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Quantifying Pollutant Emissions from Office Equipment Phase I Report

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Quantifying Pollutant Emissions from Office Equipment
Phase I Report

Literature Review, Screening Level Measurements, and Revised Phase-II Research Proposal

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Abstract

Although office equipment has been a focal point for governmental efforts to promote energy efficiency through programs such as Energy Star, little is known about the relationship between office equipment use and indoor air quality. This report provides results of the first phase (Phase I) of a study in which the primary objective is to measure emissions of organic pollutants and particulate matter from a selected set of office equipment typically used in residential and office environments. The specific aims of the overall research effort are: (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 ageing 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 includes 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 literature review and screening level experiments in Phase 1 were designed to identify substances of toxicological significance for more detailed study. In addition, these screening level measurements indicate the potential relative importance of different categories of office equipment with respect to human exposures. The more detailed studies of the next phase of research (Phase II) are meant to characterize changes in emissions with time and may identify factors that can be modified to reduce emissions. These measurements may identify “win-win” situations in which low energy consumption machines have lower pollutant emissions. This information will be used to compare machines to determine if some are substantially better than their peers with respect to their emissions of pollutants.

1 INTRODUCTION

The last few decades have seen major changes in the work environment. The economies of the US and other industrialized nations are undergoing profound transformations, with their bases shifting from manufacturing towards information technologies where professions and service jobs dominate. This means 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 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 and a display unit. 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 notebook computers spanning both work and non-work environments is on the rise.

A number of potentially harmful pollutants may be emitted from office equipment. Laser printers and photocopiers can generate ozone in varying amounts. Toner and paper dust from printing devices can become airborne resulting in the generation of 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. VOCs 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 (PBDEs) and organophosphates. Among the semi-volatile organic compounds (SVOCs) emitted from computers are triphenylphosphate and other organophosphate esters from plastic covers of video-display units (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.

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 provide compelling arguments for a systematic study of pollutant emissions. However, this is a somewhat daunting task, in part, due to the diversity of the available equipment; the rapid evolution and turnover of product lines; and the variability in operating conditions.

To address the need for a systematic study of pollutant emissions from office equipment we have developed a two-phase research plan. Phase I includes a review and analysis of the current literature on the emissions of air pollutants from office machines and screening-level experiments to broadly identify and measure pollutant emissions associated with major classes of desktop office equipment. Phase I is complete and is the main subject of this report. The goal in Phase II is to build on the screening-level experiments of Phase I to focus on important chemicals and to measure emissions and energy use with individual devices under controlled conditions using defined protocols. In the proposed workplan for this research, it was stated that the details of Phase II experiments will be provided to ARB only after the synthesis of information from the literature review and from results of the Phase I experiments. Thus, an important goal of this report is to use the Phase I results to update and set priorities for the matrix of experiments that will make up the Phase II experiments.

2 PROJECT OVERVIEW AND OBJECTIVES

The primary objectives of this research are to: 1) Identify and quantify concentrations of specific VOCs, SVOCs, ozone and particulate matter emitted by major categories of office equipment in a controlled chamber environment, 2) quantify emissions of air pollutants from individual machines within each of the major office equipment categories in a controlled chamber environment, 3) Characterize the effects of ageing 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. We begin this report with an overview of the project.

2.1 Definition of Study Phases and Specific Tasks

The project was designed to be conducted in two phases. Phase I includes a literature review and a series of screening-level experiments to identify and measure pollutant concentrations associated with major equipment categories. The screening measurements were collected simultaneously from multiple units (computers or printers) in a controlled chamber environment. In Phase II, emissions and other factors will be 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. Revisions to the Phase II research plan will be carried out only after consultation with and approval by ARB staff.

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 will study how emissions vary when equipment is operated at different energy levels such as standby, low power consumption, and high power consumption.

2.1.1 Phase I Tasks

Phase I was organized into three major tasks. Task 1 is a comprehensive review and analysis of published literature and other available information on the emissions of air pollutants from office equipment. Task 2 includes screening experiments to identify and quantify pollutants emitted by recently purchased (<3 months old) computers operating with LCD displays. A preliminary experiment was included with current generation laptop computers to provide preliminary information about the chamber performance and experimental conditions that were needed to optimize conditions for the desktop experiment. Three additional screening experiments were conducted to characterize and quantify emissions from major categories of printers including: 1) printers and multipurpose devices using color inkjet technology; 2) low- to medium-output printers and multipurpose devices employing monochrome or color laser technology; 3) high-output monochrome and color laser printers. The screening experiments were conducted with printers that had been used for approximately 12-24 months, the premise being that emissions may increase as the machines age and wear. The goal of Task 3 was to synthesize results from Tasks 1 and 2 to produce this interim report providing guidance about specific pollutants of interest that are recommended to be considered in the Phase II experiments.

A wide range of pollutants were assessed during the screening experiments. The focus for computer systems was on VOCs, low molecular weight carbonyl compounds, SVOCs, ozone and particulater matter (PM). There was particular emphasis on "criteria" pollutants for which health-based ambient concentration limits have been set (specifically ozone and PM2.5) and compounds appearing on California's list of toxic air contaminants (TACs), including polycyclic aromatic hydrocarbons, environmentally-persistent flame retardants, and other organophosphorus compounds. Pollutants measured during experiments with printers included ozone; fine particulate matter mass, black carbon (BC) organic carbon (OC) and elemental carbon (EC) along with the speciated VOCs including carbonyls; and SVOCs. Metals were also included in the original research plan but particle levels were too low to facilitate determination of specific metal concentrations.

2.1.2 Phase II Tasks

During Phase II, the research team recommends measuring pollutant emissions and energy for individual representative units within each equipment category to confirm results from Phase I. They further recommend that this second phase build on the broad characterization of specific pollutants identified in Phase I. Recommendations for Phase II include Tasks 4 through 7. Task 4 measures VOC and SVOC emissions and energy use for individual computer systems and their components to confirm result from Phase I and to further evaluate factors influencing emissions. Task 5 focuses on measures of VOC and SVOC compounds along with particle emissions and energy use for individual printing devices. The research team recommends measuring the effect of ageing on emissions for a subset of the individual units although this could be considered a lower priority. Task 6 will investigate other variables that may affect device energy use and emissions, e.g., use of non-OEM (original equipment manufacturer) printing supplies, use of recycled paper, varied types of operation, or the effects of heavy-use and/or extended ageing focusing on improved understanding of the factors leading to particulate emissions. ARB staff and the Project Advisory Committee (PAC) will be consulted about the selection of specific devices and variables for testing throughout Tasks 4-6. Task 7 will include a complete reporting of Phase II results and the synthesis of findings from the entire study.

2.2 Project Organization

The project is 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. UCB is the lead institution.

The overall research team structure is one in which the Principal Investigator (PI), Thomas McKone, serves as the lead contact between UCB, ARB and the PAC and has overall project management responsibility as well as responsibility for project synthesis and for all interim and final reports. Al Hodgson serves as Co-Investigator in charge of all work conducted at LBNL, including both experiments and laboratory analyses of fine particles, volatile organic compounds (VOCs) and sample collection and extraction for SVOCs. Professor S. Katherine Hammond serves as Co-Investigator in charge of SVOC analysis at UCB and supervises the work of Charles Perrino. Randy Maddalena and Hugo Destaillats have primary responsibility for designing and supervising the implementation of experimental protocols at LBNL including collection and processing of all samples and the supervision of research associates Marion Russell and Tosh Hotchi, both of LBNL, and Rachelle Majeske, a student hired through UCB. The responsibility and flow of authority in the project and overall project structure are illustrated in Figure 1.

