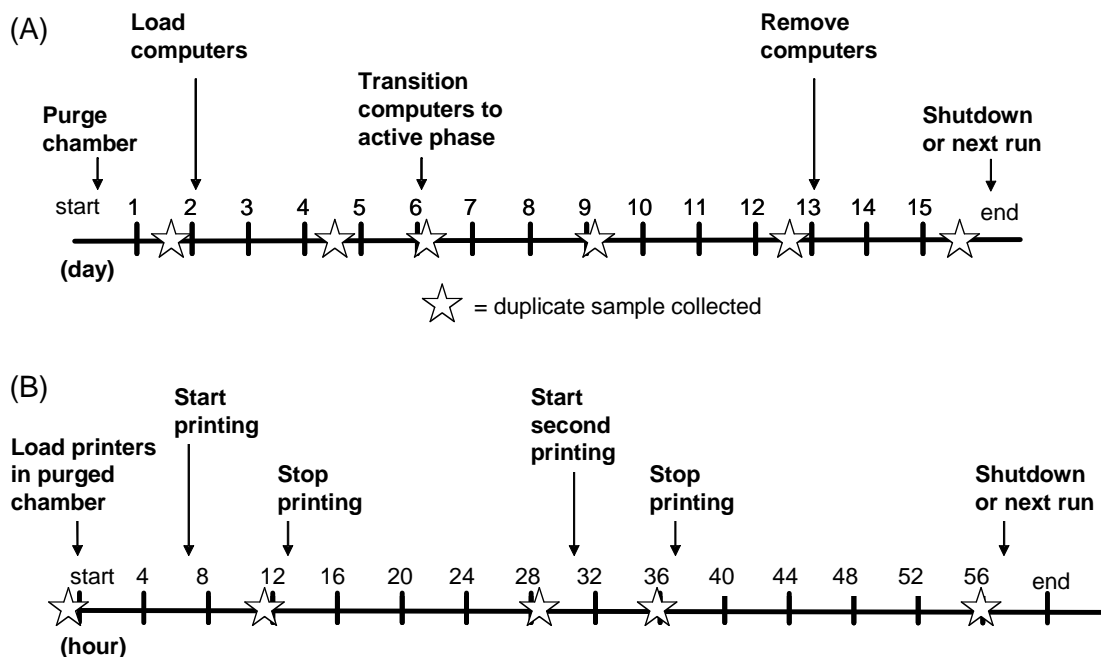


Figure 1. Typical experimental timeline for computers (A) in days and for printers (B) in hours. The different experimental phases are indicated by the text boxes and arrows. The stars indicate the approximate time when the duplicate integrated samples for VOCs (60 minutes, 100 milliliters [ml]/min), aldehydes (120 minutes, 1 liter/ minute) and SVOCs (12 hours, 20 liters/minute) were collected. Particle number concentration was determined at several time points during each experimental phase.

The *Consumers Reports* (CR) magazine (Consumers Reports 2005) provides information for selecting representative computers based on a wide range of test results (convenience, speed, multimedia, expansion, etc.) that may be considered in purchasing a computer. The CR list also includes actual units from each vendor along with price. The results are separated into three categories, including "Budget Models," "Workhorse Models," and "Macintosh." The list includes all the vendors listed in the previously mentioned sources, with one additional manufacturer. Because of the rapid evolution of computers, the CR tables and other reviews were useful as a general guide for selection of office equipment, but actual units listed in the reviews were typically replaced by newer models before our selection was made. As a result, individual units were selected to include current models from the major manufacturers. For monitor selection, the experimental premise was that the "typical" customer for a home use computer will select a computer based on "packages" offered by vendors that include both the box and monitor. Therefore, the project team selected monitors based on size (17" or 19") for the individual computers at the time of purchase by choosing from either top sellers lists or units recommended by the vendor/distributor where the box is purchased. The five desktop computers were selected for the screening experiments. Details on the computer/monitor units selected for Phase I are provided in Table 6.

Table 6. Descriptions of desktop computers used in Phase 1

Unit Identifier	DT01	DT02	DT03	DT04	DT05
Processor	AMD Sempron 3500+ Processor; 2GHz	AMD Sempron 3300+ Processor; 2GHz	1.83GHz Intel Core Duo processor	Intel Pentium 4 3.2GHz 800FSB 2M LGA775	Pentium 4 Prescott DT, 3.0GHZ, 1 MEGB, 800FSB
Operating System	Windows XP Home	Windows XP Home	Mac OS X	Microsoft Windows XP Professional	Microsoft Windows XP Professional
Memory	512MB DDR PC3200 SDRAM (2x256MB)	256MB DDR PC3200 SDRAM (1x256MB)	512MB DDR2 SDRAM	32x64 256MB 400MHz DDR DIMM	DUAL IN-LINE MEMORY MODULE, 512, 533M, 64X64, 8, 240, 1RX8
Graphics Card	Integrated ATI Radeon Xpress 200 Graphics with 128MB shared video memory	NVIDIA GeForce 6100 GPU up to 128MB of shared video memory	ATI Radeon X1600 with 128MB GDDR3 SDRAM	Molex ADD2 DVI-D Card PCI-Express	
Hard Drive	160GB 7200RPM Ultra DMA hard drive	100GB 7200RPM	160GB Serial ATA	Western Digital Caviar 120GB 8MB Cache SATA HD	40GB, S, 7.2K, WD-XL80SD-2, LEAD FREE
Primary CD/DVD Drive	LightScribe DVD+/-R/RW drive with CD writer and double layer support	48x CD-RW/DVD combo drive	Slot-loading SuperDrive (DVD+R DL/DVD+-RW/CD-RW)	LITE-ON 52X32X52X/6X CDRW/DVD COMBO DRIVE	COMPACT DISK READ WRITE/DIGITAL VIDEO DISK DRIVE COMBO, 48X, HALF HEIGHT, SONY, CHASSIS 2001
Communications	10/100BaseT network interface	10/100Mbps integrated Ethernet LAN (RJ-45 port)	10/100/1000BAS E-T Ethernet; AirPort Extreme; Bluetooth 2.0 + EDR	10/100/1000 Mb/s/sec	
Sound	Integrated audio, 6 speaker configurable	6-channel (5.1) AC'97 audio	Built-in stereo speakers; Integrated microphone; headphone/ optical digital audio output; audio line in	Intel High Definition audio subsystem based on the Realtek ALC860 audio codec	
Monitor	17-inch SyncMaster 730b	15-inch model 500G	17-inch viewable widescreen active-matrix LCD display		
Power Use (W) for Boxes					
Plugged in off	6	8	4	4	4
Sleep	12	10	5	4	2
Idle	170	130	102	225	180
Active	210–230	165–170	110	> 300	280–290

Ten printers were used in the screening experiments. These included two high-output laser-technology printers (*LP01* and *LP02*), three medium-output laser printers (*LP03*, *LP04*, and *LP05*) and five inkjet printers (*IJ01*, *IJ02*, *IJ03*, *IJ04*, and *IJ05*). Printers in the inkjet and medium-output laser technology categories were identified that fit the selection criteria regarding age by surveying colleagues at LBNL and UCB. Once identified, the printers were borrowed for the experiment. Fresh ink/toner cartridges were installed prior to use. For the high-output laser printers, two units were rented from a local office equipment rental store, and these units were used as received. Details on the specifications of the printers are provided in Table 7.

Table 7. Descriptions of printers used in Phase 1

High-output laser technology	<i>LP01</i>	<i>LP02</i>			
<i>Print speed^a</i>	33	45			
<i>Print resolution (dpi)</i>	1200	1200			
<i>Recommended monthly duty cycle (pages)</i>	150,000	200,000			
<i>Power usage (watts)</i>					
<i>active</i>	580	680			
<i>standby</i>	21	13			
Medium output laser printers	<i>LP03</i>	<i>LP04</i>	<i>LP05</i>		
<i>Print speed^a</i>	20	21	15		
<i>Print resolution (dpi)</i>	1200	600-1200	1200		
<i>Recommended monthly duty cycle (pages)</i>	10,000	20,000	7,000		
<i>Power usage (watts)</i>					
<i>active</i>	345	460	260		
<i>standby</i>	6	75	7		
Inkjet printers	<i>IJ01</i>	<i>IJ02</i>	<i>IJ03</i>	<i>IJ04</i>	<i>IJ05</i>
<i>Print speed^a</i>	11	12	8	9	18
<i>Print resolution (dpi)</i>	2400X1200	2880X720	2880X720	600X600	1200X1200
<i>Recommended monthly duty cycle (pages)</i>	3000	1,000–9,999	1,000–9,999	1,000–9,999	2000
<i>Power usage (watts)</i>					
<i>active</i>	14	17	15	25	75
<i>standby</i>	5			4	4

^a Print speed is in pages per minute

Operation of Office Equipment During Experiments

The ECMA Standard titled “Detection and Measurement of Chemical Emissions from Electronic Equipment” (ECMA 2006) recommends operating equipment at maximum duty cycle during emissions tests. For the PC laptops and desktops, commercially available software (BurnInTest, <http://passmark.com/>) was used to manage the duty cycles during the emissions experiments. The software is designed to test computer components by executing a range of actions on the hardware in the PCs (i.e., hard drive, floppy drive, CD drive, graphics card, sound card, memory, and ports). The software was installed on each PC, and the standard test procedure was run during the emissions phase of the experiments. The standard run configuration was set up to maintain the CPU at 100% while executing CPU math calculations, CPU multimedia and

streaming extensions, memory (RAM), 2-D and 3-D graphic operations, disk test, network, sound, and video operations. For the Macintosh systems, a script was developed to repeatedly copy, paste, and erase a large test file on the hard drive. Temperature, fan speed, and other variables were not monitored during the screening experiments, but the options are available for more detailed studies.

Each group of printers tested included several printers with different monthly duty cycles and different print speeds and paper handling capacities. To develop a standard print cycle that represented continuous duty for the group of printers the research team first estimated total pages per day for all printers in the category based on monthly duty cycle rating for each printer. The total print job was allocated to each printer based on a duty fraction for that printer within its group. The *duty fraction* is the fraction of pages that a particular printer would contribute to the total print job, based on the relative magnitude of its recommended monthly duty cycle. Using the medium output printers as an example, Table 8 and the paragraph below illustrate how the project team developed a standard duty cycle for each group of printers.

Table 8. Example calculations for specification of printer duty cycles in Phase 1

	<i>Monthly Duty Cycle (pages/month)</i>	<i>Print Speed (pages/min)</i>	<i>Average Daily Duty Cycle (pages/day)</i>	<i>Duty Fraction</i>
<i>LP03</i>	10,000	20	333	0.27
<i>LP04</i>	20,000	21	666	0.54
<i>LP05</i>	7,000	15	233	0.19

Based on the “average daily duty cycle” in Table 8, the total number of pages in a day for the group of medium-output laser printers would be ~1240 (recommended maximum). If one defines a typical print job as 20 pages, it is possible to specify one complete print cycle (i.e., all three printers print once in series) as 60 pages, where the *LP03*, *LP04*, and *LP05* print 17, 33, and 12 pages each per cycle, respectively. To satisfy the maximum duty (i.e., 1240 pages) requires 21 cycles over the duration of the active phase.

The input and output tray capacity for each printer dictated how often the researchers entered the chamber to empty the output trays and refill the input trays. Consideration of print speed and the 10 seconds required by each machine to print the first page (i.e., time between start of printing cycle and first page printed) provided roughly 75 minutes of active printing dispersed evenly throughout the day. The researchers distributed the active print time over about six hours to approximate a steady-state printing activity resulting in an approximate four-minute pause between each print job. After completion of the active print cycle, the printers were left idle overnight (~18 hours) before repeating experiments the next day or removing the printers from the chamber after the two consecutive sampling events. The ISO/IEC 19752:2004 standard test page (ISO 2004) was used in the room-scale experiments, and a script was developed to send the appropriate number of pages to each printer at the specified print interval.

3.1.2. Phase I Sample Collection and Analysis Methods

This section describes both how candidate pollutants were selected and how the selected pollutants were collected from the exposure chambers and analyzed chemically. It includes information on sample collection, extraction, analyses, and data interpretation.

Pollutant Selection

Pollutant selection was based on two factors. First, the information gathered from the literature review provided an expectation of the types and quantities of substances that are released from computers and printers. Second, the screening experiments themselves provided a chemical analysis that included a range of peaks on the chromatograph from the sampling devices. Peaks that had not yet been identified from other studies were further explored, and in some cases used to add a specific substance to the list of candidate analytes. The major categories of pollutants considered included VOCs (including low molecular weight carbonyls), SVOCs, particles, and ozone. The sampling and analysis methods used for each of these pollutant categories are summarized in Table 9. All of the SVOCs were collected simultaneously on the same sorbent cartridge, but specific chemical classes followed different analytical pathways after extraction. The following sections provide a more detailed list of analytes and the techniques used to collect them from the chamber and quantify their concentration.

VOC Selection, Sampling, and Analysis

The target VOC analytes for Phase I are listed in Table 10. Volatile organic compound samples were collected and analyzed generally following U.S. Environmental Protection Agency (U.S. EPA) Methods TO-1 (USEPA 1984) and TO-17 (USEPA 1999). They were collected onto Tenax-TA™ sorbent tubes (P/N CP-16251; Varian, Inc.) modified by substituting a 15-millimeter (mm) section of Carbosieve S-III 60/80 mesh (P/N 10184, Supelco Inc., Bellefonte, PA, USA) for Tenax-TA™ at the outlet end. The addition of Carbosieve allows for the collection and analysis of more volatile compounds. Prior to use, the sorbent tubes were cleaned by helium purge (~10 cc/min) at 275°C (527°F) for 60 minutes. Sorbent tubes were inserted through ports in the chamber wall during sample collection so that air could be drawn directly into the tubes from the chamber, to avoid losses of lower-volatility compounds in the sampling train and tubing. Peristaltic pumps were used to pull chamber air through the parallel sample tubes at 100 cc/min. for 30 minutes, collecting a total of three liters of air. Flows were verified using a separate calibrated flow meter at the beginning and end of each sampling event. The tubes were capped after use and either analyzed the same day or stored in a freezer until analysis. Sample stability over freezer storage times of more than two months has been confirmed previously at the LBNL lab for many of the VOCs included in this study.

Table 9. Overview of sample collection and analysis methods used in Phase 1

<i>Analyte</i>	<i>Sampling Mode</i>	<i>Collection Media</i>	<i>Sample Processing</i>	<i>Analysis Method</i>
VOCs	Integrated in duplicate	Tenax-TA + Carbosieve sorbent tubes	Thermal desorption	TDGC/MS
Volatile Carbonyls	Integrated in duplicate	DNPH-coated silica cartridges	Extract with acetonitrile	HPLC
SVOCs	12 hr 20 lpm (14.4 m ³) integrated in duplicate	Polyurethane foam + XAD TM -4	Accelerated Solvent Extraction in 1:1 Ace:Hex	GC/MS (PAHs) GC-ECD (BFRs) GC-NPD (OPs)
Particle count	Continuous		Condensation particle counter	TSI P-Trak ultrafine particle counter
PM - mass	Integrated	Teflo [®] Teflon filters	Equilibrate filters at T/RH	Gravimetric
PM - BC	Semi-integrated	Filter strip in aethelometer		Light absorption (continuous)
PM - EC/OC	Integrated	Tissuquartz fiber filters		Light absorption (on filter)
Ozone	Continuous			UV photometric

VOC = volatile organic compounds; TDGC = thermo-desorption gas chromatograph; MS = mass selective detector; DNPH = dinitrophenylhydrazine; HPLC = high performance liquid chromatograph; PAH = polycyclic aromatic hydrocarbon; PM = particulate matter; PUF = polyurethane foam; ECD = electron capture detector; NPD = nitrogen-phosphorus detector; OP = organophosphorus compounds; BC = black carbon; T/RH = temperature and relative humidity; EC/OC = elemental carbon/organic carbon.

Sorbent tubes were thermally desorbed for analysis by thermal desorption gas chromatography/mass spectrometry (TD-GC/MS) using a cryogenic inletting system (Model CP-4020 TCT, Chrompack). The system was fitted with a Tenax-packed trap (P/N CP-16425; Varian, Inc) to enhance recovery of the most volatile compounds. Desorption temperature was set to 235°C (455°F) for 6.5 minutes. The cryogenic trap was held at -100°C (-148°F) and then heated within 30 seconds to 235°C for injection. Compounds were resolved on a GC (Series 6890Plus, Agilent Technologies) with a 30 m length, 0.25 mm diameter HP-1701 column (Agilent, 19091U-233) having a 1 micrometer (µm) film thickness. The chemicals were detected using an electron impact MS system (5973, Agilent Technologies). The target compounds span an approximate volatility range bounded by n-butane and n-octadecane (C₄-C₁₈). The upper end of this boiling point range captures several of the analytes that are also included in the SVOC analytical stream, including the low-boiling phthalates and polycyclic aromatic hydrocarbons. The MS was operated in scan mode and all compounds over the detection limit (< 1 to several nanograms) were identified by initial National Institute of Standards and Technology (NIST) spectral library search, followed by comparison to reference standards. Multipoint calibrations

were prepared for target VOCs, for which pure standards were available. All pure standards and analytes were referenced to an internal standard (~120 ng) of 1-bromo-4-fluorobenzene.

The VOCs that were positively identified in this study represent approximately one-third of the total VOCs recorded in the GCMS analysis described above. The remaining unknown analytes were either tentatively identified (as aromatic or phenolic compounds) using library matches to known mass spectra or remain unknown.

Table 10. Target VOCs included in Phase I screening measurements

<i>Chemical name</i>	<i>CAS#</i>	<i>Chemical name</i>	<i>CAS#</i>
Toluene	108-88-3	1,2,3-Trimethylbenzene	526-73-8
Ethylbenzene	100-41-4	2-Methylnaphthalene	91-57-6
o-Xylene	95-47-6	Benzene	71-43-2
Hexadecane	544-76-3	Mesitylene	108-67-8
Styrene	100-42-5	n-Propylbenzene	103-65-1
Acetophenone	98-86-2	Diethylphthalate	84-66-2
1,2,3,5,-Tetramethylbenzene	527-53-7	1-Methylnaphthalene	90-12-0
Dibutylphthalate	84-74-2	1,3-Diethylbenzene	141-93-5
Naphthalene	91-20-3	n-Butylbenzene	104-51-8
Benzaldehyde	100-52-7	Isobutylbenzene	538-93-2
1,2,4,5,-Tetramethylbenzene	95-93-2		

Carbonyl Selection, Sampling, and Analysis

The target carbonyls included formaldehyde, acetaldehyde, and benzaldehyde. Since there was no acetone identified in the screening assessment, the carbonyl analysis was essentially a low-molecular-weight aldehyde assessment. Hence from this point onward the term “carbonyl” is replaced with “aldehyde” or “low-molecular-weight aldehyde” in discussions of carbonyl compounds. Samples of these low molecular weight aldehyde compounds were collected and analyzed following ASTM Test Method D 5197-92 (ASTM 1997). As with the VOCs, samples were drawn directly from the chamber onto sorbent cartridges to minimize losses. With this method, samples were collected on commercially available silica gel cartridges coated with 2,4-dinitrophenylhydrazine (DNPH, P/N WAT047205, Waters). Duplicate samples were collected in parallel at ~ 1 liter per minute (lpm) for 120 minutes using a vacuum pump. Flow rates were controlled by means of electronic mass flow controllers, and rates were verified before and after each sampling period. Sample cartridges were stored after use in the freezer until extraction. Cartridges were extracted with 2 ml of high-purity acetonitrile for analysis.

Extracts were analyzed by high-performance liquid chromatography (HPLC) using a C₁₈ reverse phase column and ultraviolet (UV) detection at 360 nm. Multipoint calibrations were prepared for the target aldehyde using commercially available hydrazone derivatives of formaldehyde, acetaldehyde, and acetone. Higher carbon-number aldehydes were quantified using sorbent sampling tubes and GC/MS following the VOC method described above.

SVOC Pollutant Sampling

Semi-volatile organic compound pollutants selected for sampling and analysis included polycyclic aromatic compounds, polybrominated diphenyl ethers (brominated flame retardants or BFRs), and organophosphate (OP) compounds (also used as flame retardants). These SVOC samples were collected on polyurethane foam plugs backed with XAD-4 sorbent loaded into Savillex Teflon cartridges. The sorbent material was pre-cleaned before loading in the cartridge using an Accelerated Solvent Extraction system (ASE 200, Dionex) with high purity solvents of decreasing polarity as sequential extractions with two times methanol (MeOH), two times dichloromethane (DCM), two times hexanes, and three times with a 1:1 mixture of acetone:hexanes. The ASE system was operated at 1500 pounds per square inch (psi), 75°C (167°F), no preheat time, a five-minute static phase, 50% flush volume, 120-second purge, and three cycles per extraction. After cleaning, the material was dried in the ASE cell with a stream of high purity nitrogen (N₂) then the XAD was transferred to the sampling cartridges. The PUF was removed from the ASE cell and dipped in clean DCM to restore the original shape then dried under a stream of high purity N₂. After drying, the sorbent material was loaded into the sampling cartridge, capped tightly, wrapped in foil, and stored in the dark at room temperature until use.

Duplicate samples were collected by pulling 20 lpm of chamber air through each of two parallel samplers with flows controlled by a dedicated taper-tube rotometer for each sample line. Samples were typically collected for 12 hours during the computer experiments and 24 hours during the printer runs. Cartridges were mounted on stainless steel tubes and inserted through access ports into the chamber and placed in a vertical orientation to prevent flow paths from forming if the sorbent material settled.

SVOC Collection Efficiency and Recoveries

Initial recovery experiments were performed using cleaned sorbent cartridges that were spiked with a mixture of all target compounds at known levels and processed using the full extraction procedure and analytical procedure for each chemical class. The standard spike recovery experiments were run in triplicate for all the SVOCs. A second recovery experiment was performed after modifying the sorbent cleanup method to include an initial hot MeOH extraction in the ASE. The modification was made to reduce background noise in the OP analysis. The second recovery experiment was run in conjunction with an assessment of breakthrough or collection efficiency and determination of the blank chamber levels. The experiment used clean SVOC sample cartridges that were spiked with a known amount of target analytes on the leading edge of the PUF. The spiked cartridges were then deployed in parallel with a clean (unspiked) cartridge and run for a full sampling period in the blank (empty) room-scale chamber. The cartridges were extracted and quantified using the full method and the total of the known amount spiked on the cartridge plus the amount collected on the parallel sample cartridge provides an estimate of the total amount expected on the spiked cartridge at the end of the sampling period assuming no losses. This value was compared to the actual amount measured on the spiked cartridge to assess recovery.

The collection efficiency of the sampling cartridges was evaluated during two separate experiments by placing a second sampler cartridge containing XAD-4 in series behind the primary sample cartridges. The primary cartridge was spiked on the leading face of the PUF with a known quantity of standard containing the analytes of interest prior to use as described above, and run in parallel with a second sampler that was not spiked with standard. The collection efficiency was calculated as $1-(m_b/m_p)$ where m_p is the mass of analyte measured in the primary sampler and m_b is the mass of analyte measured in the backup sampler.

SVOC Sampling Extraction

The PUF and XAD were extracted with 1:1 acetone:hexanes by ASE with the same conditions as used in the sorbent matrix cleanup. The extraction was repeated twice and all extracts for the sample were combined in a single concentration tube then concentrated under high purity N₂ to 0.5 ml using a Zymark TurboVap Concentration Station. The concentrated extract was transferred along with a 0.5 ml solvent wash of the concentration tube into an amber auto sample vial. After extraction, the samples were transferred along with the chain of custody form to the University of California (UC), Berkeley, (Prof. Hammond's laboratory) for analysis.

As with the VOCs, the quantified target analytes represent only a fraction of the peaks in a full scan GC/MS analysis of the extracts. Because several different detectors were used for the different analytes, there was no estimate made for the fraction of peaks that were actually identified.

SVOC Selection and Analysis

After extraction of the sample cartridges, the chemical analysis followed several different pathways depending on the chemical class being quantified. The methods are described below along with a detailed table of target chemicals selected in each class.

Polycyclic Aromatic Hydrocarbon (PAH) Analysis

The PAH analytes are listed in Table 11, along with quantification and confirmation ions and GC retention times. A 2000 µg/ml standard solution of the 16 PAHs, in benzene/methylene chloride from Supleco was serially diluted to concentrations of 250, 50, 25, 10, 5, and 2 ng/ml. Dilutions from the stock solution were prepared for each two-week period of analysis, and a full set of standards were run at least once on each day of analysis. All solutions were stored at -20°C (-4°F).

Table 11. Target polycyclic aromatic hydrocarbons in Phase I screening study

Chemical name	CAS#	Ions Monitored (m/z)	Retention Time (min)
Naphthalene	91-20-3	128, 102	11.6
Acenaphthylene	208-96-8	153,152,151,150	19.4
Acenaphthene	83-32-9	153,152,151,150	20.0
Fluorene	86-73-7	166	22.4
Phenanthrene	85-01-8	188,184,178,152	27.6
Anthracene	120-12-7	188,184,178,152	27.7
Fluoranthene	206-44-0	212,202,184,156,101	33.5
Pyrene	129-00-0	212,202,184,156,101	34.9
Benz(a)anthracene	56-55-3	228,113	40.8
Chrysene	218-01-9	228,113	41.2
Benzo(b)fluoranthene	205-99-2	253,252,250,125,126	46.7
Benzo(k)fluoranthene	207-08-9	253,252,250,125,126	46.9
Benzo(a)pyrene	50-32-8	253,252,250,125,126	49.5
Indeno(1,2,3-cd)pyrene	193-39-5	279,278,276,139,138	61.2
Dibenz(a,h)anthracene	53-70-3	279,278,276,139,138	61.6
Benzo(ghi)perylene	191-24-2	277,276,138,137	65.2

m/z = mass to charge ratio

All PAH analyses were performed on a Hewlett Packard model 6890 GC equipped with an Agilent 5972 Mass Spectrometer. A 30-m DB-17MS, (50%-Phenyl)-methylpolysiloxane fused silica capillary column, (0.25-mm (ID) inner diameter and 0.25- μ m film thickness) was used for separation. The inlet and detector temperatures were 305°C (581°F) and 280°C (536°F), respectively. The initial oven temperature was 65°C (149°F), then ramped at 5°C (2.78 °F) per minute to 280°C, held for 20 minutes and then ramped at 10°C (5.56 °F) per minute to 310°C (590°F) and held for five minutes. The MSD was operated in the selected ion-monitoring mode for enhanced sensitivity. Mass ions were previously identified by analyzing known standards in "Scan" mode and selecting the ions with the greatest abundance.

Polybrominated Diphenyl Ether (BFR) Analysis

The BFR congeners are listed in Table 12, along with the congener numbers and the GC retention times. A 2500 ng/ml stock solution of BFR congeners in nonane from Cambridge Isotope Laboratories was serially diluted to concentrations of 625, 250, 50, 25, and 5 ng/ml. The concentrations for DecaBDE (#209) were higher, and ranged from 12.5 μ g/ml to 12.5 ng/ml. Dilutions from the stock solution were prepared for each two-week analysis period, and a full set of standards were run at least once on each day of analysis. All solutions were stored at -20°C.

All analyses were performed on a Hewlett Packard model 6890 GC equipped with an Electron Capture Detector (ECD). A 15 m DB-XLB low bleed, fused silica capillary column, ID 0.25mm and film thickness 0.1 μ m, was used for separation. The inlet temperature and detector were 305°C (581°F) and 340°C (644°F), respectively. The initial oven temperature was 100°C (212°F), then ramped at 20°C (5.56 °F) per minute to 340°C and held for 20 minutes.

Table 12. Target brominated diphenyl ethers (BDE) in the Phase I screening study

Chemical Name	IUPAC#	Retention Time (min)
2,2',4'-TriBDE	17	6.6
2,4,4'-TriBDE	28	6.8
2,2',4,4'-TetraBDE	47	7.7
2,3',4,4'-TetraBDE	66	7.9
2,3',4',6-TetraBDE	71	8.0
2,2',3,4,4'-PentaBDE	85	8.6
2,2',4,4',5-PentaBDE	99	8.9
2,2',4,4',6-PentaBDE	100	9.3
2,2',3,4,4',5'-HexaBDE	138	9.4
2,2',4,4',5,5'-HexaBDE	153	9.7
2,2',4,4',5,6'-HexaBDE	154	10.2
2,2',3,4,4',5',6-HeptaBDE	183	10.6
2,3,3',4,4',5,6-HeptaBDE	190	11.1
DecaBDE	209	14.5

IUPAC = International Union of Pure and Applied Chemistry

Organophosphate Analysis

The OP analytes are listed in Table 13 along with GC retention times. Standards were prepared by weighing approximately 34 mg of each organophosphate into a 10 ml volumetric cylinder and diluting to final volume with heptane. For Tris(2-chloroethyl) phosphate (TCEP), 25 μ L of the pure liquid was pipetted into a 10 ml flask and diluted with heptane. The resulting stock solutions were then serially diluted to concentrations of 13.2, 33, 165, and 825 ng/ml, providing a four-point calibration curve. Standards were purchased from Sigma-Aldrich. Dilutions from the stock solution were prepared for each two-week period of analysis, and a full set of standards was run at least once on each day of analysis. All solutions were stored at -20°C .

Chemical analyses were performed on a Hewlett Packard model 5890 Gas Chromatograph equipped with a Nitrogen-Phosphorous detector (NPD). A 15-m DB-5 column with 0.32- μ m diameter and 0.25- μ m film thickness was used for separation. The inlet and detector temperatures were 250°C and 300°C , respectively. The initial oven temperature was held at 80°C for one minute, and then increased at 10°C (5.56°F) per minute to 120°C ; then increased by 30°C (16.67°F) per minute to a final temperature of 160°C (320°F). The baseline output of the NPD was kept at approximately 30 milliamps for the analysis.

Table 13. Target Organophosphates in the Phase I screening study

Chemical Name	CAS#	Acronym	Retention Time (min)
Triethyl Phosphate	78-40-0	TEP	4.8
Tributyl phosphate	126-73-8	TBP	11.6
Tris(2-chloroethyl) phosphate	115-96-8	TCEP	12.9
Triphenyl phosphate	115-86-6	TPP	19.0
Tris(2-butoxyethyl) phosphate	78-51-3	TBEP	19.3
Tris(2-ethylhexyl) phosphate	78-42-2	TEHP	20.0

CAS# = Chemical Abstract Service Number

Particle Sampling and Analysis

Particle concentrations were monitored using a variety of methods to characterize particle number and mass along with measures of black carbon, elemental carbon, and organic carbon. The particle sampling methods used in Phase I are summarized below.

Particle Number Count

Ultrafine particle number concentrations (particle number per cc, or PNC) were monitored either continuously or at designated intervals throughout the duration of each printer and computer screening experiment using a P-TRAK (TSI Inc.) condensation particle counter. This device allows for the detection of emissions of ultrafine particles (20 nm to > 1 µm). Samples were typically collected for one hour using a one-minute averaging time for the computers and collected continuously for the duration of the study for the printer runs.

Black Carbon, Elemental Carbon, and Organic Carbon

Semi-continuous concentrations of black carbon (BC) were tracked during the printer experiments with a portable aethelometer (Magee Scientific) operated in 7-LED mode. The aethelometer measures visible light absorption of particles collected on a quartz filter tape over time periods of a few minutes to 10 minutes. For this study, the integration time was set to five minutes, as recommended in the instrument users manual for a typical urban sampling event, and the sampling rate at 3.3 lpm, which is in the midrange for recommended sampling event duration in the instrument users manual.

Particles for EC/OC analysis were collected directly from the chamber onto quartz fiber filters (37 mm TissuQuartz®, Pall Corp.) at 20 lpm for 24 hours. Filters were pre-cleaned by baking in muffle furnace overnight at 500°C (932°F). Following collection of particles, the filters were packaged along with several blank filters and shipped FedEx to Sunset Labs, where they were used to determine elemental carbon and organic carbon content following National Institute for Occupational Safety and Health (NIOSH) method 5040.

Particle Mass

The original proposal included the use of a nephelometer to assess temporal fluctuations in particle mass concentrations and to evaluate the degree to which integrated samples collected over different periods represent conditions throughout the experiments. However, the literature review showed that particles emitted from printers were almost exclusively in the ultrafine size range, so it was determined that the particle number concentration measurements were adequate to assess fluctuations in particle emissions. To determine integrated particle mass concentrations, samples were collected on pre-weighted Teflon filters (37 mm, Teflo®, Pall Corp.) that were weighed using a Cahn 21 Automatic Electrobalance and stored in Petri dishes until use. Duplicate samples were collected in parallel by pulling chamber air directly from the chamber through each filter at 20 lpm for 24 hours. The 24-hour sampling period was selected to provide adequate integrated mass. Earlier studies found that particles emitted from printers are mostly in the ultrafine size range (< 100 nm) with no particles greater than 1 µm (Kagi et al. 2007; He et al. 2007; Seeger et al. 2006; Uhde et al. 2006; Wensing et al. 2006) so no size-selective sampling heads were used in this study. The filters were re-weighed on at least two separate

occasions both before and after deployment. Since they do not readily absorb water, Teflon filters are generally much less sensitive than quartz filters to variations in ambient relative humidity. Nevertheless, filters were equilibrated for a minimum of 24 hours at $T = 21 \pm 3^\circ\text{C}$ and $\text{RH} = 30\% - 40\%$ for at least one weighing before sampling and one weighing after sampling. A subset of unused filters was also weighed with each group of sample filters to confirm consistent operation of the balance and to quantify measurement uncertainty of each weighing event. The percent coefficient of variation for weights collected on four different filters on different days ranged from 0.01% to 0.1%.

Ozone

Ozone levels were evaluated continuously during operation of each of the equipment categories using an ultraviolet photometric ozone analyzer (Model 400; API Inc.) calibrated prior to the beginning of the project.

3.1.3. Summary of Phase I Quality Assurance Procedures

Recovery of spiked SVOCs from sampling media (PUF) was evaluated for three experiments, using prepared sample cartridges that were spiked in the lab and extracted immediately. An additional SVOC sample cartridge was spiked in the lab and deployed to the chamber for a full sample collection period (12 hours) and installed with a backup cartridge to assess both breakthrough (collection efficiency) and recovery. Duplicate samples were collected and compared for the SVOCs ($n=5$ pairs), VOCs ($n=11$ pairs), aldehydes ($n=16$ pairs), particulate matter determination ($n=2$ pairs), and EC/OC determination ($n=3$ pairs). The duplicate SVOC samples from the Phase I desktop experiment were combined to increase sample volume. Blank chamber measurements for the integrated samples (SVOC, VOCs, and aldehydes) were typically collected before and after each emission experiment. A total of 20 chamber blanks and 10 process blanks were analyzed during Phase I. For continuous measurements such as the particle number concentration and ozone, the blank chamber measurements were collected periodically throughout the duration of the study. Method detection limits (MDL) for the SVOC, VOC, and aldehyde measurements in Phase I were based on the larger of either the lowest calibration point in the chemical analysis or three times the baseline instrument signal (noise) in the analyses. Further details of the project quality objectives and measurement quality objectives are provided in Appendix B, with an emphasis on actions taken to assure sample analysis quality.

3.2. Phase I Screening Experiments: Results

Three sets of results are presented below for the Phase I experiments. The first set includes results from the initial experiment with laptop computers. This experiment was not part of the proposed work plan but was used to set up and test the chamber. It expanded the pool of computers considered, providing key insights for the next two experiments, and gave results that provided context for later computer experiments. The second set includes results from the desktop computer experiment. The third set includes results from the printer experiments. All of the results are first provided as concentrations in chamber air normalized to one air change per hour (ACH) in the chamber. In some cases these concentrations have been translated into preliminary estimates of emissions factors expressed as $\mu\text{g}/\text{unit}/\text{hr}$. For continuous emissions,

these emission factors are obtained by dividing the concentration by the number of devices in the chamber, multiplying that number by the volume of the chamber (20 m^3), and then multiplying that number by 1 ACH (hr^{-1}). In the case of particulate-matter emissions from printers, where there were intermittent particle emissions and active/idle periods, it was not informative to express this as an emission factor on a time or unit basis. For printers, emissions factors could only be developed in Phase II experiments.

3.2.1. The Initial Laptop Experiment

An initial full-scale chamber experiment was run using laptop computers to test and optimize chamber conditions and to verify methods. The experiment used a sample of five laptop computers of differing ages and from a range of manufacturers. This was a convenience sample, in that the laptops were simply selected from staff at UC Berkeley and LBNL. Figure 2 illustrates the chamber conditions and experimental timeline for the laptop experiment. Stage *A* represents the empty chamber during its conditioning over several days with the goal of determining background levels for all target substances. Stage *A* air samples were collected just prior to loading the computers in the chamber. Stage *B* represents the chamber with computers installed but not running with samples collected and measurements made just prior to turning on and initiating the computer duty cycles. Stage *C* was the actual emissions phase of the study, with all computers running. Stage *C* included three separate sampling and measurement events for target substances emitted from operating computers. Stage *D* was the post emissions phase after the computers had been removed when a second determination of chamber background was made. Ozone was measured continuously throughout all stages of the experiment. Other target analytes for the laptop experiment were aldehydes, SVOCs (PAHs, BFRs, OPs), and particulate matter. Because methods for VOC emissions were already well calibrated, VOCs were not considered in the laptop experiment.

Environmental conditions in the chamber were recorded through each stage. The measured temperature ($^{\circ}\text{C}$), percent relative humidity, pressure differential (in pascals [Pa]), and air exchange rate (h^{-1}) in the chamber (\pm one standard deviation) were respectively $21.9 (\pm 0.8)$, $36.5 (\pm 6.6)$, $7.5 (\pm 0.8)$, and $0.95 (\pm 0.02)$, over the course of the experiment. The ACH was tracked continuously during all stages with a calibrated air-flow venturi meter on the chamber inlet.

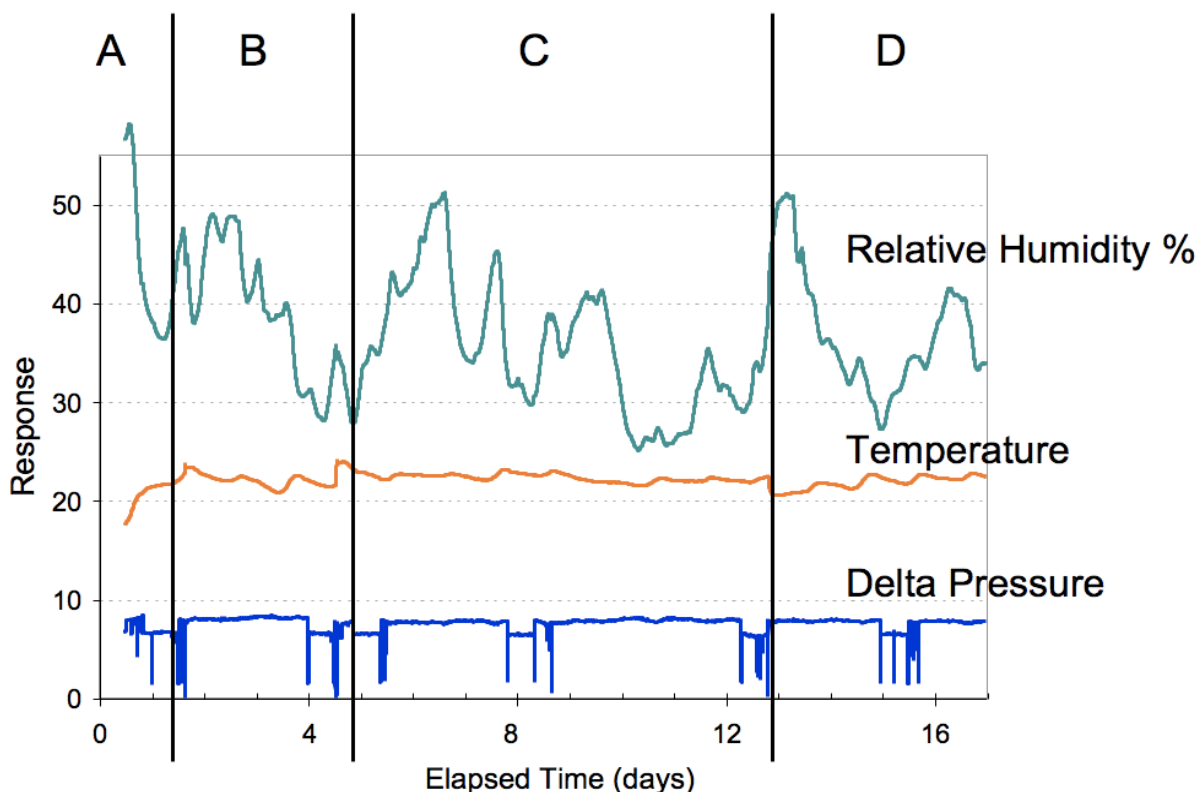


Figure 2. Experimental stages, including: (A) pre-experiment conditioning of the chamber; (B) chamber loaded with computers; (C) computers running, and (D) chamber after computers were removed. The environmental conditions shown in the figure include Delta Pressure, which is the difference between internal and external pressure (Pa) in the chamber (a drop in pressure indicates a sample was being collected), Relative Humidity, which was not controlled so the value roughly tracked changes in the ambient air conditions, and Temperature (C°).

Recovery Analyses and Detection Limits

Standard recovery analyses were run prior to the laptop experiments. Because of extensive experience with VOCs and aldehydes at LBNL, the focus of the experiment was on SVOCs for confirming detection and recovery. Analyses were run in triplicate for the SVOCs using spiked PUF cartridges. The results showed excellent performance for the PAHs, with recoveries ranging from a low of 84% ($\pm 7\%$) for naphthalene to a high of 124% ($\pm 8\%$). The BFR target compounds also showed good recoveries, ranging from a low of 71% ($\pm 10\%$) for PBDE#190 to a high of 119% ($\pm 11\%$) for PBDE#47. The exception for the BFRs was the deca congener, PBDE#209, where the recoveries from the spiked matrix were zero for all three replicates. Further investigation revealed that the PBDE#209 was being lost in the GC. Once the GC inlet, seal, and column were replaced, good recoveries were obtained for all BFR standards. The full recovery experiment was not repeated, although subsequent analyses of PUF extracts again altered the GC such that PBDE#209 was not recovered. This was later determined to possibly be related to the polyurethane foam extract, as reported by Charles et al. (2005), but changes to the sample media were not made until Phase II of the study (see Section 4.1.6 for details of the Phase II SVOC sampling). As a result, PBDE#209 is not reported for Phase I. For the target OP

flame retardants, initial recovery results were not satisfactory with recoveries ranging from a low of 66% ($\pm 31\%$) for TEP to a high of 272% ($\pm 54\%$) for TEHP, indicating interference by co-eluting contaminants. In addition, TEBP was not recovered. Because the Nitrogen/Phosphorous Detector (NPD) was used in the OP method, the researchers suspect high nitrogen containing background from the PUF sorbent material. To address this issue, the cleanup method was modified prior to the laptop experiment to include a hot methanol wash to remove polar nitrogen containing compounds prior to the laptop experiment. A second recovery experiment run during the collection efficiency determination again found PAH recoveries in the range of 74%–102% and for BFRs the recoveries ranged from 60%–143%, except for a very high calculated recovery for PBDE#28 possibly due to elevated background in the sample media and, as indicated above, a loss of the deca congener. For the OP flame retardants, the recoveries still lacked precision, ranging from zero (TEHP) to 380% (TCEP), even after changing the cleanup method to reduce background nitrogen containing compounds. Further modifications to the method were not possible due to scheduling, so the reported OP results should be considered preliminary.

Collection efficiency (breakthrough) of the SVOC sampling cartridges from field spikes, and blank cartridges were all evaluated during the laptop experiment. For the PAHs, collection efficiencies were generally near 100%. The one exception was acenaphthene for which the calculated collection efficiency was 51%. For BFRs, the collection efficiencies were also near 100% for all target chemicals except for PBDE#28—due to the elevated background. For the OP flame retardants, the collection efficiencies were near 100%, but the recoveries still lacked precision as indicated above.

The next set of experiments was carried out without performing formal measurements of method detection limits (MDL) or the limits of quantification (LOQ) for the SVOCs. However, an approximate MDL was estimated for PAHs based on the previous experience of the laboratory. This MDL likely was 0.2 ng/m^3 for the laptop experiment and 0.1 ng/m^3 for the remaining experiments, this decrease being due to a larger sample volume. An approximate MDL for BFRs was estimated to be three times the background signal. This MDL was about 5 ng/m^3 for the laptop computer experiment and 2.5 ng/m^3 for the remainder of the experiments. An approximate MDL for the OPs was estimated to be three times the standard deviation of the three measured values from spiked PUF. This MDL was about 30 ng/m^3 for the notebook computer experiment and 15 ng/m^3 for the remaining experiments, with TBEP excluded because of an interfering peak. Formal experiments to determine MDL and LOQ were not performed because of the screening nature of the Phase I experiments. It was anticipated that these factors would be calculated during Phase II but only for chemicals that were found in the emissions stream during the Phase I experiments.

Measured Concentrations of Selected Target Compounds

The laptop experiment provided an opportunity to collect, measure, and evaluate chamber air concentrations for SVOCs including PAHs, BFRs, and OPs; low molecular weight aldehydes; particulate matter; and ozone. There was a slight increase in total PAH emissions when computers are placed in the chamber, with a further increase when the computers are turned

on, followed by a steady decline as the computers continue to run. These changes appear to be primarily due to naphthalene, and to a lesser extent, acenaphthene. The PAHs heavier than pyrene were not detected.

The measurements were well below our approximate MDL for BFRs, although the field spike recovery sample collected at stage *D* in parallel with the actual sample (as described above) demonstrated that the collection efficiency and recovery of target chemicals (with exception of the PBDE#209) were adequate under the experimental conditions used.

Chamber concentration analyses for OPs included TBEP, TEP, TEHP, TBP TPP, and TCEP. The results for TBEP were excluded due to interference in the chromatography, and results for TEP were excluded due to significant levels in the field blank sample (i.e., > 110% of the measured values during the emissions phase of the experiment). TEHP was not detected. Of the three remaining target OPs, both TBP and TPP had elevated levels in the field blank. For TBP, the levels in the field blank sample were between 14%–75% of the values measured during the emissions phase, and for TPP the field blank levels were between 34%–52% of the emission phase values. Much of the increase for OPs during the emissions phase of the experiment was attributed to the TCEP, but this compound was elevated prior to installing computers in the chamber. The elevated concentration of TCEP measured during time Stage *A* was attributed to use of only one of the parallel samplers. The second sample collected during that time period had no detectable levels.

The concentrations of the target volatile aldehydes measured in the chamber with aged laptops were generally low relative to the LOQ, with no discernable increase in chamber concentrations when the laptops were installed and/or running. The low aldehyde concentrations were typical for all experiments.

Particle number concentration measured with the condensation particle counter and ozone concentrations measured continuously were both unchanged for the duration of the experiment. The air entering the chamber was filtered, so background concentrations in the chamber were typically less than 100 particles/cc, with a low coefficient of variation, while air in the room that housed the chamber ranged from 2000 to 4000 particles/cc. Ozone in the chamber was constant throughout the experiment, at 1.1 (± 0.5) ppb.

Lessons from the Laptop Experiment

The laptop experiment provided an opportunity to perform a pilot experiment in the full-scale chamber. This provided both training and insight for all future experiments, allowed for the optimization of chamber conditions, verification of methods, and an opportunity to identify potential problem areas. Standard recovery analyses were run prior to the laptop experiments, addressing all analytes but with attention on SVOCs for confirming detection and recovery. The results showed excellent performance for all VOCs and the PAHs. Following an initial problem with the deca congener, PBDE#209, which required column replacement in the GC, good recoveries were obtained for all BDE standards. For the target OP flame retardants, initial recovery results were not satisfactory—the collection efficiencies were near 100%, but the recoveries still lacked precision, even after changing the cleanup method to reduce background

nitrogen containing compounds. This indicated the need for an additional sample cleanup step and/or a different detection method.

3.2.2. Desktop Experiment Results

The desktop emission experiment was conducted with five new or recently purchased computers, all with flat-screen LCD monitors. All units were equipped with keyboard and mouse. Speakers were installed if available in the purchase package. Details on the desktop computer units were provided earlier in Table 6.

Figure 3 illustrates the chamber conditions and experimental timeline for the desktop experiment. The experimental stages are as described for the laptop experiment, where Stage *A* represents the empty chamber prior to loading computers, Stage *B* represents the chamber with computers installed but not running, Stage *C* represents the three different sampling times during the actual emissions phase of the study with all computers running at full capacity, and Stage *D* is the post-emissions phase, where the computers had been removed and the chamber allowed to re-equilibrate. Ozone was again measured continuously throughout the duration of the experiment, and the target chemicals and particle counts were collected for each experimental stage.

There was a time delay between stage *B* and *C* in the desktop run because of problems with heat buildup in the chamber. The five computers put out quite a bit of heat (computer power use provided in Table 6) so it was necessary to run a chiller on the input air and to increase the air exchange rate to maintain temperatures within appropriate ranges. This is illustrated in Figure 3. The need for this modification was not discovered until after Stage *B* had been completed. Rather than use a calibrated venturi-style flow meter to measure the higher air flow rate, the research team tracked the air changes by periodically injecting carbon dioxide (CO₂) into the chamber as a tracer gas for decay curve calculation (see Appendix C).

The chilled air input also reduced the relative humidity in the chamber, and the higher air exchange rate increased the pressure slightly for the Stage *C* sampling points and during Stage *D*. The chamber conditions prior to the use of the chiller on the air inlet were 23.7 (± 1.0)°C, 33.7 (± 8.1)%, 6.0 (± 0.7) Pa, and 0.98 (± 0.01) h⁻¹ respectively for temperature, percent relative humidity, pressure differential, and air exchange rate, respectively. After the chiller was installed, the temperature, percent relative humidity, pressure differential, and air exchange rate were, respectively, 30.1 (± 1.5)°C, 14.5 (± 1.5)%, 13.6 (± 0.6) Pa and 1.4 (± 0.03) h⁻¹.

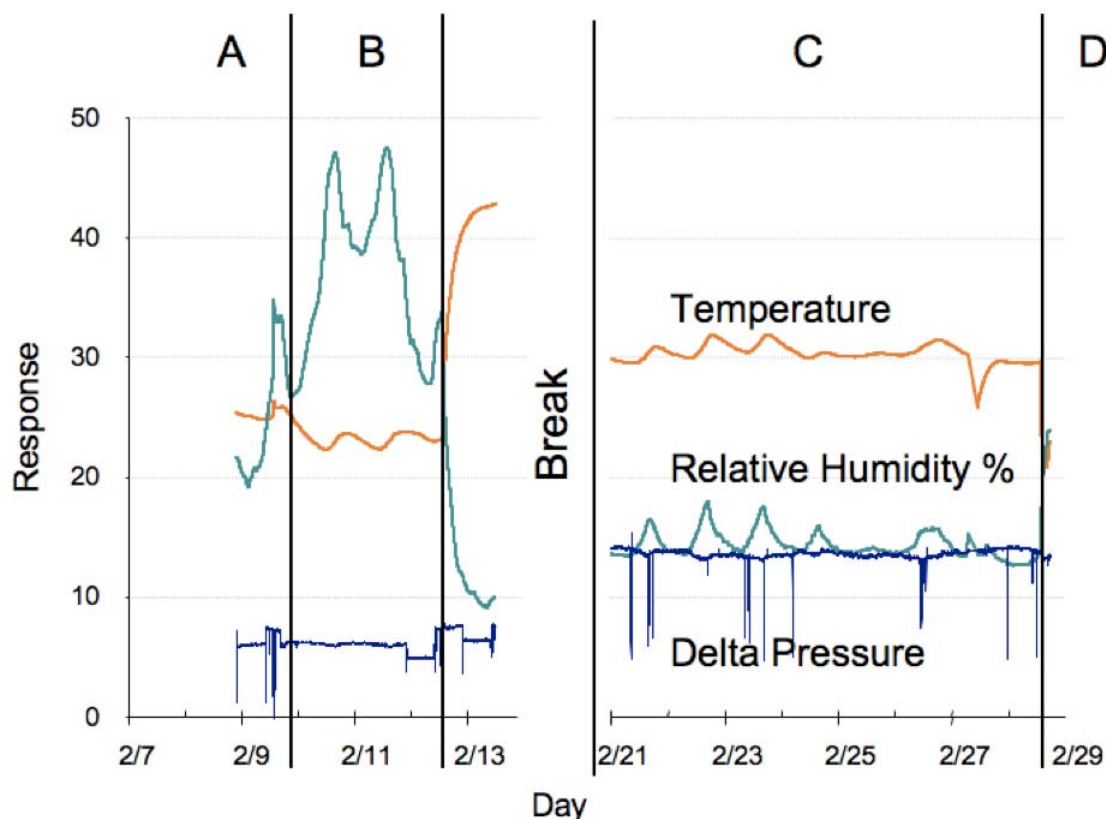


Figure 3. Experimental timeline and chamber conditions for Desktop experiment. The break between stage *B* and *C* was due to modifications to the chamber conditions that were needed to compensate for the heat load from the desktop computers and monitors. The Stage D sample was collected prior to the start of the printer experiments 8 days after the computers were removed from the chamber.

Although the relative humidity during the emissions phase of the desktop experiments was below the intended target range for the experiments, it is not expected to have a significant impact on the screening-level measurements. There are related experimental studies that support this assumption. Wolkoff (1998) studied the influence of several environmental factors on emission and found no change in the emissions of measured VOCs from polyvinyl chloride (PVC) material with changes in relative humidity. In another study, the influence of relative humidity on VOC emissions from other building materials differed, depending on the type of material (wood, paint, lacquer, or carpet) and the chemical under study (Haghighat and De Bellis 1998; Wolkoff 1998). Overall, a low relative humidity did not consistently increase or decrease emission of VOCs from building material.

VOC Concentrations and Emissions

Results for the VOCs that were positively identified (measured at levels above the MDL) in this experiment are summarized in Table 14 and illustrated in Figure 4. These results represent approximately one-third of the total VOCs recorded in the chromatograms from the emission

phase of the experiment, many of which were only tentatively identified (as aromatic or phenolic compounds) or remain unknown. The results in Figure 4 show an initial increase in chamber concentrations after the computers were installed, then another increase when the computers were turned on, followed by a steady decline over the duration of the experiment.

Concentrations of low molecular weight carbonyls including formaldehyde, acetaldehyde, and acetone were not elevated over background ($\sim 1 \pm 0.4 \mu\text{g}/\text{m}^3$) during computer operation and are not reported.

Table 14. Average chamber concentration ($\mu\text{g}/\text{m}^3$) of VOCs normalized to 1 ACH in Phase 1

<i>Chemical</i>	<i>Stage A</i>	<i>Stage B</i>	<i>Stage C day 1</i>	<i>Stage C day 3</i>	<i>Stage C day 7</i>	<i>Stage D</i>
naphthalene	0.01	0.12	0.21	0.17	0.13	0.01
hexadecane	n.d.	0.41	0.70	0.54	0.42	n.d.
dibutyl phthalate	n.d.	0.14	0.46	0.54	0.24	0.14
benzene	0.04	0.06	0.07	0.12	0.16	0.05
2-methyl naphthalene	n.d.	0.07	0.11	0.09	0.07	n.d.
1245 Tetra-methylbenzene	n.d.	0.07	0.12	0.10	0.07	n.d.
13-diethylbenzene	n.d.	0.03	0.05	0.03	0.02	n.d.
123-trimethylbenzene	n.d.	0.08	0.14	0.10	0.07	n.d.
1-methyl naphthalene	n.d.	0.03	0.05	0.04	0.03	n.d.
1235 tetra-methylbenzene	n.d.	0.19	0.35	0.22	0.21	n.d.
acetophenone	0.02	0.24	0.41	0.36	0.31	0.02
diethyl phthalate	0.02	0.03	0.05	0.05	0.05	0.02
l-butyl benzene	n.d.	0.01	0.01	0.02	0.01	n.d.
n-butyl benzene	n.d.	0.03	0.05	0.03	0.03	n.d.
benzaldehyde	0.04	0.09	0.17	0.15	0.12	0.03
ethyl benzene	n.d.	0.93	1.68	1.31	1.00	0.02
n-propylbenzene	n.d.	0.05	0.08	0.06	0.04	n.d.
mesitylene	n.d.	0.06	0.11	0.08	0.05	n.d.
o-xylene	n.d.	0.76	1.33	0.99	0.73	0.01
styrene	n.d.	0.34	0.63	0.50	0.38	0.02
toluene	0.06	2.64	4.69	3.71	2.80	0.31

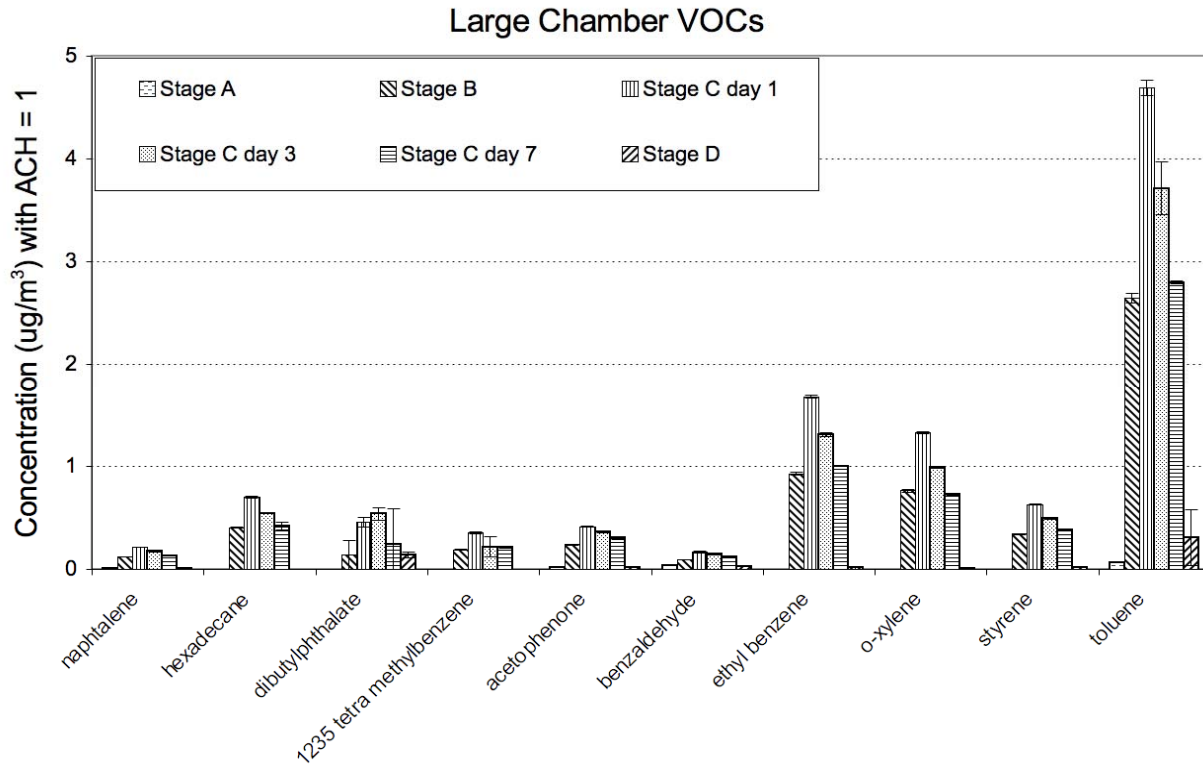


Figure 4. Results for identified VOCs in Phase I showing an initial elevation of concentrations with computers running (stage C). The concentrations of many VOCs steadily declined over time while the computers were running. The results represent the average of two samples collected in parallel. Actual values used to construct this figure are presented in Table 14. The error bars indicate the standard deviation.²

To assess emissions potential for computers, the results were converted to approximate emission rates. These emissions rates are obtained by assuming there are no significant net wall effects for the VOCs and then applying Equation 3-1.

$$E = \frac{(C - C_{bg}) \times ACH \times V}{n} \quad (3-1)$$

where E is the emission rate per computer ($\mu\text{g}/\text{h}/\text{unit}$), C and C_{bg} are the chamber concentrations for the VOC ($\mu\text{g}/\text{m}^3$) and the background concentration, respectively, ACH is the air change rate for the chamber concentrations (h^{-1}), V is the chamber volume (m^3), and n is the number of computers in the chamber during the experiment.

With the emission phase lasting over several days, the VOC concentrations are expected to have reached steady state. At these levels, there may be interaction with chamber walls but the net

¹ The standard deviation is reported in this document for results based on two or more samples. The statistic is reported to indicate the deviation between replicates but may not be reliable for decision-making or detailed analysis given the small sample size.

effect on concentration is likely to be negligible. Table 15 lists emissions rates obtained by applying Equation 3-1 to results in Table 14 with a chamber volume of 20 m³ and an ACH of 1 h⁻¹.

Table 15. Average emission rates in µg/h/unit (± standard deviation) for VOCs in Phase 1

<i>Chemical</i>	<i>First day</i>	<i>Last day</i>
toluene	70.0 (±1.34)	35.2 (±0.16)
ethylbenzene	24.4 (±0.3)	12.5 (±0.11)
o-xylene	19.5 (±0.025)	8.87 (±0.08)
hexadecane	9.52 (±0.17)	4.68 (±0.42)
styrene	8.61 (±0.11)	4.53 (±0.03)
acetophenone	7.42 (±0.14)	4.52 (±0.20)
1,2,3,5,-tetramethylbenzene	4.42 (±0.06)	2.35 (±0.03)
dibutylphthalate	4.38 (±0.47)	3.7 (±5.2)
naphthalene	3.5 (±0.0)	1.86 (±0.05)
benzaldehyde	2.90 (±0.0)	1.86 (±0.03)
1,2,4,5,-tetramethylbenzene	2.25 (±0.06)	1.17 (±0.03)
1,2,3-trimethylbenzene	2.05 (±0.03)	0.81 (±0.02)
2-methylnaphthalene	1.92 (±0.01)	1.01 (±0.03)
benzene	1.66 (±1.3)	2.04 (±0.54)
mesitylene	1.65 (±0.01)	0.65 (±0.01)
n-propylbenzene	1.24 (±0.02)	0.54 (±0.01)
diethylphthalate	0.91 (±0.32)	0.73 (±0.02)
1-methylnaphthalene	0.82 (±0.03)	0.48 (±0.01)
1,3-diethylbenzene	0.73 (±0.06)	0.29 (±0.02)
n-butylbenzene	0.68 (±0.01)	0.32 (±0.01)
isobutylbenzene	0.14 (±0.0)	0.09 (±0.00)
Total	169 (±9)	88 (±7)

Phthalate Esters

Significant background phthalates in the SVOC methods prevented us from evaluating a comprehensive number of phthalates in the emission stream. However, two of the lighter phthalate esters (diethyl- and dibutyl-phthalate) were quantified with the VOC method in which samples were collected on Tenax cartridges. Because these results are of interest, they are included here even though the phthalates were not on the initial list of target analytes. Figure 5 presents the observed concentrations for one of these phthalates, dibutyl-phthalate (DBP), over the duration of the experiment. Dibutyl-phthalate did not show the same temporal pattern as the other VOCs, indicating that interaction with the chamber walls may be a factor that affects gas-phase concentrations. For DBP, there was an apparent buildup with concentrations approaching a steady state concentration of around 500 ng/m³, while the other VOCs reached steady state concentrations more quickly. For DBP, the concentrations decayed slowly after the computers were removed from the chamber, while the other VOCs quickly returned to background levels. The slow clearance for DBP may be due to desorption from the walls of the chamber. Post-experiment blanks collected more than a week after the end of the experiment still showed measurable concentrations of DBP.

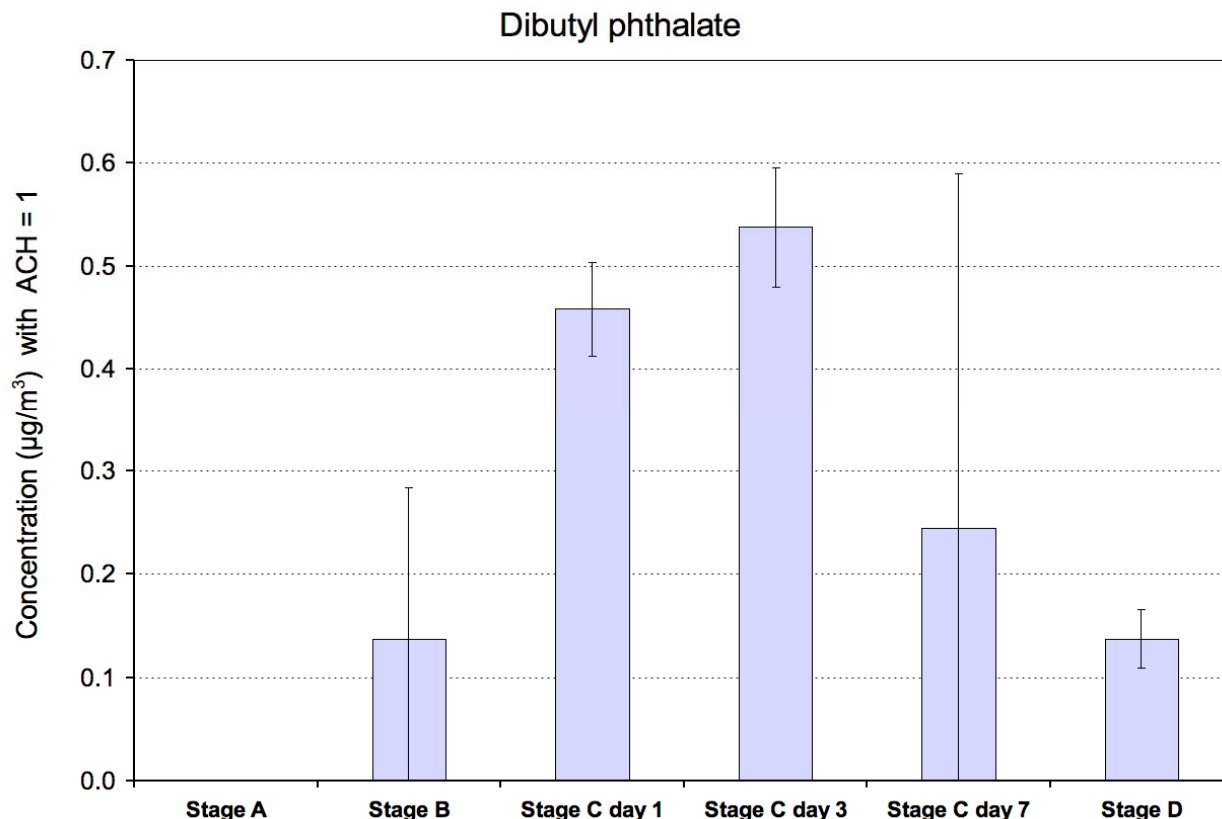


Figure 5. Concentration of phthalate ester showing possible chamber wall effects. Computers were removed from chamber on day 8. The results are the average of two samples with coefficient of variation (CV) ranging from a high of 107% to a low of 2%. Error bars represent ± 1 standard deviation from duplicate samples collected during each phase of the experiment. The statistic is provided to illustrate the deviation between replicates but the standard deviation based on only two samples may not be reliable for decision-making or detailed analysis.

SVOC Concentrations

Based on lessons learned from the laptop experiment, samples were collected for SVOC analyses at multiple time points and included several quality assurance (QA) samples. The parallel samples were combined after extraction, to increase the integrated air volume to 28.8 m³ to improve detection limits. Details for the individual chemical classes are presented below.

PAH Concentrations

The concentrations of PAHs in the chamber air for the three experimental stages are illustrated in Figure 6. Naphthalene levels were elevated when the computers were in the chamber, regardless of whether they were running or not. The other volatile PAHs (acenaphthylene through phenanthrene) were only slightly elevated over the blank chamber concentrations, and the low volatility PAHs (i.e., more than three rings) were not detected. Increased chamber temperature during the emissions phase of the experiment may have increased the amount of material volatilized from the chamber walls, contributing to the observed increase in concentration. However, prior to the emission phase the chamber temperature had increased to

over 40°C (104°F) for several hours. This was expected to reduce the amount of chemical sorbed to walls, so the contribution from wall evaporation of PAHs is expected to be negligible.

BFR Concentrations

Figure 7 illustrates the measured concentrations of BFR compounds obtained during different stages of the desktop experiment. The BFR results show a measurable difference among the blank chamber, the chamber with computers loaded, and the chamber with computers running. There is also the pattern of decreasing concentration that was seen with VOCs after Day 1. Many of these values are close to or below the qualitative MDL.

OP Concentrations

Measured concentrations of OP compounds (primarily flame retardants) obtained during different stages of the desktop experiment are illustrated in Figure 8. These results show that the concentrations of several of the target compounds were elevated during the emissions phase of the experiment as compared to the blank chamber, but all of the values are close to or below the qualitative MDL.

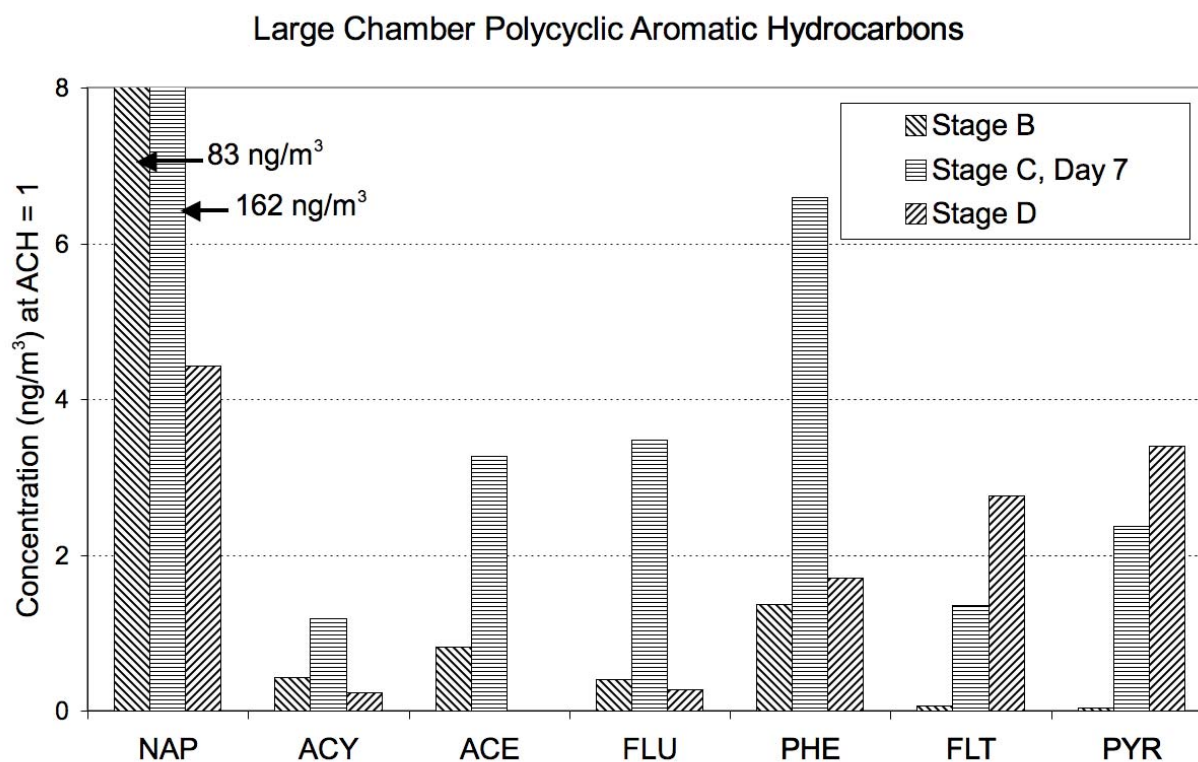


Figure 6. Results for PAHs from the desktop computer experiment. The Stage C sample was collected after 7 days of continuous operation of the computers and the stage D sample was collected 8 days after computers had been removed from the chamber. Anthracene and PAHs heavier than Pyrene were not detected.

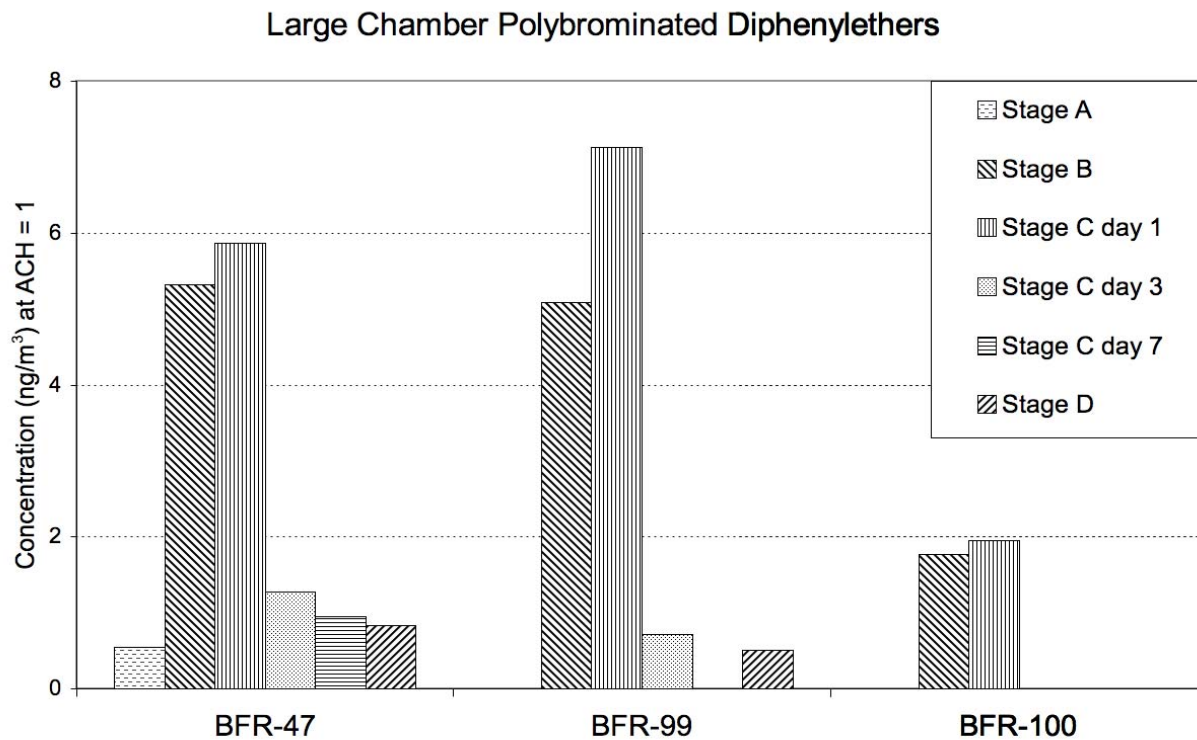


Figure 7. Results for BFRs in the desktop computer experiment show an initial increase for several congeners, with subsequent decreases as the computers aged.

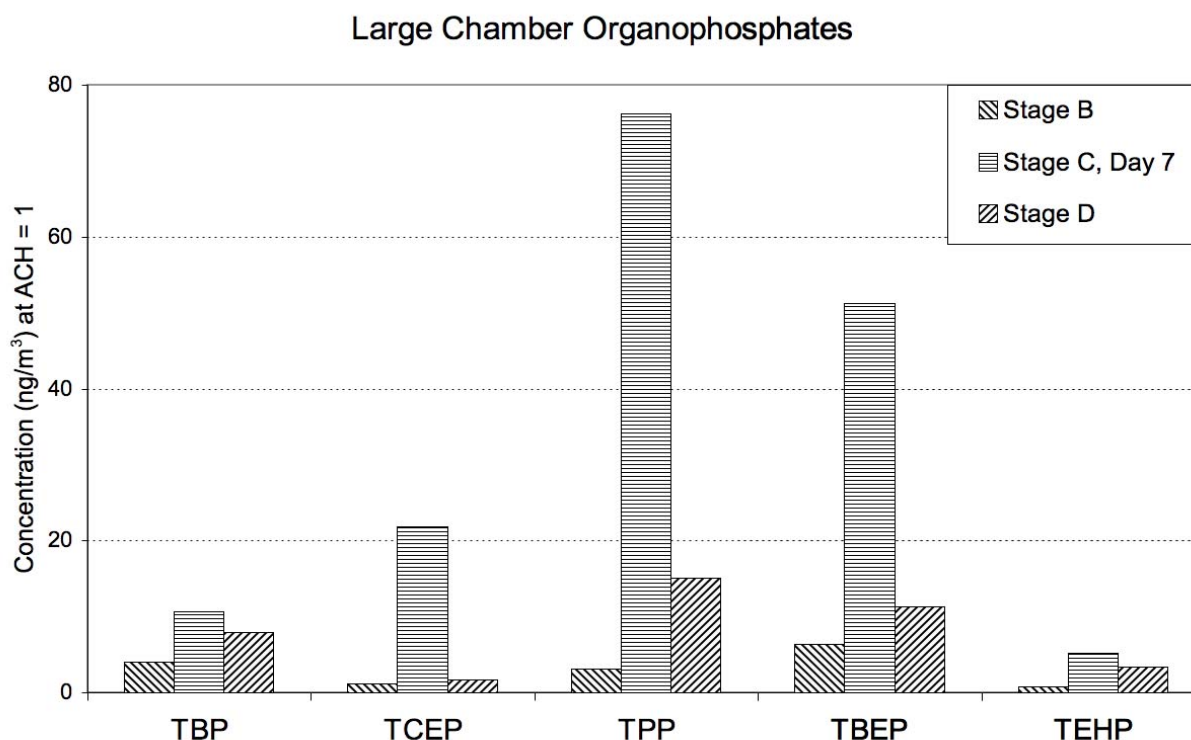


Figure 8. Results for OPs showing an increase in the concentration of several of the target chemicals during operation (Stage C) relative to the blank chamber (Stages B and D). TEP was not detected.

Particulate Matter and Ozone

Measured particle levels in the chamber during the desktop computers experiment were similar to levels during the preliminary laptop experiment, with measurements typically less than 100 particles/cc (details are provided in Appendix D, Section D.1). Ozone levels measured continuously in the chamber showed no difference with and without computers or with the computers operating.

3.2.3. Printer Experiment Results

Chamber concentrations for VOCs, aldehydes, SVOCs, ozone, particle number concentration, and particulate matter were obtained from three printer emission experiments. These three experiments were conducted in sequence. First with three medium-output laser technology printers, then with two high-output laser technology printers, and finally with five inkjet technology printers. Figure 9 illustrates a typical experimental timeline. Each set of printers was installed in the chamber and allowed to equilibrate at least 24 hours before printing was initiated. Each printer was then run in the chamber using sequentially-repeating print operations. These printing sequences were run for a period of approximately six hours of active printing, followed by approximately 18 hours idle. This print schedule was repeated for two consecutive days for each printer group. After the second day, the printers were removed, and the chamber was allowed to equilibrate for 72 hours before installing the next group of printers.

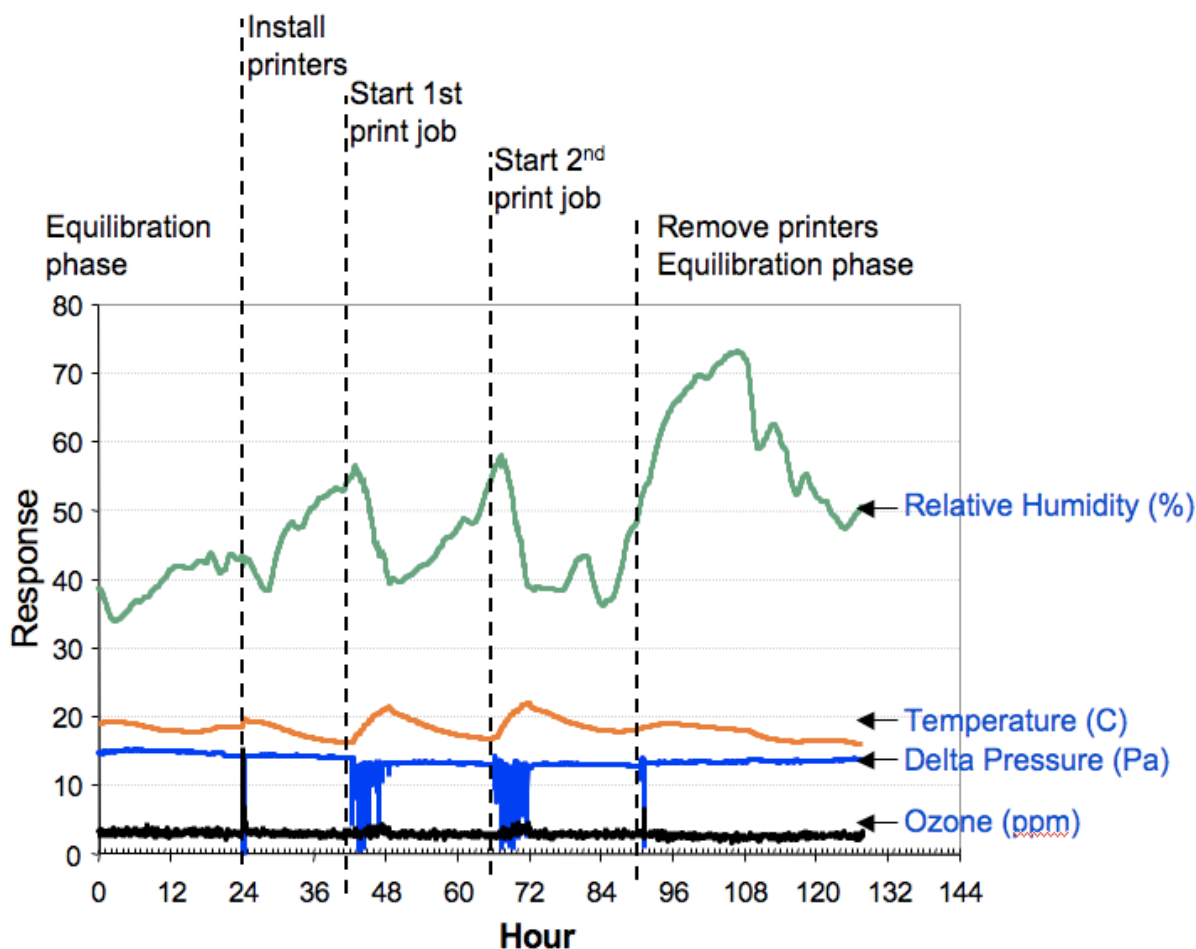


Figure 9. Chamber conditions during the medium-output laser printer emissions experiment. The experimental phases are listed across the top of the figure. This cycle was repeated for both the high-output laser printers and the inkjet printers.

Table 16 summarizes the chamber conditions during the roughly 72 hour period during which each set of printers was installed in the chamber. Fresh toner and ink cartridges were installed prior to the experiments. Because all of the laser technology printers and most of the inkjet printers selected for Phase I did not include color printing capability, all printers were operated in black and white mode for consistency. Details on the printers in each category are listed in Table 7.

Table 16. Chamber conditions (\pm standard deviation) during printer experiments in Phase 1

	<i>Number of Printers</i>	<i>Relative Humidity</i>	<i>Temperature (C°)</i>	<i>Delta Pressure</i>	<i>Air Exchange Rate (h⁻¹)</i>
High-output laser technology printers ⁽¹⁾	2	48.6 (\pm 5.3)	18.3 (\pm 0.5)	13.3 (\pm 1.1)	1.9 (\pm 0.03)
Medium-output laser printers ^a	3	45.8 (\pm 6.0)	18.7 (\pm 1.4)	13.3 (\pm 1.3)	1.9 (\pm 0.03)
Inkjet printers ^b	5	47.2 (\pm 5.5)	18.5 (\pm 0.9)	13.3 (\pm 1.3)	1.9 (\pm 0.03)

^a Based on four complete days of data, starting when printers were loaded into the chamber.

^b Inkjet conditions based on only two days of data, due to chamber malfunction on the second day of the print cycle.

VOC Concentrations

Volatile Organic Compound samples were collected during both the active (6-hour) and idle (18-hour) phases of each of two consecutive 24-hour emission experiments applied to each printer category. Concentration measurements for the high-output laser, medium-output laser, and inkjet printers are illustrated, respectively, in Figure 10, Figure 11, and Figure 12. These figures show an apparent initial increase in VOC concentrations during printing for the laser technology printers, with a decline over time. The increase in VOC concentrations with the high-output laser printers was primarily due to o-xylene (40%), toluene (11%), styrene (9%), ethyl benzene (7%), and hexadecane (7%). In the medium-duty laser printers, the increase in VOC concentrations was due primarily to toluene (26%), o-xylene (15%), styrene (13%), ethyl benzene (11%), and benzaldehyde (7%). The inkjet printers did not result in elevated VOC concentrations in the chamber.

Aldehyde Concentrations

There was no increase in the concentrations of low molecular weight carbonyls including formaldehyde, acetaldehyde and acetone for any of the printer experiments.

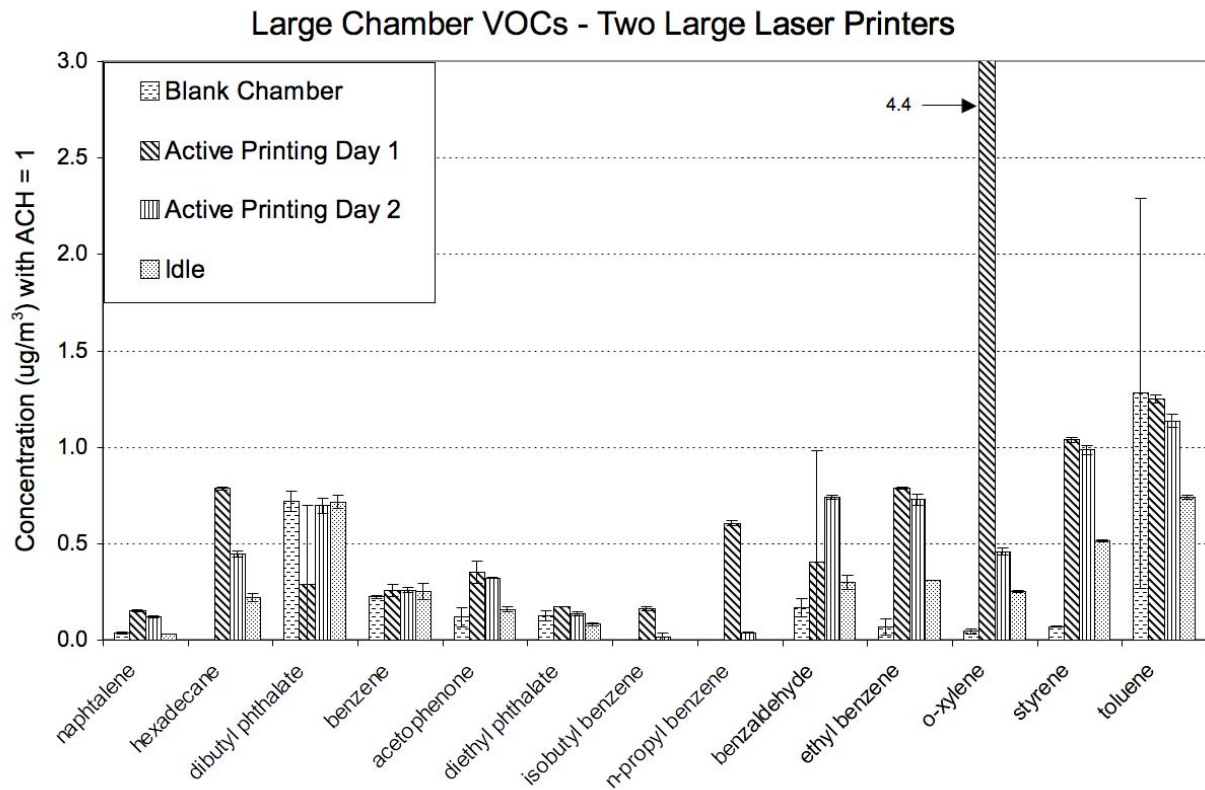


Figure 10. VOC concentrations ($\mu\text{g}/\text{m}^3$) during the experiment with two high-output laser printers. Included are results for the blank chamber without printers installed, two consecutive active printing periods, and the idle period after the second day's print job (the idle period after the first day's print job is not shown). Dibutyl phthalate and toluene concentrations in the samples were similar to those in the blank chamber. Error bars represent ± 1 standard deviation from duplicate samples collected during each phase of the experiment.

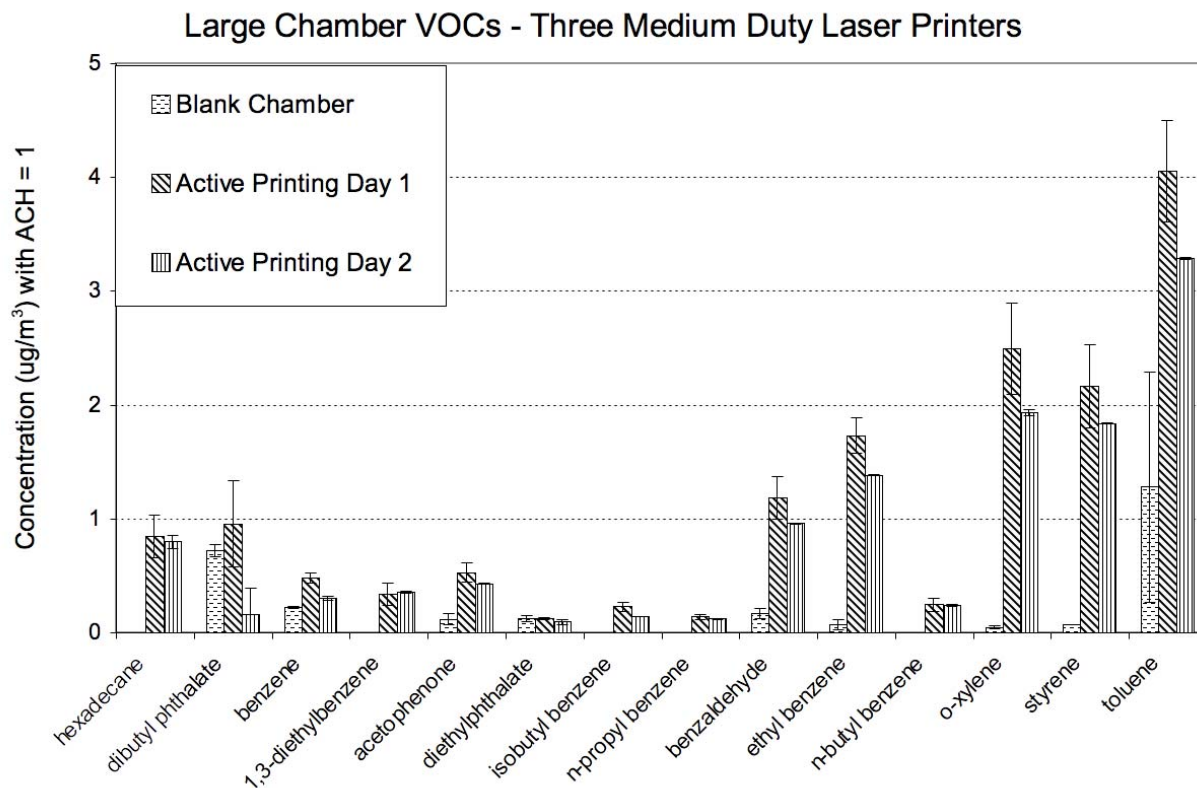


Figure 11. VOC concentrations ($\mu\text{g}/\text{m}^3$) during the experiment with three small (medium-output) laser printers. Included are results for the blank chamber without printers installed and two consecutive active printing periods. 1-methylnaphthalene and diethyl phthalate concentrations were similar to those in the blank chamber. Error bars represent ± 1 standard deviation from duplicate samples collected during each phase of the experiment.

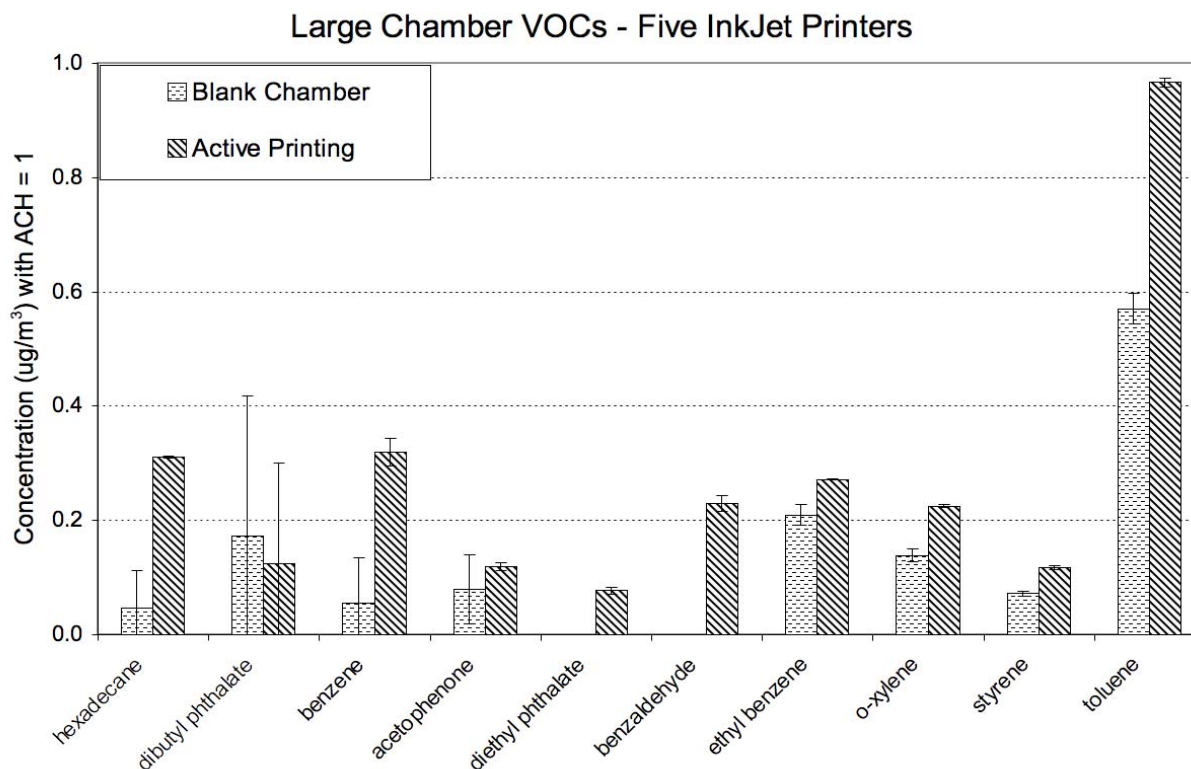
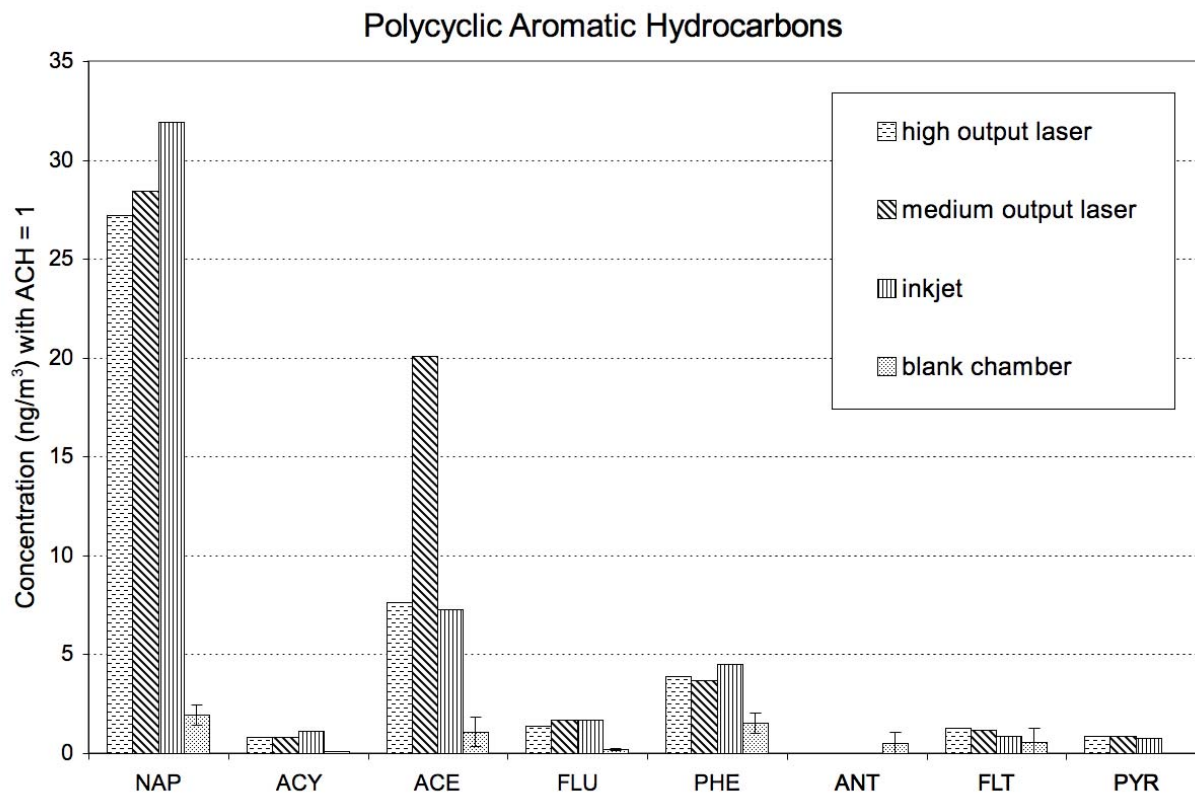


Figure 12. VOC concentrations ($\mu\text{g}/\text{m}^3$) during the experiment with five inkjet printers. Included are the results for the blank chamber without printers installed and the first day of active printing. The experiment was terminated following the first day's sampling because of a chamber malfunction. Error bars represent ± 1 standard deviation from duplicate samples collected during each phase of the experiment.