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 (Charles Perrino, Randy Maddalena and/or Hugo Destaillats), 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 technicians/students.

A project Executive Committee was formed consisting of the PI and the LBNL and UCB co-investigators. The EC met regularly to track and sustain activities on all the individual tasks and maintain effective communication among the members of the project team as well as with ARB sponsors.

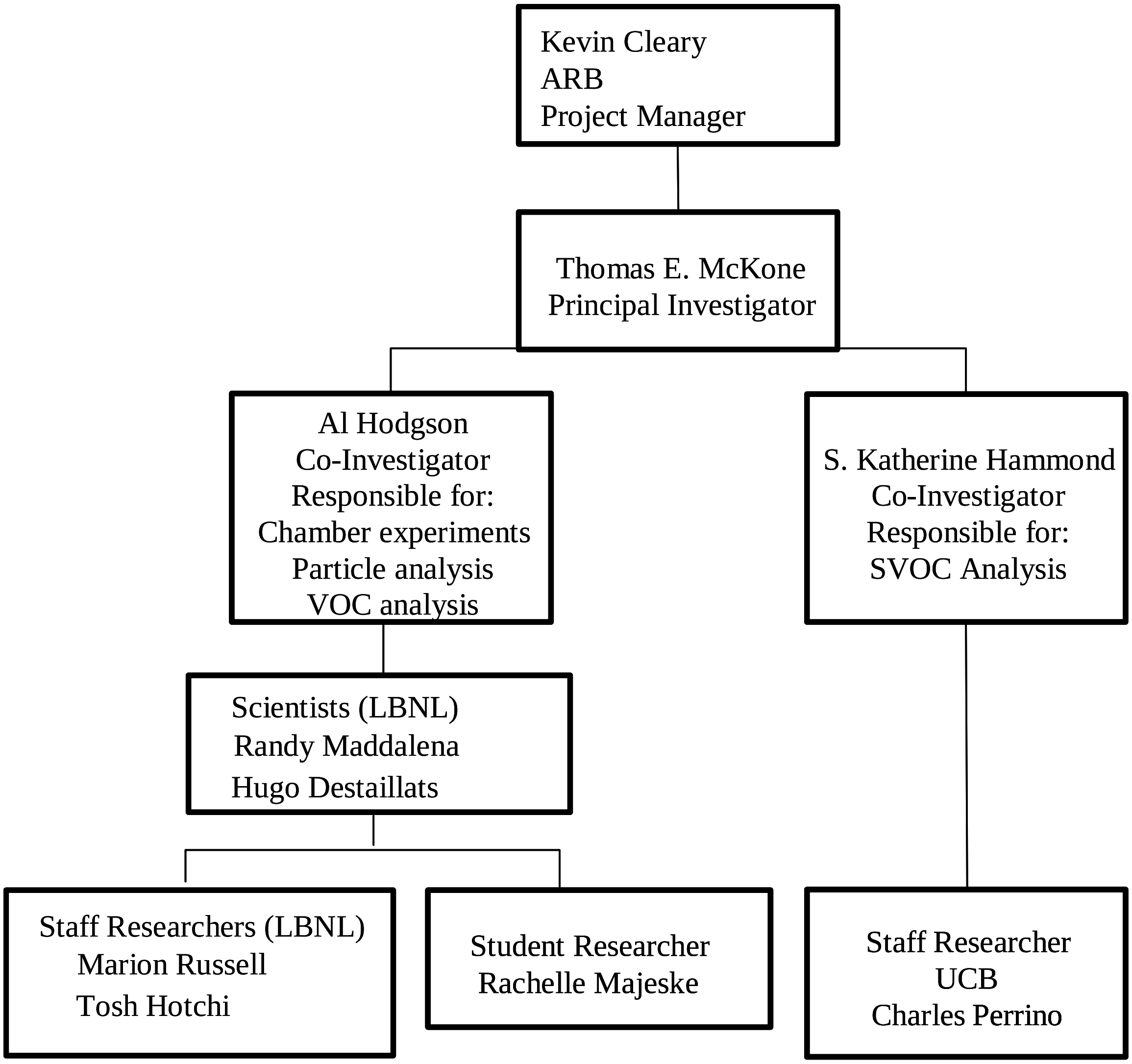

Figure 1: Project Organizational Chart

3 LITERATURE REVIEW AND EVALUATION

3.1 Introduction and Overview of Key Issues

A number of potentially harmful pollutants are emitted from office equipment. For example, office equipment has been identified as one of the sources of volatile and semi-volatile organic compounds that are associated with occupational symptoms such as eye, nose or throat irritation, headache and fatigue (Mendell et al. 2002; Wolkoff et al. 2006). In this review we summarize the existing data reported in the archival literature on this topic.

The literature reviewed in this section includes various reports on chamber pollutant concentration and emission rates from office equipment. Laser printers and photocopiers generate ozone in varying amounts. Toner and paper dust from printing devices can become airborne resulting in the generation of 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. VOCs identified in the emissions from printing devices are also summarized. These include toxic air contaminants (TACs) such as benzene, toluene, ethylbenzene, xylenes, styrene, formaldehyde and acetaldehyde. The plastic covers of video-display units (VDUs) have been shown to contain and emit triphenylphosphate and other organophosphate esters used as flame retardants. Electronic devices including office equipment contain and emit a number of brominated flame retardants such as the polybrominated diphenyl ethers (PBDEs), among other identified semi-volatile organic compounds (SVOCs). Printed circuit boards held at elevated temperature (60° C) were recently shown to emit several PBDEs. Production and use of PBDE formulations has been phased-out in Europe, and Japanese industries have voluntarily restricted the production and use of polybrominated biphenyls (PBBs), hexabromodiphenyl ether and tetrabromodiphenyl ether (Kemmlein et al. 2003b). However, use of recycled plastics containing high residual PBDE levels may re-introduce these chemicals in the manufacture of new units even after governmental regulations or voluntary restrictions are in place (Morf et al. 2005). Some of the reported emission rates of air pollutants from office equipment may be relatively low in comparison to some other known indoor sources such as building products. 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. This proximity can result in higher personal exposures than would be estimated from pollutant concentrations measured in well-mixed building air (McBride et al. 1999).

3.1.1 Public health implications

Pollutants emitted from office equipment can have potentially serious adverse health effects. Ozone emissions from office equipment have been studied in the context of understanding indoor ozone exposures (Wolkoff 1999). Inhalation exposure to toner dust has been implicated in case reports as causing respiratory impairment (Gallardo et al. 1994; Armbruster et al. 1996). Formaldehyde was recently listed by IARC as a Group I carcinogen. Acetaldehyde, and a number of the volatile aromatic hydrocarbons emitted by printers and photocopiers are Category IIa TACs. Formaldehyde, acetaldehyde and benzene are carcinogens listed by the Safe Drinking Water and Toxic Enforcement Act of 1986 (Proposition 65) with relatively low No Significant Risk Levels (NSRLs). Formaldehyde and acetaldehyde also have low (i.e., <10 μg m^{-3}) chronic Reference Exposures Levels (RELs) for noncancer effects. Triphenyl phosphate is an inhibitor of human blood monocyte carboxyleserase, has shown hemolytic toxicity, and has contact allergenic effects in humans (see references in Carlsson et al., 2000). PBDEs, which are classified as endocrine-disrupting compounds (Rudel et al. 2003), have been shown to accumulate in human breast milk (Noren and Meironyte 2000). Thirteen PBDE congeners and tetrabromobisphenol-A were quantified in serum collected from 19 computer technicians (Jakobsson et al. 2002).