SVOC Concentrations

Semi-volatile organic compound samples were collected in parallel with VOC samples over the full 24-hour cycle (6 hours printing + 18 hours idle). Of the four SVOC samples (two active and two idle) collected for each printer group, only one was analyzed. The others were retained as needed for confirmation and quality control. The results for PAHs, BFRs, and OPs are illustrated in Figure 13, Figure 14, and Figure 15, respectively. The blank chamber results reported in these figures reflect the average (\pm standard deviation) of all blank samples collected for the office equipment emissions experiments ($n=4$). Except for a slight increase in naphthalene, all SVOC concentrations were near or below the background levels and/or the MDL. The elevated level of TCEP shown in Figure 15 may be significant but difficulties with interfering peaks in the OP analysis make the results uncertain.



NAP=Naphthalene, ACY=Acenaphthylene, ACE=Acenaphthene, FLU=Fluorene, PHE=Phenanthrene, ANT=Anthracene, FLT=Fluoranthene, PYR=Pyrene

Figure 13. Results for PAH measurements while printers were operating. Samples were integrated over 24 hours. The blank chamber results are the average \pm 1 standard deviation from four measurements.

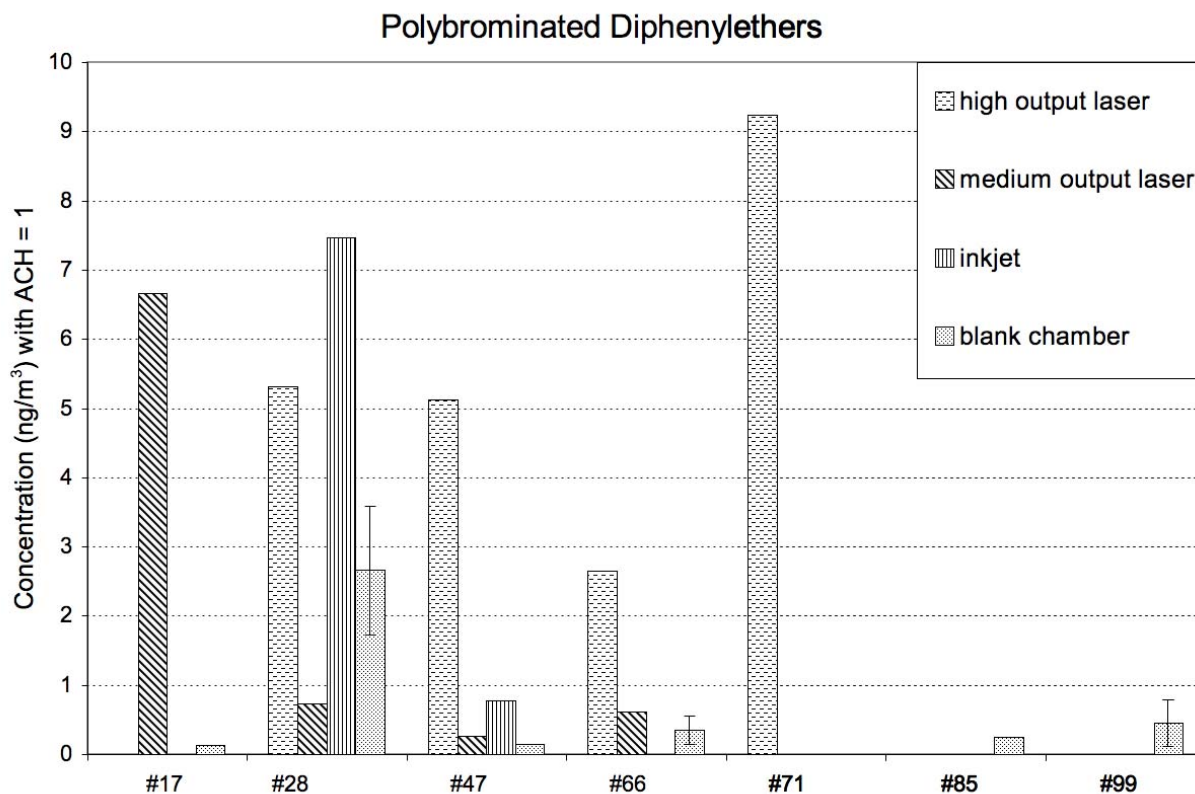


Figure 14. Results for BFR measurements while printers were operating. Samples were integrated over 24 hours. The blank chamber results are the average ± 1 standard deviation from four measurements.

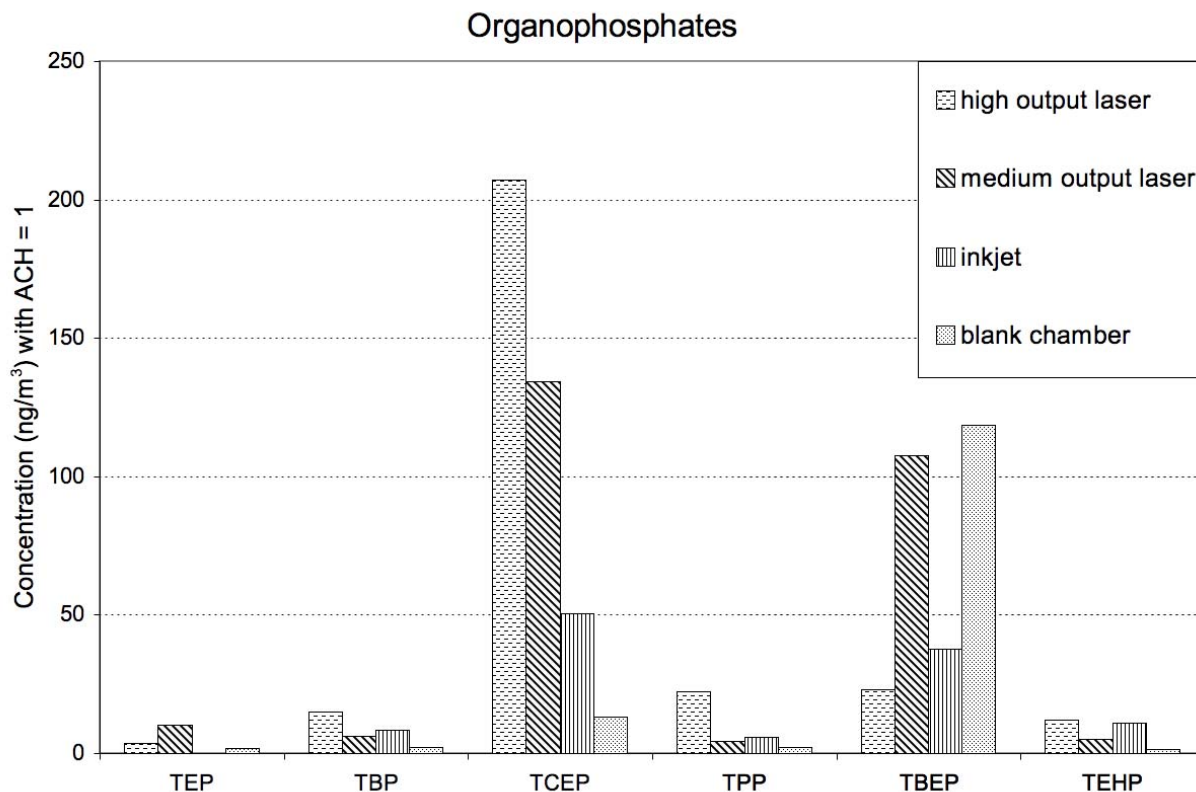


Figure 15. Results for OP measurements while printers were operating. Samples were integrated over 24 hours. The blank chamber results are the average of all experiments (n=4).

Particulate Matter and Ozone Concentrations

For all printer experiments, particle number concentrations were collected continuously during and after printing for each day, using a P-Trak condensation particle counter. The instrument was filled with alcohol prior to each use and could operate continuously for eight hours without replenishing the alcohol. The particle number counts were averaged over one-minute time steps. Results of these measurements are presented in Figure 16, Figure 17, and Figure 18, respectively, for the high-output laser, medium-output laser, and inkjet printers. Only one day of data was collected for the inkjet printers (Figure 18) because of a mechanical failure in the air handler, but the results for the inkjet printers did not show a significant increase in the particle number concentration. All of the spikes in Figure 18 are caused by room air entering the chamber when the paper was being loaded and/or refreshed in the printers. Both the high- and medium-output laser technology printers did result in significant increases in particle number concentration during printer operation. Notably high particle number concentrations were observed after a cold start, or in the case of the medium-output units, immediately following a paper jam. The reason for the second spike for the high-output laser printer on Day 1 (Figure 16) is not known. There was a short break (approximately 60 minutes) in the continuous measurement of particle number concentrations on the first day of the experiment with the

medium-output laser printers. This break was caused by a need to change the batteries in the P-Trak instrument. Subsequent experiments used a power supply for the P-Trak.

Ozone levels remained at background concentrations for all three printer experiments.

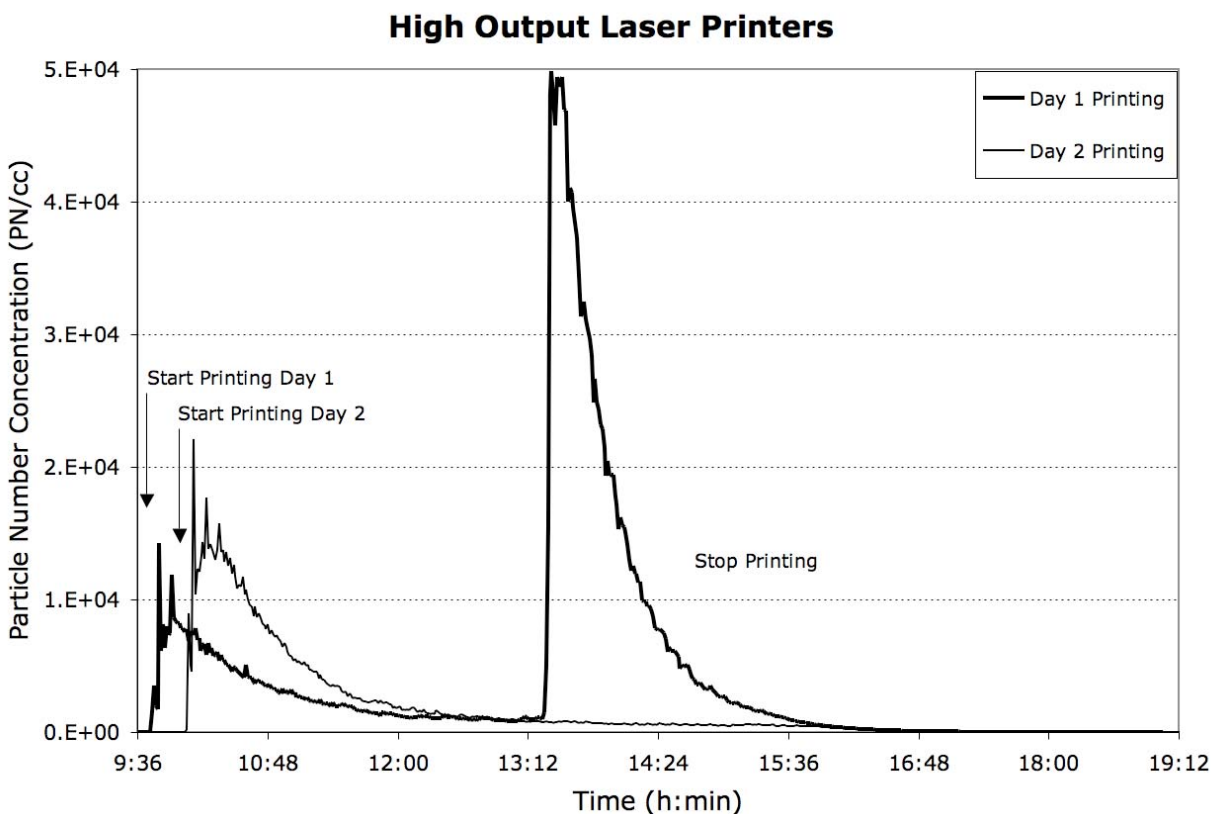


Figure 16. Particle number concentration (particles per cc) for Day 1 and Day 2 of the experiment with two high-output laser printers. The initial spike in particle counts on both days occurred immediately after cold startup of the printers.

Medium Duty Laser Printers

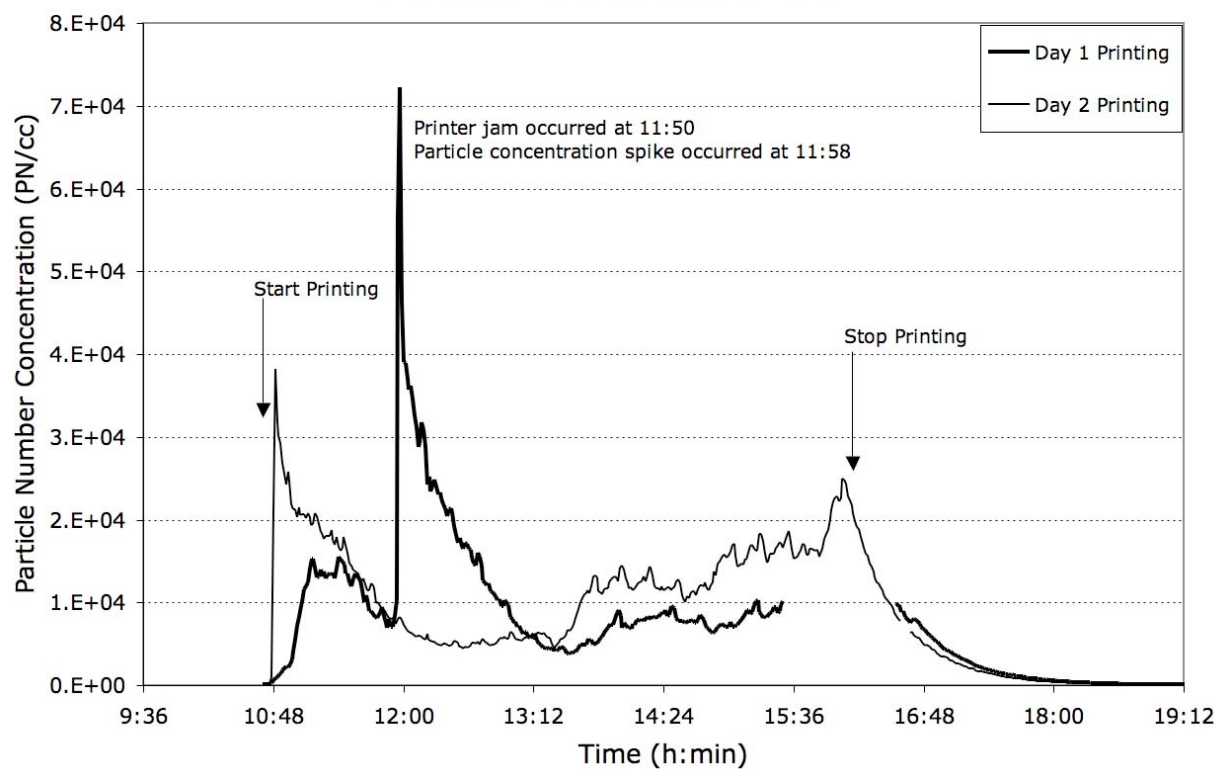


Figure 17. Particle number count concentrations (particles per cc) for Day 1 and Day 2 of the experiment with three medium-output laser printers. The break in the data for Day 1 occurred due to a short shutdown of the particle-counting instrument.

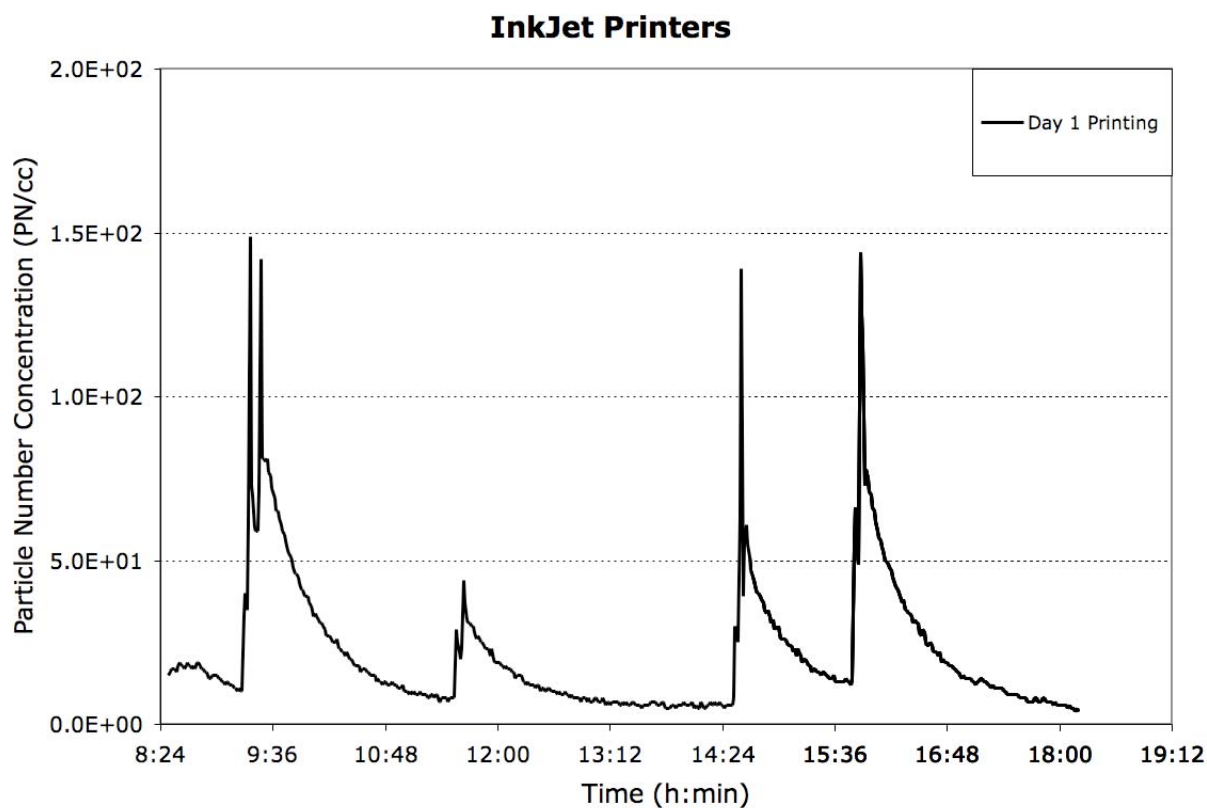


Figure 18. Particle number concentrations (particles per cc) for Day 1 of the experiment with five inkjet printers. The particle counts are near background and printing does not contribute to this background. The spikes that are seen in the figure are due to opening of the chamber door to reload paper in the printers.

Particle mass concentrations in the chamber during the two laser-technology printer experiments consistently reached a level of $1 \mu\text{g}/\text{m}^3$ for the medium-output units and $3 \mu\text{g}/\text{m}^3$ for the high-output units (blank chamber measurements were not collected for particle mass, given that particle number concentrations in the empty chamber were typically between 10 and 30 particles per cc). The results for particle mass determination are provided in Appendix D, Section D.2. Continuous measurements with an aethelometer using sampling conditions recommended for a typical urban sampling event did not detect an increase in black carbon over background. Black carbon is a measure of particulate species generated by the combustion of carbonaceous materials. These results indicate that particles generated during printing do not originate from combustion-related decomposition of chemicals during the printing process. The OC/EC analysis of the particles revealed that particle mass on filters was primarily organic carbon (details provided in Appendix D, Section D.3).

4.0 Phase II Individual Unit Experiments

Phase II of this project focused on measuring pollutant-specific emission factors and the influence of a range of environmental and operational variables on emissions for individual computer and printer units operating in an emission test chamber. This phase included four tasks. The first task focused on the measurement of chemical emissions from individual computer systems and their components to verify/refute the Phase I results, to extend these results to a more realistic atmospheric environment, and to explore the potential for near-field exposures by using a smaller emissions chamber. The second task was to develop mass-balance relationships that can be applied to the observed temporal concentration patterns in the chambers, to more accurately estimate device emission rates for some SVOCs and surface reactive chemicals as needed. The details of this approach are described in Appendix C. Because repeated measurements during extended experimental period indicated that the system was at steady-state for all measured chemicals, the approach was available, but not needed for, the third and fourth tasks. The third task was focused on emissions from individual printers with a goal of better understanding the particle emissions from printing devices—temporal trends and variations among different brands and models. The fourth and final task focused on factors that contribute to elevated emissions (primarily particles from printers, but also VOCs) and measures that can be taken to reduce these emissions. In these experiments, each device was tested using the operating cycles developed in Phase I, with some modifications for the printers in order to explore the influence of duty cycle on emissions. The sections below describe Phase II methods and results.

4.1. Phase II Methods

Methods described for Phase II experiments include the scientific/technical basis for development of the Phase II experimental design, details on the test chamber design and operation, specific procedures for selection and testing of individual computers and printers, modifications to the chemical sampling and analysis methods that were previously described in Phase I, experimental design for testing different options for mitigating emissions and exposure, and data analysis methods used for calculating emission factors for the different combinations of equipment and specific pollutants.

4.1.1. Scientific/Technical Basis for the Phase II Experimental Design

The overall experimental design, as well as many of the specific experimental protocols, are based in part on lessons from Phase I, along with input from the ARB, the Energy Commission, and the Project Advisory Committee.

Lessons from Phase I Experiments and Four Recommendations for Phase II

Results from Phase I indicate that, for many of the selected analytes, emissions are relatively low. Exceptions to this finding are particle number emissions from printers and in some cases, the OP flame retardants. However, it is important to note that the experimental design and testing system used in the Phase I screening analysis was intended to detect a wide range of pollutants by simultaneously testing multiple units from a given category of office equipment in a single large chamber. This approach is expected to diminish high emissions from any single

unit and does not provide information on emission factors for individual pieces of office equipment. As a result, the project team's two key recommendations for Phase II efforts were: (1) conduct experiments to confirm or refute the findings of any low-emissions chemicals in Phase I by measuring specific emission factors for individual units, and (2) generate experimental results on actions that can be used to mitigate or eliminate exposures to analytes with large emissions factors. Given that no particle emissions were detected during the computer experiments, no additional particle measurements (mass or number) are included in Phase II for computers. Also, given that results from the aethelometer measurements during printing were uninformative, no additional black carbon measurements were included in Phase II.

Phase I results also revealed that the initial target chemicals only represent a fraction of the chemicals detected during the VOC and SVOC analyses. Although the results for the SVOCs appeared to only identify a fraction of the chemicals present in the extract, the use of multiple detectors during the analysis for the different classes of SVOCs prevented the researchers from quantitatively stating the fraction of chemicals that were identified in the emission stream. As a result, a third recommendation for Phase II experiments was to identify, and if possible, quantify, significant unknowns in the emissions stream.

A key finding of the Phase I experiments is that ultrafine particle emissions during laser printing were elevated and episodic, particularly during initiation of the printing each day. The inkjet printer category had low emissions of both aerosols and gas-phase chemicals compared to the laser printers, although these results have not been compared to reported reference concentrations and health specific endpoints. These Phase I results lead to a fourth recommendation for Phase II experiments: to better characterize particle emissions from laser technology printing devices and to identify the potential causes of these episodic emission events as well as options to mitigate these emissions. Because particles emitted from printing devices are so small, and emission periods during active printing are short, the focus of Phase II for printing devices was on particle number emissions rather than particle mass emissions.

Goals for the Phase II Experiments

Building on lessons from Phase I, the research team developed in consultation with ARB and the Energy Commission a work plan for Phase II, including a matrix for the number and duration of individual-component experiments. The overall goals for Phase II included: (1) experiments with single devices in smaller chambers to measure specific emissions factors that confirm or refute the initial findings in Phase I, (2) efforts to evaluate previously unidentified chemicals in emissions streams, (3) experiments to characterize particle emissions from laser printers, (4) energy use measurements, and (5) experiments to provide insight into options for mitigating emissions and potential human exposures. Table 17 provides a summary of the experimental matrix used in Phase II. Included in this summary are the total numbers of devices included in each subtask. ARB and Energy Commission staff were consulted about the selection of specific devices and variables for testing.

4.1.2. Test Chamber Design

All of the Phase II experiments were carried out in a smaller continuously stirred cylindrical frame chamber constructed with a Teflon-coated aluminum frame wrapped in a transparent Teflon film, as shown in Figure 19. The chamber is large enough (~ 395 liters) to contain a single printer or computer (with monitor and peripherals) but small enough to allow the full air stream to be sampled if necessary for low-concentration SVOC measurements. The continuous stirred design provides a well-mixed system that could be sampled from several different sampling ports for low-flow measurements of VOCs, ozone, aldehydes, and particle number concentrations. Chamber materials were selected to minimize the interaction of pollutants with the chamber walls (Maddalena et al. 2002). Outside air was introduced into the top of the chamber after being conditioned by passing through a pre-filter, activated carbon, and high efficiency filter; chilled to a fixed dew point; reheated; and then humidified to 50% RH for the computer experiments using an ultrasonic humidifier on a rheostat control. The printer experiments used a lower starting RH to compensate for the significant water emissions during printing. The air exchange rate in the chamber was set at 2.5 h^{-1} for the computer emission experiments and $\sim 10 \text{ h}^{-1}$ for the printing experiments. Switching valves and multiple sample ports were used to provide continuous flow while collecting long-term integrated SVOC samples by diverting the full chamber flow through the SVOC sample cartridge or a bypass port during sample cartridge installations or changes. The chamber temperature is controlled by the room temperature and is set to 23°C (73°F). Environmental variables (T, RH, and pressure differential [inside-outside]) are logged continuously during operation. The chamber is equipped with a controlled CO_2 source and continuous CO_2 analyzer for air exchange rate determination as needed.

Prior to each emission test, the chamber film and frame are carefully wiped clean with dry Kim wipes. The chamber setup, testing, and calibration was the first major activity of Phase II.

Table 17. Experimental Matrix for Phase II

Devices	Experiments/Variables	Total Experiments	Target Analytes
Empty chamber with known emissions source	Develop a positive control to confirm detection of known sources, and explore wall interactions	4	VOCs and limited set of SVOCs, using different analytical methods
3 new computer systems	Determine temporal patterns of emissions with aging	3 experiments with each unit, plus one additional for one unit (10 total)	VOCs, aldehydes, ^a and SVOCs
2 additional new computer systems	Determine out-of-box emissions rates, one additional aging time point, and measure device variability	2 experiments for each unit (4 total)	VOCs and SVOCs
Same computer systems as above	Measure influence of on/off cycling in active computers	2	
7 medium output laser technology printers or multifunction devices	Measure initial print and extended print emission rates	7	VOCs, O ₃ , Particle number, size-resolved particle analysis, and a limited set of SVOCs ^b
7 laser printers indicated above, plus 1 inkjet	Individual device variability	8, including replicate runs for QA	
Printers and computer components listed above	Evaluate how aging, toner choices, paper choices, and operation schedules affect emissions	10	

^a The aldehyde emissions were assessed using the initial three computers. Aldehyde emissions from printers were not assessed because of the longer sampling time required.

^b The number of SVOCs that could be included is limited to those that could be collected along with the VOCs because the sample duration was determined by both humidity buildup and by the need to refresh paper during printing. Further explanation is provided in Section 4.1.4.



Figure 19. Test chamber used during Phase II experiments

4.1.3. Computer Selection and Testing

All Phase II individual computer experiments used the chamber described above to measure a range of volatile and semi-volatile organic compounds emitted from individual computers and their components. Components included monitor, keyboard, mouse, speakers, and cables. Selected computers were purchased directly from manufacturers.

Computer Selection

To augment the selection criteria used in Phase I, where the goal was to include units from each of the major manufacturers, the Phase II computer selection effort sought to identify units that were expected to contain elevated levels of bromine and/or other organic compounds of interest. A portable X-ray fluorescence (XRF) analyzer tuned to bromine was borrowed from the Department of Toxic Substance Control and used to screen several of the computers and printers from the Phase I experiments. Although bromine was detected in a number of the units and the computer peripherals that were tested, primarily in the mouse, the results did not provide a clear picture of which units might have elevated emissions. Results from the bromine screening assessment are provided in Appendix E. Information on relating XRF results for bromine content to potential emissions is not currently available in the literature. Pressure from regulatory agencies and environmental groups are having an impact on the use of brominated flame retardants (Betts 2008). This impact can be seen on a number of computer manufacturer's websites,³ where they announce their shift away from brominated flame retardants in their product streams. This indicates that even if a particular model of computer from Phase I of this project was identified by the XRF analyzer to have bromine, that would not in itself be evidence that a new model in the same product line would also have bromine. Therefore, rather than selecting office equipment from a particular product line based on bromine measurements in older units, our selection of test units for Phase II was aimed at expanding the set of computers tested in Phase I for different manufacturers.

New computers from normal manufactured batches were selected from major computer manufacturers who were identified as top picks in current consumer review magazines and/or websites. One laptop and four desktop units were purchased directly from manufacturer's websites; configured by a computer technician at the University of California, Berkeley (UCB); and tested at Lawrence Berkeley National Lab. The five computers and their characteristics are described in Table 18.

³ Dell computers chemical use policy - <http://www.dell.com/>; HP computers Global Citizenship Policy - www.hp.com/hpinfo/globalcitizenship/gcpolicy.html; Apple 2008 Environmental Update - www.apple.com/environment/update/; IBM Computers Voluntary Initiatives - www.ibm.com/ibm/environment/initiatives/.

Table 18. Description of computers used in Phase II

Unit Identifier	Monitor	Energy Use Rate in Watts (off/idle/active) ^a
DT06	19-inch 1907FPc	1/ 57/ 96
DT07	19-inch LCD	3/ 82/ 92
LT01	15-inch LCD	2/ 25/ 47
DT08	19-inch FPD1975w TFT LCD	3/ 75/ 90
DT09	19-inch CTL LCD widescreen	0/ 75/ 101

^a All LCD monitors consumed 29 watts when they were on.

Computer Handling, Preparation, and Testing

After acquisition, the computers and their components were stored in original packaging in a conditioned office space or staging area until ready for testing. Twenty-four hours prior to the start of an initial emissions test, the computer was unpacked and all packaging material was removed from the room. The computer was assembled with all components on a clean workbench in the staging area and the following details were recorded in the test report: manufacturer; brand name; serial number; model; configuration; external dimensions; packaging type; dates of production, arrival at lab, and unpacking; storage time; and environmental storage conditions. The computer was turned on and the duty-cycle software (PassMark BurnIn Version 4.0) was installed, and the default cycle was initiated for a six-hour test run. The computer was then shut down and unplugged from the power source and left in the staging area for approximately 12 hours (overnight) prior to loading in the test chamber for the initial measurement.

Five different computers were used to determine initial out-of-box emission factors, emission factors as a function of processor age, and emission factors during different on/off duty cycles. In general, each experiment followed the experimental path depicted in Figure 20. All five computers were tested new to determine their initial “out-of-box” emission factors. After determining the initial emission factors, three of the computers were artificially aged by running continuously through a prescribed duty cycle for approximately 100 hours and then the emissions measurements were repeated. The same three units were again aged an additional 100–150 hours and tested a third time. One of the units was aged an additional 200 hours and tested a fourth time. For the remaining two units, after the initial out-of-box emission factors were measured, the units were each returned to the chamber. Their emissions were measured during either a continuous on/off cycling routine or a continuously repeating cycle consisting of five minutes when the unit was on and active followed by five minutes when the unit was off. Afterwards, these two units were again tested to represent a second aging period using the full operational duty cycle.

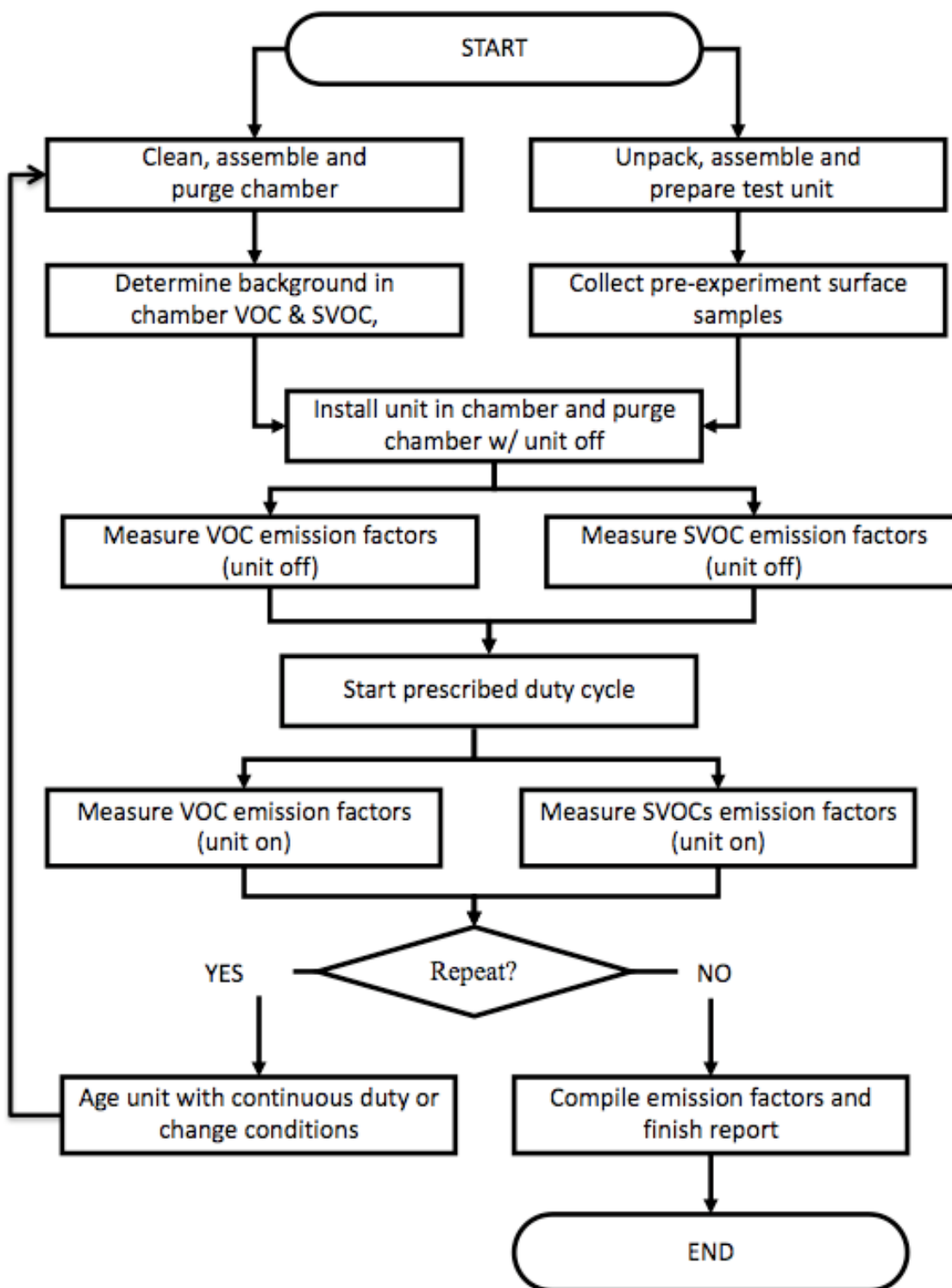


Figure 20. Experimental flow chart for determination of chemical emissions from individual computers. The experimental protocol illustrated in Figure 20 and described above is based on Standard ECMA-328 (ECMA 2006) but modified to include the determination of SVOCs in the emission stream.

Sampling Periods and Durations

For each of the 16 computer emissions experiments described above, integrated samples were collected from the chamber to represent: (1) background in the chamber (C_{bg}), (2) emission rates with the unit turned off (C_{off}), and (3) emission rates during computer operation (C_{on}). Integrated samples were typically collected for 30 minutes at 100 cc/min. for VOCs, 120 minutes at 1 liter per minute (lpm) for aldehydes, and 12 hours at 16.5 lpm for SVOCs. For the C_{bg} measurement, the SVOC sample collection was started approximately 6 hours (~15 air changes) after the start of chamber purge and run overnight (12 hours). Background VOC (and aldehyde when included) samples were collected after the SVOCs measurement was completed and prior to installing the test computer. After background VOC/aldehyde samples were collected the chamber was opened (all flows and setting remained on), the computer, monitor, and peripherals were installed, and the chamber was closed and purged again. The first VOC measurement for the C_{off} phase was collected after ~ three air changes per the ECMA 328 Standard recommendation, then again after several hours and/or just prior to moving to the next experimental phase. The SVOC sample collection for the C_{off} phase was initiated approximately 6 hours after closing the chamber and run overnight (~ 12 hours) followed by a second 12-hour sample collected the following day. The consecutive samples were compared to assess whether the measured chemical concentrations represented steady-state (i.e., concentrations are not increasing) and to evaluate experimental error for the test system by comparing the two samples to see if the results indicated that steady state had been achieved. After the C_{off} measurements were collected, the computer was powered up, and the duty cycle was initiated. Adjustments to T and RH were made to maintain the target conditions within the chamber accounting for the heat generated by the active computer. The first VOC measurement during the active phase was again collected after three air changes per the ECMA 328 Standard, then after several hours and/or just prior to the end of the experiment. The first of two 12-hour consecutive SVOC samples for the C_{on} phase was collected after approximately 6 hours of operation and then again the following day. For the low molecular weight aldehydes, at least one sampling period for each C_{bg} and C_{off} phase was included with duplicate aldehyde samples collected during the C_{on} phase.

After the ~ 32-hour operating period during which SVOCs, VOCs, and aldehydes were sampled, the computer was powered off and removed from the test chamber, and the chamber was allowed to purge in preparation for the next experiment. The results were used to calculate pollutant-specific emission factors for each computer and experiment combination, as described in Section 4.1.7.

4.1.4. Printer Selection and Testing

The specific needs of the emissions studies and the intervention/mitigation studies were to identify and quantify pollutants from individual printing devices and gather evidence to help identify the source of these pollutants in the printing process, so that steps can be taken to mitigate potential exposure. Although the pollutants of most interest are ultrafine particles, understanding particle emissions also requires an assessment of VOC and ozone emissions because of potential for secondary aerosols to form. Semi-volatile organic compound analytes included in the large chamber experiments in Phase I were not measured for printers in Phase II

because the experiment duration was limited by both the buildup of moisture in the chamber during active printing and by the need to refresh the paper at relatively short time intervals. For recommendations regarding experimental methods specifically for the determination of SVOC emissions from printers, see Section 6.4.

Printer Selection

The literature review and the results from Phase I indicate that it is printer technology rather than manufacturer that affects particle emissions. The group-level results from Phase I further indicated that print technology (inkjet versus laser printers) and not printer size (medium versus high output) had the biggest impact on particle emissions. Printer selection for Phase II was guided primarily by the team's interest in the mechanism of pollutant generation, with specific emphasis on particle emissions, so this effort had a focus on medium-duty laser printers that would fit easily in the small test chamber. In addition to characterizing unit-specific emission factors for particles, ozone, and VOCs, the printer selection for Phase II was also guided by the need to make general comparisons of emission rates as they relate to:

- inkjet versus laser printing technology,
- variability of emissions with brand and model, and
- variation of emissions with age of device.

Eight printers were selected to meet these objectives, and several of the same units were used to explore additional factors related to emissions and possible options for mitigating these emissions and exposures. It is important to note that the aim of the selection process was to provide a test bed for printers that allowed us to assess both the variability of and causative factors for pollutant emissions from printers, not to construct a representative "sample" of printers from the current market in California. However, the final set of printers provide a cross-section of major manufacturers. Two additional printers were initially tested in the emission chamber to identify conditions that lead to elevated particle emissions and to develop a standard printing scenario for use in subsequent experiments. These printers are not included in the final reported unit specific emission rates because of paper feed malfunctions that prevented a complete emissions testing profile.

The final set of selected printers included seven medium-duty laser printers that were used to explore aging, print cycle, consumable selection and capacity factors, as well as one inkjet printer used to compare emissions from that different print technology. The list of printers and their characteristics are provided in Table 19.

Table 19. Description of printers used in the Phase II

Printers	Type	Cartridge	Manufacture Date	Power use during standby / operation (W)
<i>LP06</i>	Laser	Q5957A	March 2006	6 / 850
<i>LP07</i>	Laser	Q5957A	Sept. 2005	5 / 720
<i>IJ06</i>	Inkjet	A FINE PG-50 Black	Out of box (manufacture date not listed)	2 / 13
<i>LP08</i>	Laser	Q2612A	July 2007	2 / 350
<i>LP09</i>	Laser	(Innovera) IVRML1210	June 2002	5 / 560
<i>LP10</i>	Laser	Q5917a	Dec. 2004	2 / 600
<i>LP11</i>	Laser	OEM ^a cartridge with original purchase	March 2007	12 / 800
<i>LP12</i>	Laser	Non-OEM refill cartridge and new cartridge TN540	Nov. 2004	5 / >1000

^a OEM = original equipment manufacturer

Printer Handling, Preparation, and Testing

All of the printers tested in Phase II were late-model printers that were selected from a list of printers offered for testing by individuals at LBNL and UCB. Selected printers were picked up from the owners one to two days prior to initiation of testing and transported to the lab where they were wiped down with dry Kim wipes to remove visible dust from the external surfaces. Any paper that was loaded in the printer was removed, and the tray was filled with fresh paper. Generally the printers were tested as received, with the exception being the mitigation experiments aimed at identifying the source of particle and VOC emissions.

The eight different printers selected for testing are summarized in Table 19. All of the printers were used to determine unit-specific emission rates for ozone, VOCs, and ultrafine particles (UFPs). The UFP emission rates were determined for both cold-start prints and for extended printing jobs with varying page count. Five of the printers were used to measure size-resolved particle number concentrations using the condensation particle counter (TSI 3022A CPC) and optical particle counter (Lasair 1003) operating in parallel. Two units were tested to measure the importance of toner selection, two units were tested to compare paper selection, and one unit was tested to assess the impact of toner coverage on the printed page. Two of the units had the same manufacturer and model but different fabrication dates, to test variation across units from the same product line. One of the units was tested repeatedly on different days to better characterize experimental variability. Finally, all of the experiments logged the power use during printing to explore the relationship between power consumption and emissions. The individual experiments are detailed in Table 20.

Table 20. Details of specific factors tested in the emissions mitigation experiments in Phase II

Factor Tested	Device Type	Number of Devices Used	Number of Experiments
How aging of computers affects VOC and SVOC emissions	Computers	5	7 (plus five standard emission experiments)
How on/off cycling affects VOC and SVOC emissions	Computers	2	2 (plus two standard emission experiments)
How age of printers affects VOC, ozone, and particle emissions	Printers	8	8
Determination of size fraction for UFPs	Printers	5	5
Assess variation of VOC and UFP emissions for units from same manufacturer and product line	Printers	2	2
Print cycle—cold start versus warm printing for particle emission rates	Printers	8	8
Use of original equipment manufacturer (OEM) versus non-OEM toner and old versus new OEM toner	Printers	2	4
Assess how toner coverage on printed page affects VOC, ozone, and particle emissions	Printer	1	3 (plus one standard emission experiment)
Use of different paper types (high quality versus economy brand)	Printer	2	2

Sampling Periods and Durations

Ozone, particle number concentrations, and power use (W) were monitored continuously along with chamber conditions (T, RH, and ΔP) throughout the emissions experiments. Integrated samples for the VOC analysis were collected to represent the background and the different operational stages. Aldehydes were not collected during the printer experiments due to the longer sampling period required. The VOCs were collected for between 10 and 30 minutes, depending on the experimental phase, the number of pages printed, and the print speed. All samples were collected at 100 cc/min. The longer sample period was conducted to look at background measurements when concentrations in the chamber were expected to be low. Both the measured concentrations and sampling duration were used in the algorithm for estimating emission rates, as described in Section 4.1.7. The actual sample collection time and the print duration are incorporated into the emission estimation algorithm so sample collection duration was optimized for each experimental phase.

The protocol for collecting emissions measurements follows the experimental path that is illustrated in Figure 21 and detailed in this section. In summary, after the chamber is cleaned, closed, and purged, and the printer is cleaned and loaded with fresh paper as described above, integrated background measurements of VOCs are collected from the empty chamber as described in Section 4.1.6, and data logging is initiated for real-time measurements of UFPs and ozone (and other environmental and power-consumption variables). The UFP and ozone data is collected continuously throughout the duration of the experiment. After the background VOC sample is collected, the printer is installed in the chamber, plugged into the watt meter and

connected to a laptop computer with appropriate printer drivers installed. The computer is mounted outside the chamber and a single test page is printed to insure communication is established between computer and printer. Then the chamber is closed and the purging phase initiated. The chamber is allowed to purge until the particle and ozone concentrations return to background levels (< 5 particles/cc and < 2 ppb ozone) before collecting the idle-phase VOC sample. After the background and idle phase samples are collected for VOCs, the active phase sampling is initiated.

The active-phase VOC sample collection is initiated simultaneously with a single extended print job (≥ 100 pages), and sampling is continued for up to 15 minutes, then a second VOC sample cartridge is started and run for an additional 30 minutes. The actual sample duration and integrated VOC concentrations measured during background, idle, active, and post-active phases are used to estimate emission rates for the idle and active phases, as summarized in Section 4.1.7 and detailed in ECMA Standard 328 (ECMA 2006).

For the particle emissions estimate, a series of print jobs are run beginning with a cold printer then continuing with a number of prints with varying page count. The resulting particle and ozone concentration time series are used to estimate emissions for each print job and the subsequent unit-specific emission factors, as described in Section 4.1.7.

The process is repeated for each printer and then for each mitigation experiment after adjusting the various factors to explore pollutant sources and potential mitigation strategies. The standard test page used for all the emission measurements was a 5% toner coverage pattern as recommended by ECMA (2006). Blank test pages were also used, along with 10% and 20% coverage pages for some of the experiments.

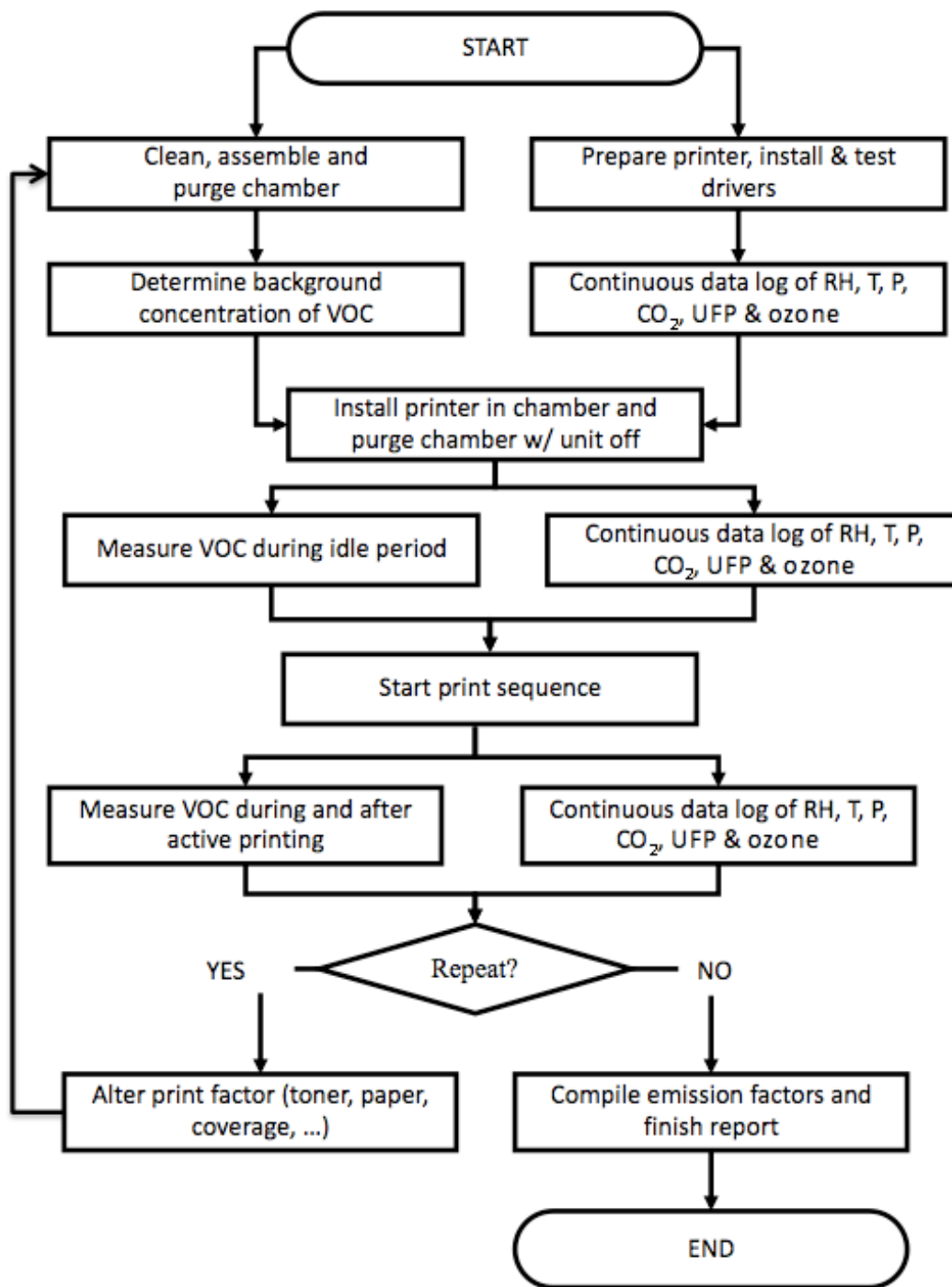


Figure 21. Experimental flow chart for determination of emissions from printers

4.1.5. Exploring Options for Mitigating Emissions and Exposures

The last experimental task of Phase II was to vary operating conditions for computers and printers in order to identify factors that affect device energy use and emissions. Examples of such factors include, for both computers and printers, equipment aging and varied operational states. For printers, the effects of heavy use, the use of non-OEM toner type, variation in toner coverage, and paper type were also evaluated. The major goal of this task was to identify which among these factors can be applied to reduce emissions, as well as the mechanism by which emissions are reduced. This required the development of an experimental matrix of individual devices and conditions that resulted in the highest observed emissions in earlier experiments that were used to estimate the base-line emission rates. Once the units and conditions were identified, each individual unit was tested following the procedures described above. A subset of experiments was dedicated specifically to evaluating potential emissions and exposure mitigation strategies. This effort explored seven factors requiring 32 experiments lasting one to three days each. Table 20 details the experiments used for this task.

4.1.6. Phase II Sample Collection and Analysis Methods

Phase II sample collection and analysis methods were guided by the methods and results of Phase I. In the period between Phase I and Phase II, new analytical equipment replaced many of the test systems at LBNL. In addition, a number of unknown peaks in the analytical results of Phase I were identified and quantified in Phase II, and findings from Phase I—along with a recently published ARB study (Charles et al. 2005)—identified possible problems with using PUF sorbent for sampling PBDE-209. Each of these changes or findings led to modifications in the methods for Phase II.

This section provides a summary of all pollutants analyzed for the Phase II study, along with details on sample collection and analysis methods. Where the methods are unchanged from Phase I, the reader is referred back to Section 3.1.2. Where changes have been made or new analytes added, this new information is provided. The quality assurance plan for the overall study is given in Appendix A.

VOC Selection, Sampling, and Analysis

The list of VOC target analytes was expanded for Phase II. The additional analytes are listed in Table 21. Due to newer equipment there were also some modifications to the protocol. Volatile organic compound samples were collected onto multi-sorbent tubes (Gerstel P/N 012347-005-00; or equivalent) with primary bed of Tenax-TA® sorbent backed with a section of Carbosieve®.

After sample collection, sorbent tubes were spiked with a known amount of 1-bromo-4-fluorobenzene, then thermally desorbed for analysis by thermal desorption gas chromatography/mass spectrometry (TD-GC/MS) using a thermo-desorption auto-sampler (Model TDSA2; Gerstel), a thermo-desorption oven (Model TDS3, Gerstel), and a cooled injection system (Model CIS4; Gerstel). The cooled injection system was fitted with a Tenax-packed glass liner (P/N 013247-005-00; Gerstel) and initially cooled to -10°C (14°F). Desorption temperature for the sample tube was 25°C (77°F) with a 0.5-minute delay, followed by a 60°C/min (33.3 °F/min) ramp to 250°C (482°F) and a four-minute hold time. The cryogenic trap was held at -10°C (14°F) and then heated within 0.2 minutes to 270°C (518°F) at a rate of 12°C/s

(6.7 °F/s), followed by a three-minute hold time. Compounds were resolved on a GC (Series 6890Plus; Agilent Technologies) equipped with a 30 meter HP-1701 14% Cyanopropyl Phenyl Methyl column (Model 19091U-233; Agilent Technologies) at an initial temperature of 1°C (34°F) for 0.5 minutes then ramped to 40°C (104°F) at 25°C/min. (13.9 °F/min), to 115°C (239°F) at 3°C/min. (1.7°F/min), and finally to 250°C (482°F) at 10°C/min., (5.6°F/min) holding for 10 minutes. Multipoint calibrations were prepared for target VOCs and referenced to the internal standard. The target compounds span an approximate volatility range bounded by n-butane and n-octadecane (C₄–C₁₈). The upper end of this boiling point range captures several of the analytes that are included in the SVOC analytical stream, including the low-boiling phthalates and the low-boiling polycyclic aromatic hydrocarbons.

Table 21. Additional VOCs included in Phase II measurements

<i>Chemical Name</i>	<i>CAS#</i>	<i>Chemical Name</i>	<i>CAS#</i>
Hexanal	66-25-1	Dodecane	112-40-3
p-Xylene	106-42-3	Phenol	108-95-2
α-Pinene	7785-70-8	Tridecane	629-50-5
β-Pinene	18172-67-3	Tetradecane	629-59-4
3-Carene	13466-78-9	Pentadecane	629-62-9
d-Limonene	5989-27-5	TMPD-MIB (Texanol) ^a	25265-77-4
Octanal	124-13-0	Butylated Hydroxytoluene	128-37-0
2-ethyl-1-Hexanol	104-76-7	TMPD-DIB (TXIB) ^b	6846-50-0
Nonanal	124-19-6		

^a TMPD-MIB, Texanol 2,2,4-Trimethyl-1,3-pentanediol monoisobutyrate

^b TMPD-DIB, TXIB, 2,2,4-Trimethyl-1,3-pentanediol diisobutyrate

Aldehyde Selection, Sampling, and Analysis

As in Phase I, the low-molecular-weight-aldehyde target analytes included formaldehyde, acetaldehyde, and acetone. Samples of these low molecular weight aldehydes were collected and analyzed following ASTM Test Method D 5197-92 (ASTM 1997). More details on the aldehyde analysis are available in Section 3.1.2.

SVOC Selection, Sampling, and Analysis

Semi-volatile organic compound pollutants selected for sampling and analysis in Phase II included polycyclic aromatic compounds, polybrominated diphenyl ethers (brominated flame retardants or BFRs), and organophosphate compounds (also used as flame retardants). Integrated SVOC samples were collected using sampling cartridges consisting of a 33 ml ASE cell body containing ~ 10 g XAD-2 loaded between two glass wool plugs. Air was pulled directly from the chamber through sampling cartridge. Prior to assembling this system, the XAD-2 and glass wool was baked in a muffle furnace, and the cartridge components were detergent-washed and solvent-cleaned. After assembly, the XAD-filled cartridges were further cleaned by accelerated solvent extraction using acetone as the final rinse solvent. After use, the XAD-2 was spiked with an internal standard and extracted with dichloromethane (DCM) by ASE. Extracts were concentrated in a Turbovap tube under a stream of nitrogen to 0.5 ml, then

solvent exchanged to iso-octane and quantitatively transferred to an auto-sample vial for analysis.

Analysis of three SVOC classes (polycyclic aromatic hydrocarbons and polybrominated diphenyl ethers) were performed on a Varian CP-3800 gas chromatograph (GC) coupled to a Varian 4000 ion trap mass spectrometer (MS). The ion trap was run in an internal electron ionization configuration using Rapid MS chromatography. Analytes were separated on a Rapid MS 10 m column (10 m x 0.53 mm x 0.25 μ m, VF-5ms, Varian) with a 5% phenyl, 95% dimethylpolysiloxane phase. Samples were injected onto the column with a Varian CP-8400 auto sampler. Generally a 1 μ L sample size was used for the analysis. The organophosphate SVOCs were analyzed on a Hewlett Packard model 5890 GC equipped with a Nitrogen-Phosphorous detector (NPD). A 15-m DB-5 column with 0.32-mm diameter and 0.25- μ m film thickness was used for separation. Details on each method are provided in Appendix F.

Particle Sampling and Analysis

Particle number concentrations were monitored during the printer experiments using a condensation particle counter (TSI 3022A CPC) rather than the P-Trak particle counter that was used during Phase I. Although the chamber design provides a well-mixed system, the sample inlet for the particle samplers was located in the upper part of the chamber, to prevent sampling directly from an exhaust port on the printers. No particle measurements were collected during the computer experiments. The TSI 3022A CPC was used to improve detection of ultrafine particles. The minimum-size particle diameter at which 50% of particles are detected using the TSI 3022A CPC is 7 nm (compared to 48 nm for the P-Trak), and the maximum size particle is $> 3 \mu$ m. The maximum concentration detected is 10^7 particles per cc, with the accuracy reported as $\pm 12\%$ to $5 \times 10^5 \text{ cm}^{-3}$ and $\pm 20\%$ at $> 5 \times 10^5 \text{ cm}^{-3}$. Although the TSI 3022A CPC can detect larger particles, most particles emitted by printers are expected to be in the ultrafine size range ($< 100 \text{ nm}$). To identify whether the particles counted by the TSI 3022A CPC were in the ultrafine size range, the size-resolved particle number concentration was measured using a Lasair 1003 optical particle counter (OPC) for a subset of the printer experiment. The OPC measured particle number concentration in seven size fractions from 0.1–2.0 μ m diameter, with a maximum concentration of $1.4 \times 10^4 \text{ cm}^{-3}$ and accuracy $< 10\%$. The results presented in Appendix G confirm that particle emissions from printers are predominantly in the ultrafine size range. Particle mass measurements were not collected during either the computer or printer experiments for Phase II.

Ozone

As in Phase I, ozone levels were evaluated continuously during the operational period of each of the individual printer experiments in Phase II. This was done using an ultraviolet photometric ozone analyzer (Model 400; API Inc.) calibrated prior to the beginning of the project. Rapid changes in chamber humidity during printing events caused a false signal in the ozone analyzer output. This was corrected by installing nafion tubing between the test chamber and the analyzer to provide a constant moisture content in the sample stream.

Selecting, Sampling, and Analyzing the Significant “Unknown” Organics

Significant unknown peaks identified in the SVOC and VOC analyses of Phase I were numbered and identified by retention time in the column. Tentative identification was provided using the National Institute for Standards and Technology (NIST) library for mass-spectrometry analyses. A more rigorous identification was conducted by comparing retention times and mass spectra to reference standards when these were available. A determination about whether unknowns should be included in the reported results was made in consultation with ARB staff but was also dependent on the available budget. Based on this process, a set of cyclic siloxanes were selected from the set of unknowns as compounds that should be analyzed in the Phase II results. A siloxane is any chemical compound composed of units of the form R_2SiO , where R is a hydrogen atom or a hydrocarbon group. A siloxane has a branched or unbranched backbone of alternating silicon and oxygen atoms -Si-O-Si-O-, with side chains R attached to the silicon atoms. A cyclic siloxane is a siloxane compound whose molecules contain a number of atoms bonded together to form a ring. The cyclic siloxanes that were identified and analyzed in office equipment emissions include the following letter/number codes and full names:

- D3 or Cyclotrisiloxane, hexamethyl
- D4 or Cyclotetrasiloxane, octamethyl
- D5 or Cyclopentasiloxane, decamethyl
- D6 or Cyclohexasiloxane, dodecamethyl
- D7 or Cycloheptasiloxane, tetradecamethyl
- D8 or Cyclooctasiloxane, hexadecamethyl

4.1.7. Calculation of Emission Factors

Unlike the Phase I experiments that used groups of devices in a large chamber, the Phase II experiments used individual devices placed in a small chamber. The experimental design of Phase I made it necessary to report pollutant concentration in the chamber air normalized to a standard air exchange rate rather than device specific emission factors. In contrast, all results for Phase II are reported as device-specific emissions rates with units of mass per time per device, that is $\mu\text{g}/\text{h}/\text{unit}$, during different operational phases. We obtain these emission rates in several different ways, depending on whether we are collecting an integrated sample (VOCs, SVOCs, aldehydes) or quasi-real time measurements (i.e., particle number and ozone concentrations). In general, the mass of pollutant collected during a specific time interval was analyzed and recorded, along with the duration of each collection period, and used with the measured ACH in the chamber to calculate the emission rate.

The time-series chamber concentration for ozone and particle number were tracked directly and respectively by the ozone analyzer and CPC and/or OPC and recorded on two separate data loggers.

The concentrations for SVOCs were estimated from an integrated air sample that captured the full air stream flowing from the chamber exit port. The concentration of SVOCs is the chemical

mass (μg) divided by the sample flow rate (m^3/h) and sample duration (h). Alternatively, the mass can be divided by $\text{ACH} \times V \times \text{sample_duration}$.

The VOCs and aldehydes were sampled at a flow rate that was less than the total flow through the chamber. As a result, the concentration during the sampling period was estimated as the mass collected divided by the sample flow rate and sampling duration.

The subsections below provide details on how the chamber concentration is used to estimate emission rate for each chemical class for computers and printers.

Determining Emission Rates for VOCs, Aldehydes, and SVOCs that achieve Steady-State Concentrations

For computers and for inactive printers where emissions are continuous and the experiments can be run long enough to achieve steady-state concentration in the chamber, the measured concentrations can be used to determine emission rates for a specific device and operating phase. These emission rates ($\mu\text{g}/\text{h}/\text{unit}$) are calculated as:

$$ER_{ji} = (C - C_{bg}) \times \text{ACH} \times V \quad (4-1)$$

Where ER_{ji} is the unit-specific emission factor for the j th computer and i th time period or operational phase of an experiment, C is the measured steady-state chamber concentration, C_{bg} is the background concentration in the chamber, ACH is the air change rate per hour, and V is the chamber volume in cubic meters. ACH is determined either directly from flow measurement and the active air volume in the chamber or by tracer gas decay curve method, as described in Appendix C, Section C.1.

Determining Emission Rates for SVOCs that Sorb to Wall Surfaces

When there is significant partitioning to chamber surfaces for some chemicals, then the system may not reach steady-state during the experimental period, due to reversible binding to wall surfaces. To check for this condition, multiple measurements were collected over several days during the computer emissions experiments. Long-term SVOC measurements were not collected during the printer experiments due the short duration of the active printing phase, but the steady-state condition of the higher-boiling VOCs in the printer experiments were also assessed with multiple samples collected over the duration of the experimental phase.

If a chemical was not at steady state, then the concentration measured in the chamber would continue to increase over time. As described in Appendix C, Section C.2, when the concentration is continuing to increase, the system will behave as if the chamber volume were greater than the actual volume, and an adjusted chamber volume or clearance rate is needed. In this study, repeated measurements of the SVOCs and high-boiling VOCs during the computer experiments did not indicate a continued increase in concentration over time. For example, the sum of organophosphates measured in the computer experiments did not show any upwards trend over a five-day active phase. To the contrary, most of the concentrations actually dropped over time. This finding may be due to a drop in emissions with unit aging, as seen with the VOCs. More detailed short-term studies of SVOCs sorbing to surfaces is an area of future research that is beyond the needs of this study to assess emissions factors. The emission rates

for the SVOCs that were measured in Phase II are therefore estimated with the system at steady state.

Determining Emission Rates for VOCs that Do Not Achieve Steady-State Concentrations Using Integrated Samples

Because of the relatively short duration of the printing events, long-term SVOC emissions were not measured for the printers. Printer emissions, which occur during the active printing phase, do not result in steady-state concentrations, even in the small chamber with relatively fast air exchange rates. Moreover, the sampling time required to recover a sufficient mass of analyte from the chamber is on the order of 10 to 30 minutes for VOCs. With actual print times ranging from a few minutes to about 15 minutes, the situation precludes the use of real-time steady-state sampling for printing events. Instead, the approach here for assessing VOC emissions used time-integrated samples collected during the idle phase and during and after active printing, along with an assumption of constant emission during printing. These measurements were used to construct the actual emissions curve over relatively short time periods. The procedure, which is described in detail in ECMA Standard 328 (ECAM 2006), is illustrated in Figure 22. In this example case, the emissions from the idle phase, an active 12-minute print cycle (consisting of some 200 printed pages), and the post-printing phase is captured using three 30-minute integrated air samples. The chamber is purged for at least 100 minutes before sampling begins. This process provides sufficient information to estimate an emission rate in micrograms per hour per unit and/or per page for the printing device being studied using Equation 4-2 (Equation B.21 in the ECMA Standard 328 [2006]). The emission rate estimation equation from the ECMA standard is repeated here for completeness, but the reader is referred to the original standard (ECMA 2006) for details on the solution to the mass balance.

The overall equation (4-2) as presented in the ECMA standard is

$$SER_{ope} = \frac{C_{ope} \cdot n^2 \cdot V \cdot t_G - SER_{pre} \left[\exp(-n(t_G - t_{ope})) + n(t_G - t_{ope}) - 1 + (1 - \exp(-n \cdot t_{pre})) \cdot (1 - \exp(-n \cdot t_G)) \right] - SER_{bg} \cdot n \cdot t_G}{\exp(-nt_G) - \exp[-n(t_G - t_{ope})] + nt_{ope}}$$

where SER_{ope} is the standard emission rate during the operating phase, C_{ope} is the average concentration during the operating phase (i.e., the second measurement indicated in Figure 22) ($\mu\text{g}/\text{m}^3$), n is the air exchange rate (h^{-1}), V is the chamber volume (m^3), t_G is the sampling duration during the operating phase (h), SER_{pre} is the standard emission rate during the pre-operating phase ($\mu\text{g}/\text{h}$) determined at steady state (see Equation 4-1) using the first sample measurement indicated in Figure 22, t_{ope} is the operating phase duration (h), t_{pre} is the pre-operating phase duration (h), and SER_{bg} is the standard emission rate measured in the empty chamber ($\mu\text{g}/\text{h}$) (see Equation 4-1 for the steady-state solution, where the background measurement is collected prior to loading the test unit in the chamber).

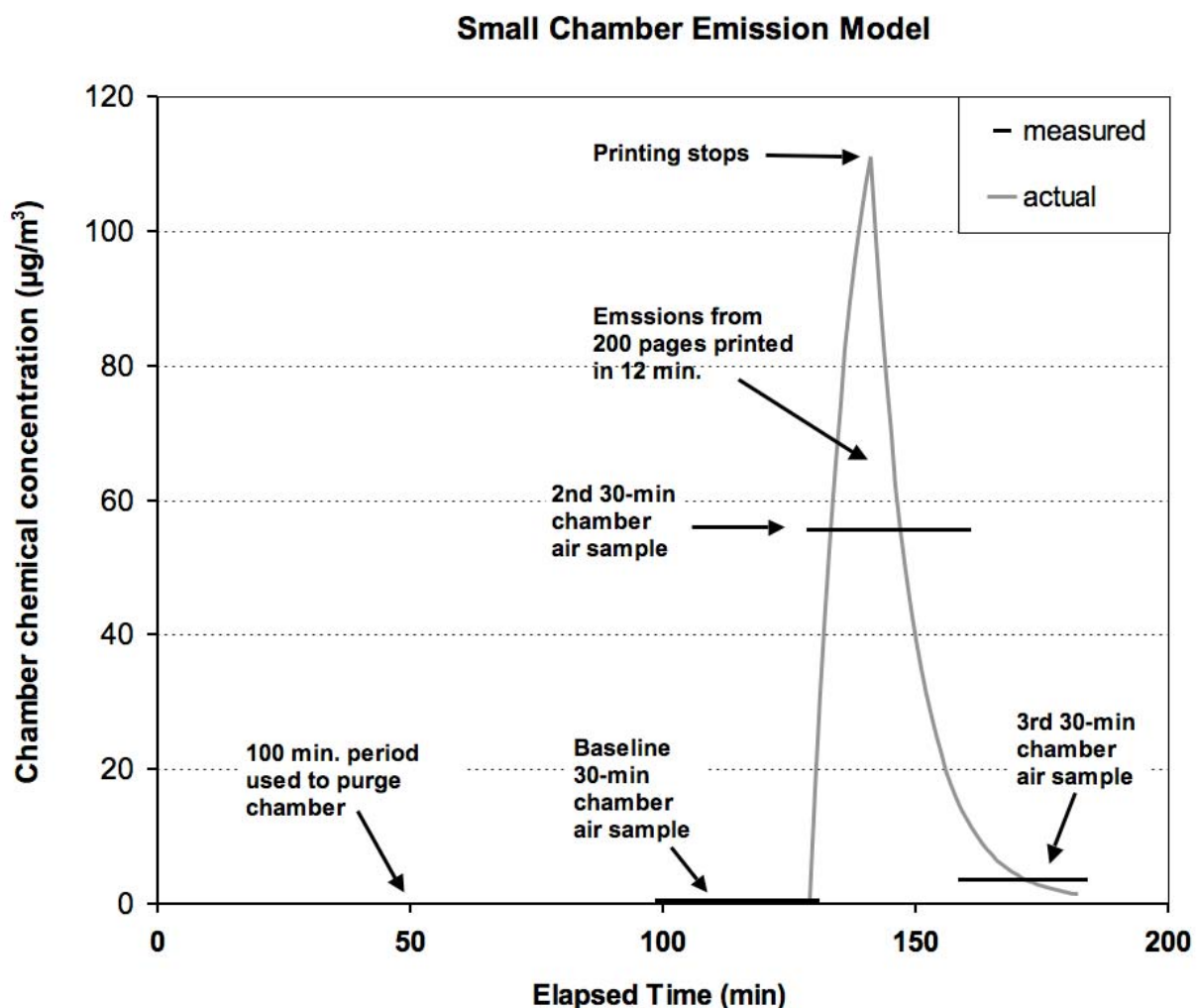


Figure 22. An illustration of how three 30-min. integrated air samples from the small chamber are used to construct the actual time history of VOC emissions from a 12-min. print cycle (approximately 200 pages).

Determining Aerosol and Ozone Emissions Rates Using Concentration Time-Series Data

The particle emissions from printers are intermittent and the pattern varies across different printers. The instruments used for measuring particle number concentrations and ozone can collect information with averaging times of 10 s and 5 s, respectively, providing near real-time data. This avoids the problem described above for VOCs in tracking short-term releases from printing events using integrated samples. In the case of particles and ozone, the concentrations were measured during successive time steps over each printing event. This information was used to calculate the emission rate during each time step (Δt) of each printing event using the chamber mass balance, where, during any time interval t_1 to t_2 , the change in concentration is described by

$$\frac{dC(t)}{dt} = -C(t)Q + \frac{E}{V} \quad (4-3)$$

Where E is the emission rate, V is the active chamber volume, and Q is the disappearance rate of the chemical from the chamber. Solving Equation 4-3 and rearranging for the emission rate during each sampling time step gives

$$E_{\Delta t} = V \times Q \times \frac{C_t - C_{t-1} \times \exp(-Q \times \Delta t)}{1 - \exp(-Q \times \Delta t)} \quad (4-4)$$

where $E_{\Delta t}$ is the emission rate ($\mu\text{g h}^{-1}$) during a time step Δt , V is the chamber volume (m^3), C_t is the concentration measured during the sampling period (t), and C_{t-1} is the concentration during the previous sample period, and Q is the overall disappearance rate for particles or ozone—and is an empirically determined parameter that includes removal by ventilation (i.e., ACH) as well as all other loss pathways (h^{-1}) such as particle accumulation, irreversible binding to surfaces, or chemical reactions. As described in more detail in Appendix C, Section C.2, the disappearance rate is estimated from the actual concentration trace following termination of emissions.

The emission rate for a given print job is the average of emission rates during each time step during the actively printing period assuming no emissions occur when the printer is idle. This calculation is repeated for each of the different print jobs to characterize the emission factor for the given printer. Unlike the VOC measurements, where we use integrated samples that cannot detect difference in emission rates during a single print, the quasi-real-time data for ozone and particles allow emissions to be assessed during different phases of a given print.

The Relationship Between Chamber Volume and Estimated Emission Rates

The equations described above use the volume of the test chamber to estimate concentrations and/or emissions. The effective volume of the test system may be less than that actual volume of the empty chamber, due to both the space taken up by—and the ventilation behavior of—the equipment being tested. Although the external chamber dimensions can easily be measured and used to define the empty volume, and the external volume of the equipment being tested can be measured, the actual volume taken up by the equipment in the chamber is unknown because both printers and computers are designed to be well-ventilated boxes, in order to manage heat loading. This rapid ventilation rate in the equipment, particularly during the active phase, is likely much faster than the air exchange rate in the test chamber, so the ventilated space within the equipment can be assumed well mixed with the chamber air and thus not to reduce the effective volume of the test chamber. Nevertheless, the internal components of printers, computers and some peripherals do take up space, and this factor can affect the estimated emission rates. Measuring and summing the volumes of the individual components of a typical desktop computer (keyboard, mouse, monitor, motherboard, hard drive, disk driver, power source, and case) gives a total for unvented space of approximately 15 liters.

Bias in the estimate of emission rates is indirectly proportional to the reduction of chamber volume caused by dead space volume in the equipment being tested. A dead space volume in the test equipment of 15 liters biases the calculated emission rates reported in this document upwards by as much as 5%-10%. The authors of this report note that this bias is within the range of experimental error and thus made no corrections to the calculations of emission rates to account for the dead-space volume of the test equipment.

4.2. Phase II Results

All Phase II results are presented as emission rates per unit. For computers, which run continuously, emission rates are presented with units of micrograms per hour ($\mu\text{g/h}$) or nanograms per hour (ng/h) during different operational phases. For printers, which run through intermittent printing jobs, unit-specific emission rates are presented as either particle count or micrograms per hour of active printing, particle count or micrograms per page printed, and/or particle count or micrograms per print job. Only VOCs were detected during the idle phase for printers, and these are reported with units of micrograms per hour.

In the sections below, results are provided for computer emissions of VOCs, aldehydes, and SVOCs. Computer results are presented first. Here the results address emissions from new (“out-of-the-box”) computers, how these emissions change in time, and how on/off cycling impacts emissions. After computer results, come printer results, which point out factors that affect VOC, ozone, and particulate matter emissions. The last set of results are from a series of experiments used to explore factors that can alter the emission rates from computers and printers.

4.2.1. Computer Emission Rates Measurements

Unit-specific emission rates are presented here for VOCs, SVOCs, siloxanes, and aldehydes. Background levels measured in the chamber during the computer experiments are provided in Appendix H. Because there were no measurable emissions of particulate matter or ozone from computers, there are no results for these pollutants presented for computers. Computer emissions are presented as new (“out-of-the-box”) levels, and then as time-varying levels as the computer “ages.” In addition, the impact of on/off cycling relative to continuous (constant-on) operation is presented.

Computer “Out-of-Box” Emission Rates

Figure 23 provides the results for VOC emission rates from the pre-operational (off) measurements, and Figure 24 provides results for VOC emission rates during the first active period of computer operation. Both figures list results for all target VOCs that were emitted from at least one unit at a rate exceeding $5 \mu\text{g/h}$ in either the pre-operational or active phase. In comparing these figures, it is important to note that the y-axis scale is four times larger in Figure 24, compared to Figure 23. So these results show a significant increase for almost all VOCs of emission rates in going from the pre-operational to the active period; that is, once a computer is taken out of the box and turned on. Table 22 lists all measured out-of box computer unit-specific emission rates ($\mu\text{g/h/unit}$) (\pm standard deviation) for VOCs, two-ring PAHs, and siloxanes during the pre-operation phase. Table 23 lists all measured out-of box computer unit-specific emission rates ($\mu\text{g/h/unit}$) (\pm standard deviation) for VOCs, two-ring PAHs, and siloxanes during the first active operational phase. Background concentrations in the test chamber for these chemicals are given in Appendix H.

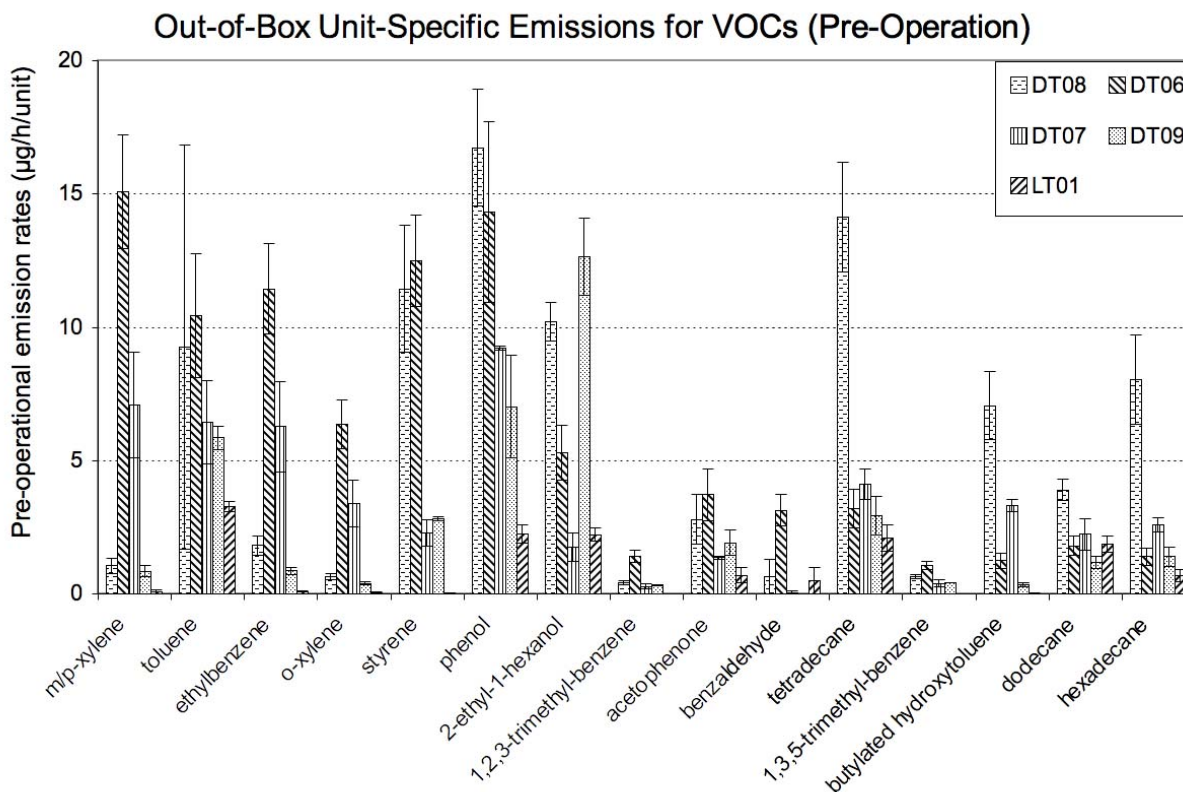


Figure 23. Unit-specific emissions factors (µg/h/unit) for VOCs emitted from new computers taken out of the box but not yet turned on (pre-operational). Error bars represent ± 1 standard deviation based on replicate measurements collected while computers were idle with sample sizes for DT06, DT07, DT08, DT09, and LT01 were 4, 2, 3, 3, and 2, respectively.

Semi-volatile organic compounds analyzed included PAHs, brominated flame retardants (BFRs), and organophosphate flame retardants (OPFR). The only PAHs that were identified above the MDL for the individual computer experiments (both in pre-operational and active emissions) are naphthalene, 1-methyl naphthalene, and 2-methyl naphthalene. Computer emissions rates for these compounds are listed in Table 22 (pre-operational) and Table 23 (active). There were no BFRs identified above the MDL from the individual computer experiments. There were six OPFRs identified and measured during active operation of the individual computers. These are triethyl phosphate (TEP), tributyl phosphate (TBP), tris(2-chloroethyl) phosphate (TCEP), triphenyl phosphate (TPP), tris (2-butoxyethyl) phosphate (TBEP), and tris (2-ethylhexyl) phosphate (TEHP). The levels during idle operation were somewhat lower and difficult to detect reliably, as were the levels when the computers were off. So only the “active” emissions are reported here. Measured results from this experiment are presented in Figure 25, which shows unit-specific emissions factors in nanograms per hour per unit for OPFRs emitted from new computers taken out of the box during active operation.

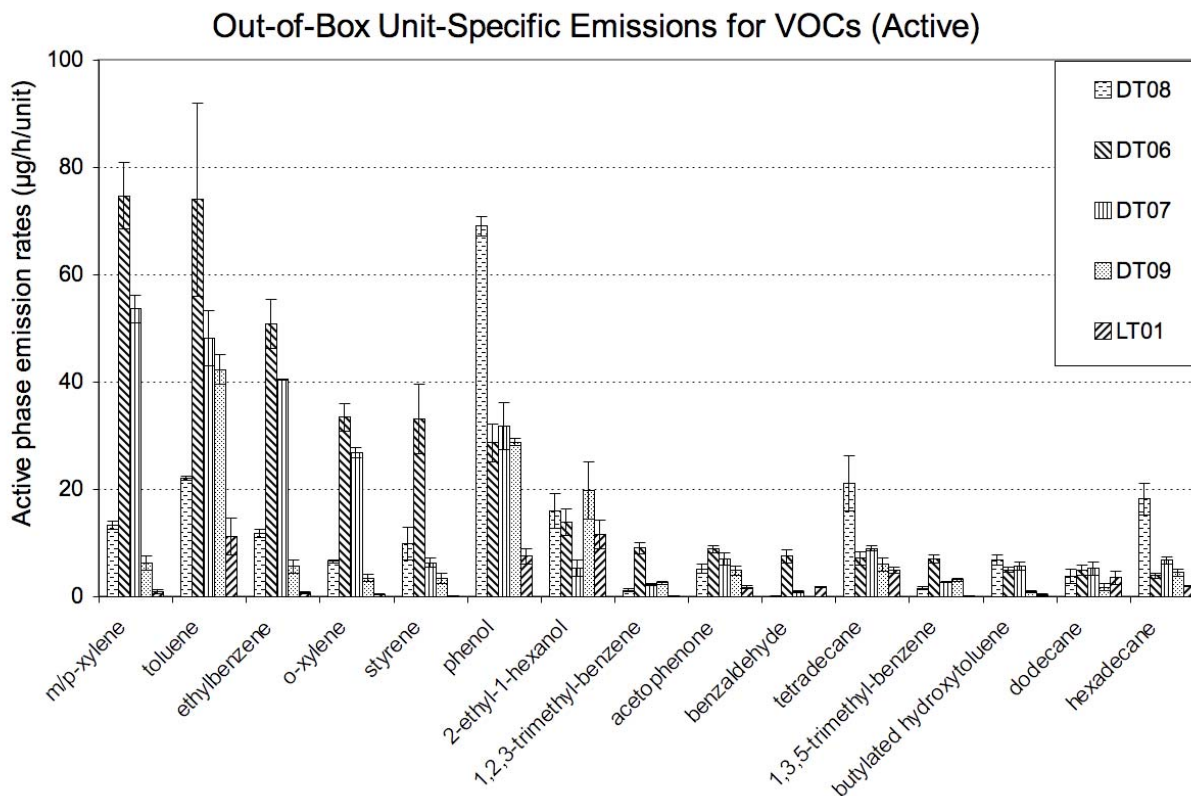


Figure 24. Unit-specific emissions factors ($\mu\text{g}/\text{h}/\text{unit}$) for VOCs emitted from new computers taken out of the box during their first active operation (active). Error bars represent ± 1 standard deviation based on replicate measurements during active computing with sample sizes for *DT06*, *DT07*, *DT08*, *DT09*, and *LT01* of 3, 3, 3, 4, and 2, respectively.

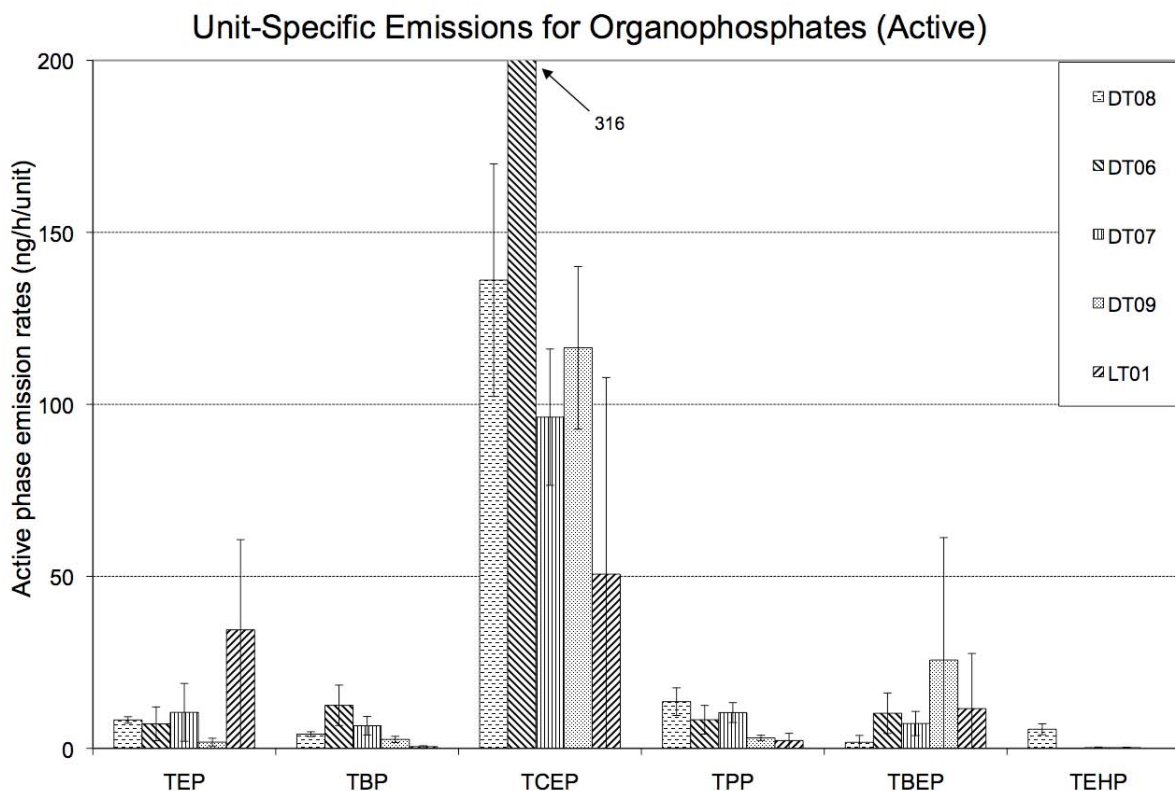


Figure 25. Unit-specific emissions factors (ng/h/unit) for OPFRs emitted from new computers taken out of the box during active operation. Error bars represent ± 1 standard deviation based on five replicate measurements collected during active computing.

Figure 26 provides the results for siloxane emission rates from the pre-operational measurements, and Figure 27 provides results for siloxane emission rates during the first active period of computer operation. In comparing Figure 26 and Figure 27, which both have the same y-axis scale, the siloxane emissions are similar between the pre-operational and active periods. Some siloxane emissions appear to decrease from the pre-operational to the active period.

Pre-operational, active, and aging emissions of low molecular weight aldehydes were also evaluated during this experiment. Results for these are provided in the next section, which describes the results of experiments that measure emissions changes as computers age.

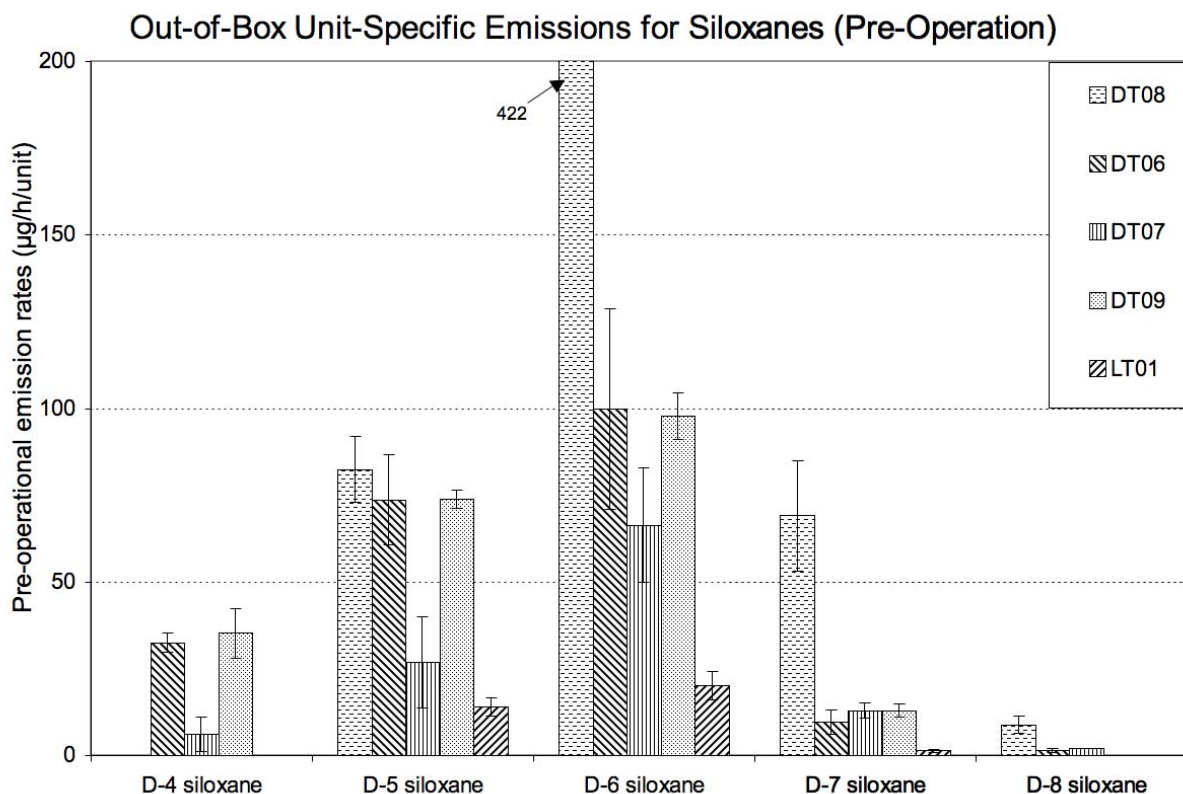


Figure 26. Unit-specific emissions factors ($\mu\text{g/h/unit}$) for siloxanes emitted from new computers taken out of the box but not yet turned on (pre-operational). Error bars represent ± 1 standard deviation based on replicate measurements collected while computers were idle with sample sizes for the *DT06*, *DT07*, *DT08*, *DT09*, and *LT01* of 4, 2, 3, 3, and 2, respectively.

No value is reported if the chamber concentration for that chemical is less than three times the average background in the empty chamber for the experiment, and the standard deviations were excluded if only one sample had a valid number.