Other adverse human consequences also may be attributed to office equipment. A study of sick building syndrome (SBS) among office workers in Copenhagen, Denmark, revealed a positive association between SBS symptoms and office equipment (Skov et al. 1989). In this study, significant involvement in either photocopying or the use of a video display terminal was positively associated with symptom prevalence for work-related mucosal irritation and work-related general symptoms. The Helsinki Office Environment Study, conducted in 1991, assessed symptoms and associated factors among 2,700 office workers in 41 buildings (Jaakkola and Jaakkola 1999). These researchers found that "photocopying was related to nasal irritation, and video display terminal work to eye symptoms, headache, and lethargy." Such symptoms may be a consequence of factors other than, or in addition to air pollutant emissions. However, a recent panel study, which isolated the effect of pollutant exposure from other factors, found that exposure to emissions from new computers caused degradation in perceived air quality, some increase in SBS symptoms, and decreased performance of office work (Bakó-Biró et al. 2004).

3.1.2 Energy use implications

Data from developed countries show that 30-50% of primary energy is consumed in non-industrial buildings (residences, offices, schools, hospitals, etc), representing an energy demand comparable to the transport sector and larger than the industrial consumption. Nearly half of building energy is dissipated through air exchange, and additional losses are estimated from the operation of mechanical ventilation systems (Liddament and Orme 1998). The total primary energy use attributable to space conditioning (heating and air conditioning) plus ventilation in U.S. residential and commercial buildings was estimated in 12.4 exajoules per year, which is about 12% of the total primary U.S. energy use (Interlaboratory-Working-Group 2000). For that reason, improving the energy efficiency of buildings and residences is one of the most effective ways of reducing the environmental footprint of urban development. Because energy savings must be compatible with preserving the health and comfort of building occupants, indoor air quality is a critical parameter to consider. If pollutant emissions from office equipment require enhanced ventilation to maintain healthful and productive indoor environments, there will be a corresponding energy penalty attributable to the office equipment due to increased thermal conditioning and air movement loads. By avoiding the need for increased ventilation, reduction of pollutant emissions from office equipment also can have important indirect energy benefits in addition to the benefits derived from energy-savings features.

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 electric power use in the U.S.

(http://enduse.lbl.gov/Projects/InfoTech.html). Kawamoto et al. (2000) estimated that the total energy use for office equipment in the U.S. in 1999 was 71 terawatt-hours (TWh), with the largest categories being desktop computers (20%), displays (20%), minicomputers (17%), copiers (11%), mainframe computers (9%), and laser printers (9%). This breakdown reflects the trend of desktop computers accounting for an increasing share of computing resources in modern offices. 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.

3.2 Experimental methods used in emission characterization

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 provide compelling arguments for systematic studies of pollutant emissions. However, this is a somewhat daunting task, in part, due to the diversity of the available equipment; the rapid evolution and turnover of product lines; and the variability in operating conditions. Studies designed to investigate emissions of office equipment are by force limited to explore only a reduced spectrum of equipment, pollutants and operation conditions. For that reason, a large variability in reported emission levels is often observed.

3.2.1 Emission chambers

Direct determination of pollutant emissions by office equipment is carried out with environmental chambers. In Table 1, we present an overview of chamber dimensions, materials and operation conditions, in addition to conditions proposed in the industry standard ECMA-238 (ECMA, 2001). A specific challenge associated with a comprehensive study of office equipment emissions is the difficulty of measuring the emissions of SVOCs using this technique. 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 PBDEs has been described by Kemmlein et al. (2003) in a study where chamber concentrations of tri-, tetra- and penta- congeners emitted by a printed circuit board held at 60°C increased with time over a period of 50 or more days. In another experiment, the same authors found that heating the chamber following removal of the test specimen evolved significant masses of sorbed PBDEs. This procedure was used to quantitatively recover sorbed SVOCs, thus overcoming chamber effects (Hoshino et al. 2003). In a similar experimental chamber study for the determination of phthalate esters released by PVC-coated wall coverings, Uhde et al. (2001) employed a cooled plate (fogging chamber) to collect and quantify the SVOCs that condensed on the chamber walls. During a 14-days test period, analyte concentrations in the cooled plate were in the same range as those determined in the air samples collected during the same period.

Table 1. Exposure chamber conditions reported in various studies.

Dimensions (m^3)	Internal surfaces	Temp, RH	Equipment analyzed	Pollutants detected	References
23 and 35	aluminum, stainless steel.	26-31 ^{o}C 30-35 %	copiers	VOCs ozone carbonyls particles	(Leovic et al. 1996; Leovic et al. 1998)
2.4	stainless steel	23 ± 2 ^{o}C 55 ± 5 % RH	copier printer all-in-one	VOCs ozone carbonyls particles	(Lee et al. 2001)
33	stainless steel	23 ± 0.5 ^{o}C 50 ± 5 % RH	copiers	VOC particles	(Brown 1999)
12	stainless steel and glass	23 ± 2 ^{o}C 50 % RH	printers	VOC ozone particles	(Heimann and Nies 2001; Smola et al. 2002)
4.5	stainless steel	23 ^{o}C, 50 % RH	computer copier printer	VOCs	(Berrios et al. 2005)
22 and 54	stainless steel	23 ^{o}C 50 % RH	computer copier printer	VOCs	(Berrios et al. 2005)
1	stainless steel	23 ± 1 ^{o}C 50 ± 3 % RH	computers	SVOCs	(Kemmlein et al. 2003)
0.02 and 0.001	glass	23 – 60 ^{o}C 50 – 8 % RH	printed circuit boards	SVOCs	(Kemmlein et al. 2003)
6.5 10^{-3}	glass	35–200 ^{o}C 50 ± 5 % RH	notebook computer	VOC SVOC	(Hoshino et al. 2003)
1	glass	22 ^{o}C	computers	VOC carbonyls	(Nakagawa et al. 2003)
Volume ratio: 1:2,5 to 1:20	Stainless steel, glass, aluminum	23 ± 2 ^{o}C 50 ± 5 % RH	electronic equipment	VOC, ozone, PM	(ECMA, 2001)

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).

3.2.2 Analytical methods

In most applications, chamber air samples were collected during operation and idle periods. Ozone was measured continuously with photometric monitors (Brown 1999). Particles were also continuously monitored using a PM_{10} aerosol monitor (Brown 1999; Lee et al. 2001). Total VOCs were in some cases monitored continuously with a photoionization detector (Lee et al. 2001). All other samples were collected on various substrates that integrate emissions over the period analyzed. Speciation of analytes of interest was carried out subsequently by chromatography after sample preparation steps involving extraction and, in some cases, derivatization.

Volatile organic chemicals (VOCs) were typically 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 a canister (Lee et al. 2001). In all cases, VOCs were identified and quantified by gas chromatography/mass spectroscopy (GC/MS).

Volatile carbonyls were collected in 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).