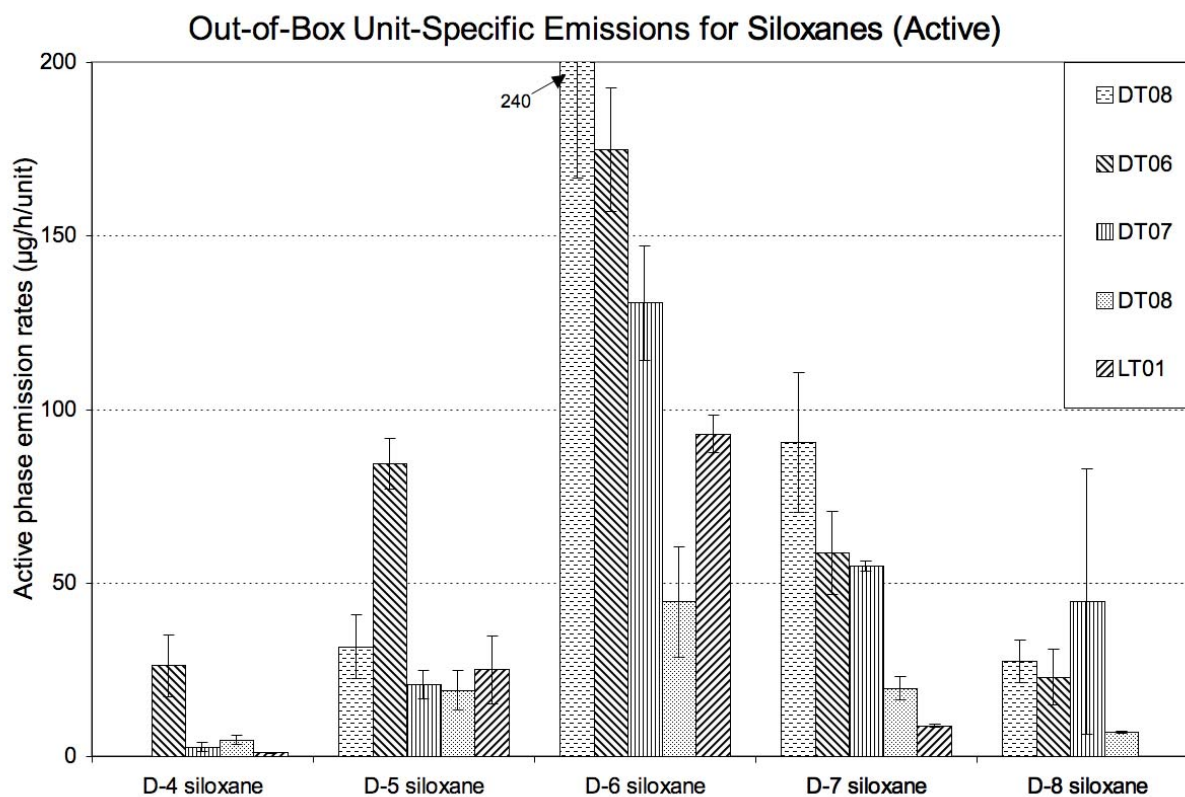


Figure 27. Unit-specific emissions factors ($\mu\text{g/h/unit}$) for siloxanes emitted from new computers taken out of the box during their first active operation (active). Error bars represent ± 1 standard deviation based on replicate measurements during active computing with sample sizes for the *DT08*, *DT06*, *DT07*, *DT09*, and *LT01* of 3, 3, 3, 4, and 2, respectively.

Table 22. Out-of box unit-specific emission rates ($\mu\text{g}/\text{h}/\text{unit}$) (\pm standard deviation)^a for computers during the pre-operation phase

	<i>DT06</i>	<i>DT07</i>	<i>LT01</i>	<i>DT08</i>	<i>DT09</i>
D4 Siloxane	32.53 (± 2.87)	6.11 (± 4.97)			35.27 (± 7.16)
D5 Siloxane	73.71 (± 13.09)	26.75 (± 13.16)	14.03 (± 2.61)	82.37 (± 9.48)	73.81 (± 2.57)
D6 Siloxane	99.92 (± 28.92)	66.39 (± 16.41)	20.19 (± 4.01)	421.58 (± 50.84)	97.87 (± 6.73)
D7 Siloxane	9.77 (± 3.50)	12.89 (± 2.21)	1.33 (± 0.38)	69.06 (± 16.01)	12.98 (± 1.88)
D8 Siloxane	1.49 (± 0.68)	1.98 (± 0.01)		8.90 (± 2.61)	
Toluene	10.44 (± 2.34)	6.45 (± 1.57)		9.24 (± 7.58)	5.85 (± 0.45)
Ethylbenzene	11.44 (± 1.70)	6.27 (± 1.69)		1.83 (± 0.36)	0.86 (± 0.12)
m/p-Xylene	15.08 (± 2.13)	7.08 (± 2.00)			
o-Xylene	6.35 (± 0.91)	3.40 (± 0.88)		0.66 (± 0.11)	
Styrene	12.51 (± 1.71)	2.30 (± 0.50)		11.45 (± 2.38)	2.82 (± 0.08)
propyl-benzene	0.49 (± 0.06)	0.30 (± 0.09)		0.91 (± 0.13)	0.37 (± 0.02)
1,3,5-trimethyl-benzene	1.07 (± 0.16)	0.39 (± 0.12)		0.65 (± 0.07)	0.42 (± 0.01)
2-methylprop benzene	0.10 (± 0.02)				
1,2,3-trimethyl-benzene	1.40 (± 0.23)	0.28 (± 0.10)			
Benzaldehyde					
1,3-diethyl-benzene,	0.14 (± 0.02)	0.08 (± 0.02)		0.53 (± 0.06)	0.28 (± 0.02)
butyl-benzene	0.15 (± 0.03)	0.08 (± 0.02)		0.16 (± 0.03)	0.14 (± 0.01)
2-ethyl-1-Hexanol	5.28 (± 1.03)		2.22 (± 0.24)	10.22 (± 0.73)	12.64 (± 1.45)
1,2,3,4-tetramethyl benzene	0.30 (± 0.06)	0.10 (± 0.02)	0.03 (± 0.01)	0.18 (± 0.03)	0.15 (± 0.02)
1,2,3,5-tetramethyl benzene	0.74 (± 0.13)	0.21 (± 0.04)	0.05 (± 0.01)	0.50 (± 0.05)	0.41 (± 0.06)
Dodecane	1.81 (± 0.35)	2.23 (± 0.60)	1.87 (± 0.31)	3.90 (± 0.41)	1.19 (± 0.23)
Acetophenone	3.72 (± 0.98)			2.80 (± 0.95)	1.92 (± 0.48)
Phenol	14.33 (± 3.40)	9.24 (± 0.08)	2.25 (± 0.33)	16.74 (± 2.19)	7.02 (± 1.91)
Naphthalene	0.68 (± 0.18)	0.25		0.67 (± 0.11)	0.78 (± 0.19)
Tetradecane	3.21 (± 0.72)	4.12 (± 0.57)	2.08 (± 0.49)	14.15 (± 2.06)	2.93 (± 0.71)
2-methyl-Naphthalene	0.22 (± 0.05)	0.15		0.26 (± 0.04)	0.23 (± 0.06)
1-methyl-Naphthalene	0.12 (± 0.03)	0.06		0.14 (± 0.03)	0.11 (± 0.03)
Hexadecane	1.39 (± 0.32)	2.59 (± 0.26)	0.70 (± 0.23)	8.04 (± 1.68)	1.40 (± 0.36)
Butylated Hydroxytoluene	1.25 (± 0.28)	3.32 (± 0.23)		7.07 (± 1.26)	0.35 (± 0.07)
Dibutylphthalate		1.61 (± 0.37)			

^a The standard deviation is determined from replicate experiments and/or replicate measurements collected during an emissions experiment. Replicate measurements were determined by combining measurements from consecutive samples and recalculating the emission rate.

Table 23. Out-of-box unit-specific emission rates ($\mu\text{g}/\text{h}/\text{unit}$) (\pm standard deviation) for computers during the active (operational) phase where power use during active phase (watts) was provided for reference below the unit name

	<i>DT06</i> (96 watts)	<i>DT07</i> (92 watts)	<i>LT01</i> (47 watts)	<i>DT08</i> (90 watts)	<i>DT09</i> (101 watts)
D4 Siloxane	26.14 (± 8.99)	2.68 (± 1.31)	1.07 (± 0.17)		4.79 (± 1.31)
D5 Siloxane	84.43 (± 7.23)	20.73 (± 4.18)	24.97 (± 9.80)	31.60 (± 9.24)	19.04 (± 5.75)
D6 Siloxane	174.85 (± 17.72)	130.67 (± 16.62)	92.93 (± 5.39)	240.46 (± 73.8)	44.53 (± 15.83)
D7 Siloxane	58.68 (± 11.93)	54.90 (± 1.35)	8.83 (± 0.42)	90.49 (± 20.1)	19.68 (± 3.44)
D8 Siloxane	22.89 (± 7.93)	44.74 (± 38.30)		27.58 (± 6.12)	7.01 (± 0.31)
Toluene	74.03 (± 18.01)	48.18 (± 5.19)	11.28 (± 3.42)	22.02 (± 0.36)	42.36 (± 2.74)
Ethylbenzene	50.91 (± 4.59)	40.52 (± 0.11)	0.77 (± 0.13)	11.75 (± 0.78)	5.67 (± 1.27)
m/p-Xylene	74.74 (± 6.16)	53.64 (± 2.53)		13.29 (± 0.73)	6.20 (± 1.33)
o-Xylene	33.48 (± 2.53)	26.92 (± 0.98)		6.58 (± 0.28)	3.46 (± 0.65)
Styrene	33.18 (± 6.52)	6.35 (± 0.86)		9.87 (± 3.01)	3.42 (± 0.88)
propyl-benzene	2.45 (± 0.26)	1.68 (± 0.01)		1.94 (± 0.34)	2.18 (± 0.19)
1,3,5-trimethyl-benzene	7.03 (± 0.80)	2.75 (± 0.05)		1.59 (± 0.31)	3.17 (± 0.24)
2-methylprop benzene	0.50 (± 0.08)	0.23		0.10 (± 0.03)	0.21 (± 0.03)
1,2,3-trimethyl-benzene	9.08 (± 1.05)	2.24 (± 0.17)	0.19 (± 0.06)	1.16 (± 0.30)	2.58 (± 0.21)
Benzaldehyde	7.53 (± 1.30)				
1,3-diethyl-benzene,	0.85 (± 0.11)	0.46	0.07 (± 0.01)	0.96 (± 0.21)	0.87 (± 0.14)
butyl-benzene	0.87 (± 0.11)	0.57	0.08 (± 0.01)	0.30 (± 0.07)	0.45 (± 0.08)
2-ethyl-1-Hexanol	13.91 (± 2.53)	5.40 (± 1.54)	11.65 (± 2.68)	16.01 (± 3.31)	19.83 (± 5.40)
1,2,3,4-tetramethyl benzene	1.30 (± 0.15)	0.76	0.13 (± 0.02)	0.23 (± 0.06)	0.37 (± 0.08)
1,2,3,5-tetramethyl benzene	2.97 (± 0.32)	1.77 (± 0.03)	0.21	0.61 (± 0.17)	1.00 (± 0.23)
Dodecane	4.91 (± 0.98)	5.26 (± 1.29)	3.53 (± 1.27)	3.74 (± 1.35)	1.78 (± 0.70)
Acetophenone	8.86 (± 0.61)	7.07 (± 1.18)		5.22 (± 0.92)	4.87 (± 0.81)
Phenol	28.72 (± 3.55)	31.80 (± 4.45)	7.60 (± 1.43)	69.12 (± 1.81)	28.79 (± 0.66)
Naphthalene	2.45 (± 0.35)	1.44 (± 0.48)	0.45 (± 0.12)	0.78 (± 0.22)	2.22 (± 0.36)
Tetradecane	7.17 (± 1.24)	9.04 (± 0.43)	4.94 (± 0.64)	21.15 (± 5.17)	6.03 (± 1.24)
2-methyl-Naphthalene	0.72 (± 0.07)	0.60 (± 0.05)	0.11 (± 0.02)	0.40 (± 0.09)	0.71 (± 0.10)
1-methyl-Naphthalene	0.39 (± 0.04)	0.28		0.22 (± 0.05)	0.39 (± 0.05)
Hexadecane	3.93 (± 0.48)	6.78 (± 0.65)	2.02 (± 0.06)	18.19 (± 2.99)	4.51 (± 0.63)
Butylated Hydroxytoluene	4.98 (± 0.50)	5.70 (± 0.75)	0.33 (± 0.16)	6.89 (± 0.96)	1.02 (± 0.22)
Dibutylphthalate	0.19 (± 0.14)	2.32 (± 0.33)		0.97 (± 1.64)	

Emissions Changes with Time: The Impact of “Aging”

To assess the impact of aging on pollutant emissions, the VOC emission rate measurements were repeated at several different age points, where age was based on the elapsed processor time while the computer was turned on and active. The measured emission rates at each time point for each chemical was first normalized by dividing it by its out-of-box emission rate to obtain the relative change in the emission rate as a function of processor age. Next, for each computer, all chemicals with initial emission rates greater than 5 µg/h/unit were used to calculate the average fraction remaining at each time point. The results of this calculation are shown in Figure 28. The error bars are the standard deviation of the fraction of each chemical remaining at each age point. Also shown in this figure is a line showing the trend of decreasing emissions with increasing processor age. The emissions decay curve [$y=a+bln(x)$] is simultaneously fit to the emission rate data for all computers and all measured VOCs that had starting emission rates greater than 5 µg/unit/h. The best fit line was determined by minimizing the sum of square errors between the measured emissions and the model estimates. This curve indicates that VOC emissions are decreasing at an approximate rate of 0.12% per hour of active processor time, or roughly 3% per day of processor operation. The composition of the emission stream at each time point is illustrated for the desktop computer *DT06* in the pie charts in Figure 29, where the six VOCs listed make up 98% of the mass in the VOC emissions (excluding siloxanes).

The aging of siloxanes emissions were determined separately. These compounds showed some evidence of aging with elapsed processor time, but the results were not definitive, so the researchers elected not to conclude whether there is a significant aging effect for siloxanes. If there is an aging effect for siloxanes, it is rather slow compared to VOCs.

Pre-operational, active, and aging emissions of low-molecular-weight aldehydes were also evaluated during this experiment. Only two aldehydes—formaldehyde and acetaldehyde—are included. The higher molecular weight carbonyls are included in the VOC analysis. Table 24 summarizes the preoperational, active and aging emissions of these two compounds for three of the five computers included in this experiment. For these machines the decrease of formaldehyde emissions with processor age followed a trend similar to VOCs, with emissions rates decreasing at roughly 3% per day of processor time.

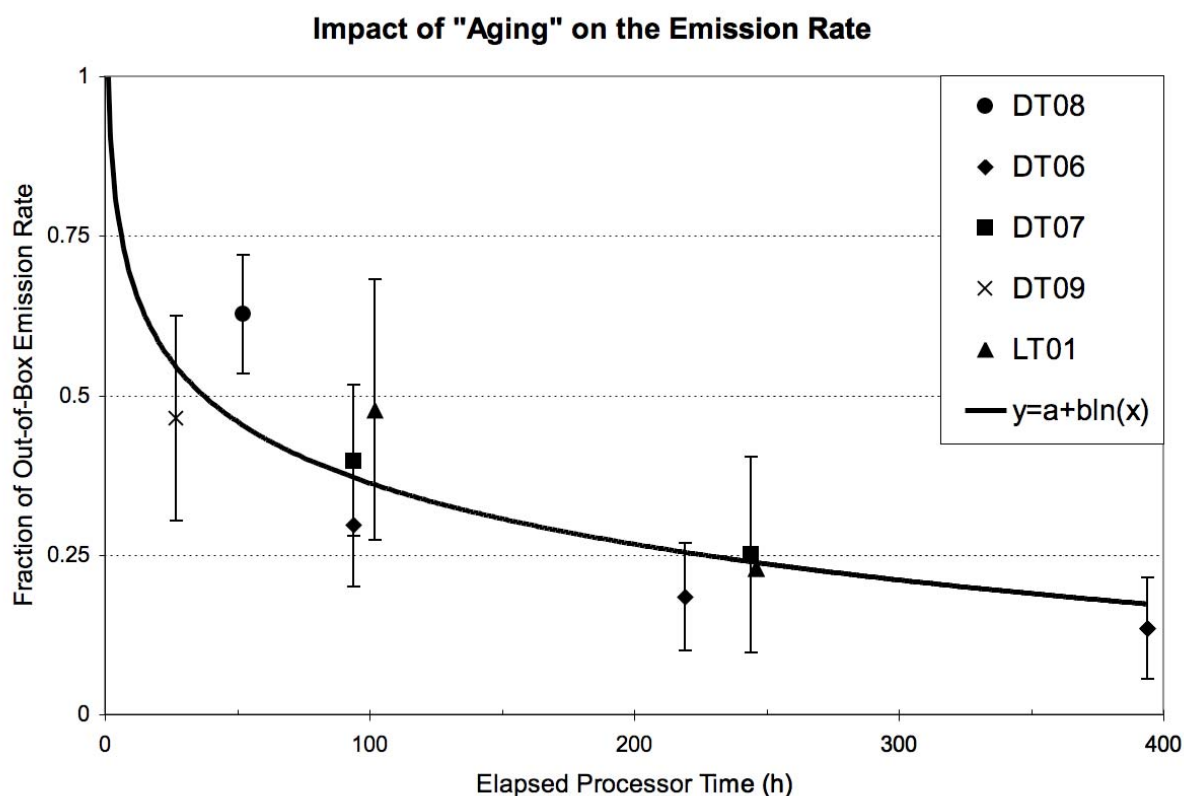


Figure 28. The decrease of total VOC emissions as a function of processor time for five units. Emission rates are reported as a fraction of the “out-of-box” emission rate for each unit normalized to the initial out-of-box emissions. The error bars represent ± 1 standard deviation for all chemicals with initial emission rates greater than $5 \mu\text{g}/\text{unit}/\text{h}$. The sample sizes for the *DT06*, *DT07*, *DT08*, *DT09*, and *LT01* were 10, 11, 11, 6, and 3, respectively. Also shown is a logarithmic model fit to these observations, showing that the rate of decrease in VOC emissions is approximately 0.12% per hour, or 3% per day (after about 100 hours of operation).

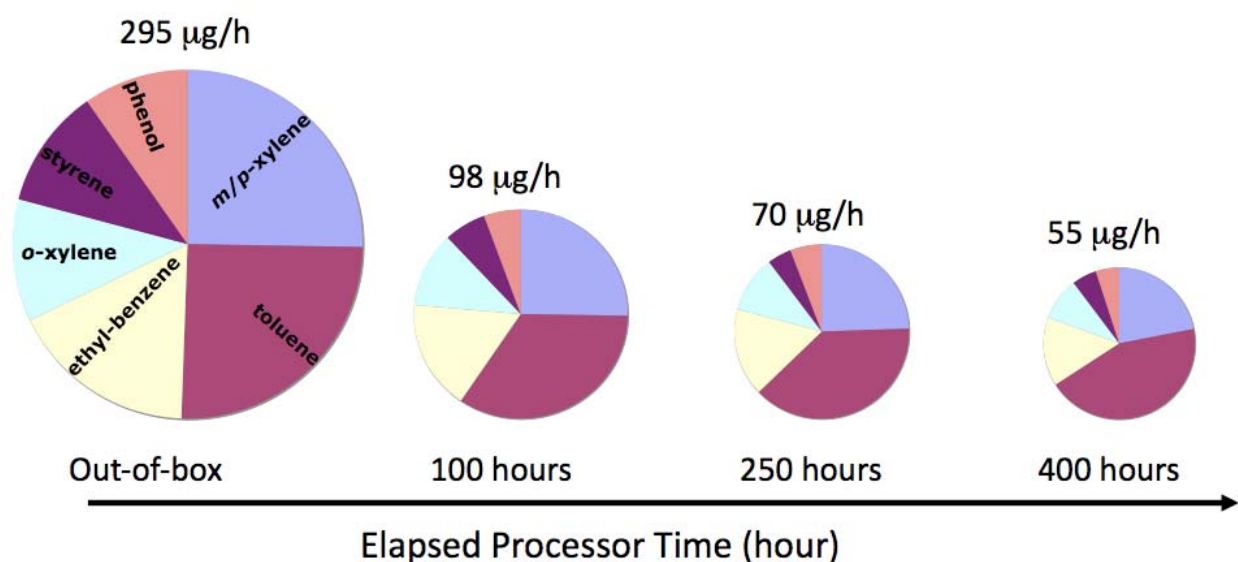


Figure 29. The composition of the emission stream for the *DT06* computer, where the listed chemicals make up 98% of the total mass in the emissions, excluding siloxanes.

Table 24. Low-molecular-weight aldehyde emission rates (µg/h/unit) for individual computers in Phase II

	<i>DT06</i>	<i>DT07</i>	<i>LT01</i>
Formaldehyde			
Pre-operation	1.69	2.34	1.04
Out-of-box	32.06	26.44	2.95
~ 100 hours	17.39	10.82	2.81
~ 250 hours	11.15	6.28	
Acetaldehyde			
Pre-operation	0.34	3.02	
Out-of-box	4.40	10.28	2.37
~ 100 hours	2.45	3.39	1.12
~250 hours	2.40	2.92	

The Impact of On/Off Cycling on VOC and Siloxane Emissions

Following the aging experiment, the next experiment was designed to assess how on/off cycling affects computer emissions. The aging experiments demonstrated that VOC and aldehyde emissions decrease with time when computers are run continuously. But what happens when computers are turned on and off, rather than being on continuously? Will emission rates age as quickly as they did for computers that are left on continuously, or will emission rates change during repeated startups?

For this experiment, two computers—*DT08* and *DT09*—were selected and tested for both VOC and siloxane emissions in a scenario where the machines repeatedly cycled on and off. For the

DT09 computer, this experiment lasted for 39.5 hours of processor time. The “out-of-box” computer was started up and run for six hours during software loading and testing. Then it was turned off. It was placed in the chamber, and after idle phase samples were collected, the unit was turned on and put in continuous operation from processor hours 6 to 23. During this time the “out-of-box” emission samples were collected. From hours 23 to 37.5, the computer was turned on and off repeatedly, and a sample was collected from hours 23.5 to 37.5. Then from hours 37.5 to 39.5, the computer was put back in continuous active operation for the last sample, which represented a second processor age point.

For the *DT08* computer, this experiment lasted for 55.5 hours of processor time. Once again, the “out-of-box” computer was started up and run for six hours during software loading and testing. Then it was turned off. It was placed in the chamber, and after collecting the pre-operational sample it was turned on and put in continuous operation from processor hours 6 to 10 for the first sample collection. From hours 10 to 48.5 it was turned on and off in five-minute intervals. That is, the computer was turned off and allowed to cool down for five minutes and then turned on for five minutes. For this experiment the sample was collected during hours 31 to 47. Then from hours 48.5 to 55.5, the computer was put back in continuous active operation for the final emissions sample.

The results from the “on/off” experiments include emissions rates for both VOCs and siloxanes. Figure 30 shows VOC emission rates from *DT09*, and Figure 31 shows VOC emissions rates from *DT08*. Figure 32 shows siloxane emission rates from the *DT09* and Figure 33 shows siloxane emissions rates from *DT08*. Only chemicals with initial emission rates greater than 5 µg/unit/h are included. For each sampling period, the emission rates illustrated in Figures 30 to 33 are based on the time the computer was actually running rather than the elapsed time of the experiment. The first sample reported in each figure is considered the “out-of-box” emission rate.

The on/off cycling experiments provide emission rates at different ages (processor time) for each unit. Similar to the aging experiments, the results from the on/off cycling experiments indicate that there is a reduction of VOC emission as the processor ages. The *DT09* computer that was continuously cycled on and off had a combined emission rate for the major constituents listed in Figure 30 that was 42% (± 17) of the out-of-box emissions rate at 39 hours, compared to a predicted value of 49% based on decay curve from the experiment data discussed in the previous section. Although no formal statistical analysis was performed, the results suggests that for continuous cycling that does not give the unit time to cool, the emissions during active computing and the rate at which those emission decrease with age are not different from a continuously operating computer. The *DT08* computer that was cycled on/off at five-minute intervals, had a combined emission rate for the major constituents after 52 hours of processor time that was 63% (± 10) of the original out-of-box emission rate, compared to a predicted value of 45%. The emission rate did not decrease as quickly for the computer that cycled on a five-minute interval compared to a continuously active unit. Allowing the computer to cool down between cycled runs (i.e., leaving the unit off for five minutes before starting again) seems to have resulted in a reduction in emissions during the on/off cycling phase and a subsequent reduction in the rate of aging for the emissions stream. For siloxanes the aging rate is much

slower and more inconsistent among different machines, so it is more difficult to conclude whether on/off cycling has any impact on siloxane emissions.

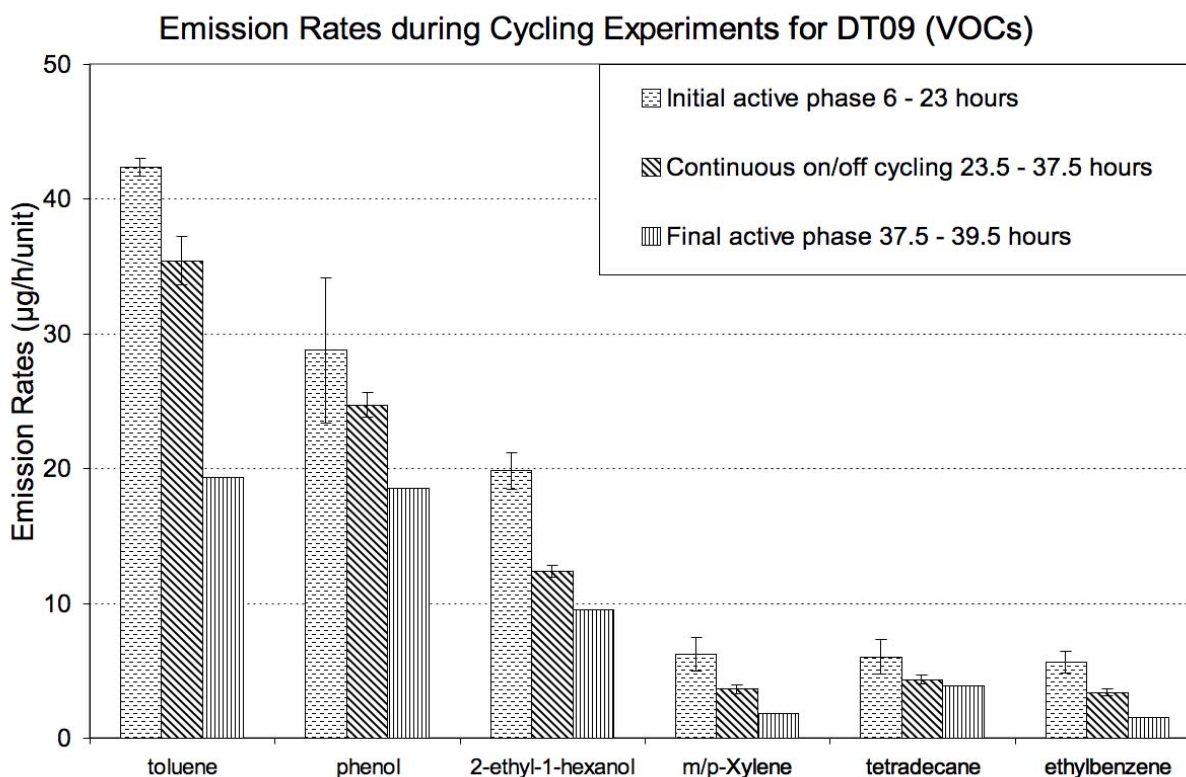


Figure 30. VOCs emission rates from the *DT09* computer during the on/off cycling experiment. Only chemicals with initial emission rates greater than 5 µg/h/unit are included. For each sampling period, the emission rates are based on the time the computer was actually running. Error bars represent ± 1 standard deviation based on replicate measurements during initial active computing (n=4) and during the cycling phase (n=4).

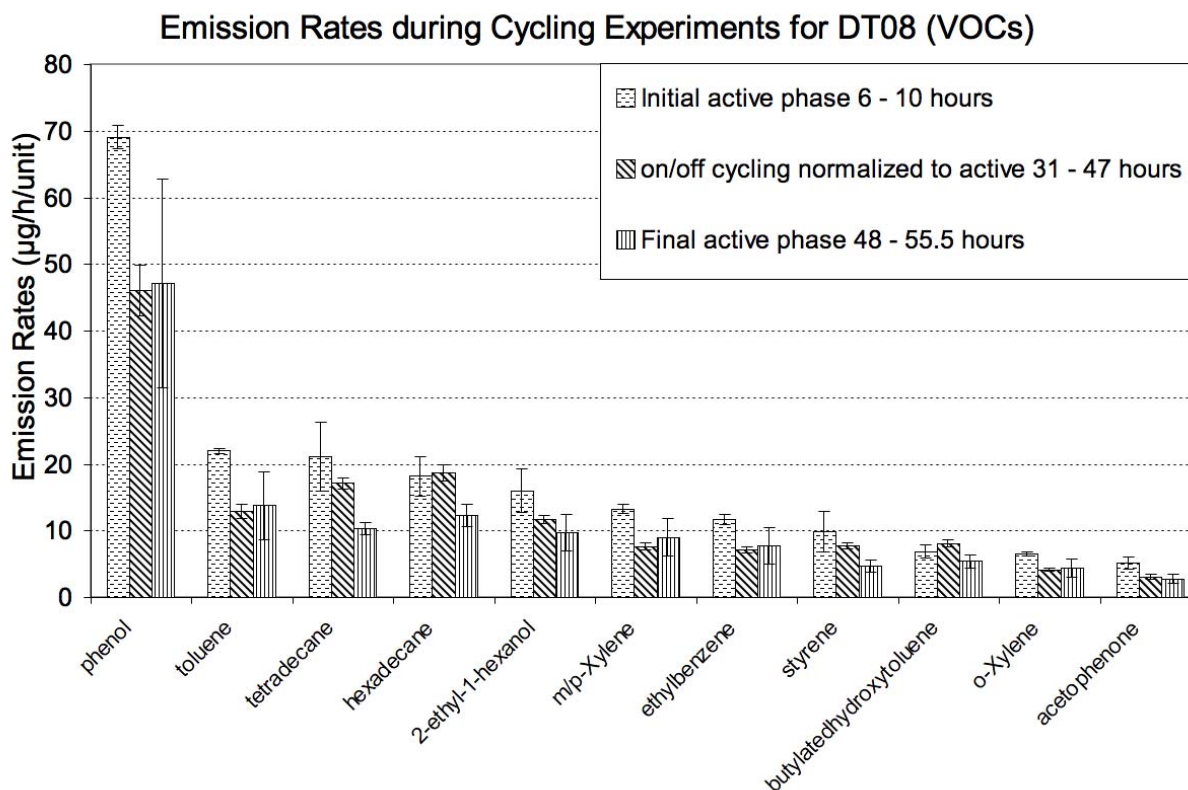


Figure 31. VOCs emission rates from the *DT08* computer during the on/off cycling experiment. Only chemicals with initial emission rates greater than 5 µg/h/unit are included. For each sampling period, the emission rates are based on the time the computer was actually running. Error bars represent ± 1 standard deviation based on replicate measurements during initial active computing (n=3), during the cycling phase (n=4), and during a final active phase (n=3).

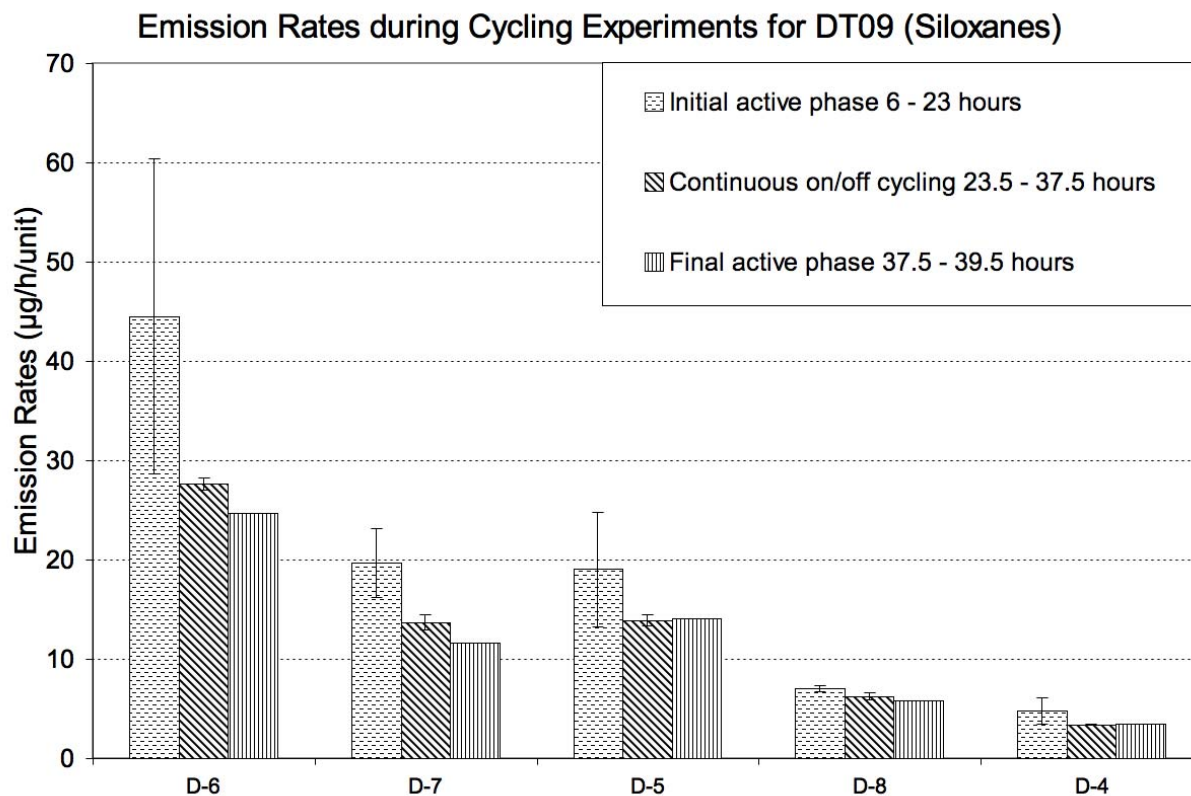


Figure 32. Siloxane emission rates from the *DT09* computer during the on/off cycling experiment. Only chemicals with initial emission rates greater than 5 µg/h/unit are included. For each sampling period, the emission rates are based on the time the computer was actually running. Error bars represent ± 1 standard deviation based on replicate measurements during initial active computing (n=4) and during the cycling phase (n=4).

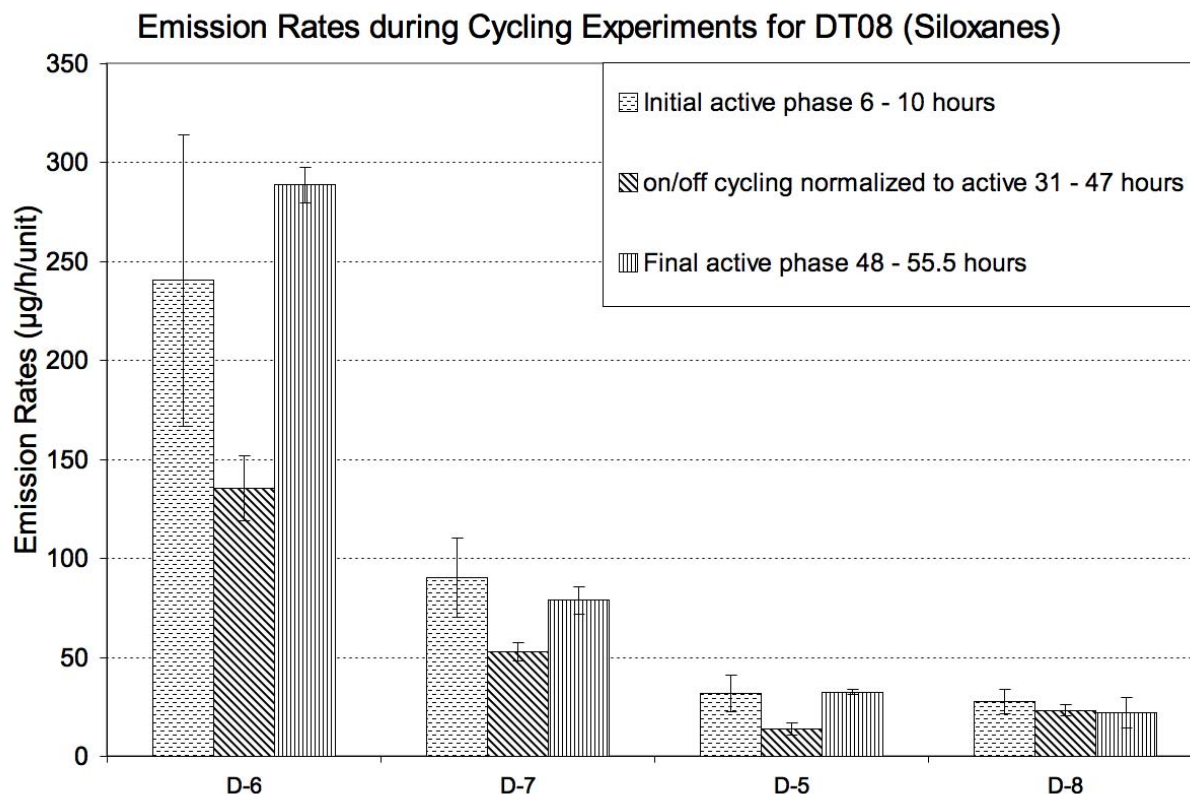


Figure 33. Siloxane emission rates from the *DT08* computer during the on/off cycling experiment. Only chemicals with initial emission rates greater than 5 µg/h/unit are included. For each sampling period, the emission rates are based on the time the computer was actually running. Error bars represent ± 1 standard deviation based on replicate measurements during initial active computing (n=3), during the cycling phase (n=4), and during a final active phase (n=3).

Power Use and Emissions for Computers

The relationship of emissions to power use for the computers in this study was first evaluated by plotting the total measured VOC emissions for each computer against the power use for that computer where power use (W) was measured during the active phase of computing (Figure 34). The lowest point on both the power use and emission axis is the laptop unit (LT01). If we exclude the laptop, there is no apparent correlation of total VOC emissions and power use because all of the desktop units tested have similar power consumption during active computing. The lowest point on the emissions curve for the desktop units is the “white-box” computer (DT09). The other three units with elevated power use and emissions are all name-brand desktop computers (DT06, DT07, and DT08). It should be noted that power consumption is likely a direct indication of both heat load in the computer and ventilation rate of the box, both of which could affect emission rates.

All of the units in the power-versus-emissions experiments were performing similar tasks and for the desktop units the difference in power consumption was not great. The correlation

between power use during active computing and emissions for individual VOCs was calculated, and the results are summarized in Table 25. The chemicals in bold are the highest contributors to the emissions stream, as indicated in Figure 24. The highest correlation is found only when the name-brand computers are assessed and the laptop and the “white-box” unit are excluded. It is noted here that the evaluation of the relationship between emissions and power use were performed across multiple units performing equivalent tasks, and not for the same unit performing different tasks, although it would be possible to run individual units under different computing loads.

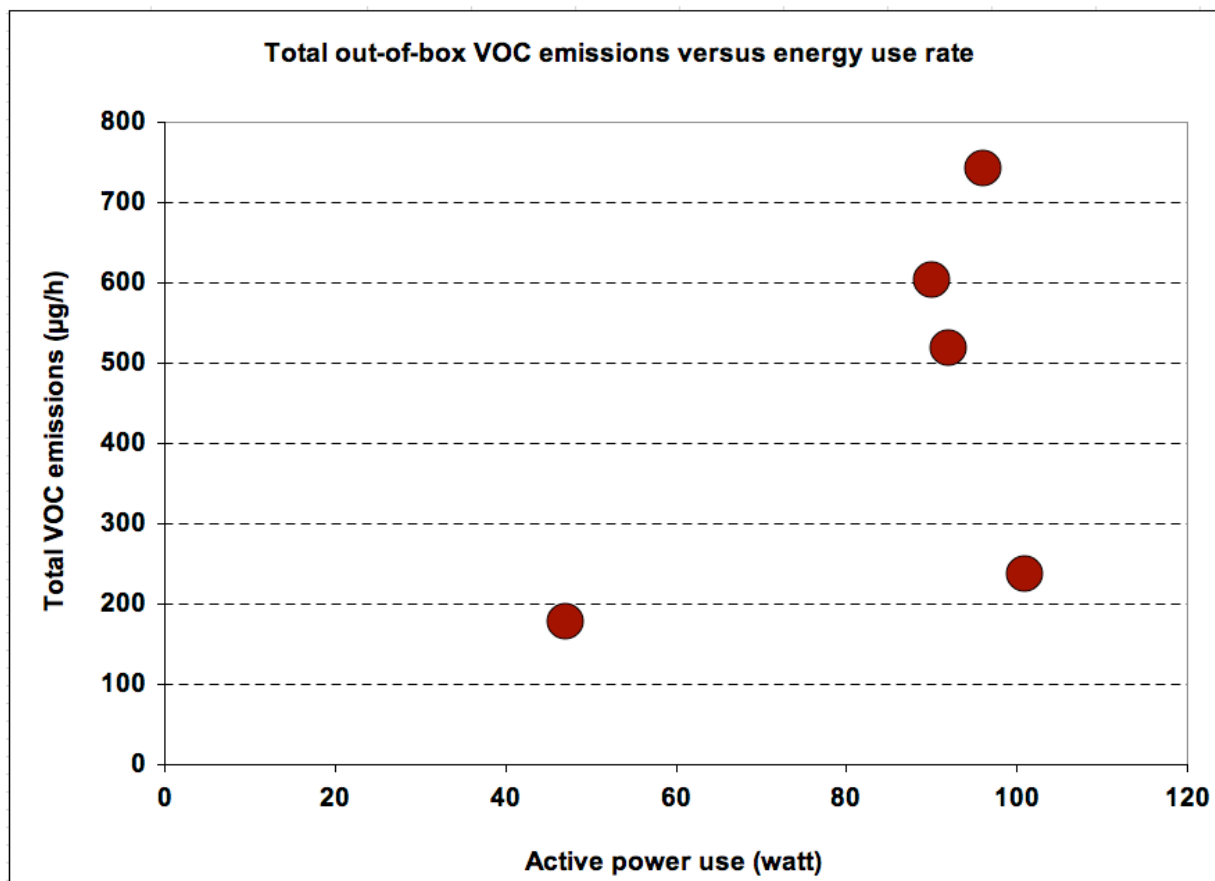


Figure 34. The relationship of out-of-box total VOC emissions to power use for computers. The lowest point is the laptop unit and the point with the higher power usage, but low emissions is the white-box unit.

Table 25. Correlation between power use during active computing and individual VOC emissions for all units combined, desktop units only, and name brand units only

Chemical	All units	Desktops	Name-brand units
m/p-Xylene^a	0.46	-0.16	0.93
Toluene	0.69	0.38	0.98
Ethylbenzene	0.48	-0.21	0.90
o-Xylene	0.47	-0.19	0.89
Styrene	0.43	-0.01	0.90
Phenol	0.53	-0.70	-0.80
1-Hexanol,2-ethyl-	0.28	0.57	0.00
Benzene,1,2,3-trimethyl-	0.50	0.30	0.98
Acetophenone	0.77	-0.10	0.98
Benzaldehyde	0.07	0.13	0.98
Tetradecane	0.26	-0.77	-0.83
Benzene,1,3,5-trimethyl-	0.66	0.39	0.99
ButylatedHydroxytoluene	0.51	-0.97	-0.95
Dodecane	0.00	-0.66	0.59
Hexadecane	0.30	-0.74	-0.87
Benzene,1,2,3,5-tetra...	0.58	0.15	0.98
Benzene,propyl-	0.97	0.60	0.78
Naphthalene	0.76	0.84	1.00
Benzene,1,2,3,4-tetra...	0.51	0.11	0.98
Benzene,butyl-	0.72	0.25	0.99
Benzene,1,3-diethyl-	0.86	0.21	-0.03
Naphthalene,2-methyl-	0.93	0.83	0.94
Benzene,(2-methylprop...	0.65	0.34	1.00
Naphthalene,1-methyl-	0.94	0.90	1.00
Dibutylphthalate	0.26	-0.70	-0.53

^a Chemicals written in bold text are those with the largest contribution to the emissions stream as reported in Figure 24.

4.2.2. Printer Emission Rates Measurements

Unit-specific printer emission rates are presented here for VOCs, ozone, and particulate matter. Particulate matter emissions are assessed as particle number concentration for ultrafine particulate matter (UFP). A series of experiments were used to characterize the temporal trends in printer emissions and the variability among different printing devices. These experiments used seven medium-output laser technology printers or multifunction devices and one inkjet printer. Because the Phase I study provided good characterization of inkjet emissions and demonstrated that inkjet printers do not emit significant quantities of particulate matter or ozone, only one inkjet printer was included in the individual-printers study. The first set of seven experiments focused on characterizing initial print and extended print emission rates—primarily for laser printers. The next set of eight experiments focused on power consumption and emissions variability among the individual printers.

VOC and Siloxane Emissions

Volatile organic compound and siloxane emissions were collected from the empty chamber during printer experiments and from printers during periods when the printers were on-and-idle and periods when they were actively printing. The results from the blank chamber experiments are provided in Appendix H. The results from the first set of printer emissions experiments are provided in Table 26, where the average “idle-phase” emissions ($\mu\text{g/h}$) for the laser printers ($n=7$) are compared to those from the inkjet printer. The idle phase is the period when the printer is first turned on but not yet printing. The average emission rate among the seven laser printers is referred to as the *category-specific* emission rate for idle phase, where the printers were turned on but not actively printing. These category-specific emissions are used later to evaluate any impact of different emissions control strategies. The unit-specific emissions for each printer used to determine the category specific emission rates are provided in Appendix I. Only results above the method detection limit (MDL) are included in the results. Volatile organic compounds and siloxane results are combined in this table. The results from the second set of experiments when the units are actively printing are provided in Table 27. Here the average emissions rates in $\mu\text{g/h}$ from the active printing phase for seven laser printers are again compared to those from the inkjet printer. The active period is when the printer is actually printing pages and warmed up after an idle phase. The average emission rate among the seven laser printers is referred to as the category specific emission rate for active printing. These category specific emissions are used later to evaluate the impact of different emissions control strategies.

Printer VOC and siloxane emissions were also characterized as mass emitted per printed page during the active printing period. For the top fifteen identified chemical emissions (by mass emitted from printers), Figure 35 presents the emission rates expressed as micrograms per page printed. The information used to construct this figure is provided in Appendix I. Both VOCs and siloxanes were among the top fifteen, but no SVOCs were among the top fifteen emitted compounds. The table shows that there are significant differences in the emission rate per page even among printers from the same manufacturer (*LP06*, *LP07*, *LP08* and *LP10* are from one manufacturer while *LP11* and *LP12* are from a different manufacturer) and even between

essentially the same printer model (*LP06* and *LP07* are the same make and model just different production dates). This figure shows that the inkjet printer (*IJ06*) has significantly lower emissions per page-hour than the laser printers.

Table 26. Comparison of laser printers and inkjet printer emission rates ($\mu\text{g}/\text{h}/\text{unit}$): idle phase

Chemical	<i>Laser Printers^a</i>		<i>Inkjet</i>
	Emission Rate $\mu\text{g}/\text{h}/\text{unit}$	Stdev	Emission Rate $\mu\text{g}/\text{h}/\text{unit}$
Benzene	1.04	0.12	
Cyclotrisiloxane, hexamethyl-	14.40	8.17	12.27
Toluene	1.06	1.31	0.38
Hexanal	3.09	2.90	1.31
Ethylbenzene	0.29	0.17	0.11
p-Xylene	0.45	0.47	
1R-.alpha.-Pinene	0.16	0.23	
o-Xylene	0.22	0.22	
Styrene	0.68	0.66	1.36
D4-Siloxane	5.18	6.90	2.23
Benzene, propyl-	0.05	0.03	
D-Limonene	0.50	0.70	
Benzene, 1,2,3-trimethyl-	0.41		
Benzaldehyde	1.20	0.61	1.24
Octanal	7.56	8.70	
Benzene, 1,3-diethyl-	0.47	0.42	
Benzene, butyl-	0.09		
D5-Siloxane	2.73	1.99	0.87
1-Hexanol, 2-ethyl-	0.98	1.14	2.26
Nonanal	2.74	1.62	
Dodecane	0.24	0.24	
Acetophenone	0.90	0.58	1.93
Phenol	2.03	1.51	3.12
Tridecane	0.39	0.35	
Tetradecane	1.31	1.14	1.51
Pentadecane	0.52	0.36	2.41
TMPD-MIB, Texanol	0.11	0.16	
Hexadecane	0.14	0.10	2.40
Butylated Hydroxytoluene	0.02	0.03	
TMPD-DIB, TXIB	0.40	0.40	
Diethyl Phthalate	0.23	0.12	
Dibutyl Phthalate	0.34	0.13	

^a Category-specific emissions for the Laser Printer category are averages of unit-specific emissions for all the printers tested, whereas InkJet results are from a single printer.

Table 27. Comparison of laser printers and inkjet printer emission rates (µg/h/unit): active printing

Chemical	<i>Laser Printers^a</i>		<i>Inkjet</i>	
	Emission Rate µg/h/unit	Stdev	Emission Rate µg/h/unit	Stdev
Benzene	5.63	1.80		
D3-Siloxane	135.82	108.80	29.22	±10.58
Toluene	55.77	81.46	0.30	±0.30
Hexanal	343.06	235.71	2.99	±1.03
Ethylbenzene	70.42	85.09	0.00	0.08
p-Xylene	102.19	141.52		
1R-.alpha.-Pinene	6.08	3.10		
o-Xylene	58.51	59.78		
Styrene	79.97	50.94	1.24	0.35
D4-Siloxane	116.84	204.52	4.57	1.31
Benzene, propyl-	6.56	1.10		
3-Carene	8.52			
Benzene, (2-methylpropyl)-	4.84			
D-Limonene	69.04	110.79		
Benzene, 1,2,3-trimethyl-	135.19			
Benzaldehyde	85.23	48.48	1.75	0.51
Octanal	116.40	73.93		
Benzene, 1,3-diethyl-	104.62	11.17		
Benzene, butyl-	6.68			
D5-Siloxane	113.11	126.18	1.87	0.56
1-Hexanol, 2-ethyl-	66.66	70.79	2.11	0.04
Nonanal	192.04	119.70		
Dodecane	42.68	27.22		
Acetophenone	42.02	38.33	2.18	0.57
Phenol	63.85	49.21	3.19	0.89
Tridecane	154.29	223.55		
Tetradecane	531.82	328.45	1.09	0.26
Pentadecane	217.51	184.77	1.73	0.28
TMPD-MIB, Texanol	15.21	8.17		
Hexadecane	31.94	17.56	1.74	0.40
Butylated Hydroxytoluene	9.34	10.98		
TMPD-DIB, TXIB	12.32	6.06		
Diethyl Phthalate	3.70	1.97		
1-Hexadecanol	5.53	3.90		
Dibutyl Phthalate	7.18	0.23		

^a Category specific emissions for the Laser Printer category are averages of unit-specific emissions for all the printers tested; whereas the InkJet results are from a single printer.

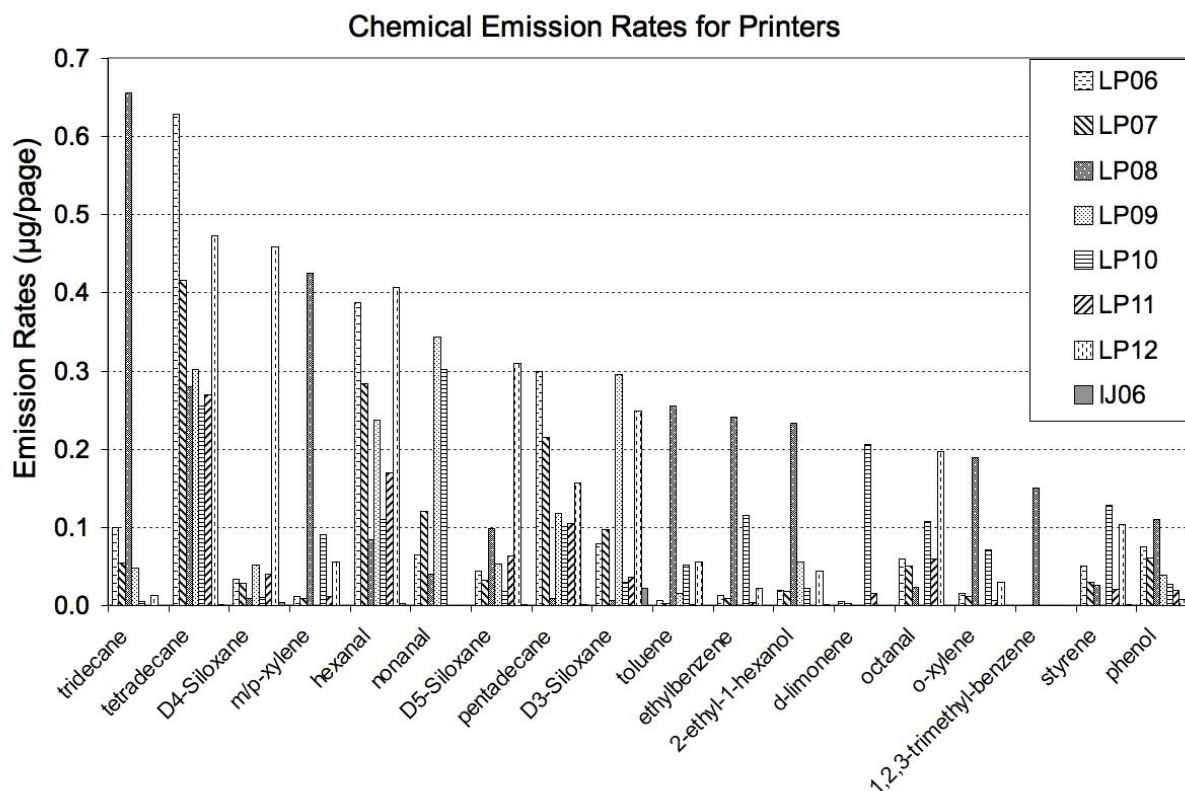


Figure 35. A comparison of emission rates expressed as µg per page printed (µg/page) among the eight printers tested. Only the top fifteen identified chemical emissions by mass are listed. One printer (IJ06) is an inkjet printer, all others are laser printers.

Ozone Emissions

Ozone was measured continuously during each printer experiment. Only print jobs greater than 100 pages were used to evaluate ozone emissions, and only prints that exceeded 10 ppb ozone in the chamber (~ 3 times background levels) during printing were quantified. Ozone emission rates were quantified as described in Section 4.1.7. If the chamber concentration did not exceed 10 ppb then the result was characterized as either “trace emissions” or “non-detect,” depending on whether an increase in the ozone concentration could be seen during printing.

Of the eight printers tested, two had no detectable increase in ozone concentration during printing, four showed trace emissions of ozone, and two had quantifiable emissions. For the units with quantifiable emissions, the emission rate was not constant throughout the printing period. This is illustrated in Figure 36, where the emission rate peaks at the start of the print job then drops to a sustained emission rate for the remainder of the print job. The printer ozone emission profile illustrated in Figure 37 shows a case where emissions increase over the duration of the print job with constant power use, and then the power periodically spikes during the idle period after printing. In both figures, the power use (W) is included to show the period of active printing and temporal changes in the power usage, illustrating the difference in printing technology and processes. The pattern of ozone emission and power use are consistent

across repeated print jobs for a given printer. As a result, we elected to report the time-averaged ozone emissions during the active printing phase.

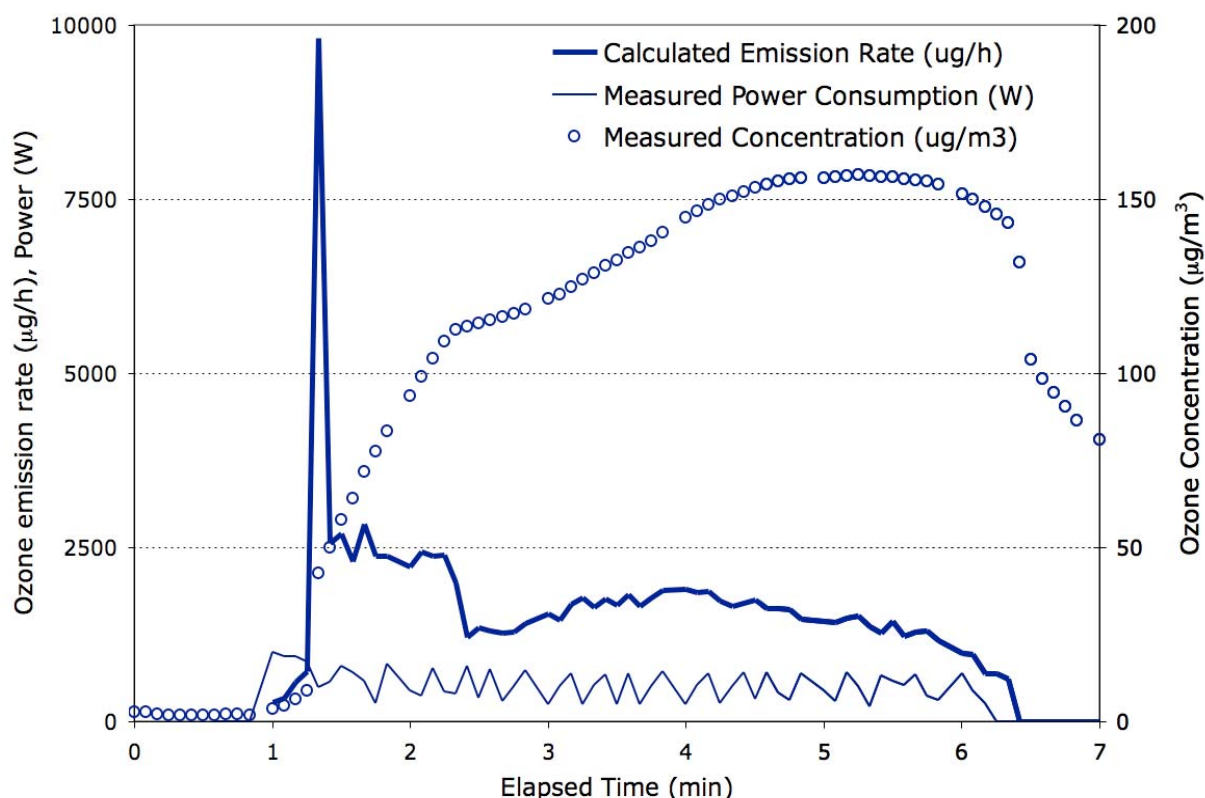


Figure 36. The *LP12* ozone emissions profile, showing ozone emissions ($\mu\text{g/h}$), the corresponding power use (W) on the primary y-axis, and the chamber concentration of ozone ($\mu\text{g/m}^3$) on the secondary y-axis during a 100-page print job. This printer shows an initial spike in the emission rate (heavy solid line) and then a relatively constant power use during printing.

The time-averaged ozone emissions (\pm one standard deviation) measured during active printing was $583 \pm 111 \mu\text{g/h}$ and $1750 \pm 92 \mu\text{g/h}$ for the *LP11* and the *LP12*, respectively, where the emission rate for the first unit was measured three times on the same day, and the second unit was measured six times on three different days. The standard deviation represents experimental variation from run to run rather than temporal variation in emissions during a given run. Of the eight printers tested, printers *LP11* and *LP12* (from the same manufacturer) both had quantifiable emissions, printers *LP06*, *LP07*, *LP08*, and *LP10* from a second manufacturer had trace ozone emissions, and the *IJ06* (inkjet) and *LP09* from a third and fourth manufacturer had no detectable ozone emissions. The full ozone emissions profile for each printer tested is provided in Appendix J.

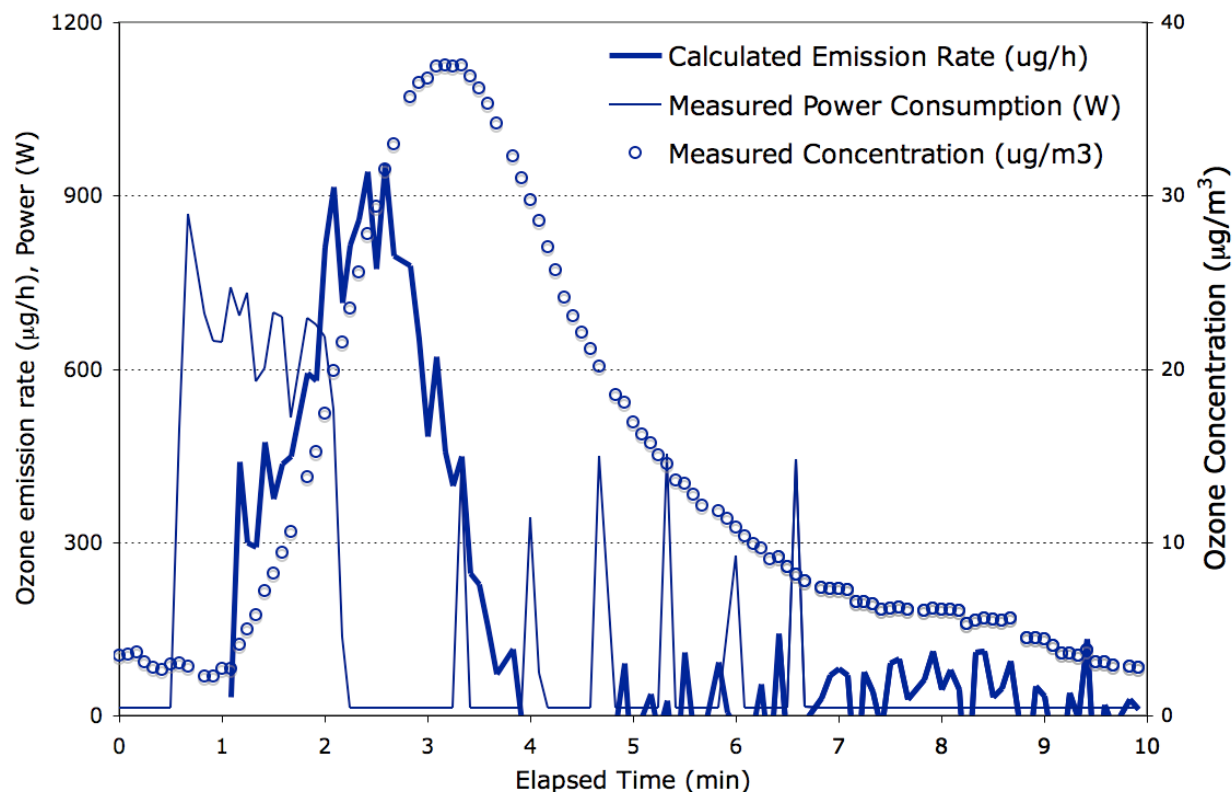


Figure 37. Printer *LP11* ozone emissions profile, showing ozone emissions ($\mu\text{g/h}$) and power use (W) on the primary y-axis and chamber concentration of ozone ($\mu\text{g/m}^3$) on the secondary y-axis, during a 100 page print job. This printer has an emission rate (heavy solid line) that increases over the course of the print job, with constant power use during printing followed by intermittent spikes in power during the idle phase.

Particle Number Emissions

Size-resolved particle number concentration (PNC) data was collected for a subset of printer emissions experiments, to determine the particle size fraction in the measured particle number concentrations. The total particle number concentration for particles > 100 nm (as measured using a Lasair model 1003 optical particle counter, or OPC) compared to the results from the condensation particle counter (CPC) (measuring particles > 7 nm) consistently found that the particles emitted from printers are predominantly less than 100 nm diameter. The total particle number concentration measured by the Lasair (sample channels from 0.1–2 μm) was typically less than 1 particle number (PN)/cc. It is possible to have more particle mass in the fine fraction and still have more particle numbers in the ultrafine range, but the results clearly show that printer emissions based on particle number are almost entirely in the ultrafine size fraction. More detailed results from the particle size evaluation are provided in Appendix G.

Particulate number emissions measurements were obtained from each of the eight printers (seven laser printers and one inkjet printer) in a series of experiments designed to measure emissions from different print jobs, ranging from short one-page cold-start prints to extended and repeated prints from warm units. There were no significant particle emissions (significantly

above chamber background) from the inkjet printer (IJ06) and only a small amount of particle emissions from one of the laser printers (LP08). However, each of the other laser printers emitted significant (much greater than chamber background) levels of ultrafine particles.

The emission profile varied between printers, but typically the laser printers generated an initial burst of UFP for the first cold-start print followed by somewhat lower sustained emissions for subsequent warm prints. The magnitude of the initial burst of particles varied among the different laser printer makes and models, but a typical pattern for the particle trace during a full emissions test for a given printer is illustrated in Figure 38.

In the case illustrated in Figure 38 the printer is LP06. The printer is called on to print some number of pages (1, 10, 20, 50, or 100) at fixed intervals that do not allow the unit to cool down following the initial print. The particle number concentration (C_t in Equation 4.3) is tracked continuously (data points represented by open circles in Figure 38) at 10-second intervals (Δt in Equation 4.3), along with power demand. The first print job of one page takes the printer from a cold (off) state to an operational state and generates an initial steep increase of particle concentration. The power trace in the figure shows that power is used only during active printing for this unit. Often the particle clearance following this initial print is used to estimate particle clearance rate (Q in Equation 4.3). Particle clearance rate includes removal by ventilation, deposition of particles to chamber surfaces, and aggregation of particles. All of these processes are lumped together in a single observed particle clearance rate. For details on calculation of emission rates from the data presented in Figure 38, see Section 4.1.7.

After the printer was warmed up, the remaining series of nine print jobs (including one with a paper jam) illustrated in Figure 38 occurred at 10-minute intervals, but the actual print time was only a few seconds to minutes, depending on the number of pages printed. So there was a period of at least nine minutes between print jobs in which the printer was in an idle state. For some of the printers, the release of particles was primarily associated with the transition from idle state to printing state, rather than with the actual printing. During this transition period the print drum of the laser printer was conditioned (that is, warmed up). It is this warm-up phase that appears to be associated with the particle emissions.

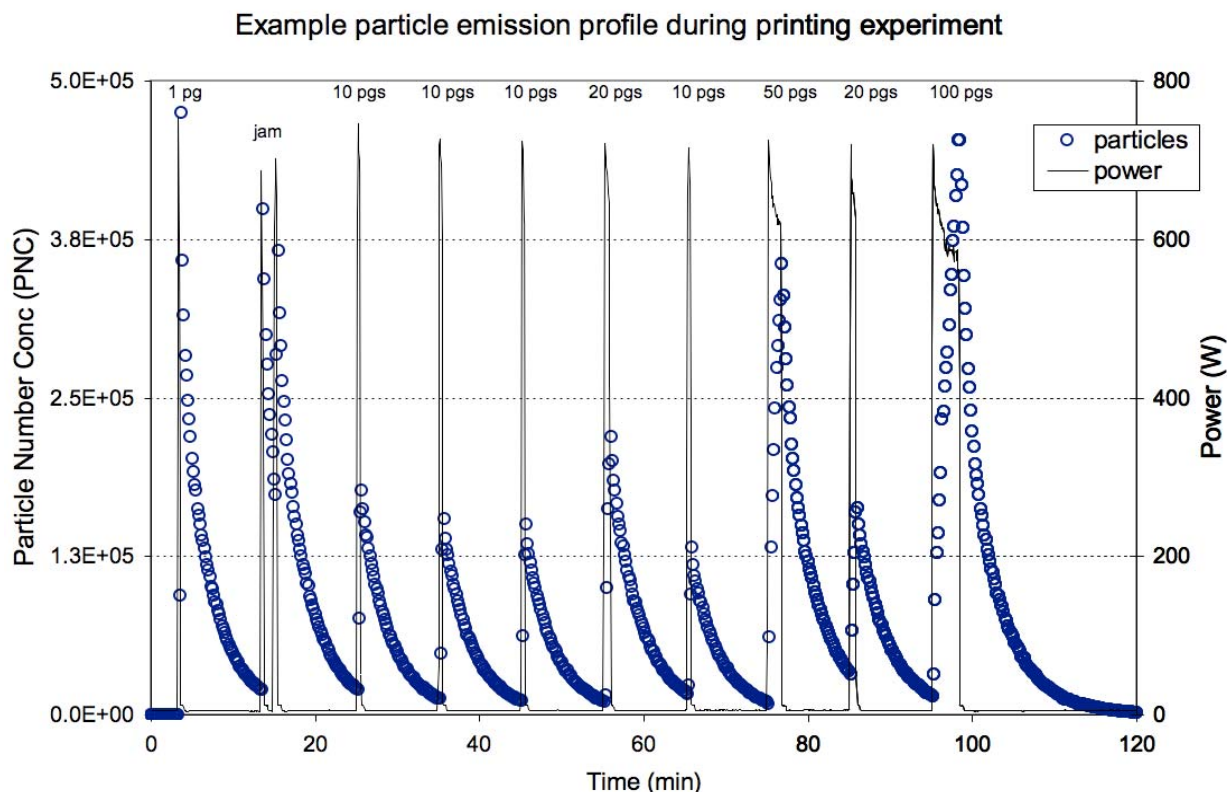


Figure 38. The time profile of particle number concentration (PNC, particles/cc) in the chamber with repeated print jobs using a laser printer (in this case, the laser printer LP06) showing how the release of particles links to power use during a series of printing events. A similar print profile is used for each printer to determine cold-start (first print) and warm print (subsequent prints) emission rates. In this case, the second print resulted in a paper jam, so that part of the PNC trace could not be used in the calculation of emissions. The start and duration of each active print job in the emission profile is indicated by the power consumption curve. The number of pages printed is listed across the top of the chart above each print job.

The particle number concentration (PNC, particles per cc) illustrated in Figure 38 represents the particle concentration in the 395 L chamber housing the printer. During the first print, the concentration rose to almost 500,000 PNC in the chamber. This is a level that is much higher than a typical level of fine/ultrafine PNC in urban atmospheres, and it is significantly higher than long-term average archetypal levels of fine/ultrafine PNC that is typically found indoors for residential environments. Early studies (for example, Wallace 1996) and more recent reviews (Riley et al. 2002) and measurements (He et al. 2007) for indoor/outdoor levels of fine/ultrafine particles indicate that number concentrations in urban atmospheres are in the range of 10,000 to as much 100,000 PNC or more, and that the archetypal levels of ultrafine particles indoors are in the range of 1,000 to 50,000 fine/ultrafine PNC for residential environments. But the 500,000 PNC refers to a test chamber, so it is not necessarily relevant to the impact that might occur in a specific working or residential environment. To relate these measured chamber concentrations to different (and likely much larger) volume environments with much different particle loss rates, the actual emission rate should be expressed in units that can relate specific printer duty cycles to emissions. A cumulative emission can be obtained by estimating the emission rate

during each time step, based on changes in the particle concentration and the total loss rate of particles within the chamber (see Appendix C). Results from this approach are illustrated in Figure 39 for a series of 10-page print jobs. Particle emission rates exceeded 1.3×10^{13} PN/h or 2.3×10^9 PN/s during active printing. For a 32-second print job in this specific example, this is equivalent to releasing ~ 70 billion particles (32 seconds \times 2.3×10^9 UFP per second equals 7.4×10^{10} UFP released) from the printer.

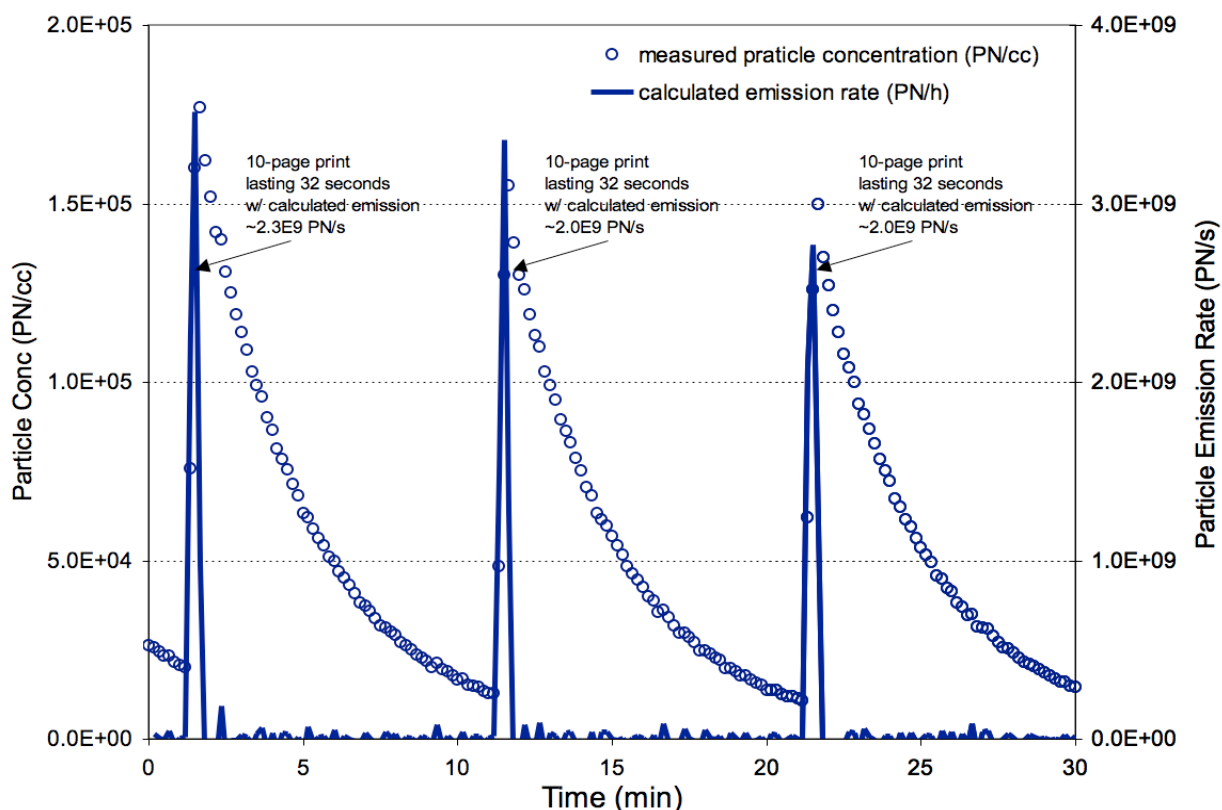


Figure 39. An illustration of how the measured particle concentration (PCN) relates to the calculated particle emission rates from a series of print jobs. Three successive print jobs from the previous figure are shown with average emission rates calculated over each 32-second (10-page) print. The calculated emissions range from 2.3×10^9 particles per second to 2.0×10^9 particles per second.

The experiment described above was repeated for the single inkjet printer and each of the seven medium-output laser printers. For each device, researchers measured both the emission rate in two different functional metrics (PN/second and PN/page) and the integrated emissions (PN/print job) from the initial (cold) print and from the series of warm-start prints with varying page counts. The particle emission rates for warm prints are compared across the different printer brands and models in Figure 40. The cold-start emission rates are provided in Section 4.2.1 on mitigation strategies, where these emissions are used as a basis for assessing the impact of different strategies.

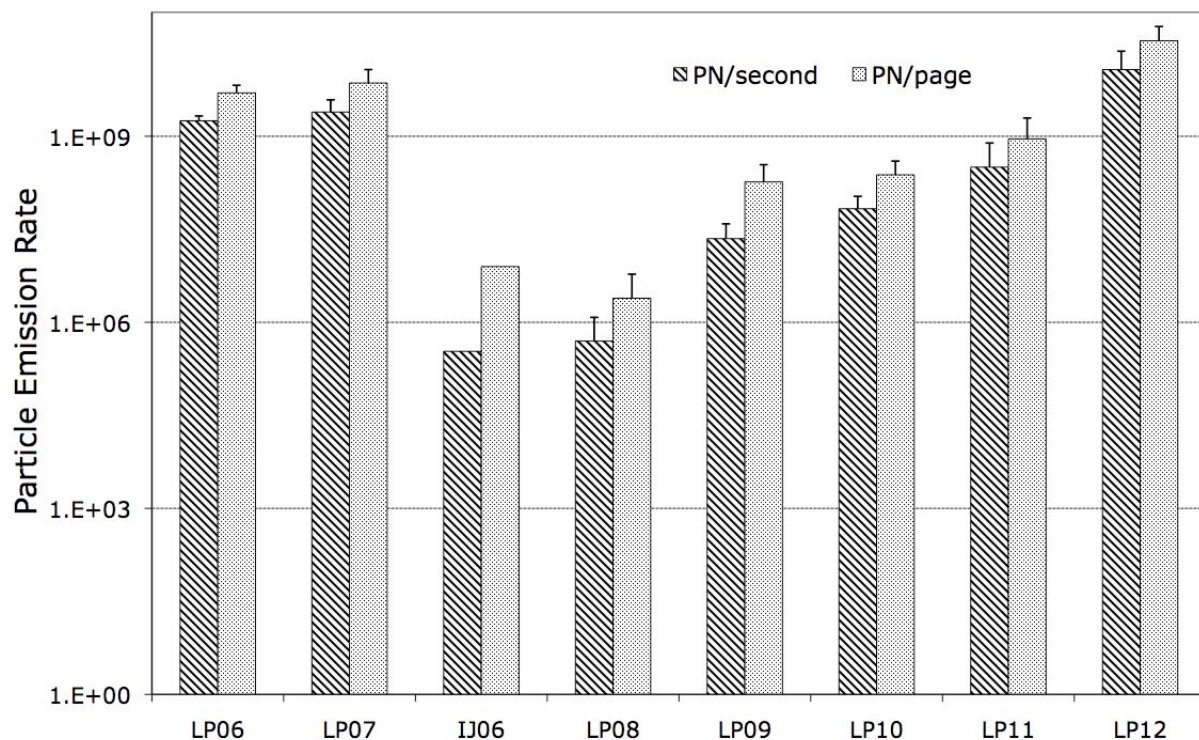


Figure 40. Unit-specific particle emission rates (particles per second, or particles per page) for a range of medium-duty laser printers and one inkjet printer (*IJ06*). Error bars represent 1 standard deviation of emission rates determined from multiple experiments, including replicate page counts, varying page counts and, for some units, replicate experiments conducted on different days. Experimental sample sizes used to estimate the emission rates were as follows; *LP06* n=8, *LP07* n=10, *IJ06* n=1, *LP08* n=5, *LP09* n=4, *LP10* n=8, *LP11* n=6, and *LP12* n=7.

The overall results from forty experiments with six different medium-duty laser printers (excluding *LP08*) representing cold-start and warm prints with a wide range of page counts and print duty cycles has a geometric mean (GM) of 4.8×10^8 PN/second of active printing with a geometric standard deviation (GSD) of 12.5. The GM (GSD) for emissions in units of PN/page-printed is 2.1×10^9 (12.5), and the overall integrated emission as PN/print-job is 2.9×10^{10} (12.6). The detailed results for the individual printers, page counts, print durations, and cold-start prints are provided in Appendix K, along with a time-series plot of each experiment showing both PNC and power use during each print job.

Power Use and Emissions for Printers

The relationship between VOC emissions and power use during active printing was evaluated by plotting the sum of the measured VOC emission rates for the laser printers against the manufacturer's reported power rating for each unit. The power use during operation for each unit is reported in Table 19.

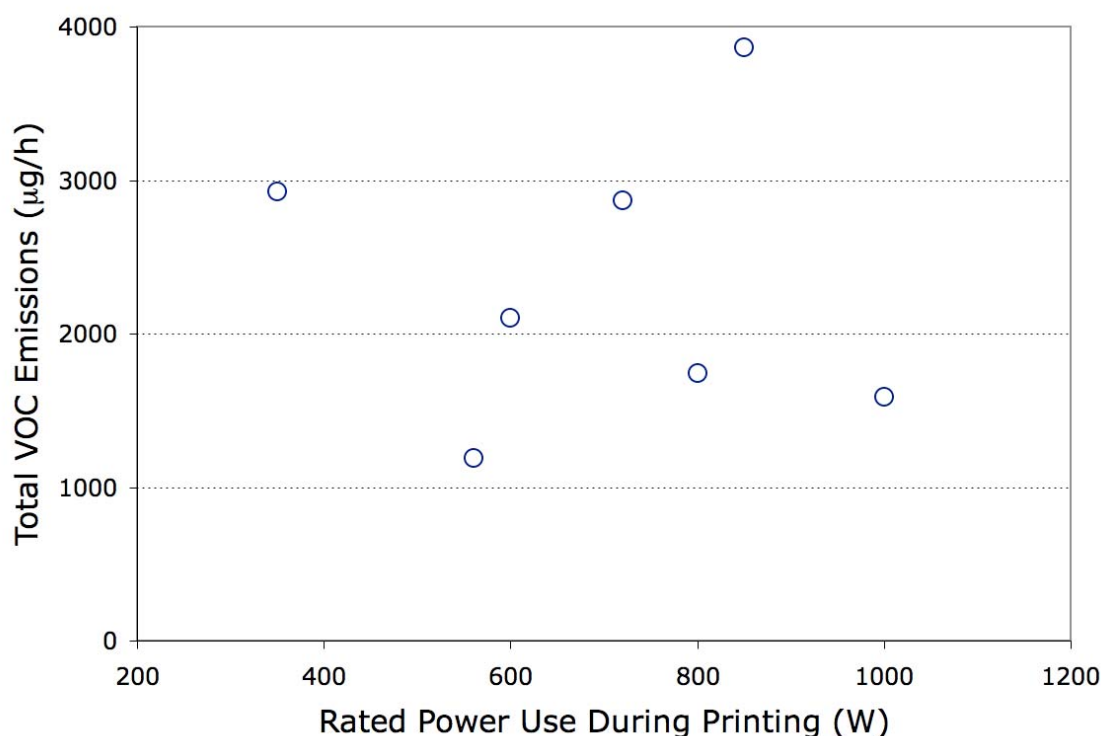


Figure 41. Plot of the measured VOC emissions during printing against the manufacturer's reported power rating showing that there is no relationship between VOC emissions and power for the tested laser printers.

The results (plotted in Figure 41) show that VOC emissions are not related to power use for printers. All of the machines were performing equivalent tasks (i.e., 100-page print jobs) during the emissions measurements.

The unit-specific particle emissions (i.e., excluding cold-start prints) were also evaluated against power usage, and the results are plotted in Figure 42. In this case, there is a strong and direct

relationship between power and particle emissions, where the more-efficient units emitted less particles during printing. As with the VOC assessment, all the printers were performing equivalent tasks made up of a series of prescribed print jobs of varying page-counts.

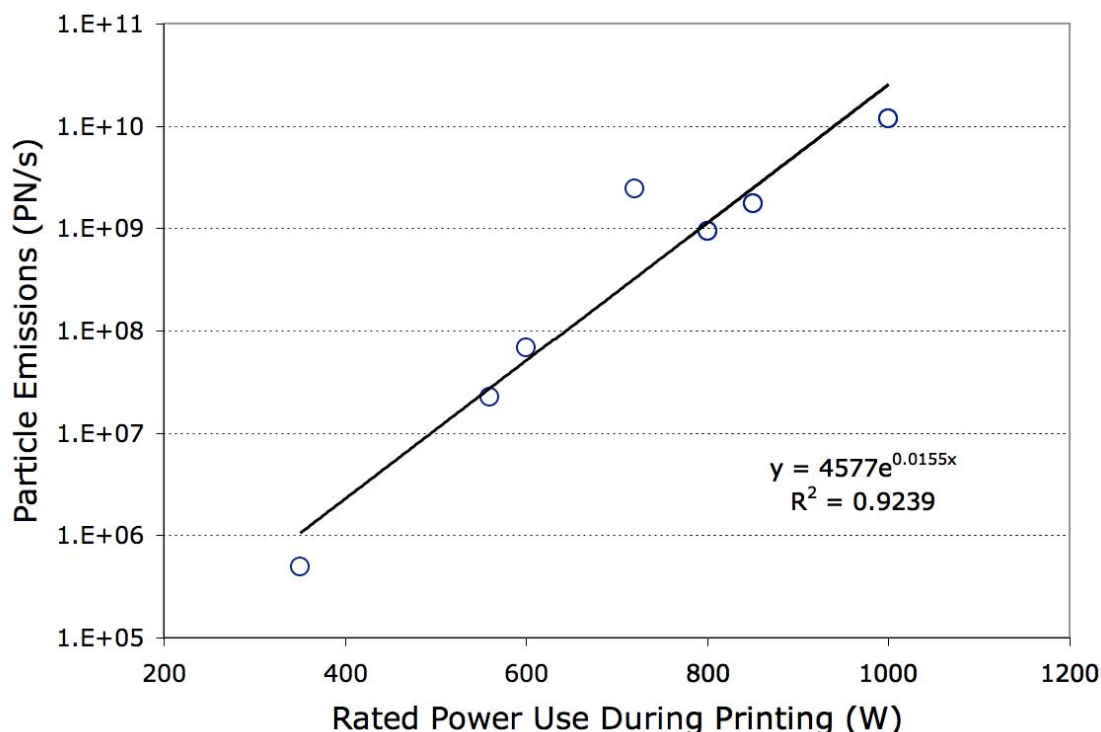


Figure 42. Plot of the unit-specific particle emissions from laser printers and the rated power use for active printing, showing a strong and direct relationship for the tested printers.

As with the evaluation of power use impacts for computers, it is noted here that the emissions from printers were evaluated for units with different power ratings performing similar tasks rather than for the same unit run under a range of power loadings. For printers, the power use during printing cannot be modified within a particular unit, so comparisons across different units performing similar tasks provides the only opportunity to measure the relationship between emissions and power consumption.

4.2.3. Mitigation of Emissions and Exposures

A subset of the Phase II experiments was dedicated specifically to evaluating potential emissions and exposure mitigation strategies. This effort included 10 experiments lasting 1–3 days each, using the small test chamber and measurement techniques applied in previous tasks. These experiments were designed to explore the following issues:

- How aging of computers impacts VOC and SVOC emissions
- How age, brand, and model of printer affects VOC, ozone, and particle emissions
- Print cycle—cold start versus warm printing for particle emission rates
- Use of original equipment manufacturer (OEM) versus non-OEM toner

- Assess how toner coverage on printed page affects VOC, ozone, and particle emissions
- Use of different paper types (high quality versus economy brand)

For each of these issues, the paragraphs below provide information on the number of computers/printers used in the experiment, the results obtained, and the implications of these results.

How Aging of Computers Affects VOC and SVOC Emissions

To address the issue of aging for computers, five computers were evaluated in twelve different experiments. All of the computers were tested to determine their “out-of-box” emission rates and then removed from the test chamber. Three of the computers were set up to run continuously for an extended period to artificially age the processors. After a pre-determined period, the three computers were re-tested. Emissions from two of the computers were measured at three different ages (including out-of-box), and one was measured at four age periods. There were also on/off cycling experiments carried out with two additional computers run for an extended period, where emissions were measured at the beginning and end of the extended operation period. For each experiment the fraction of each VOC and/or SVOC chemical emission rate remaining after aging was measured for a series of time points (based on the elapsed processor time while the computer was active). These measured emission rates were then divided by the out-of-box emission rate to obtain the relative change. The results of this experiment are described in more detail in Section 4.2.1. In this experiment, it was shown that VOCs age at a rate of about 3% per 24-hour period of processor time. Semi-volatile organic compounds and siloxanes showed little evidence of an aging effect.

How Age, Brand, and Model of Printer Affects VOC, Ozone, and Particle Emissions

To assess how printer age, brand, and model affect emissions, one inkjet and seven laser printers were evaluated. The printers ranged in age from 1 to 68 months with three models from one manufacturer and two models from a second manufacturer. Two of the printers were the same make/model but with different ages. In this case the printer’s actual production date was used to establish age, rather than actual time of operation as was done with the computer experiments, where processor time was tracked. For each printer experiment the total measured VOC mass emitted per hour during active printing and the particle emission rate in PN/second was recorded. Figure 43 provides the results of this analysis and shows that the inkjet technology has much lower VOC emissions than the seven laser printers, but that the laser printers vary no more than a factor of three among themselves for VOC emissions without showing any clear age or brand trend. The inkjet and one of the laser-technology printers had particle emissions that were several orders of magnitude lower than the other laser technology printers. But this effort did not include a large enough pool of printers to document any significant trends in emissions with age, brand, or model.

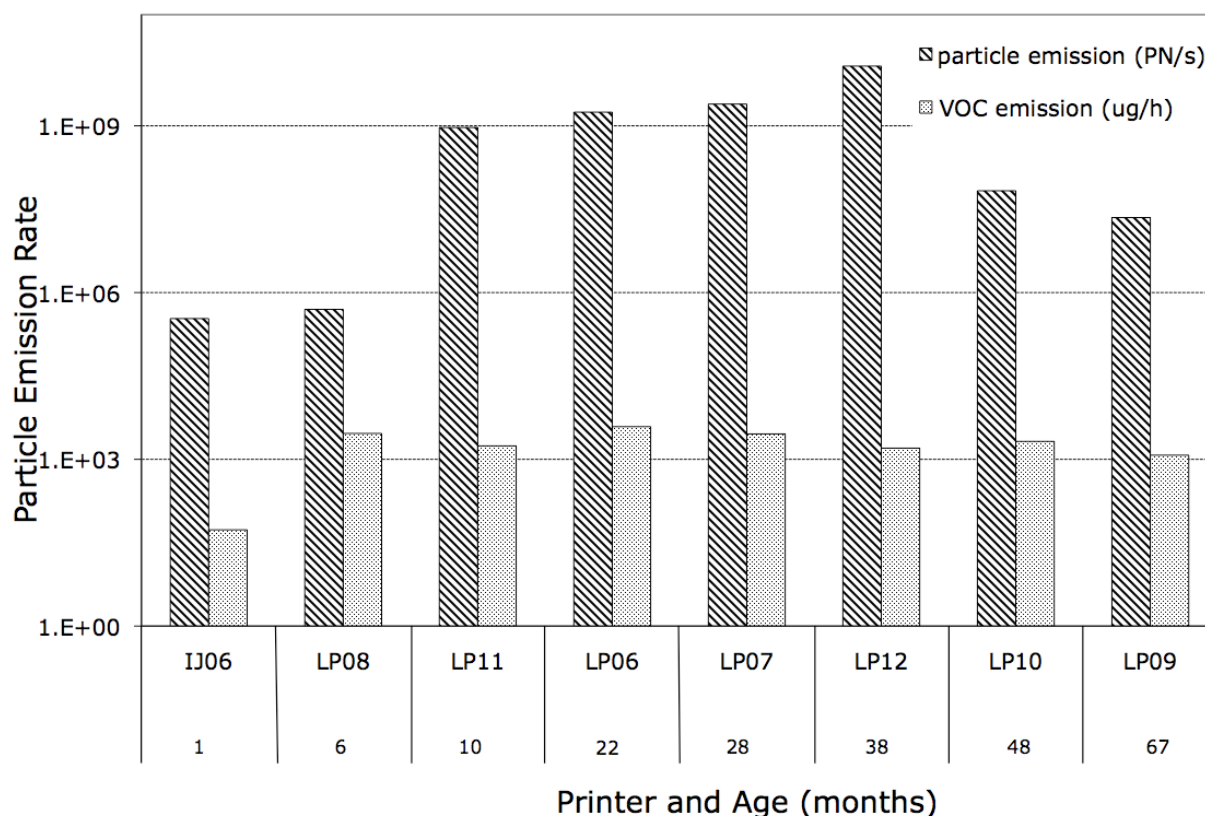


Figure 43. Variation of printer VOC ($\mu\text{g}/\text{h}/\text{unit}$) and particle (PN/second) emissions across ages, brands, and models during active printing, where VOCs represent the total measured VOCs

Print Cycle: Impact of Cold Start Versus Warm Printing on Particle Emission Rates

Preliminary experiments indicated that particle emissions were elevated significantly above background levels during the initial cold-start print. This appeared as a short burst of UFP. This burst of particles occurred on most of the laser technology printers, and, as illustrated in Figure 44 for cold-start printing, is almost completely independent of the number of pages printed and the duration of the initial print. Here particle emissions from a cold-start 100-page print lasting 316 seconds are compared to those from a cold-start one-page print lasting 27 seconds. This suggests that the initial burst of particles from a cold or startup print is not dependant on the number of pages or duration of the print job. In contrast, the warm-print emissions seem to depend on the duration of print or number of pages printed, as illustrated earlier in Figure 38. Therefore, the two emission factors are reported separately.

To evaluate the magnitude of this initial cold-start particle burst, each printer (excluding the inkjet) was tested from a cold-start at least once, and one of the printers was tested on four different days. In Figure 45, these cold-start results are compared to the unit-specific emission rate from the series of warm-start prints. Six of the seven laser printers tested had an increased rate of emission during the first few seconds of a cold-start print relative to a warm-start print. The LP10 printer had similar emission rates, determined during cold and warm prints. In

contrast, all other laser printers had cold-start emission rates that were between two and seven times greater than the warm print emission rates.

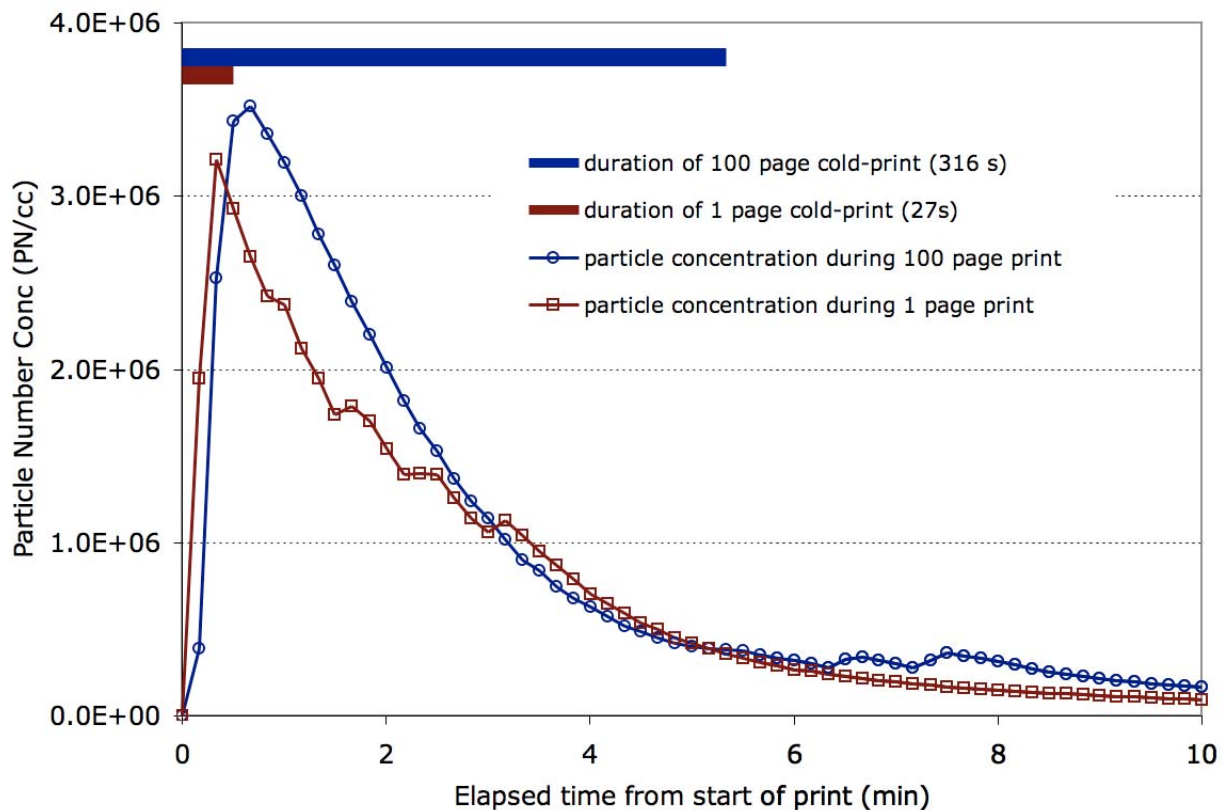


Figure 44. Comparison of the PNC profile from two cold-start prints with differing page count and print duration (illustrated by solid lines at top of figure) showing that the initial burst of particles from startup of a cold printer does not depend strongly on duration of print job or number of pages printed. This result indicates that the mechanism of emissions from a cold-start print job is different from that of emissions from a warm printer.