SVOCs were collected in PUF cartridges. After extraction, identification and quantification were carried out by GC/MS for most analytes. High pressure liquid chromatography (HPLC/DAD) was used as an alternative technique for those analytes that were not amenable to GC analysis, such as Bisphenol A bis (diphenyl phosphate) (Kemmlein et al. 2003). In a test where the whole chamber was heated to 200°C after the emissions ended and the specimen was removed, SVOCs were directly collected on Tenax and analyzed by GC/MS using thermal desorption (Hoshino et al. 2003). This simple method was possible to carry out with a notebook computer in a relatively small chamber, but is not practical for most of the other tested equipment due to difficulties with heating larger chambers.

3.3 Characterization of emissions from office equipment

3.3.1 Emissions from desktop and notebook computers

VOCs emission rates from desktop and notebook computers are reported in Table 2. When available, chamber concentration data are also reported in this table. Emission rates are reported separately for computers operating with cathode-ray tube (CRT) monitors and with thin-film transistor (TFT) monitors. Typically the total VOC emissions (TVOC) are higher for computers with CRT than with TFT monitors. VOC emissions include aromatic hydrocarbons

Table 2. Reported volatile organic chemicals (VOCs) and ozone emitted by personal computers

Chemical	Emission rate (µg h^{-1} $unit^{-1}$)	Chamber concentration (µg/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		
Valeraldehdye	3.1		
Hexaldehyde	4.6		
Aromatic hydrocarbons	103		
TVOC	180		
Desktop PCs in operation – TFT monitor			
Formaldehyde	9.7		(Nakagawa et al. 2003)
Acetaldehyde	1.5		
Valeraldehdye	0.5		
Hexaldehyde	2.7		
Aromatic hydrocarbons	32		
TVOC	113		
Desktop PCs in operation –CRT and TFT monitors combined [a,b]			
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[c]			
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: we report the range of values determined for 3 different units

b: the article does not indicate which unit is provided with CRT or TFT monitor

c: two values are reported, corresponding to idle/operating conditions.

and volatile carbonyls, particularly formaldehyde. Notebook emissions are significantly lower than desktop units, both for idle and operating conditions. For notebooks, the chemical composition of emissions is also more diverse, including alcohols, carboxylates and ketones. The number of studies is limited but generally the results indicate that a wide range of VOCs are emitted from computers with emission rates for total VOCs between 100 and 200 $\mu g\ h^{-1}$ unit^{-1}.

Table 3 provides SVOC emission rates for desktop computers during the computer operation period, together with chamber concentrations corresponding to the desktop study and concentrations for the notebook study. Organophosphorous flame retardants were measured during computer operation, but brominated flame retardants sorbed to the chamber walls and were only detected after computer operation by thermal desorption after heating the chamber to 120 °C. Where calculated, the emission rates for the SVOCs are in the low ng per hour per computer range.

Table 3. Reported semivolatile chemicals (SVOCs) emitted by personal computers

Chemical	Emission rate (ng h^{-1} $unit^{-1}$)	Chamber concentration (ng/m^3) [a]	References
Desktop PCs in operation			
Hexabromo benzene		1	(Kemmlein et al. 2003)
RDP	2	13 (100 d)	
BDP	44	20 (100 d)	
TCPP	24		
TPP	25	85 (100 d)	
		94 (1 d) 8.6 (183 d)	(Carlsson et al. 2000) *b*
Desktop PCs after operation (from chamber surfaces)			
[illegible]E 47		150	(Kemmlein et al. 2003)
BDE 100		28	
BDE 99		61	
TBBPA		64-446	
Notebook computer			
DBP	110 / 650		(Hoshino et al. 2003)

a: the number of days in operation is indicated between parenthesis.

b: video display units

3.3.2 Emissions from printers and copiers

Table 4 presents VOCs and ozone chamber concentrations determined during idle and operation periods for laser printers, ink-jet printers and a multifunction machine (which included fax, color printer, copier and scanner). Aerosol particles (PM_{10}) concentrations (in µg/m^3) for the same equipment are reported in Table 5. Wensing et al (2006) reported particle size distributions of aerosols emitted by ten different hardcopy devices (laser printers and multi-functional devices). Ultrafine particles (< 100 nm) predominated in every case: measured particle numbers were in the range 500 – 343,000 #/cm^3 for particles > 7nm, but significantly lower (6 – 38,000 #/cm^3) for particles > 100 nm. Levels of VOCs were highest from laser printers in all categories reported in **Error! Reference source not found.** and Table 5, and, although the difference was generally small, operating units had higher levels than idle units. Additional reports from recent conference proceedings that do not specify the nature of the equipment investigated is included in Table 6. Although the individual chemicals reported in Table 6 are higher than those reported in **Error! Reference source not found.**, the total VOC results are consistent.

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Table 4. Volatile organic chemicals (VOCs), ozone and particulate matter (PM10) emitted by printers.

When reported, time of operation is indicated in parenthesis.

Chemical	**Laser printers [a,b] Chamber concentration (ppbv)**		**Ink-jet printers [a] Chamber concentration (ppbv)**		***All-in-one office machines*** **[a] Chamber concentration (ppbv)**		**Unspecified printers [c] Emission rate (μg h^{-1} unit^{-1})**
	idle	**in operation**	**idle**	**in operation**	**idle**	**in operation**	
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	207-996
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	
m,p-Xylene	1.2	1.6-1.7	0.86	0.92	0.9	0.9	84-520
Styrene	2.7-4.0	3.2-5.3	1.14	1.43	1.2	1.9	1132
o-Xylene	0.9-1.0	2.0-2.3	0.69	0.68	0.58	0.58	1128
1,4-Dichlorobenzene			0.34	0.32	0.34	0.35	
1,3-Dichlorobenzene			0.34	0.32	0.34	0.35	
1,2-Dichlorobenzene			0.21	0.21	0.26	0.22	
1,2,4-Trichlorobenzene			0.86	0.63	0.23	0.2	
Hexachlorobutadiene			0.37	0.36	0.88	0.64	
d-limonene							59
Butoxymethyl oxirane							1370
Ozone		9-10 1 – 13 *(20 m)*		5-6		6	
PM_{10}		65		20-38		41	
TVOC		300 – 1400 *(20 – 60 m)*					2500 – 43500

a: Lee et al, 2001

***b*:** Smola et al, 2002

c: Berrios et al, 2005 (the high end of the TVOC range is affected by one unit that exhibited extremely high emissions of an unidentified VOC).

Table 5. Reported PM$_{10}$ emitted by printers

Printing device	Chamber concentration (μg/m^3)	Reference
Laser printers	65	(Lee et al. 2001)
Ink-jet printers	20-38	
All-in-one office machine	41	

Table 6. Reported pollutants from printing or photocopy devices (not specified)

Chemical	Emission rate (μg h^{-1} unit^{-1})	Chamber concentration (μg/m^3) [a]	References
Benzene	6 - 1500		(Jungnickel et al. 2003)
	43.5 (10 h)	2.2 - 8.7 (10 h)	(Rochstroh et al. 2003)
Styrene	1044 (10 h)	52 - 209 (10 h)	
TVOC	8700 (10 h)	435 - 1740 (10 h)	
	870 (idle)	43.5 - 174 (idle)	
Ozone	1740 (10 h)	87 - 348 (10 h)	

a: the time of operation is indicated between parenthesis.

A relatively larger body of experimental data is available for emissions of VOCs and ozone from copier machines and this information is summarized in Table 7. In general, the emissions from photocopiers are much higher than for printers and multifunctional devices but the variability among the studies is also high.