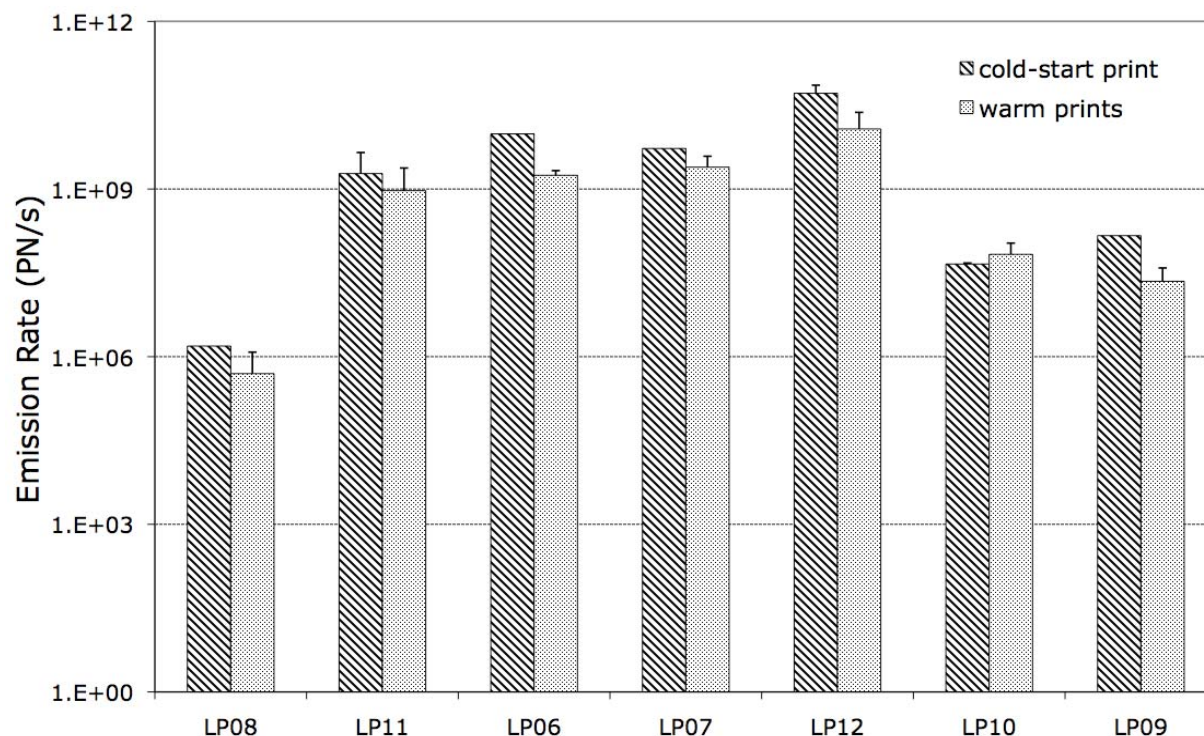


Figure 45. Comparison of warm print particle emission rates to cold-start print emission rate for tested printers. Error bars represent ± 1 standard deviation. Cold-start prints were measured on five separate occasions for the *LP12* printer with a precision (coefficient of variation) of $\sim 40\%$. Replicate cold start measurements were also collected for the *LP11* and *LP10* printers. The cold-start emission was not measured for the inkjet printer.

Influence of Toner Selection on VOC, Particle and Ozone Emissions

Two printers (*LP09* and *LP12*) were tested before and after replacing the toner cartridge, to evaluate the contribution that the choice of cartridge had on emissions of VOCs and particles. For the *LP09* printer, the original equipment manufacturer's recommended cartridge was replaced with a fresh original equipment manufacturer (OEM)-recommended cartridge. For the *LP12* printer, the original cartridge was an after-market refilled cartridge, which was replaced with a new OEM-recommended cartridge (TN540) and the corona wire was cleaned as recommended in the cartridge installation instructions. Particle emissions and ozone emissions were determined before and after changing the cartridge for both printers, while changes in VOC emissions were only evaluated for the *LP12* printer.

For VOCs, there were relatively small changes in emissions for hexanal and the larger alkanes (tetra- and penta-decane), but the other VOC emissions tended to increase after installing the new OEM-recommended cartridge, particularly for the three siloxanes possibly indicating a different toner composition. Overall, the total measured VOC emissions increased by a factor of two with the fresh OEM toner. In contrast, the measured particle emissions from both printers decreased with the installation of fresh toner cartridges. Emission rates from cold-start 100-page prints (PN/second) decreased by a factor of three (4.6×10^7 reduced to $1.4 \times 10^7 \pm 4.6 \times 10^6$) for the

LP09 printer and a factor of ten ($3.0 \times 10^{10} \pm 1.1 \times 10^{10}$ reduced to $2.7 \times 10^9 \pm 6.1 \times 10^8$) for the LP12 printer. Only extended cold-start prints were run in this experiment so it was not clear whether the reduction in particle emissions was due to a reduction in the initial cold-start particle burst or a reduction in the overall emission rate. There was no measurable change in ozone emission rates in the LP12 printer after changing the toner cartridge (and cleaning the corona wire).

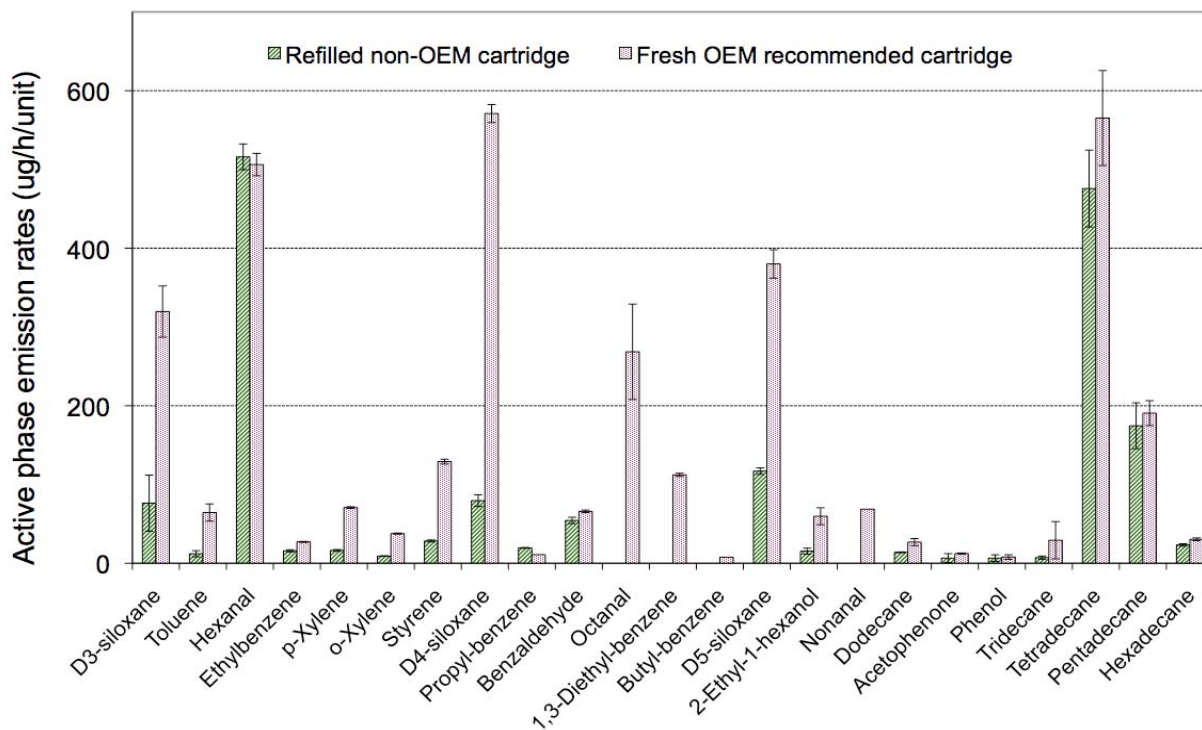


Figure 46. Comparison of VOC emissions during active printing using an older non-OEM recommended refilled cartridge and a new OEM recommended cartridge. Error bars represent ± 1 standard deviation based on replicate measurements for the fresh OEM-recommended cartridge and replicate measures for the refilled non-OEM cartridge.

Influence of Paper Brand Selection on VOC and Particle Emissions

One printer (LP08) was tested with two different brands of paper: Xerox Business 4200 and Boise HDp laser-printer paper. Volatile organic compounds and particle emissions were measured separately for each paper use. There was no clear difference in the particle emissions profile, although the unit tested had a much lower particle emissions than the other printers tested. For the VOC emissions, there was an apparent difference in emissions for several of the chemicals measured. This is illustrated in Figure 47. The differences are particularly pronounced for the alkanes, where the combined increase in tri- and tetra-decane emission rates were more than double with the Xerox paper as compared to the Boise paper. The apparent change in VOC emission profile warrants further study to determine what chemicals may be related to paper as compared to the toner, and whether paper selection would influence particle emissions for units that normally have higher levels of particle and/or ozone emissions.

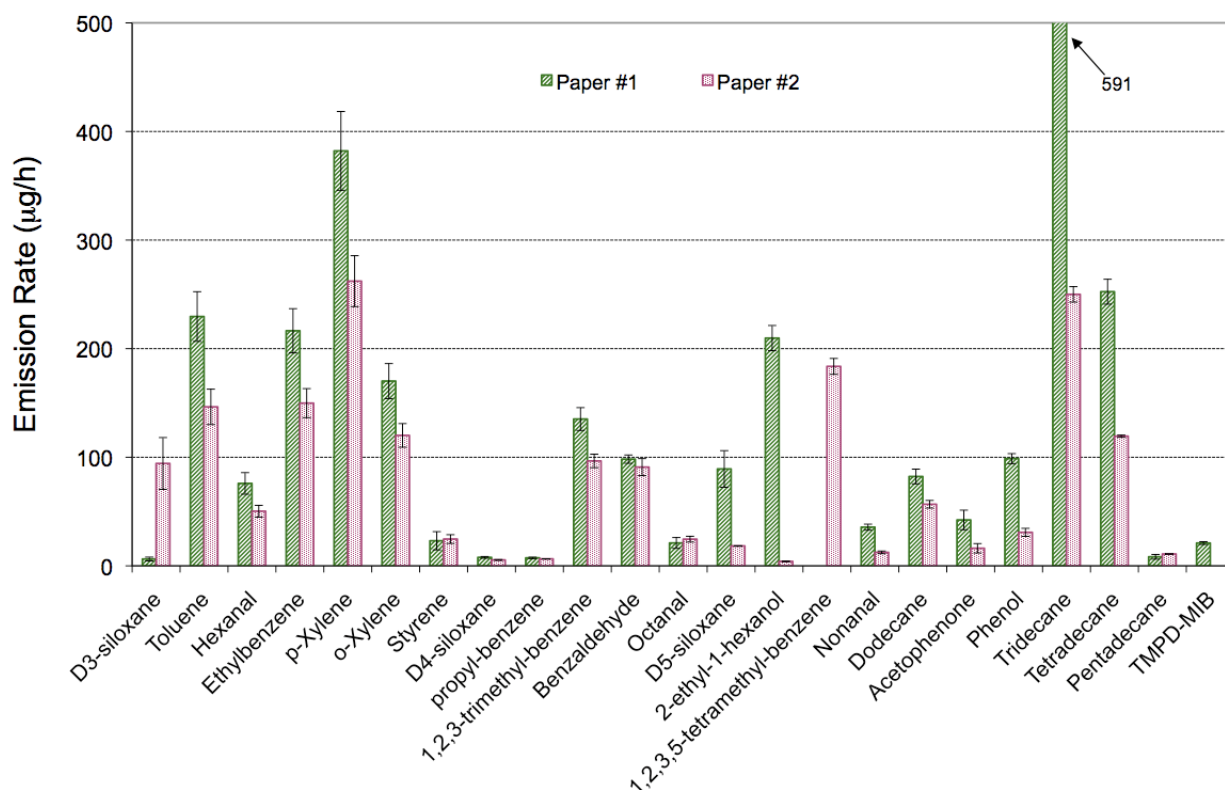


Figure 47. Comparison of the VOC emissions profile during active printing with LP08 and the use of two different paper brands. Error bars represent ± 1 standard deviation based on replicate measurements for each paper.

How Toner Coverage on the Printed Page Affects VOC, Ozone, and Particle Emissions

The printer with the highest measured emissions of ozone and particles was selected to explore the influence of toner coverage on emission rates. For each toner coverage level, ozone and particles were monitored continuously, and VOCs were measured during active printing. The standard print page pattern (5% coverage) was modified to achieve ~10% and ~20% coverage on the printed page (black only). Prior to evaluating the toner at 0%, 10%, and 20% coverage, a series of print jobs were run to clear the printer of residue. Figure 48 shows the change in measured particle emission rate for several sequential print jobs of varying page count. The emission rates are plotted at the mid-point of each print job. For example, the clearance experiment started with a one-page print (data point plotted at 0.5) followed by a series of 10-page print jobs (plotted at 5.5, 15.5, 25.5), followed by a 40-page print job (plotted at 45.5), and then two 60-page print jobs (plotted at 75.5 and 105.5), illustrating the change in emissions-increasing consecutive page counts. The results show an initial decrease in particle emission rate as the number of blank pages printed increases and approaches a minimum value ($\sim 5 \times 10^8 \pm 1 \times 10^8$). These clearance runs demonstrate that there is a residue effect for particle emissions where buildup from prior print jobs can contribute to particle emissions from subsequent print jobs, but also that there is a lower and continuous emission that is not dependent on toner use but may be coming from lubricant or other materials in the printer.

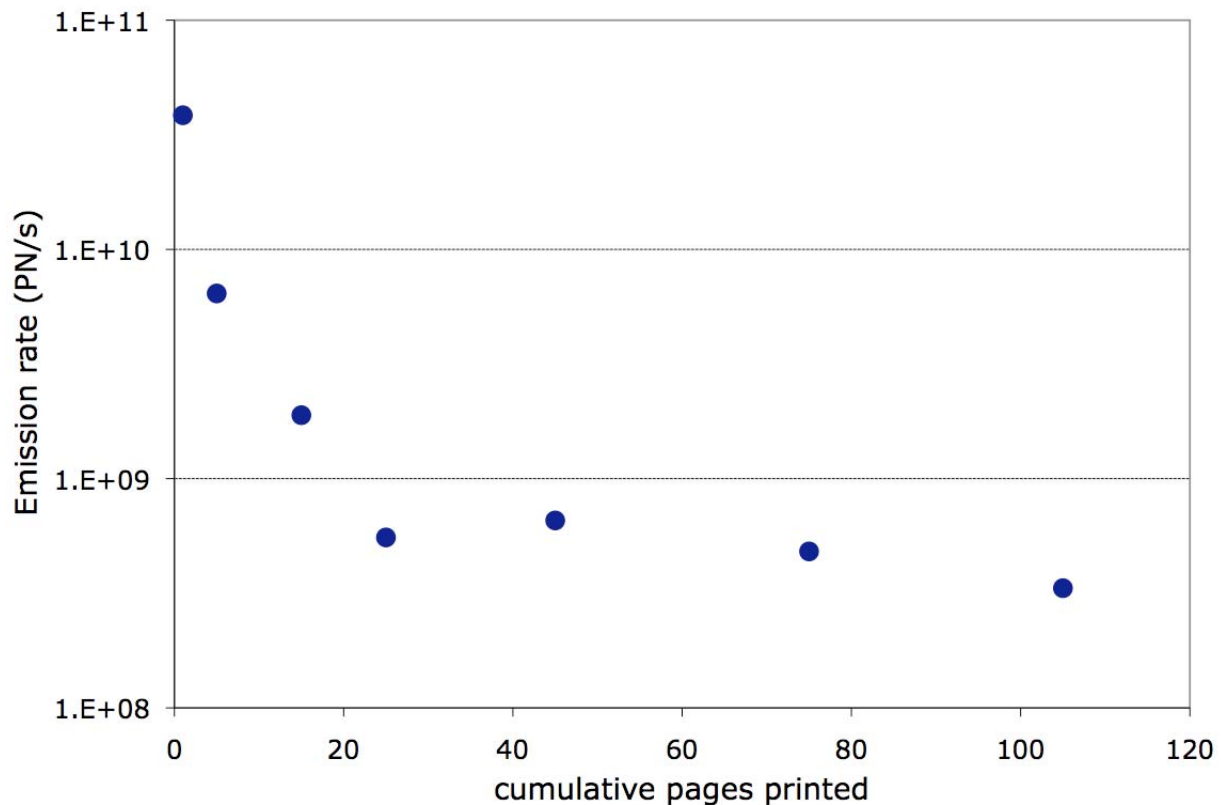


Figure 48. Change in particle emission rate (PN/second), with increasing number of consecutive blank printed pages using the *LP12* printer showing the approach to a minimum value. Each data point indicates the emission rate calculated from individual print jobs run at 10-minute intervals.

Following the clearance runs, a series of cold-start print jobs were carried out starting with 0% toner coverage (i.e., blank pages printed), followed by a 10%-coverage, and finally a 20%-coverage print job. The resulting particle traces during each print job are overlain in Figure 49. The particle concentration trace clearly changes with increasing toner coverage, from 0% to 20% percent coverage. Because the curves illustrated in Figure 49 are from cold-start prints, the increase of emissions with increasing toner may be due to a combination of residue in the unit accumulated from prior print jobs and the amount of toner used during the current print job.

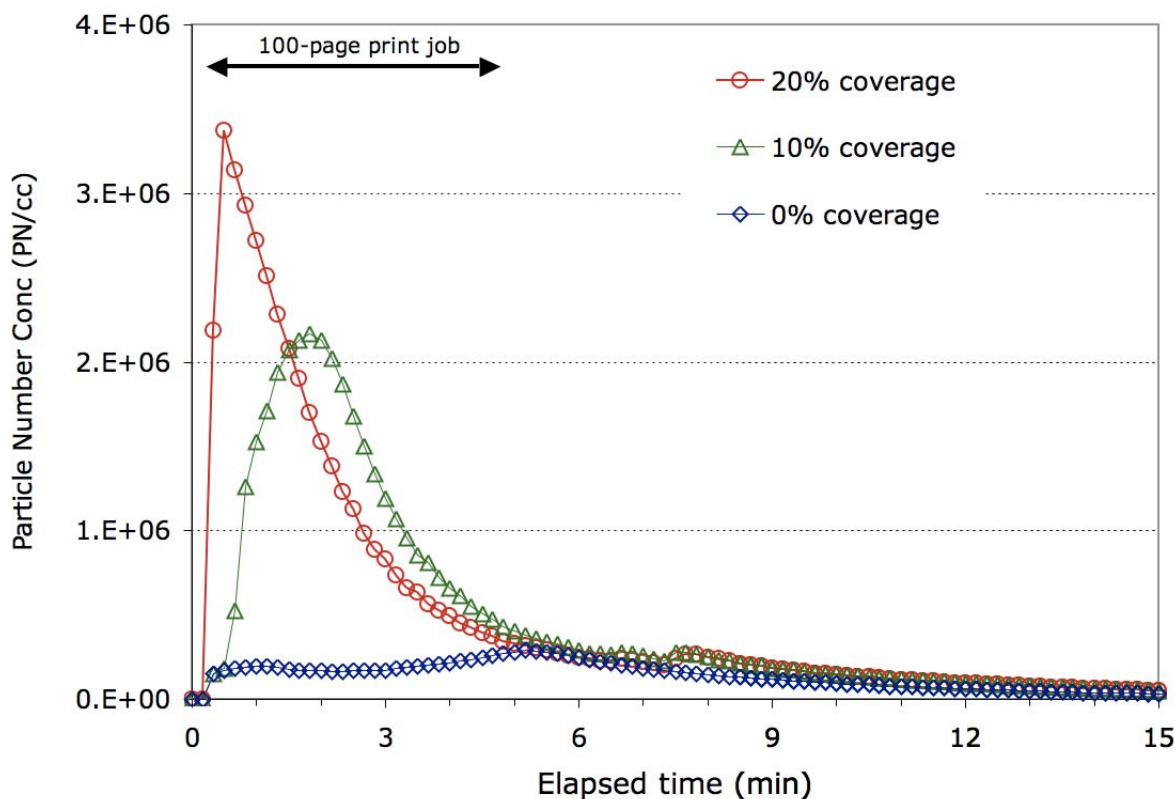


Figure 49. Particle concentration trace for each of three different cold-start print jobs, with differing toner coverage on the pages. The successive prints show an increasing burst during the early phase of active printing, indicating residue buildup from earlier prints.

Volatile organic compound emissions were also measured for each of the cold-start prints with differing toner coverage, to evaluate the contribution of toner to chemical emissions. The correlation between the measured emission rates from each experiment and the toner coverage was evaluated, and the chemicals with correlation coefficients greater than 0.9 are plotted in Figure 50, while those with correlation coefficients less than 0.9 are plotted in Figure 51. The results support the finding from the experiments using different paper brands that the alkanes (tri-, tetra-, and penta-decane) and the hexanal are likely coming from a source other than the toner. The VOCs that are not correlated with toner may be due to the paper, fuser oil, or some other component of the printer machinery. These results also demonstrate that a range of VOCs are emitted from the toner itself, either directly during the print job or from secondary release of residues that build up over consecutive print jobs.

Ozone emissions were not affected by difference in the toner coverage, with resulting emission rates of 1708, 1693, 1688, and 1684 $\mu\text{g}/\text{h}$ for the 0%, 5%, 10%, and 20% coverage print jobs, respectively.

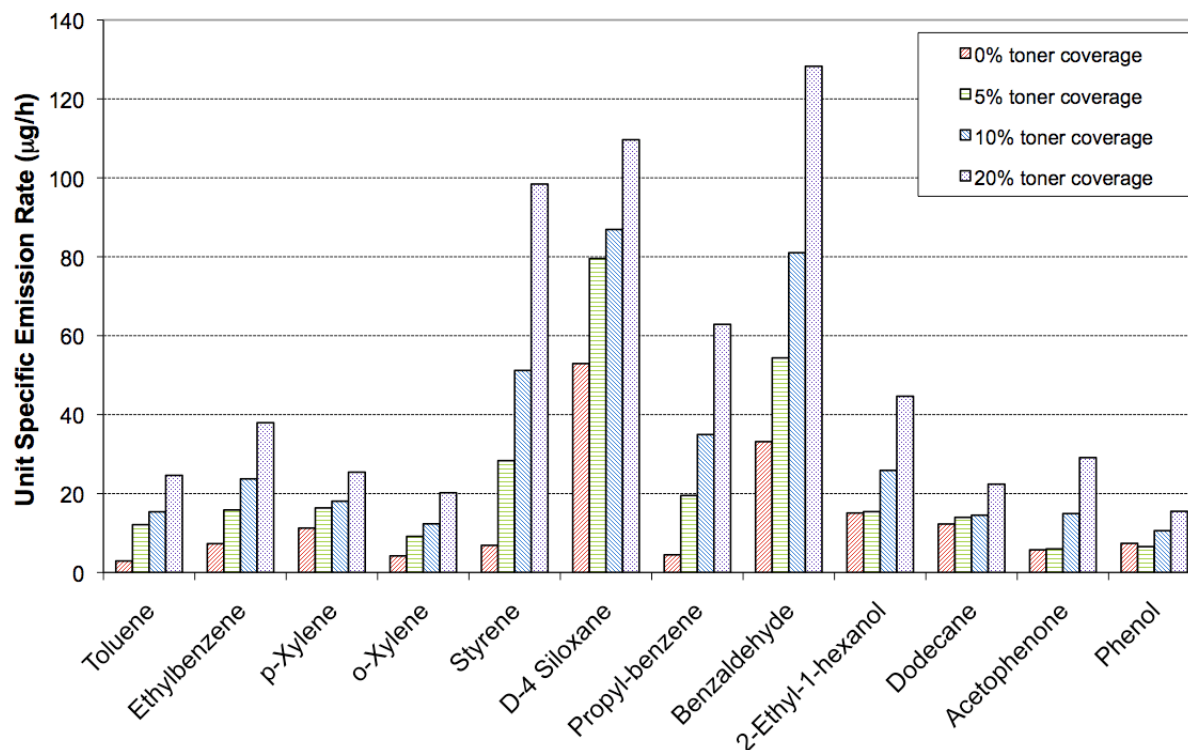


Figure 50. VOC emission rates ($\mu\text{g}/\text{h}/\text{unit}$) for chemicals that have emission rates that correlate ($r > 0.9$) with toner coverage on the printed page, indicating that toner may be the source of these chemicals

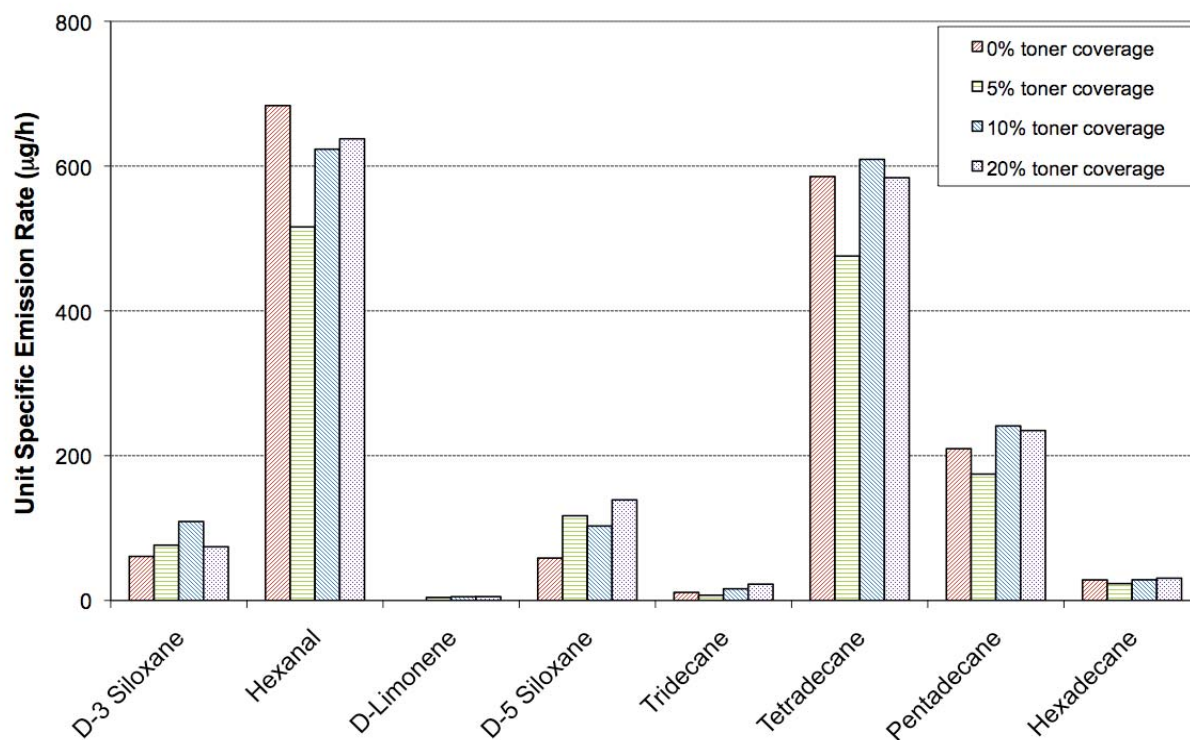


Figure 51. VOC emission rates (µg/h/unit) for chemicals that have emission rates that do not correlate with toner coverage on the printed page, indicating that the source may not be toner related.

5.0 Discussion

The use of office equipment in residential environments has become common and will likely continue to increase. Computers and printers are found in almost every office environment and in a large number of residential environments. The need for greater energy efficiency means that many of these environments will have reduced ventilation. Both consumers and environmental health scientists are concerned about the potential impacts of office equipment emissions.

This project was the first effort to use a pair of controlled chamber environments to systematically assess the full range of pollutant emissions from desktop computers and printers. The integration of a detailed literature review, screening measurements in a large chamber, and emissions studies on individual components in a small chamber provided the opportunity to formulate effective and informative measurement protocols.

5.1. Measurements and Results

Emissions were measured and evaluated for six categories of pollutants—VOCs, low-molecular-weight aldehydes, SVOCs, siloxanes, ozone, and particulate matter (PM as particle number concentrations). Both computers and printers produced quantifiable emissions of many VOCs. Computers show an “aging” effect in that the VOC and possibly SVOC emissions decrease as operating time increases. Cycling the computers on and off did not significantly alter emission rates over time relative to continuous operation. The emission rates for VOCs and SVOCs from printers do not decrease with age. But it should be noted that this assessment did not look at an individual unit over time but at different models with different fabrication dates. Variability of emission among models may mask any age-related difference but the absence of an aging effect may also be attributable to emissions coming from consumables like toner and paper or printer drum conditions, which are either continuously replenished or constant. Formaldehyde and acetaldehyde releases were measured for computers, and these emission rates showed an aging effect similar to the other VOCs.

Three classes of SVOC were considered for computers and printers—polycyclic aromatic hydrocarbons (PAHs), brominated flame retardants (BFRs), and organophosphate flame retardants (OPFR). Emissions from each of these chemical classes were observed for both computers and printers in the room-scale experiments from Phase I. Printer PAH emission rates in these experiments exceed those from computers, but both types of devices do not appear to be significant sources of indoor PAH. Computers and printers had similar and continuous emission rates of some BFRs. Both computers and printers had continuous emissions of OPFR, but printers were somewhat higher. Siloxanes were added to the set of analytes following an evaluation of “unknowns” from the Phase I results. Siloxane emissions came from both computers and printers, did not show a significant aging effect, and also did not change much when the computer power was off.

Emissions of ozone and PM were not detected for computers or inkjet printers. Ozone emissions from laser printers range from non-detectable levels to the low $\mu\text{g}/\text{h}$ range during active printing, but given relatively short duration of active printing events, the overall emissions of

ozone from printing is relatively low (compared to what can be brought to the indoor environment from ambient air). However, the ozone levels within the laser printing devices are likely higher and could have an impact on particle formation. Laser printers give off large initial bursts (large number counts) of fine to ultrafine particle emissions. These releases depend somewhat on the number of pages printed but are more strongly associated with start up and with warm up (printing after a long delay) events. This appears to be related to the conditioning of the printer drum and is discussed more below.

5.2. Interpretation of Results

This section addresses the significance of the emissions results both for particles and chemicals. Let us consider chemicals first. For the most part, the experiments reported here identify what can be measured coming out of computers and can help quantify emission rates during specific activity states. The results indicate that computers and printers emit similar amounts of siloxanes and that active printers emit significantly more VOCs and SVOCs than out-of-box computers that are active. However, it is important to note that the active phase for printing can often be very short relative to the active phase for computing. The total number of identified VOCs, SVOCs, and siloxanes coming out of new and operating computers includes 40 compounds and amounts to 300 to 500 $\mu\text{g}/\text{h}$ of total chemical emissions. In contrast, the total number of identified VOCs, SVOCs, and siloxanes in the emission stream from active printers include 30 compounds, with emission rates during printing between 2,000 to 4,000 $\mu\text{g}/\text{h}$ (33 to 67 $\mu\text{g}/\text{min}$) of total chemical emissions. For both computers and printers, most of the emissions stream is made up from less than ten substances. However, there are different mixes of VOCs/SVOCs coming out of computers and printers.

To interpret the significance of these emissions, some comparison tables were developed. Table 28 provides a list of the 32 aldehydes, VOCs, SVOCs, and siloxanes with the highest measured emissions averaged among all computers tested. The emission factors used in Table 28 are the measured out-of-box emission rates averaged across all computers tested in Phase II, including the laptop. The range of emission rates for any given chemical and computer was within a factor of two of the average value. Nevertheless, the average emissions are used in the comparison. Also listed in this table are representative measurements of indoor levels available for these substances from two recent studies (Hodgson and Levin 2003; Hippelein 2004). Hodgson and Levin (2003) compiled measured concentrations of VOCs in indoor air for residences by reviewing a series of studies with VOC indoor concentrations measured in North America since 1990. Hippelein (2004) summarized background concentrations of individual and total VOCs in residential indoor air in Germany. These two studies included many of the VOC and SVOC compounds that are key emissions from computers and printers. Table 29 provides a list of the 35 aldehydes, VOCs, SVOCs, and siloxanes with the highest contribution to the total emission stream averaged among all laser printers tested (excluding the inkjet) during active printing cycles, along with representative measurements of indoor levels available for these substances from Hodgson and Levin (2003) and Hippelein (2004). The maximum measured emission rate for any given chemical and printer was a factor of 2.2 (± 1.0), the average value reported in Table 29, but the average is used in the comparison.

The emissions data in Table 28 and Table 29 were used to compare computers (out-of-box and active) and active printers in terms of the 45 highest VOC, SVOC, and siloxane emissions in micrograms per hour observed among all devices. This comparison is shown in Figure 52. The plotted emissions are the averages for each chemical among all devices tested. For computers, emissions decrease with time (see Figure 28) and for both computers (Tables 22 and 23) and printers (Tables 26 and 27) emissions during idle operation are lower than during active operations or printing. Not all substances are linked to both computers and printers. But Figure 52 reveals that printers appear to be more important than computers as sources of chemical emissions and exposure.

To provide more of an exposure context for these emission rate measurements, they were converted using a simple mass balance model into potential indoor concentrations and placed in columns three and four of Table 28 and Table 29. To convert the emission rates into equivalent indoor levels, two exposure scenarios were used:

1. a small room of 20 m³ volume with 0.2 air-change per hour, and
2. a 100 m³ room with 0.2 air-change per hour.

These scenarios provide a means of evaluating the emissions measurements here with the representative indoor concentration reported in Hodgson and Levin (2003) and Hippelein (2004). These scenarios also provide a screening-level estimate of how computers and/or printers might affect exposures and indoor concentrations. The air exchange rates are selected to be in the low but plausible range for California residences. Computers and printers can easily be used in residential environments where the air exchange rate (AER) is below the California Building Code minimum requirement of 0.35 h⁻¹. For example, when Piazza et al. (2007) carried out a survey of ventilation practices in California, they found that many houses are under-ventilated, and they estimated that only 10% to 50% of new houses meet the minimum requirement of 0.35 h⁻¹. More recently Offermann et al. (2008) conducted a multi-season study of ventilation in 108 new single-family, detached homes in California and found that 32% of the households never opened their windows or doors for ventilation, especially in the winter months. The homes without mechanical ventilation systems had outdoor air exchange rates below 0.35 h⁻¹. Offermann et al. (2008) concluded that new single-family detached homes in California are built relatively tight, and in those homes where the windows/doors are not opened for ventilation, the outdoor air exchange rates are typically low (e.g., 0.2 h⁻¹). It should also be noted that: (a) when the whole-house AER gets low, the room-to-room air mixing within the house will likely control exposure concentrations for point sources such as office equipment and can be higher than the whole-house AER, (b) there are proximity effects (McBride et al. 1999) near point sources that can make exposures for the person near the source higher than the room average, and (c) short-term AERs during office equipment use can be much lower than the 24-hour average measured in surveys. With all of these issues considered, a room AER of 0.2 h⁻¹ was selected as a screening value. In Table 28 and Table 29, the concentrations derived from the two scenarios are listed in columns three and four.

Table 28. Summary comparison of chemical emissions from computers, and how concentrations in 20 m³ and 100 m³ rooms with 0.2 ACH compare to those observed in residential environments

Substance	Emit µg/h	Conc. µg/m ³ in 20m ³	Conc. µg/m ³ in 100 m ³	Hippelein (2004) µg/m ³	Hodgson & Levin (2003) µg/m ³	Exposure potential	Key Indoor source?
D6 Siloxane	136	34	6.8	0.82		Yes	Yes
D7 Siloxane	46.5	11	2.3			?	?
Toluene	39.5	9.9	2.0	12.0	12.5		
D5 Siloxane	36.1	9.1	1.8	0.82	12.7	Yes	
Phenol	33.2	8.3	1.6		5.77	Yes	
p-Xylene	29.7	7.5	1.5	0.20	5.65	Yes	Yes
Ethylbenzene	21.9	5.5	1.1	1.40	2.30	Yes	
D8 Siloxane	20.6	5.2	1.1			?	?
Formaldehyde	20.0	5.0	1.0		20.9		
o-Xylene	14.1	3.6	0.70	1.40	2.22	Yes	
1-Hexanol, 2-ethyl-	13.3	3.3	0.65	2.80	7.89	Yes	
Styrene	10.6	2.6	0.55	1.00	1.00	Yes	
Tetradecane	9.66	2.4	0.50	0.86	40.7	Yes	
Hexadecane	7.09	1.7	0.35	0.35		Yes	?
D4 Siloxane	6.94	1.7	0.35	0.82		Yes	?
Acetophenone	5.56	1.4	0.30	1.00		Yes	?
Acetaldehyde	5.50	1.4	0.30		5.42		
Dodecane	3.84	0.95	0.20	0.75		Yes	
Butylated Hydroxytoluene	3.78	0.95	0.20			?	?
Benzene, 1,2,3-trimethyl-	3.05	0.75	0.15			?	?
Benzene, 1,3,5-trimethyl-	2.93	0.75	0.15			?	?
Benzaldehyde	2.07	0.50	0.10		1.65		
Benzene, propyl-	1.66	0.40	0.10	0.53	0.54		
Naphthalene	1.47	0.35	0.05			?	?
Benzene, 1,2,3,5-tetramethyl	1.31	0.35	0.050			?	?
Naphthalene, (1 & 2 methyl)	0.77	0.20	0.050			?	?
Dibutyl phthalate	0.70	0.15	0.050			?	?
Benzene, 1,3-diethyl-	0.64	0.15	0.05			?	?
Benzene, 1,2,3,4-tetramethyl	0.56	0.15	0.05			?	?
Benzene, butyl-	0.45	0.10	0.025		1.65		
Benzene, (2-methylpropyl)-	0.21	0.050	0.010			?	?
tris(2-chloroethyl) phosphate	0.15	0.050	0.010			?	?

Table 29. Summary comparison of chemical emissions from printers, and how concentrations in 20 m³ and 100 m³ rooms with 0.2 ACH compare to those observed in residential environments

Substance	Emit ^a µg/h	Conc. µg/m ³ in 20m ³	Conc. µg/m ³ in 100 m ³	Hippelein (2004) µg/m ³	Hodgson & Levin (2003) µg/m ³	Exposure potential	Key Indoor source?
Tetradecane	532	130	27	0.86	40.7	Yes	Yes
Hexanal	343	86	17	9.4	61.5	Yes	Yes
Pentadecane	218	54	11	0.51	4.3	Yes	Yes
Nonanal	192	48	9.6	8.0	18.0	Yes	Yes
Tridecane	154	39	7.7	1.2	1.1	Yes	Yes
D3 Siloxane	136	34	6.8	0.82		Yes	Yes
Benzene, 1,2,3-trimethyl-	135	34	6.7			?	?
D4 Siloxane	117	29	5.8	0.82		Yes	Yes
Octanal	116	29	5.8		1.0	Yes	Yes
D5 Siloxane	113	28	5.6	0.82	12.7	Yes	Yes
Benzene, 1,3-diethyl-	105	26	5.2			?	?
p-Xylene	102	26	5.1	0.2	5.7	Yes	Yes
Benzaldehyde	85.2	21	4.2		1.7	Yes	Yes
Styrene	79.9	20	4.0	1.0	1.0	Yes	Yes
Ethylbenzene	70.4	18	3.5	1.4	2.3	Yes	Yes
D-Limonene	69.0	17	3.4	8.4	20.0	Yes	
1-Hexanol, 2-ethyl-	66.	17	3.3	2.8	7.9	Yes	Yes
Phenol	63.8	16	3.2		5.8	Yes	
o-Xylene	58.5	15	2.9	1.4	2.2	Yes	Yes
Toluene	55.8	14	2.8	12	12.5	Yes	
Dodecane	42.7	11	2.1	0.92	1.2	Yes	Yes
Acetophenone	42.0	10	2.1	1.0		Yes	Yes
Hexadecane	31.9	8.0	1.6	0.35		Yes	Yes
TMPD-MIB, Texanol	15.2	3.8	0.75			?	?
TMPD-DIB, TXIB	12.3	3.1	0.60			?	?
Butylated Hydroxytoluene	9.34	2.3	0.45			?	?
3-Carene	8.52	2.1	0.45	4.7	22.8		
Dibutyl Phthalate	7.18	1.8	0.35			?	?
Benzene, butyl-	6.68	1.6	0.35		1.6	Yes	
Benzene, propyl-	6.56	1.6	0.35	0.53	0.5	Yes	
1R-.alpha.-Pinene	6.08	1.5	0.30	12	22.8		
Benzene	5.63	1.4	0.30	2.1	2.9		
1-Hexadecanol	5.53	1.4	0.30			?	?
Benzene, (2-methylpropyl)-	4.84	1.2	0.25			?	?
Diethyl Phthalate	3.70	0.95	0.20			?	?

^a Average of all laser printers tested during active printing.

The screening estimates in the third and fourth columns of Table 28 and Table 29 do not address the ability of surfaces to increase the effective residence time of some SVOCs, as discussed in Appendix C. So it must be recognized that some SVOCs can behave as though the chamber (or room) has a larger volume and retention time. In addition, both printers and computers are often in an idle state, and this exercise does not explicitly account for the actual time printing and actively running the computer. So this should be considered a preliminary screening exercise.

To identify chemicals of concern, concentrations in both the 20 m³ and 100 m³ volumes are compared to the measurements of Hodgson and Levin (2003) and Hippelein (2004). When the 20 m³ scenario concentration exceeds the background measurements from either study, it indicates the compound is potentially important for exposure studies addressing the person near the computer or printer. When the 100 m³ scenario concentration exceeds the background measurements from either study, it is considered as the potential for a significant contribution of a chemical to indoor air from computers or printers. These results are expressed in columns seven and eight of Table 28 and Table 29, where a “Yes” indicates a potentially significant impact to either indoor exposure or indoor concentrations. A question mark indicates compounds that are not included in the work of Hodgson and Levin (2003) and Hippelein (2004).

The emissions from printers and computers during active printing or processing are compared in Figure 52, showing that printers generally have the highest emission rates for a range of VOCs. However, the time that printers are active is likely to be much less than the time that computers are active. The comparison in Table 28 and Table 29 is summarized graphically in Figure 53 and Figure 54. Figure 53 compares predicted concentrations in a 0.2 ACH, 20 m³ room receiving computer and printer emissions to concentrations observed in German and North America residences. The substances released by printers produce levels that are mostly at or above observed indoor levels—indicating a high potential for proximity exposure—but the results do not consider the duration of a typical print cycle. Computers produce lower levels than printers for most compounds considered, but still present the potential for significant exposures in small spaces. Relative to other indoor sources, the computers and printers tested are potentially important indoor sources for the following substances: dodecamethyl cyclohexasiloxane (D6 Siloxane), octamethyl cyclotetrasiloxane (D4 Siloxane), decamethyl-cyclopentasiloxane (D5 Siloxane), m/p-xylene, styrene, ethylbenzene, 2-ethyl-1-hexanol, phenol, and o-xylene. Figure 54 shows that, once the room size increases to 100 m³, the predicted contributions of active printer and computer emissions to room concentrations become smaller but are still significant relative to observed concentrations for many substances. Figure 54 indicates that all computer emissions (except D6 Siloxane) give rise to indoor levels within or well below observed ranges of residential concentrations, while emissions from printers generally give rise to indoor levels within or above observed residential concentrations. In considering these results, one should note that many residential or office environments can have a number of computing and printing devices in the same room.

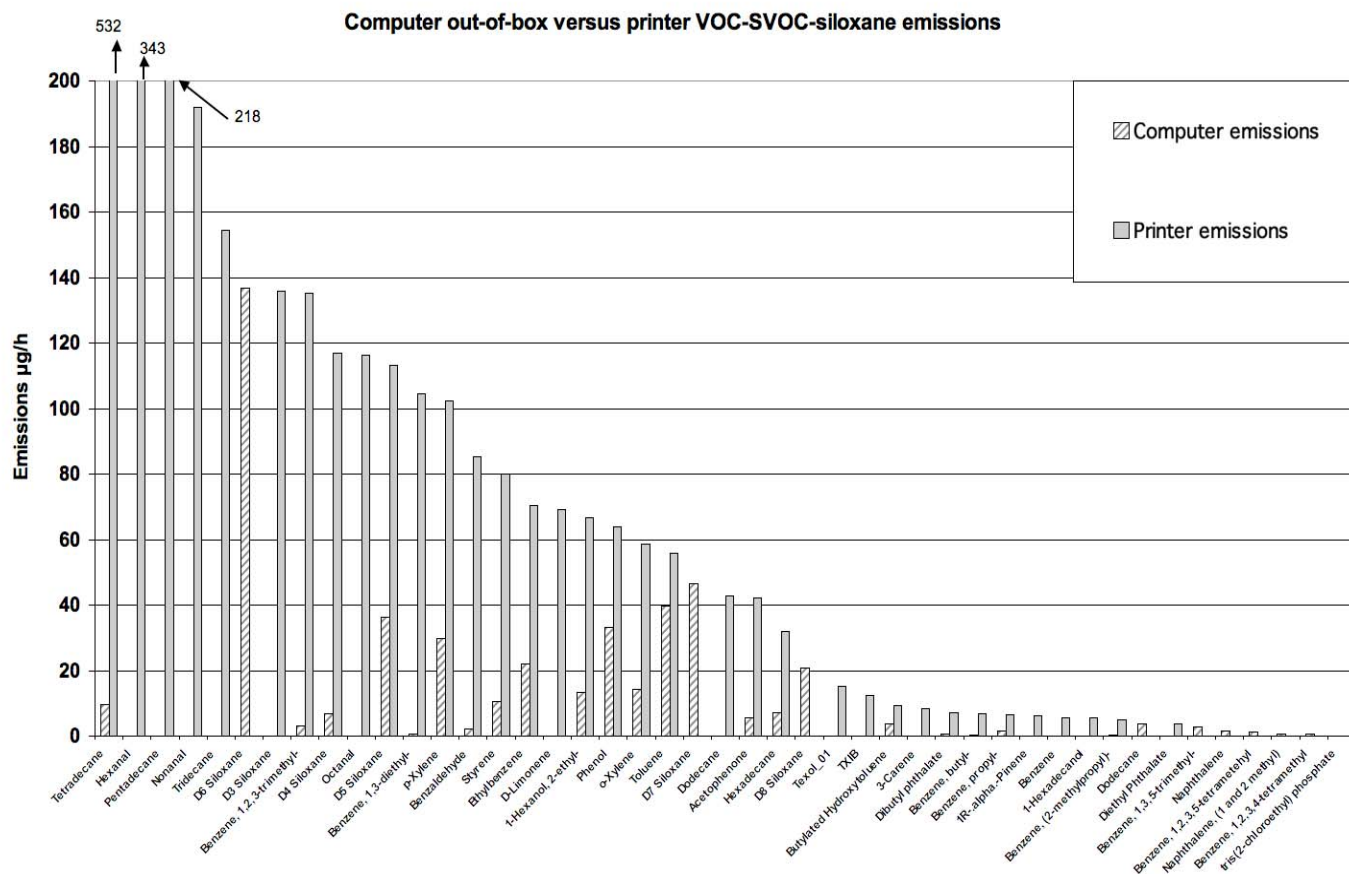


Figure 52. Summary comparison of chemical emissions for out-of-box-computers and printers during active operation

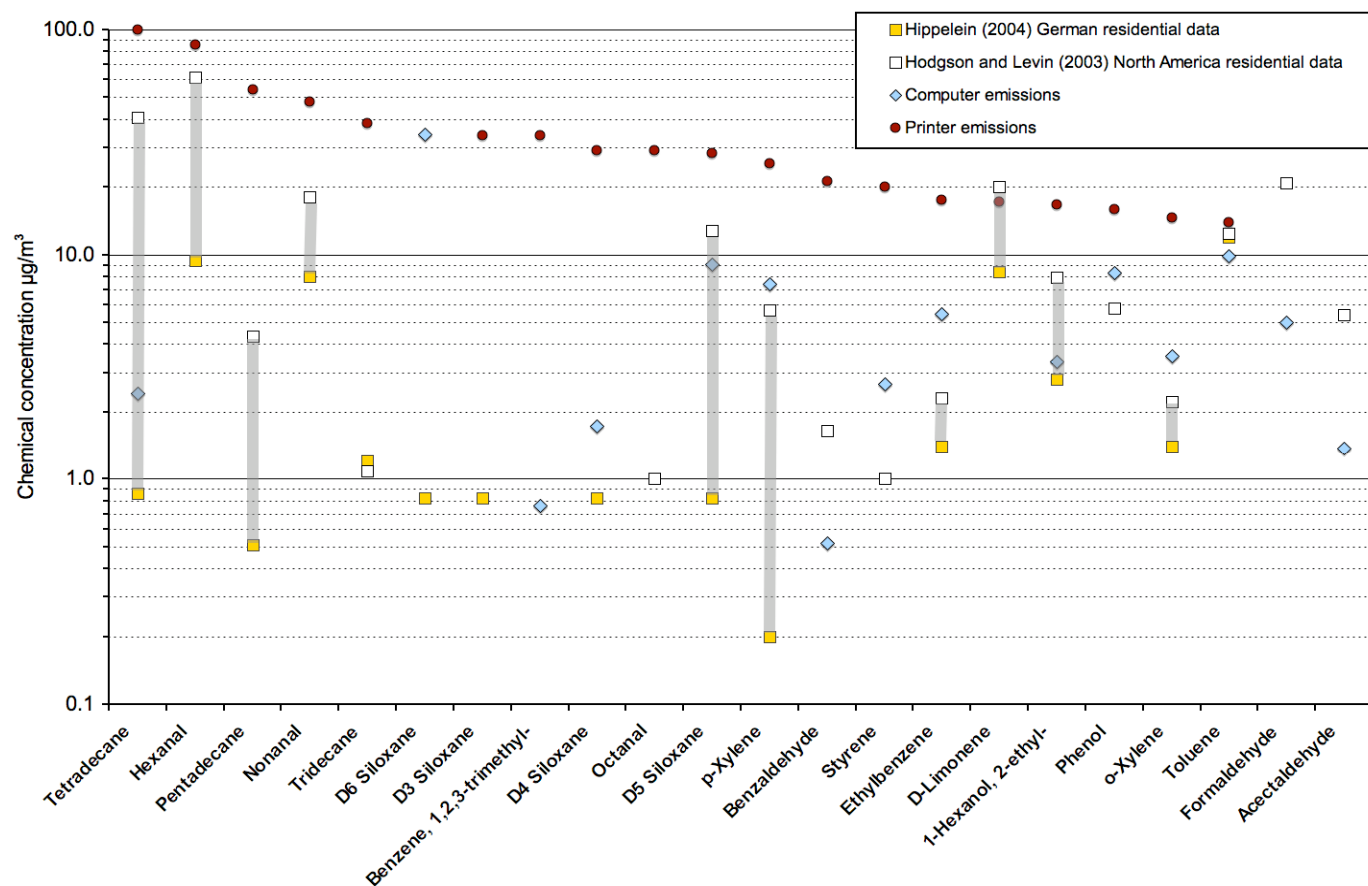


Figure 53. Comparison of predicted concentrations in a 20 m³ room with 0.2 ACH from computer and printer emissions to those observed in German and North American residences

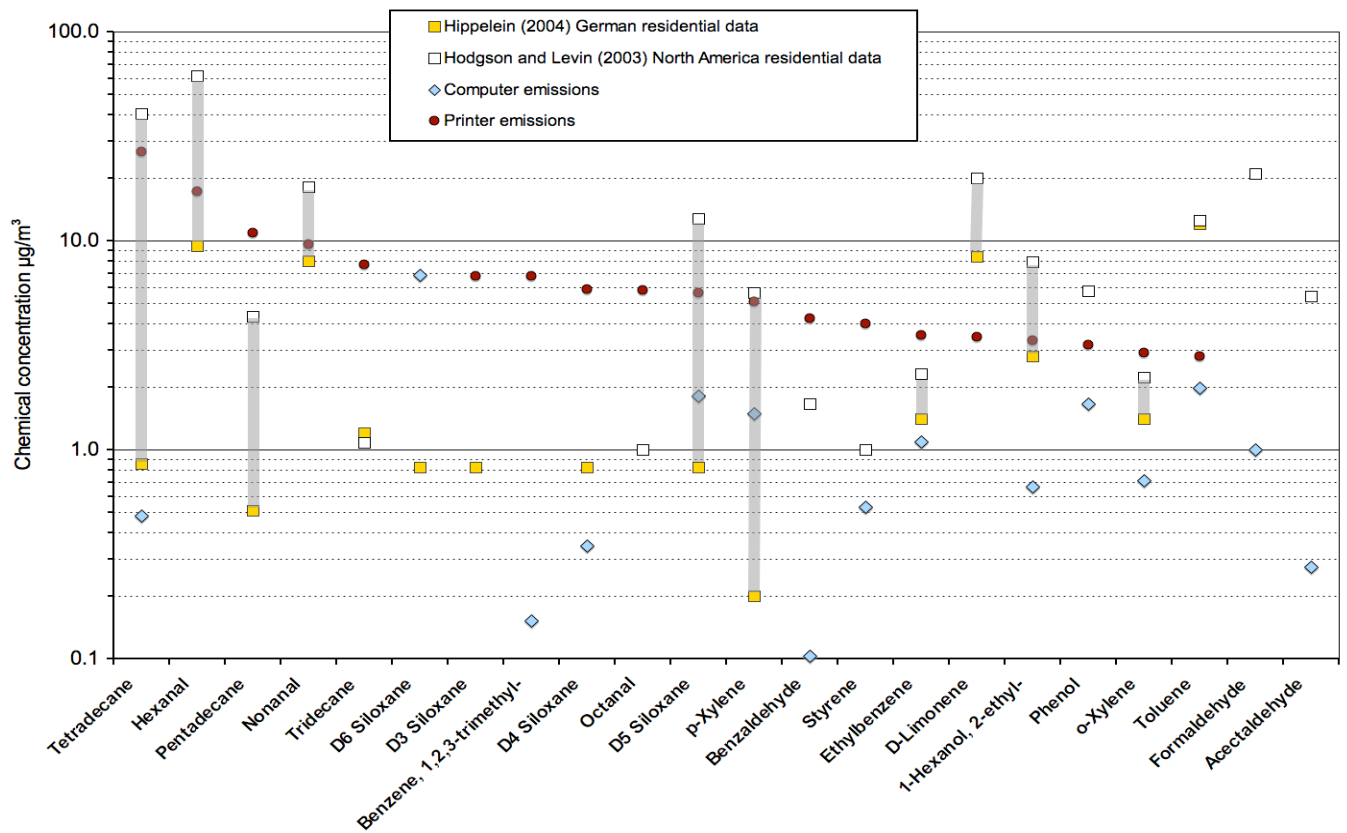


Figure 54. Comparison of predicted concentrations in a 100 m³ room with 0.2 ACH from computer and printer emissions to those observed in German and North American residences

To provide additional perspective on the emissions of VOCs and SVOCs, the results here are also placed in the context of health-protective guidelines. A review of both national and state guidelines was carried out. It included the California Chronic Reference Exposure Levels (CRELs) (OEHHA 2008a), Acute Reference Exposure Levels (ARELs) (OEHHA 2008b), No Significant Risk Levels (NSRLs) for carcinogens and Maximum Allowable Dose Levels (MADLs) for chemicals causing reproductive toxicity (OEHHA 2008c), and the Reference Dose (RfD) and Reference Concentration (RfC) from the U.S. EPA IRIS database (USEPA 2008). Eighteen of the compounds listed in either Table 28 or Table 29 are listed in one or more of these health-based guidelines. It should be noted that compounds without available guidelines are not necessarily safe. Table 30 lists these eighteen compounds, the available guideline numbers, and the corresponding concentration for a release to a 20 m³ room with 0.2 ACH. In almost all cases the computer and printer emissions give rise to concentrations well below guideline levels. However, formaldehyde emissions from computers and dibutylphthalate emissions from printers are possible exceptions.

The experiments here draw attention to siloxanes that come out of both computers and printers at relatively high levels. These are compounds that should be of continuing interest to ARB and the Energy Commission. Only a few siloxanes are described in the literature with regard to exposure and health effects, and it is therefore difficult at this point to make broad conclusions and comparisons of the toxicity and/or health risks associated with these compounds (Lassen et al. 2005). Many siloxanes are relatively persistent both in the environment and within the human body. Toxicity data cover primarily the cyclic siloxanes D4 (octamethylcyclotetrasiloxane) and D5 (decamethylcyclopentasiloxane). For these, acute toxicity tests show very low toxicity by oral, dermal, and inhalation routes (Lassen et al. 2005). But there is some indication that D5 is a potential carcinogen (USEPA 2003), and D4 has been observed to impair fertility in rats by inhalation and has thus been classified as a substance toxic to reproduction in Category 3 with the risk phrase "Possible risk of impaired fertility" (Lassen et al. 2005).

Table 30. Comparison of the various health-based guidelines to room concentrations from computer and printer emissions for the 20 m³ room scenario

Substance	CREL µg/m³	AREL µg/m³	NSRL/ MADL µg/d (and derived air conc. in µg/m³)^a	EPA RfD mg/kg-d (and derived air conc. in µg/m³)^b	EPA RfC µg/m³	Computer emission conc. 20 m³ scenario µg/m³	Printer emission conc. 20 m³ scenario µg/m³
Formaldehyde	9	94 (1 h)	40 (2)	n/a		5.0	-
Acetaldehyde	9		90 (4.5)		9	1.4	-
Acetophenone				0.1 (350)		-	0.95
Benzaldehyde				0.1 (350)		0.50	21
Benzene	60	1300 (6 h)	6.4			-	1.4
Dibutylphthalate			8.7 (0.44)	0.1 (350)		0.15	1.8
Diethylphthalate				0.8 (2800)		-	0.95
Ethylbenzene	2000		54 (2.7)	0.1 (350)	1000	5.5	18
Naphthalene	9		5.8 (0.29)	0.02 (70)	3	0.35	-
Naphthalene, 1-methyl-				0.004 (14)		0.20	-
Naphthalene, 2-methyl-				0.004 (14)		0.20	-
Phenol	200	20,000 (1 h)		0.3 (1050)		8.5	16
Styrene	900	21,000 (1 h)		0.2 (700)	1000	2.7	20
Toluene	300	37,000 (1 h)	7000 (350)	0.08 (280)	5000	10	14
o-Xylene	700	22,000 (1 h)		0.2 (700)	100	3.6	15
p-Xylene	700	22,000 (1 h)		0.2 (700)	100	7.5	25

^a The NSRL/MADL intake with units µg/d is converted to an equivalent concentration in µg/m³ by dividing it by 20 m³/d—the assumed default breathing rate.

^b The RfD with units mg/kg-d is converted to an equivalent concentration in µg/m³ by dividing it by 20 m³/d (the assumed default breathing rate), multiplying it by 70 kilograms (kg) (the assumed default body weight), and multiplying by the conversion 1000 µg/mg.

In addition to chemical emissions there is the issue of particles. Experimental results here indicate that inkjet printers have very small particulate-matter releases, but that laser printers can release up to 1.8×10^{12} particles during the few seconds when the printing drum is conditioned from an idle state (see results for LP12 cold prints in Appendix K) to prepare for a print and the print is initiated. When this number of particles is released to a 20 m^3 volume, a concentration of 50,000 particles/cc will be added to the ambient concentration. When this number of particles is released to a 100 m^3 volume, a concentration of 10,000 particles/cc will result. These particles are mostly in the ultrafine range (less than $0.1 \text{ }\mu\text{m}$ in diameter), which means they are rapidly removed from air by accumulation and surface binding. Results here indicate that these particles are removed from the study chamber at a rate up to 40% faster than removal by ventilation alone. So these concentrations are short-lived and are removed often before the next print job. As a result, the long-term average concentration in a room with a printer and 100 m^3 of volume will be much lower than 10,000 particles/cc. As noted in Section 4, early studies (for example, Wallace 1996) and more recent reviews (Riley et al. 2002) and measurements (He et al. 2007) for indoor/outdoor levels of fine/ultrafine particles indicate that number concentrations in urban atmospheres are in the range of 10,000 to 100,000 particle/cc and that the archetypal levels of ultrafine particles indoors are in the range of 1,000 to 50,000 fine/ultrafine particles/cc for residential environments. This indicates that although laser printers might be a significant contributor to short-term exposures, they may not necessarily contribute significantly to the long-term cumulative exposure to ultrafine particles.

5.3. The Source of Particle Emissions from Laser Printers

The work here clearly demonstrates significant bursts of ultrafine particle (UFPs) emissions from laser printers, but it has not shown the mechanism by which these particles are formed within the printers. Moreover, the work to date has not determined what accounts for variations among different laser printers regarding the magnitude of this emission. The research group has three working hypotheses: (1) at the start of each print cycle, the drum within the laser printer becomes quite hot, such that heating the drum inside the printer could lead to the formation of UFPs, especially if it is dirty or soiled with toner residue from previous prints, (2) ozone formed within the printer reacts with volatile chemicals within the printer to form UFP, and (3) heating the paper and toner or fuser oil vaporizes semi-volatile chemicals and significant amounts of water that rapidly condense to form particles as the printer exhaust stream cools.

The first hypothesis has merit in that it is common for hot surfaces to form particles due to a combination of events. Both the drum and the corona wire within the printers become hot during the printing process. There was an opportunity to compare particle emissions between experiments where the corona wire was or was not cleaned, and these comparisons showed only a small reduction in particle emissions, although the toner cartridge was replaced as well. This leaves the hot drum as the key source for this hypothesis. There were no experiments here to compare emissions with a drum that was clean with one that was not, although repeated printing of blank pages reduced emissions then increasing toner usage led to an increase in emissions.

The second hypothesis, ozone-mediated UFP formation, has been demonstrated as a mechanism of particle formation when ozone comes in contact with volatile cleaning solvents (Destailats et al. 2006a). In the cleaning product experiments, this particle formation was observed in a small chamber when the inlet ozone was 120 ppb. But because there was rapid reaction of ozone with the chamber surface, the ozone concentrations available for reacting with cleaning solvents was typically less than 10 ppb. The experiments here measured ozone levels coming out of the printers at 2–3 ppb as background, but two of the printers had significant emissions (580–1750 $\mu\text{g}/\text{h}$ during active printing). The printer with the highest measured ozone emissions also had the highest measured particle emissions. But the other printer with elevated ozone emissions did not have particle emissions that were elevated above the other printers that had only trace or non-detected ozone emissions. The measured increase in ozone at the printer outlet for some of the printers means that it is likely that much higher ozone levels have formed within the printers and could be sufficient to react inside the printer to form UFPs before the exhaust exits the printer.

The third hypothesis is based on the observation that a significant amount of higher molecular weight alkanes are measured in the emission stream during active printing for several of the printers that also have elevated particle emissions. In addition, a significant amount of water is released during printing, as moisture is driven out of the paper as it is warmed by the print drum.

All hypotheses are being explored and others are being solicited. But this issue will likely not be resolved without more research on what is happening inside the printers.

6.0 Summary and Conclusions

6.1. Summary

This report describes the methods and results from a study in which the primary objective was to measure emissions of organic pollutants, ozone, and particulate matter from a selected set of office equipment typically used in residential and office environments. Although office equipment has been a focal point for government efforts to promote energy efficiency, little is known about the relationship between office equipment use and indoor air quality.

6.1.1. Background and Motivation

This study was motivated by the widespread and growing use of office equipment by a large fraction of the California (and U.S.) population in their workplaces, homes, and schools, and the incomplete and fragmented evidence of this equipment as a source of health-relevant air pollutants. The last few decades have seen major changes in the work environment. Fewer people spend their workdays in factories and conversely a higher proportion can be found in offices. Revolutionary developments in information technology have increased the quantity of and transformed the nature of equipment to be found in proximity to the California population both at work and at home. It is now common for each person's home or office workspace to contain a desktop computer, a display unit, and often a printer. Office equipment has become more prevalent in home environments. By 2000 more than half of U.S. households had at least one computer (Newburger 2001). In addition, the use of laptop computers spanning both work and non-work environments is on the rise. These issues provide compelling arguments for a systematic study of pollutant emissions.

The specific aims of this research effort were to: (1) use screening-level measurements to identify and quantify the concentrations of air pollutants of interest emitted by major categories of distributed office equipment in a controlled environment; (2) quantify the emissions of air pollutants from generally representative, individual machines within each of the major categories in a controlled chamber environment using well defined protocols; (3) characterize the effects of aging and use on emissions for individual machines spanning several categories; (4) evaluate the importance of operational factors that can be manipulated to reduce pollutant emissions from office machines; and (5) explore the potential relationship between energy consumption and pollutant emissions for machines performing equivalent tasks. The study included desktop computers (CPU units), computer monitors, and three categories of desktop printing devices. The printer categories are: (1) printers and multipurpose devices using color inkjet technology; (2) low- to medium output printers and multipurpose devices employing monochrome or color laser technology; and (3) high-output monochrome and color laser printers.

The study included three components, a literature review and evaluation, and two experimental phases. Experimental Phase I included screening-level experiments designed to identify substances of interest for more detailed study. These screening-level measurements were used to indicate the potential relative importance of different categories of office equipment with respect to emission rates. Experimental Phase II involved more detailed studies of individual

devices to characterize changes in emissions with time and identify factors that can influence emissions. These measurements identified situations in which low energy consumption machines have lower pollutant emissions.

6.1.2. Literature Review Approach and Findings

The recent literature on indoor pollution reveals that a number of potentially harmful pollutants may be emitted from office equipment. The first task of this project was a comprehensive review and analysis of published literature and other available information on the emissions of air pollutants from office equipment. This review focused on experimental methods used to characterize emissions and identified critical research needs in this field. The office equipment evaluated in this review included computers (desktops and notebooks), printers (laser, ink-jet, and all-in-one machines) and photocopy machines. Pollutant categories considered included volatile organic compounds (VOCs), ozone, particulate matter, and several semi-volatile organic compounds (SVOCs). The literature review helped establish the research objectives for the current project—to provide a systematic process to measure the contribution of office equipment to the indoor concentrations and exposures for a number of important pollutants.

The literature review was structured to provide information on three issues relevant to the overall project elements. These are (1) the use of emission chambers, (2) the selection of office-equipment operation modes, and (3) chemical analytes and detection methods.

The literature review provided important input for experimental methods and revealed both the current state of knowledge and information gaps about pollutant emissions from office equipment. For some pollutants the link between office equipment emissions and indoor air concentrations is relatively well established, but most pollutants emitted from office equipment can also come from other sources, and their source apportionment is less straightforward. The review indicated the need to distinguish between computers and printers when characterizing emissions from office equipment.

The current literature establishes computers as sources of VOCs and some SVOCs, but not of ozone and particulate matter. Existing studies clearly show that computers emit a range of VOCs, although in most cases the relatively low emission rates suggest that these are less significant than other indoor and outdoor sources. Computers are typically not a source of ozone or particulate matter, although re-emission of ambient particles deposited in the units has been demonstrated. The existing literature is limited with regard to information on SVOCs. Emission factors for brominated and organophosphate flame retardants indicate levels for individual SVOC pollutants are in the nanogram per hour range. Although these numbers are significantly lower than VOCs, many SVOCs that raise health concerns are found to be retained indoors because of strong partitioning to surfaces and dust. Computers are suspected as possible long-term sources of these SVOCs. The influence of office equipment on the burden and distribution of indoor SVOCs through redistribution of particulate matter requires further investigation. This is particularly important for brominated flame retardants. Another timely issue identified in the literature review is the need to better quantify phthalate emissions by correcting for background levels.

Printers have been characterized as an indoor source of VOCs, SVOCs, particulate matter, and ozone. Emissions of VOCs from printers are generally higher than for computers, particularly for styrene, toluene, xylene, and other alkylbenzenes but the variability between devices and between experiments is also high. Significant levels of particulate matter are generally found during operation of printers, copiers, and multifunctional devices. But there have been few systematic studies to explain the time history and source of these emissions. For ozone, emission rates are unclear, but there is a concern that even low levels of ozone emitted by printers might react with other VOCs, either within the machine or outside, resulting in secondary pollutants and generation of ultrafine particles.

6.1.3. Phase I Experiments

Phase I experiments were designed as screening studies to identify a wide range of potentially important pollutants from new or recently purchased office equipment—including computers and printers. Phase I experiments were set up to screen five categories of equipment. The first included in-use laptop computers that were used to collect preliminary emission measurements and test the experimental design and instrumentation. The second category included new desktop computers with monitors. The last three categories included medium- and large-output laser printers and inkjet printers.

Phase I Experimental Methods

The Phase I screening-level experiments involved multiple components placed in a large chamber to identify and measure pollutant concentrations associated with major office-equipment categories. All Phase I experiments were conducted in a 20 m³ room-scale stainless steel test chamber with a dedicated clean-air flow-through ventilation system designed to minimize the introduction of ambient particles, VOCs, and SVOCs to the chamber air. Temperature, humidity, and pressure differential (inside/outside) were maintained at set levels and continuously monitored. The experimental duration was approximately two weeks for computer runs and four days for each of the three printer runs. Office equipment was tested under different operational phases including off, on/idle, and on/active, and the duration of each phase was selected to allow the experimental system to approach steady state, providing the opportunity to detect the widest range of pollutants. The chamber air was sampled for VOCs, carbonyls, ozone and particulate matter.

Phase I Experimental Results

Screening-level emissions concentrations were measured and evaluated for five categories of pollutants—VOCs, low-molecular-weight aldehydes, SVOCs, ozone, and particulate matter (PM). Both computers and printers produced detectable emissions of many VOCs. The only low-molecular-weight aldehyde emissions found in this study were formaldehyde releases from computers. Three classes of SVOC were identified for both computers and printers—polycyclic aromatic hydrocarbons (PAHs), brominated flame retardants (BFRs), and organophosphate flame retardants (OPFRs). Emissions of chemicals from each class were observed for both computers and printers. Printer PAH emission rates exceed those from computers, but both types of devices did not appear to be significant sources of indoor PAH. Computers and printers had similar and continuous emission rates of BFRs. Both computers

and printers had continuous emissions of OPFRs, but printers were somewhat higher. Based on Phase I results, siloxanes were added to the set of analytes, following an evaluation of “unknowns” from these screening studies.

6.1.4. Phase II Experiments

Phase II of this project used a smaller chamber to measure device-specific emission rates for a broad set of substances and identify the impact of a range of environmental and operational variables on emission rates for individual computer and printer units.

Phase II Experimental Methods

Methods developed for Phase II experiments included the overall experimental design; chamber mass balance evaluations; computer and printer selection; options for mitigating emissions; and exposure, chemical sampling, and sample analysis. All of the Phase II experiments were carried out in a smaller 395-L cylindrical frame chamber constructed with Teflon-coated aluminum top and bottom plates and supports wrapped in a transparent Teflon film. It is large enough to contain a single printer or computer (with monitor and peripherals) but small enough to allow the full air stream to be sampled for the SVOC assessment. The overall goals for the Phase II experimental methods included: (a) confirmation of Phase I results using single devices in smaller chambers, (b) evaluation of previously unidentified chemicals in emissions stream, (c) characterization of particle emissions from laser printers, (d) measurements of energy use, and (e) insight on efforts to mitigate emissions and the potential human exposures. Substances collected and analyzed from these experiments included a subset of the VOCs and SVOCs collected in Phase I: siloxanes, ozone, and particulate matter.

Phase II Experimental Results

Emissions rates from individual printers and computers were measured and evaluated for six categories of pollutants—VOCs, low-molecular-weight aldehydes, SVOCs, siloxanes, ozone, and particulate matter (PM), which was measured as particle number (PN).

Both computers and printers produced detectable emissions of many VOCs. Individual computers showed an “aging” effect in that the VOC and (possibly) SVOC emissions decrease as operating time increases. This aging effect does not seem to be affected by cycling the computer on and off as compared to a continuously operating unit. However, allowing the unit to cool between repeated runs appears to slow the emission rate relative to continuous operation and continuous on/off cycling. Printers were observed to emit VOCs with each print sequence. These emissions were not observed to decrease with age, which is based on the fabrication date for the different units tested. We hypothesize that the lack of aging effect for printers is because emissions are related, at least in part, to the toner use or printer drum conditions, which are either continuously replenished or constant. The formaldehyde emission rate from computers showed an aging effect similar to VOCs.

Three classes of SVOC were sampled from individual computers—PAHs, brominated flame retardants (BFRs), and organophosphate flame retardants (OPFR). Emissions from each of these chemical classes were detected. Printer PAH emission rates for the two-ring PAHs exceed those from computers. But both computers and printers do not appear to be significant sources of

indoor PAH. Computers had continuous emission rates of some BFRs, but many of the identified compounds were below the limit of detection, making some of the results difficult to interpret. Computers also had continuous emissions of OPFR. Siloxane emissions from printers and computers failed to show a significant aging effect, and also did not change significantly when the computer power was off.

Ozone emissions were not detected for computers but were detected in laser printers. Inkjet printers had no detectable emissions of ozone. Ozone emissions from laser printers were relatively low for most of the units tested (compared to what can be brought to the indoor environment from ambient air), but two printers had elevated ozone emissions. The ozone levels within the laser printing devices are likely higher and could have an impact on particle formation.

Emissions of PM were not detected for computers but were clearly present in laser printer emissions. Inkjet printers had no detectable emissions of PM. Laser printers gave off intermittent bursts (large number counts) of fine to ultrafine particle emissions. Similar results have been reported by Schripp et al. (2008). These releases can be attributed to at least two distinct mechanisms. The first occurs during cold-start print jobs, where emissions are not linked to print duration or to the number of pages printed and can thus be specified in terms of particles emitted per print job (PN/print). This emissions mechanism appears to be related to the conditioning of the printer drum and is discussed more in the next paragraph. In addition to the cold-start emissions burst, laser printers also emit ultrafine particles during active printing. Based on the range of uncertainty in the measurements and variability across different printers, particulate matter emissions during active printing were characterized as particles emitted per second of active printing (PN/second), or particles emitted per page printed (PN/page).

6.2. Conclusions

Intermittent emissions of ultrafine particles (UFP) from laser printers are the least understood and potentially the most important indoor pollutant releases from the categories of office equipment tested in this project. Knowledge of the health implications of UFP is increasing (Kreyling et al. 2006), and there is evidence that particle number concentrations of UFP may be related to health outcomes (Penttinen et al. 2001). Ultrafine particle emissions during laser printing are elevated and episodic, particularly during initiation of a printing event. These emissions can give rise to indoor particle number concentrations that can exceed urban indoor and outdoor levels (Hoek et al. 2008) and near roadway levels (Zhang et al. 2004). Nevertheless, the composition of particles emitted from printers are likely to be much different from that of near-roadway and ambient particles. Experimental results here indicate that inkjet printers have very small particulate-matter releases relative to the laser printers. Results here reveal that the lower temperature (power) used by the inkjet technology is at least partly responsible for the lower emissions. But this has not been fully documented, and the basic difference in the print technology is also a likely contributor to the difference between emissions from inkjet and laser printers. A laser printer can release up to 1.8×10^{12} particles during the initial seconds of operation, when the printer is preparing for and initiating a print job (see cold-print results for LP12 in Appendix K). When the initial burst of particles is released from a laser printer into a

volume of 20 m³, a concentration of 50,000 particles/cc can be reached. When this number of particles is released to a volume 100 m³, a concentration of 10,000 particles/cc will result. But these emissions are not continuous and are rapidly removed by accumulation, attachment to surfaces, and room ventilation. As a result, the long-term average contribution to the particle number concentration in a room with a printer and 20 m³ of volume will be much lower than 50,000 particles/cc. As noted above, ultrafine-particle number concentrations in urban atmospheres are in the range of 10,000 to several 100,000 particle/cc, and the archetypal long-term average levels of ultrafine particles indoors can range from 1,000 to as much as 50,000 or more. This indicates that although laser printers might be a significant contributor to short-term and near-field exposures, which may be detrimental to vulnerable populations that work in close proximity to office equipment, printers likely do not contribute significantly to the long-term cumulative exposure to ultrafine particles at the room scale.

The lack of standardization makes the growing body of literature on office equipment emissions confusing and difficult to interpret. This study provides all concentration data using a standard volume and normalized all results to one air change per hour, to make results comparable when reporting chamber concentrations. For individual equipment, all results are reported as emissions rates—mass/unit/hr for chemical species and number of particles per unit of time or per operation (page or print job). Because VOCs, ozone, PAHs, phthalate esters, and fine particulate matter can originate from a variety of sources, the effective use of replicable controlled emissions studies for these pollutants is a significant contribution of the present study. The use of large chambers with groupings of equipment as a screening experiment followed by the use of small chambers with individual components was an effective strategy for systematically identifying and quantifying emissions factors for office equipment.

It also is important to distinguish between computers and printers in summarizing results. The total number of identified VOCs, SVOCs, and siloxanes emitted by new and operating computer includes some 40 compounds and amounts to 300 to 500 µg/h of total chemical emissions. The total number of identified VOCs, SVOCs, and siloxanes emitted by an active printer includes some 30 compounds and amounts to 2,000 to 5,000 µg/h of total chemical emissions. In a small 20 m³ room with 0.2 air change per hour, most of the substances released by computers and many of those released by printers produce levels indoors that are at or below typical indoor levels from other sources. But there are notable exceptions. Relative to other combined indoor sources, computers are potentially important indoor sources for the following substance: dodecamethyl-cyclohexasiloxane (D6), decamethyl-cyclopentasiloxane (D5), and p-xylene. Relative to other indoor sources, printers are potentially important indoor sources for the following substance: ultrafine particles, tetradecane, hexanal, pentadecane, nonanal, tridecane, hexamethyl-cyclotrisiloxane (D3), octanal, decamethyl-cyclopentasiloxane (D5), p-xylene, benzaldehyde, styrene, ethylbenzene, 2-ethyl-1-hexanol, o-xylene, dodecane, acetophenone, and hexadecane.

It is important to put this work in the context by considering exposure, health implications, energy costs, and technology options. In light of the diversity of available office equipment, the rapid evolution and turnover of product lines, changes in manufacturing processes, and variability in operating conditions, the values summarized in this study represent initial

estimates of emissions and their implications. Most of the chemicals did not exceed health-based standards for SVOCs, VOCs, and formaldehyde using the simple room-scale mass balance model, but formaldehyde emissions from computers and dibutylphthalate emissions from printers are possible exceptions where the modeled room-scale concentrations exceed California Proposition 65 levels and, for formaldehyde, come close to the current California Chronic Reference Exposure Level. There are no indoor standards for PM_{2.5} or ozone; however, to understand the potential health implications of the indoor concentrations for these pollutants, the concentrations were compared to outdoor Ambient Air Quality Standards (AAQS 2008). Testing found PM_{2.5} emissions from the devices to be low, and the resulting exposure levels would not likely exceed the 24-hour National Ambient Air Quality Standards of 35 µg/m³. Two printers had elevated levels of ozone, but the exposure from these devices also would not likely exceed the California one-hour ozone AAQS of 0.09 ppm (180 µg/m³).

Although the concentrations of most pollutants were low, personal exposures may be significantly larger than those estimated through average pollutant indoor concentrations, when users are close to the emissions source over extended periods of time. The magnitude of emissions, the link from emissions to personal exposure, the toxicological significance of the chemicals emitted, and the costs and impacts of alternate materials should all be considered in order to evaluate potential importance of human exposures and health risks.

In addition to possible health effects, air pollutants emitted by office equipment can affect work performance and productivity. Overall productivity losses due to building-related symptoms in the United States have been estimated between \$20 billion and \$70 billion per year (Mendell et al. 2002). However, identification of chemical sources that induce or exacerbate these productivity effects is complicated by the combined presence of multiple indoor sources and environmental factors.

Two additional economic impacts of office equipment are the direct energy requirements of individual units, and the indirect energy requirements of the ventilation needed to compensate for heat gain and/or dilution of indoor pollutant emissions. Data from developed countries show that 30%–50% of primary energy is consumed in non-industrial buildings (such as residences, offices, schools, and hospitals). Direct energy use associated with office equipment is currently estimated at 3% of all electric power use in the U.S. (Kawamoto et al. 2001). Indirect energy use for ventilation to remove indoor air pollutants and heat generated by office equipment also increases the overall building energy consumption and should be considered when assessing the overall impact of office equipment.

6.3. Benefits of this Work to California

The results from this study offer benefits to a number of California programs that confront and/or potentially impact indoor air quality. Among the key factors related to indoor air quality assessment are the pollutant source characteristics within specific buildings and rooms. Chemicals are emitted from a wide range of building materials, consumer products, and office equipment. Assessments of indoor air quality can benefit from the emission factors provided in this work. These factors cover a range of chemical and particulate pollutants and capture

several categories of office equipment, as well as a range of different equipment use patterns or duty cycles. The results of this study provide valuable input to a number of ongoing and emerging environmental health programs in the State of California. Of particular note are the value of these results to the Environmentally Preferable Purchasing program, the Green Chemistry initiative, the California Environmental Contaminant Biomonitoring Program, and California's Energy Efficiency Standards for Residential and Nonresidential Buildings.

California's Environmentally Preferable Purchasing (EPP) program provides guidance to State agencies for the purchase of a wide range of products, including electronic equipment. The State has adopted the Electronic Product Environmental Assessment Tool (EPEAT) to identify electronic devices with reduced environmental impact.⁴ The EPEAT assessment tool includes desktop and laptop computers, as well as monitors, but currently does not include selection criteria for printing devices. In addition, the selection criteria for computers and monitors do not include VOC and SVOC emissions, although the use of certain environmentally sensitive materials such as mercury, cadmium, lead, polyvinyl chloride, and some flame retardants are considered along with power consumption. The results presented in this report can assist the State's EPP program in its review of assessment criteria that relate to indoor air quality for computers and monitors and its efforts to establish assessment criteria for printing devices. The measured emission factors for pollutants from computers and printers show large differences across devices, manufacturers, and models providing opportunities to identify low-emitting equipment. For printers, the ability to screen for particle number concentrations at the exhaust vent of the active unit can provide insight into the relative emissions. However more detailed experimental systems, such as those demonstrated in the current project, are required to assess actual pollutant emissions factors.

The California Green Chemistry initiative has a strong emphasis on assuring that chemicals and products used in California are sustainable. Access to detailed emissions factors for both printers and computers will assist the mission of this program.

The California Environmental Contaminant Biomonitoring Program (CECBP) is working to develop a statewide probabilistic sample of blood and urine analytes that will improve our knowledge of the magnitude and range of chemical exposures within the California population. As this program sets priorities for substances to "biomonitor," better access to computer and printer emissions factors will be a valuable input. In addition, emissions factors for computers and printers will help this program determine sources of exposure once biomonitoring sample data become available.

Emerging construction practices and the need for improved energy efficiency, as described in the California Energy Efficiency Standards for Residential Buildings (Title 24, Part 6),⁵ will result in tighter buildings that may require mechanical ventilation systems to control indoor air contaminant levels and humidity. A number of factors need to be balanced when determining

⁴ For a description of the State of California's Environmentally Preferable Purchasing program, see www.ciwm.ca.gov/EPP/

⁵ For details on California Energy Efficiency Standards, see www.energy.ca.gov/title24/.

the necessary level of ventilation in a home. These include humidity and temperature control, power usage, and the control of indoor air contaminants. Efforts to link ventilation requirements and energy efficiency standards will likely also benefit from this study. In particular, ventilation/energy-efficiency trade-off studies need this study's compilation of emission factors for office equipment, as well as its information on the relationship between pollutant emissions and power consumption and/or heat generation by office equipment.

6.4. Recommendations

The results and experience from the current study lead to a number of recommendations for future research, as described in the following paragraphs. Each paragraph begins with the recommendation in *italics*, followed by a short background and justification for the recommendation.

There is a need for additional research to consider emissions from other types of office equipment and other functions or operations. This study focused on desktop computers with flat screen (LCD) monitors and a small set of printing devices representing inkjet and laser printers. Similar work should be completed to assess emissions from other office equipment such as photocopiers or other printer functions such as the printing of pictures on photo paper or two-sided printing with and without color. In addition, a more focused study of the relationship between computer use and emissions would be helpful for identifying the source of pollutants and possible mitigations strategies. For example, in the current study we measured emissions from computers in the off, idle, and active states, but the active state was generally run at full operational load. It would be possible to run the computers at a range of operational loads or power usage that could provide more resolution for relating emissions to use.

There is a need for targeted research to explain the pattern and source of ultrafine particle emissions from printers so that effective mitigation strategies can be recommended. The work here demonstrates the significance of intermittent bursts of UFP emissions from laser printers, but has not shown the mechanism by which these particles are formed within the printers. Moreover, the work to date has not determined what accounts for variations among different laser printers regarding the magnitude of this emission. The research group has three working hypotheses: (1) at the start of each print cycle, internal components of the laser printer such as the print drum, become quite hot, leading to formation of UFPs, especially when these components have paper and ink residue, (2) ozone formed within the printer reacts with VOCs to form UFP, and (3) heating the paper and toner vaporizes semi-volatile chemicals and significant amounts of water vapor, which rapidly condense to form particles as the gas cools.

There is a need for research focused specifically on the SVOC emissions from office equipment, including printers, to provide insight into the long-term low level emission patterns that may accumulate indoors. Both the scientific literature to date and the experimental phases of this current study indicate that the levels of VOC emissions from computers and printers are not significantly higher than other indoor sources. However, comparable data for SVOCs is lacking for the indoor environment. Although this study provides some SVOC measurements for computers and printers, based on large chamber experiments and for computers based on the

small chamber experiments, SVOC measurements from printers in the small chamber was limited by the focus on VOCs, ozone, and particles. Measuring the long-term emissions of SVOCs from office equipment will require research designed specifically for this class of pollutants. The factors that influence the emission of SVOCs may ultimately be different from other emissions. In addition, it is challenging to relate measured emission rates determined in artificially clean chambers to SVOC exposure concentrations in real environments where interactions with surfaces and particles can occur and potentially alter the indoor fate of these chemicals. The accumulation of SVOCs at indoor surfaces, including surfaces of the office equipment, can contribute to other exposure pathways, such as dermal contact. Semi-volatile organic compound emissions experiments should be designed to consider surface chemistry and gas/particle interactions. These factors should also be considered when interpreting results from these studies.

Research tracking the changes in the emission stream is needed, primarily for SVOCs, as new chemicals enter the consumer products market. There were noticeable temporal changes in the chemicals detected in the emissions stream, even over the short duration of the current study. Flame retardant use appears to be shifting from BFRs to OPFRs. New plasticizers are entering the market place as phthalates are phased out in some applications. In addition, this study shows growing levels of the siloxanes D3, D4, D5, and higher coming from printers and computers. The source of these siloxanes in the units tested is not currently known, but the implications of this trend may warrant further study as new toxicological data emerge for this class of chemicals (Greve et al. 2008; Quinn et al. 2007; Siddique et al. 2007). It also remains unclear what role the siloxanes, particularly the higher molecular weight siloxanes, play in the formation of ultrafine particles in printer emissions.

Research on activity patterns related to office equipment use is needed to relate measured emission rates to exposure concentrations and contact rates. One thing that was not available for this study is information on how computers and printers are actually used in residential environments. Computers and printers have different emissions, depending on whether they are off, on and in idle mode, or on in an active mode. This study provides emissions factors for each of these modes of operation, but does not provide data on corresponding use patterns. The long-term indoor emissions from these devices will depend on the relative fraction of time they spend in each of these states. Any future exposure and risk assessments based on this study will require this information. There is a need for research to assess patterns of use for these devices so that the emissions rates developed here can be used to assess indoor emissions on a longer-term basis. This suggests the need for field research to better understand where and how computers are used in residences. Part of this research should focus on understanding the importance of proximity with respect to exposure and intake of emissions from office equipment. Personal exposure to pollutants emitted from office equipment may be enhanced or diminished due to a proximity effect, where users remain close to a source for an extended duration or move to a cleaner environment. Proximity can be particularly important in the case of SVOCs, ultrafine particles, and reactive species, where interaction with surfaces and rapid transformations can occur.

7.0 References

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8.0 List of Inventions Reported and Copyrighted Materials Produced

None to report.

9.0 Glossary of Terms, Abbreviations, and Symbols

General Abbreviations

AAQS	Ambient air quality standards
ACH	Air changes per hour
AER	Air exchange rate
ARB	Air Resources Board
AREL	Acute reference exposure limits
ASE	Accelerated solvent extraction system
ASTM	American Society for Testing and Materials
BC	Black carbon
BDE	Brominated diphenyl ether
BFR	Brominated flame retardant
CPC	Condensation particle counter
CREL	Chronic reference exposure limits
CRT	Cathode-ray tube (computer monitor)
DCM	Dichloromethane
DNPH	2,4-dinitrophenylhydrazine
EC	Elemental carbon
ECMA	European Computer Manufacturers Association
GC-ECD	Gas chromatography – Electron Capture Detector
GC/MS	Gas chromatography – Mass spectrometry
GC-NPD	Gas chromatography – Nitrogen phosphorous detector
GM	Geometric mean
GSD	Geometric standard deviation
HPLC	High performance liquid chromatography
IRIS	Integrated Risk Information System
ISO/IEC	International Organization for Standardization/International Electrotechnical Commission
LBNL	Lawrence Berkeley National Laboratory
LCD	Liquid crystal display (flat screen computer monitor)
LOQ	Limit of quantification
lpm	Liters per minute
MADL	Maximum allowable dose level
MDL	Method detection limit
MSD	Mass selective detector
MeOH	Methanol
N ₂	Nitrogen
NIOSH	National Institute for Occupational Safety and Health
NIST	National Institute of Standards and Technology
NSRL	No significant risk level
OC	Organic carbon

OEHHA	California Office of Environmental Health Hazard Assessment
OEM	Original equipment manufacturer
OP	Organophosphate
OPC	Optical particle counter
OPFR	Organophosphate flame retardants
PAC	Project Advisory Committee
PAH	Polycyclic aromatic hydrocarbon
PBDE	Polybrominated diphenyl ethers
PFA	Perfluoroalkyl compounds
PFOS	Perfluorooctane sulfonate
PIER	Public Interest Energy Research Program
PPBv	Parts per billion by volume
PPM	Parts per million
PM	Particulate matter
PNC	Particle number concentration (particles per cc)
psi	Pounds per square inch
PUF	Polyurethane foam
QA	Quality assurance
RfC	Reference concentration
RfD	Reference dose
RH	Relative humidity
SMPS	Scanning mobility particle sizer
SVOC	Semi-volatile organic compounds
TACS	Toxic air contaminants
TDGC/MS	Thermodesorption gas chromatography – mass spectrometry
TFT	Thin film transistor (computer monitor)
T/RH	Temperature and Relative Humidity
TVOC	Total volatile organic compounds
UCB	University of California, Berkeley
UFP	Ultrafine particles
USEPA	United States Environmental Protection Agency
UV	Ultraviolet
VDU	Video-display units
VOC	Volatile organic compounds
ΣVOC	Sum of measured VOCs
W	Watts
XRF	X-ray fluorescence analyzer

Symbols

C_{bg}	Background concentration in empty test chamber
C_{off}	Concentration in chamber with idle office equipment installed
C_{on}	Concentration in chamber with active office equipment
ΔP	Pressure differential in chamber (inside – outside)

Δt	Duration of an experimental time step
Q	Removal rate constant for ozone and particles
V	Volume

Brominated Flame Retardants (BFRs)

Deca-BDE	PBDE-209
PBDE-209	Fully brominated diphenyl ether congeners #209
PBDE-17	2,2',4-Tribromodiphenylether
PBDE-28	2,4,4'-Tribromodiphenylether
PBDE-47	2,2',4,4'-Tetrabromodiphenylether
PBDE-66	2,3,4,4'-Tetrabromodiphenylether
PBDE-99	2,2',4,4',5-Pentabromodiphenylether
PBDE-100	2,2',4,4',6-Pentabromodiphenylether
PBDE-153	2,2',4,4',5,5'-Hexabromodiphenylether
PBDE-154	2,2',4,4',5,6'-Hexabromodiphenylether
PBDE-183	2,2',3,4,4',5',6-Heptabromodiphenylether
PBDE-190	2,2',3,3',4,4',5,6-Heptabromodiphenylether
PBDE-209	Decabromodiphenylether
¹³ C-PBDE-209	¹³ C-Decabromodiphenylether
BTBPE	1,2-Bis(2,4,6-tribromophenoxy)ethane
TBBPA	Tetrabromo bisphenol A

Organophosphate Chemicals

BDP	Bisphenyl A bis (diphenyl phosphate)
DOPP	Di-n-octylphenyl phosphate
IPDPDP	Isopropylphenyl diphenyl phosphate
PPDPP:1-2	Propylphenyl diphenyl phosphate
RDP	Resorcinol-bis-biphenyl phosphate
TBEP	Tris(2-butoxyethyl) phosphate
TBPDPP	tert-Butylphenyl diphenyl phosphate
TBP	Tributyl phosphate
TCEP	Tris(2-chloroethyl) phosphate
TCP	Tricresyl phosphate
TCPP:1-3	Tris(chloropropyl) phosphate
TDCPP	Tris(1,3-dichloro-2-propyl) phosphate
TEEdP	Tetraethyl ethylene-diphosphonate
TEHP	Tris(2-ethylhexyl) phosphate
TEP	Triethyl phosphate
TNBP	Tri(n-butyl) phosphate
TPP	Triphenyl phosphate

Polycyclic Aromatic Hydrocarbons

NAP	Naphthalene
ACY	Acenaphthylene
ACE	Acenaphthene
FLU	Fluorene
PHE	Phenanthrene
ANT	Anthracene
FLT	Fluoranthene
PYR	Pyrene

Perfluoroalkyl Sulfonamides

EtFOSE	N-ethyl perfluorooctane sulfonamidoethanol
MeFOSE	N-methyl perfluorooctane sulfonamidoethanol
MeFOSEA	N-methyl perfluorooctane sulfonamido ethylacrylate

Phthalate Esters

BBP	Butyl benzyl phthalate
BEHA	Bis(2-ethylhexyl) adipate
DBP	Di-n-butyl phthalate
DCHP	Dicyclohexyl phthalate
DEHP	Di(2-ethylhexyl) phthalate
DEP	Diethyl phthalate
DIP	Diisobutyl phthalate
DMP	Dimethyl phthalate
DMPP	Dimethylpropyl phthalate
DPP	Dipropyl phthalate

Other

TMPD-MIB	Texanol, 2,2,4-Trimethyl-1,3-pentanediol monoisobutyrate
TMPD-DIB	TXIB, 2,2,4-Trimethyl-1,3-pentanediol diisobutyrate

Cyclic Siloxanes

D3 Siloxane	Cyclotrisiloxane, hexamethyl-
D4 Siloxane	Cyclotetrasiloxane, octamethyl
D5 Siloxane	Cylopentasiloxane, decamethyl
D6 Siloxane	Cyclohexasiloxane, dodecamethyl
D7 Siloxane	Cycloheptasiloxane, tetradecamethyl
D8 Siloxane	Cyclooctasiloxane, hexadecamethyl

Appendices

- Appendix A. Phase I Report
- Appendix B. Quality Objectives
- Appendix C. Chamber Mass Balance Evaluation
- Appendix D. Particle Characterization During Phase I Experiments
- Appendix E. Bromine Screening Experiments Performed After Phase I
- Appendix F. Phase II SVOC Analytes and Analysis Methods
- Appendix G. Particle Size Evaluation for a Subset of Printers in the Phase-II experiments
- Appendix H. Background Concentrations in the Small Chamber During Phase II Experiments
- Appendix I. Printer-Specific Emissions Rates for VOCs
- Appendix J. Ozone Emission Data for Individual Printers in Phase II Experiments
- Appendix K. Detailed Particle Emission Data for Individual Printers in Phase II Experiments

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