Table 7. Reported volatile organic chemicals (VOCs), ozone and particulate matter emission from photocopy machines

Chemical	Emission rate (μg h^{-1} unit^{-1})	Chamber concentration (μg/m^3)		Reference
		idle	in operation	
Toluene	110 - 760 540 - 2000			(1) (2)
Ethylbenzene	<50 - 28000 23000 - 29000	4.1	552 – 608	(1) (2) (3)
m,p-Xylene	100 - 29000 22000 - 29000	4.5	467 – 515	(1) (2) (3)
o-Xylene	<50 - 17000 12000 - 15000			(1) (2)
Styrene	300 - 12000 6300 - 8400			(1) (2)
Styrene / o-Xylene		3.1	354 – 390	(3)
Isopropylbenzene	150 - 160			(2)
n-Propylbenzene	<50 - 2100 360 - 460	<0.4	7.8	(1) (2) (3)
Benzaldehyde	<100 - 3800 980 - 1500	1.3	25 – 26	(1) (2) (3)
α-Methylstyrene	<50 - 330 500 - 730	1.3	16 – 18	(1) (2) (3)
1,2,4-Trimethylbenzene		0.6	3.6 - 4.2	(3)
Butylbenzene		<0.4	14 – 15	(3)
Acetophenone		1.6	11 – 13	(3)
Methoxyethylbenzene		0.9	6.6	(3)
C_9-ester		<0.5	23	(3)
Butenyl benzene		1.1	28 – 37	(3)
n-Decane	<50 - 450			(1)
2-Ethyl-1-hexanol	130 - 14000			(1)
Limonene	<50 - 1100			(1)

Nonanal	1100 - 3900			(1)
n -Undecane	62 - 2000			(1)
n -Dodecane	75 - 960			(1)
Formaldehyde	<500 - 2600 1900 - 3200			(1) (2)
Acetaldehyde	<500 - 1200 510 - 1300			(1) (2)
Acetone	<100 - 2800			(1)
Propionaldehyde	<100 - 260			(1)
2-Butanone	<100 - 380 n.d. - 600			(1)
Butyraldehyde	<100 - 840 n.d. - 410			(1) (2)
Valeraldehyde	<100 - 540			(1)
Hexanal	100 - 1200 n.d. - 950			(1) (2)
TVOC		49	1630 – 1900	(3)
Ozone	1300 - 7900 1700 - 3000			(1) (2)
PM (respirable fraction)	1420-2950	6-11	19-22	(3)

(1) (Leovic et al. 1996)
(2) (Leovic et al. 1998)
(3) (Brown 1999)

3.4 Ambient measurements of pollutants emitted from office equipment

Several studies report ambient measurements of pollutants emitted by office equipment in the indoor environment. In many cases, the source of certain chemicals present in the air or in dust cannot be attributed exclusively to emissions from office equipment. However, the authors of the cited studies indicate computers, printers and/or copier machines as a likely significant source. A summary of data from these studies are provided in Table 8 through Table 12, indicating the country or region of origin for the samples. This information is relevant considering that the formulation of additives such as plasticizers and flame retardants may vary due to different practices or regulations.

3.4.1 Volatile organic chemicals (VOCs)

In Table 8, we list VOCs reported in two studies as primarily emitted by office equipment. Several other VOCs listed in the studies (Wolkoff et al. 2006) are not included in Table 8 if they originated from sources other than office equipment. Such is the case of VOCs derived from the use of cleaning products (terpenes or 2-butoxyethanol) and of ozone, which is usually present in indoor environments as a consequence of outdoor air ventilation and infiltration. In a study performed in three photocopy centers (Stefaniak et al. 2000), a large variability was observed from one center to the other, with ambient concentrations differing by 2 or 3 orders of magnitude in some cases.

Table 8. Measurements of office equipment relevant volatile organic chemicals (VOCs) in the indoor environment

Chemical	*Concentration*	*Sampling site*	*References*
Pentane	0.8-6.2 ppb	Three photocopy centers (USA)	(Stefaniak et al. 2000)
Toluene	3-4800 ppb		
1,4-Dichlorobenzene	3.8 ppb		
m,p-Xylene	1.7-2.9 ppb		
Hexane	1.6 ppb		
Ethylbenzene	1.0-0.4 ppb		
1,2,4-Trimethylbenzene	0.4-269 ppb		
o-xylene	0.6-0.9 ppb		
Phenol	7.8 ppb		
Nonane	0.6-525 ppb		
Decane	0.6-639 ppb		
Octane	0.5 ppb		
Undecane	0.5 ppb		
1,3,5-Trimethylbenzene	304 ppb		
Decane	3-2370 μg/m^3	Office environments (review with data from Europe and USA)	(Wolkoff et al. 2006)
Toluene	28-9500 μg/m^3		
p-Xylene	10-59 μg/m^3		
Formaldehyde	38-310 μg/m^3		
Hexanal	34-520 μg/m^3		

3.4.2 SVOCs: Phthalate esters

Table 9 lists measurements of phthalate esters from two different studies carried out recently in the USA and Germany. Notably, four of the most common constituents of this class (Diethyl phthalate (DEP), Di-n-butyl phthalate (DBP), Butyl benzyl phthalate (BBP) and Di(2-ethylhexyl) phthalate (DEHP)) were present at relatively similar levels in both studies. However, other reported analytes were only present in one of the studies. Phthalate esters are used as plasticizers in a wide variety of plastic and polymeric materials. For that reason, it is difficult to apportion the contribution of office equipment to the total pollutant measured in each case. Considering the phthalate esters emission rates and chamber concentrations reported in Table 3, this source is probably negligible with respect to others such as vinyl flooring, synthetic fabrics or furniture.

Table 9. Ambient levels of phthalate esters in the indoor environment

Chemical	*Concentration*	*Sampling site*	*References*
DEP	130-4300 ng/m^3 (air) nd –111 µg/g (dust)	Indoor air and dust in residences (USA).	(Rudel et al. 2003)
DBP	52-1100 ng/m^3 (air) nd –352 µg/g (dust)		
BBP	nd-480 ng/m^3 (air) 4-1310 µg/g (dust)		
DEHP	nd –1000 ng/m^3 (air) 17-7700 µg/g (dust)		
DCHP	nd –280 ng/m^3 (air) nd –63 µg/g (dust)		
DEHA	nd –66 ng/m^3 (air) 1-391 µg/g (dust)		
DPP	nd –27 ng/m^3 (air) nd –31 µg/g (dust)		
DIP	11-990 ng/m^3 (air) nd –39 µg/g (dust)		
DBP	1218-2453 ng/m^3 (air) 56-130 µg/g (dust)	Indoor air and dust in apartments (Germany)	(Fromme et al. 2004)
BBP	37-75 ng/m^3 (air) 86-218 µg/g (dust)		
DEHP	191-390 ng/m^3 (air) 775-1542 µg/g (dust)		
DEP	807-1860 ng/m^3 (air) 45-160 µg/g (dust)		
DMP	1182-4648 ng/m^3 (air) 11-46 µg/g (dust)		
DMPP	697-1466 ng/m^3 (air) 55-144 µg/g (dust)		

3.4.3 SVOCs: Polybrominated Diphenyl Ethers (PBDE)

In Table 10 we summarize concentrations of PBDEs measured in home dust and in air from several indoor environments where occupational exposure to PBDEs was expected to be high. Those included the dismantling hall of a recycling plant for electronic products, a plant for assembly of circuit boards, a teaching hall and an office with computers. We also report data for total PBDE measured in four houses and two laboratories in the US. As expected, higher levels of PBDEs were detected in the dismantling plant. By contrast, sampling carried out in homes only detected PBDEs associated with dust particles, but not in air samples although the sources of the PBDEs in the house dust is not known.

Table 10. Ambient levels of brominated flame retardants in the indoor environment

Chemical	*Concentration*	*Sampling site*	*References*
BDE 47	nd-10 μg/g	Dust in residences (USA)	(Rudel et al. 2003)
BDE 99	nd-22 μg/g		
BDE 100	nd-3.4 μg/g		
BDE 47	0.35-2.1 ng/m^3	Air in dismantling hall of an electronics recycling plant (Sweden)	(Sjodin et al. 2001)
BDE 100	0.063-0.52 ng/m^3		
BDE 99	0.54-5.5 ng/m^3		
BDE-85	0.1-0.24 ng/m^3		
BDE-154	0.13-1.0 ng/m^3		
BDE-153	0.88-11 ng/m^3		
BDE-183	6.3-44 ng/m^3		
BDE-209	12-70 ng/m^3		
BTBPE	5.6-67 ng/m^3		
BB-209	1.6-14 ng/m^3		
TBBPA	6.9-61 ng/m^3		
BDE 47	<0.1-0.39 ng/m^3	Assembly of circuit boards (Sweden)	(Sjodin et al. 2001)
BDE 100	<0.009-0.058 ng/m^3		
BDE 99	<0.06-0.15 ng/m^3		
BDE-85	<0.006 ng/m^3		
BDE-154	<0.002-0.013 ng/m^3		
BDE-153	<0.004-0.033 ng/m^3		
BDE-183	0.014-0.11 ng/m^3		
BDE-209	<0.04-0.32 ng/m^3		

BTBPE	<0.003-0.041 ng/m^3		
BB-209	<0.009-0.024 ng/m^3		
TBBPA	0.11-0.37 ng/m^3		
BDE-183	0.0046-0.012 ng/m^3	Office with computers (Sweden)	(Sjodin et al. 2001)
BDE-209	<0.04-0.087 ng/m^3		
BTBPE	<0.003-0.0058 ng/m^3		
TBBPA	0.01-0.07 ng/m^3		
BDE 47	0.72-0.8 ng/m^3	Teaching hall (Sweden)	(Sjodin et al. 2001)
BDE 100	0.053-0.059 ng/m^3		
BDE 99	0.35-0.41 ng/m^3		
BDE-85	0.0085-0.011 ng/m^3		
BDE-154	0.012-0.013 ng/m^3		
BDE-153	0.022-0.023 ng/m^3		
BDE-183	0.011-0.012 ng/m^3		
BDE-209	<0.04-0.17 ng/m^3		
BTBPE	0.003-0.0048 ng/m^3		
TBBPA	0.035-0.15 ng/m^3		
Total PBDE	76-2088 pg/m^3(house) 358-410 pg/m^3 (labs)	House and laboratory air (North America)	(Shoeib et al. 2004)

3.4.4 SVOCs: Organophosphate flame retardants (OPFR)

Data for OPFR from five studies are reported in Table 11. These samples include residential and occupational indoor environments where exposure to OPFR is likely to be dominated by office equipment. Some OPFR were present in all or almost all the samples considered: TBP, TCEP, TPP, TBEP and TEHP. However, each of these studies also identified OPFR that were unique from those samples, indicating also a large variability of possible sources and additive formulations. In one of the studies (Marklund et al. 2003), the analysis of surface wipes from a computer screen and cover showed high levels of these chemicals which clearly indicated that the computer is a potential source of the OPFR detected in the environments but the magnitude of this source is unknown.

Table 11. Ambient levels of organophosphate flame retardants in the indoor environment

Chemical	*Concentration*	*Sampling site*	*References*
TPP	12-40 ng/m^3	Air in dismantling hall of an electronics recycling plant (Sweden)	(Sjodin et al. 2001)
IPPDPP	3.4-15 ng/m^3		
PPDPP:1	1.3-5.1 ng/m^3		
PPDPP:2	0.7-3.1 ng/m^3		
TBPDPP	0.2-1.9 ng/m^3		
TBP	9-18 ng/m^3		
TCEP	15-36 ng/m^3		
TCPP:1	10-19 ng/m^3		
TCPP:2	3.7-7.1 ng/m^3		
TCPP:3	0.6-1.5 ng/m^3		
TBEP	20-36 ng/m^3		
TBP	7.6-35 ng/m^3	Air in Schools (Sweden)	(Carlsson et al. 1997)
TNBP	9.8-64 ng/m^3		
TCEP	18-250 ng/m^3		
TCPP:1	14-35 ng/m^3		
TCPP:2	5.1-16 ng/m^3		
TCPP:3	nd-2.9 ng/m^3		
TPP	nd-0.8 ng/m^3		
TBEP	1.4-5.9 ng/m^3		
TEHP	nd-10 ng/m^3		
TBP	2.5 ng/m^3	Office air (Sweden)	(Carlsson et al. 1997)
TNBP	18 ng/m^3		
TCEP	11 ng/m^3		
TCPP:1	31 ng/m^3		
TCPP:2	12 ng/m^3		
TCPP:3	1.4 ng/m^3		
TPP	0.7 ng/m^3		
TBEP	2.2 ng/m^3		
TBP	17 ng/m^3	Office air in the absence of video display unit (Sweden)	(Carlsson et al. 2000)
TNBP	10 ng/m^3		
TCEP	7.4 ng/m^3		
TCPP:1	7 ng/m^3		

TCPP:2	2 ng/m^3		
TCPP:3	0.2 ng/m^3		
TPP	94 ng/m^3(first day) 8.6 ng/m^3(at 183 days)	Emitted by video display unit	
TBEP	18-25 µg/g	Home dust (Sweden)	(Marklund et al. 2003)
TCEP	0.19-0.27 µg/g		
TCPP	0.47-0.93 µg/g		
TDCPP	0.39-1.1 µg/g		
TPP	0.85-0.99 µg/g		
TEEdP	0.29-0.56 µg/g		
TEHP	0.06-0.07 µg/g		
TBP	0.21-0.61 µg/g		
DOPP	<0.03-0.2 µg/g		
CLP1	0.03-0.04 µg/g		
TPrP	0.02 µg/g		
TBEP	270 µg/g	Office dust (Sweden)	(Marklund et al. 2003)
TCEP	48 µg/g		
TCPP	73 µg/g		
TDCPP	67 µg/g		
TPP	6.8 µg/g		
TEEdP	0.44 µg/g		
TEHP	0.43 µg/g		
TBP	0.35 µg/g		
TBEP	170-940 ng/m^2	Wipes from computer screen and cover (Sweden)	(Marklund et al. 2003)
TCEP	210-220 ng/m^2		
TCPP	220-370 ng/m^2		
TDCPP	170-290 ng/m^2		
TPP	3300-4000 ng/m^2		
TEEdP	290-560 ng/m^2		
TBP	30-70 ng/m^2		
DOPP	130-450 ng/m^2		
TBP	4.5-8.1 ng/m^3	Office air (Switzerland)	(Hartmann et al. 2004)
TCEP	23-56 ng/m^3		

TPP	2.0-3.1 ng/m^3		
TBEP	nd-1.2 ng/m^3		
TEHP	nd-0.6 ng/m^3		
TCP	nd-0.37 ng/m^3		
TCPP	nd-130 ng/m^3		
TBP	1.7-17 ng/m^3	Electronics store air (Switzerland)	(Hartmann et al. 2004)
TCEP	2.2-8.2 ng/m^3		
TPP	1.4-5.7 ng/m^3		
TEHP	nd-2.8 ng/m^3		
TCP	nd-0.21 ng/m^3		

3.4.5 Emerging indoor SVOCs: Perfluoroalkyl compounds (PFA)

In Table 12 we summarize air concentrations of perfluoroalkyl sulfonamides measured in four houses and two laboratories. These chemicals are derived from perfluorinated surfactants that are widely used in a variety of applications that include coatings and surface treatment for electronic equipment. Potential health effects of these chemicals are relatively unknown, but their environmental persistence and their transformation in stable degradation products/metabolites such as perfluorooctane sulfonate (PFOS) is attracting increasing attention to this emerging class of indoor pollutants.

Table 12. Ambient levels of fluorinated semivolatile chemicals in the indoor environment

Chemical	Concentration	Sampling site	References
MeFOSE	667-4046 pg/m^3	House air (North America)	(Shoeib et al. 2004)
EtFOSE	364-1799 pg/m^3		
MeFOSEA	4.53-283 pg/m^3		
MeFOSE	11.1-1698 pg/m^3	Lab air (North America)	(Shoeib et al. 2004)
EtFOSE	4.75-1917 pg/m^3		

3.5 Health effects and sensory irritation

Pollutants emitted by computers and printers may be linked to health effects reported in the office environment. Asthma and allergies affect 6% and 20% respectively of the 89 millions US workers in nonagricultural, nonindustrial indoor settings. More than 20% also report nonspecific acute effects of indoor work exposures or conditions – “sick building syndrome”, SBS – including irritation symptoms, headache and fatigue with a frequency higher than weekly. The estimated productivity losses due to building-related symptoms are substantial, between 20 and 70 $B yr-1 (Mendell et al. 2002). Identification of chemical sources that induce or exacerbate these health effects is complicated by the combined presence of various possible sources in the office environment. Recent reports indicate that indoor VOCs are associated with asthma and other building-related symptoms (Andersson et al. 1997; Rumchev, Spickett et al. 2004). There is also increasing evidence from laboratory studies that the sources of these pollutants, including building products and office equipment, are associated with increased non-specific symptoms (Wolkoff, Wilkins et al. 2006). Few studies evaluate the effect of a single pollutant source, and sources other than office equipment may generate a significant contribution. For example, emissions from carpet were positively correlated with decreasing perceived air quality, the severity of headaches and the decreased performance of office work (Wargocki et al. 2002). A recent study evaluated the effect of emissions from personal computers in the office environment. The PCs were found to be strong indoor pollution sources, even after they had been in service for 3 months. The presence of new PCs increased the percentage of people dissatisfied with the perceived air quality from 13 to 41% and increased by 9% the time required for text processing. The most significant VOCs reported in that study included phenol, toluene, 2-ethylhexanol, formaldehyde, and styrene (Bakó-Biró, Wargocki et al. 2004). Little information is available on health effects associated with office equipment emissions, and a direct link can only be inferred from the existing data.

3.6 Summary

Despite earlier concerns that office equipment is a potential source for indoor pollutants, computers studied to date have only found TVOC levels on the order of 100 and 200 µg h^{-1} unit^{-1}. Although phthalate esters have only a limited number of direct emissions measurements from computers, these chemical are known additives of plastics and are measured in indoor environments so focused measurements of emissions from office equipment should be collected. Ozone and particulate matter emissions from computer equipment has not been reported. For the SVOCs, the limited number of estimated emission factors for brominated and organophosphate flame retardant compounds are in the ng per hour range but these compounds are found indoors and computers continue to be suspected as possible sources. Emissions of VOCs from printers and copiers are higher than for desktop computers particularly for certain compounds (styrene, toluene, xylene, alkylated benzenes) but the variability between devices and between experiments is also high. The contribution from printers to ozone levels indoors is unclear but significant levels of particulate matter are generally found during operation of printers, copiers and multifunctional devices. A range of methods have been used to study emissions from office equipment although standardized methods have recently been released (ECMA 2006).

4 PHASE I SCREENING EXPERIMENTS

This study was designed to support the assessment of indoor exposures to airborne contaminants released from distributed office equipment. The Phase I experiments were designed as screening studies to look for a wide range of potentially important pollutants from new or recently purchased office equipment. The number of vendors, variety of equipment offered by each vendor and across vendors and the continuing rapid evolution of technology limited our ability to identify a sample of equipment that would be representative of the current stock of computers in California households. Thus, the study design used a "composite" approach combining units from several different major manufacturers for each category of office equipment to increase our coverage of different makes and models recognizing that this approach does not provide information on individual units. The number of units that we studied in a given grouping was ultimately limited by the size of the test chamber and the need to compensate for heat generated by operating units.

The screening part of this study included three distinct experimental phases. The first used laptop computers to collect preliminary emission measurements but also to test the experimental design and instrumentation before investing in new office equipment for the second (new desktop units) and third (printers) experimental phases.

4.1 Methods

The following sections describe the materials and methods for each experiment including details on the chamber conditions, selection and operation of office equipment, sample collection, extraction, and analysis and quality assurance measures. The measured chamber conditions for each experiment are included in the results in Section 4.2.

4.1.1 Experimental Design

4.1.1.1 Overview of Experimental Approach

The same general approach was used for all screening experiments. Experiments were conducted in a 20-m^3 stainless steel test chamber with a dedicated clean-air ventilation system designed to minimize ambient particles, VOCs and SVOCs in the chamber air. The experiments were run in the dark to minimize photodegradation of pollutants. Temperature of the inflowing air was controlled to maintain 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 temperatures under differing heat loads from the equipment.

The complete experiment took 7-10 days for each computer run and 4 days for each of the three printer categories. Equipment was operated on a continuous (computers) or repeating (printers) duty cycle to provide a steady state emission scenario and maximize the likelihood of pollutant detection. Pollutant concentrations were measured either continuously (ozone, particle count, black carbon) or by collecting and analyzing integrated air samples (VOCs, SVOCs, particle mass). Duplicate samples were collected in parallel during three different stages of an experiment to characterize 1) concentrations in the empty chamber both before and after the emissions run, 2) concentrations in the chamber with office equipment installed but not plugged in and 3) concentrations with the equipment operating. Three different samples were collected during the emissions phase for the computers and two consecutive days were sampled for the printers.

4.1.1.2 Office Equipment Selection

An important part of the screening analysis for office equipment emissions is selection of a relevant sample of computers. Relevant in this context refers to computers that are likely to be used/found in California residences. 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 available to non-Members. 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 $4500.00 but the level of detail needed in the current screening study did not justify purchase of such a detailed report. However, this information would be valuable if future studies require statistically representative samples of computers in California.

Rather than use detailed survey information, our office equipment selection process was based on a survey of current articles in trade journals, consumer magazines and information from customer satisfaction surveys that are readily available to consumers. The journal *PC World* recently summarized the Gartner and IDC reports on global PC sales (Krazit, 2005). The top four manufactures in US sales include Dell, HP, Gateway and Apple Computer. These results actually represent the top six computer vendors because HP includes Compaq (merged in 2002) and Gateway includes eMachines (merged in 2004). Information on the non-name brand computer systems, sometimes referred to as “whitebox computers” is not readily available but likely makes up a small fraction of sales relative to the name-brand units. An earlier article (CNN/Money, 2004) also included IBM among the leaders in domestic computer sales. But IBM has been acquired by Lenovo and their future role in the domestic home PC market is not clear. The American Customer Satisfaction Index (ACSI) Second Quarter Scores for Manufacturing/Durable Goods & E-Business (last update: August 16, 2005) (ACSI, 2005) lists five vendors plus an “All Others” category. The list in order of ACSI score includes Apple, Dell, “All Others”, HP, Gateway and HP-Compaq (ACSI, 2005).

The Consumers Report (CR) magazine (CR, 2005) provides useful information selecting representative computers their list of computers based on a wide range of test results (convenience, speed, multimedia, expansion, etc.). 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 previously mentioned with the addition of Sony. 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.

For monitor selection, our 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, we 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. Details on the actual units selected are summarized in Table 19 in Section 4.3.2.

Printers in the inkjet and medium output laser technology categories were identified that fit our selection criteria regarding age by surveying colleagues at LBNL and UCB. Once identified, the printers were borrowed for the experiment. Fresh ink cartridges were installed prior to use. For the high output laser printers, we rented two units from a local office equipment rental store and these units were used as received. Details on selected printers are provided in Table 23 in Section 4.3.3.

4.1.1.3 Operation of Office Equipment

The ECMA Standard titled "Detection and measurement of chemical emissions from electronic equipment" (ECMA-328, August 2001) recommends operating equipment at their 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, sound 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/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 includes several printers with different monthly duty cycles and different print speeds and page capacities. To develop a standard print cycle for the group of printers we first estimated total pages per day for all printers in the category combined based on monthly duty cycle rating for each printer. This total print job was allocated to each printer based on a duty fraction for that printer in the group, which 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, the following illustrates how we developed a standard print job for a group of printers. Table 13 summarizes the values used in the calculation.

Table 13. Example calculations for printer duty cycle

	monthly duty cycle (pp/month)	*print speed (pp/min)*	*average daily duty cycle (pp/day)*	*duty fraction*
HP LaserJet 1160Le	10,000	20	333.	0.27
Brother HL-5170DN	20,000	21	666.	0.54
HP LaserJet 3015	7,000	15	233.	0.19

Based on the “average daily duty cycle” in Table 13, the total number of pages in a day for the group of medium output laser printers would be ~1240 (recommended maximum). If we define a typical print job as 20 pages, we can specify one complete print cycle (i.e., all three printers print once in series) as 60 pages where the HP1160, HL5170 and HP3015 print 17, 33 and 12 pages each per cycle, respectively. To satisfy the maximum duty (i.e., 1240 pages) requires 21 cycles.

The input and output tray capacity for each printer dictated how often we entered the chamber to empty the output trays and refill the input trays. Looking at print speed and taking into account that each machine requires about 10 seconds to print the first page (i.e., time between start of printing cycle and first page printed) then we had roughly 75 minutes of active printing per day. We distributed the active print time over about 6 hours resulting in about a 4 minute pause between each print job. After completion of the active print cycle, the printers were left idle overnight (~ 18 hour) before repeating the second 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 and a script was developed to send the appropriate size print request to each printer.

4.1.2 Sampling and Analysis Methods

The sampling and analysis methods for each pollutant category are summarized in Table 14. All of the SVOCs were collected simultaneously on the same sorbent cartridge but followed different analytical pathways after extraction. Details for each sample collection, extraction and analysis method are described below.

4.1.2.1 VOC sampling and analysis

VOC analytes are listed in Table 15. VOC samples were collected and analyzed generally following USEPA Methods TO-1 and TO-17 (USEPA 1999). VOCs were collected onto Tenax-TA™ sorbent tubes (P/N CP-16251; Varian, Inc.) modified by substituting a 15-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 at 275 °C for 30 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 120 minutes. Flows were verified using a separate calibrated flow meter at the beginning and end of sampling periods. 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 2 months have been confirmed previously in our lab for many of the VOCs included in this study.

Table 14. Sample collection and analysis methods.

Analyte	*Sampling Mode*	*Collection media*	*Sample processing*	*Analysis method*
VOC and aldehydes	Integrated	Tenax-TA + Carbosieve sorbent tubes	Thermal desorption	GC/MS
Volatile Carbonyls	Integrated	DNPH-coated silica cartridges	Extract with acetonitrile	HPLC
SVOCs	12 hr 20 lpm (14.4 m^3) integrated in duplicate	Polyurethane foam + XAD-4	Accelerated Solvent Extraction in 1:1 Ace:Hex	GC/MS (PAHs) GC-ECD (PBDEs) GC-NPD (OPs)
Particle count	Continuous		Condensation	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; GC = gas chromatograph; MS = mass selective detector; DNPH = dinitrophenylhydrazine; HPLC = high performance liquid chromatograph; PAH = polycyclic aromatic hydrocarbon; OVS = OSHA versatile sampler; PUF = polyurethane foam; ECD = electron capture detector; FPD = flame photometric detector; NPD = nitrogen-phosphorus detector; PBDE = polybrominated diphenyl ethers; 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 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 ^{o}C for 6.5 minutes. The cryogenic trap was held at -100 ^{o}C and then heated within 30 seconds to 235 ^{o}C for injection. Compounds were resolved and detected with an electron impact GC/MS system (Series 6890Plus and 5973, Agilent Technologies). The compounds span an approximate volatility range bounded by n-butane and n-octadecane (C_4-C_{18}). The MS was operated in scan mode and all compounds over the detection limit (< 1 to several ng) were identified by comparison to reference standards. Retention times and ionic spectra for most common VOCs including many HAPs and TACs are recorded in libraries constructed by LBNL staff. Any peak that could not be matched to the LBNL library was checked against the NIST spectral library. Multipoint calibrations were prepared for target VOCs for which pure standards were available. Pure standards are referenced to an internal standard 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 15. Target VOCs included in Phase I Screening Measurements

Chemical name	*CAS#*	*Chemical name*	*CAS#*
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	Diethylphtalate	84-66-2
1,2,3,5,-Tetramethylbenzene	527-53-7	1-Methylnaphthalene	90-12-0
Dibuthylphthalate	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		

4.1.2.2 Carbonyl sampling and analysis

The target carbonyls included formaldehyde, acetaldehyde and benzaldehyde. Samples of these low molecular weight carbonyl 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 lpm 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 C_{18} reverse phase column and UV detection at 360 nm. Multipoint calibrations were prepared for the target carbonyls using commercially available hydrazone derivatives of formaldehyde, acetaldeyde and acetone. Higher carbon-number carbonyls were quantified using sorbent sampling tubes and GC/MS following the VOC method described above.

4.1.2.3 SVOC sampling and analysis

SVOC samples were collected on polyurethane foam 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 including 2 extractions with MeOH, 2 extractions with DCM, 2 extractions with hexanes and 3 extractions with a 1:1 mixture of acetone:hexanes. The ASE system was operated at 1500 psi, 75 °C, no preheat time, a 5 minute static phase, 50% flush volume, 120 second purge and 3 cycles. After cleaning, the sorbent material was dried under a stream of high purity N_2 then transferred to the sampling cartridges, capped tightly, wrapped in foil and stored in the dark at room temperature until use.

Duplicate samples were collected by pulling 20 L/min of chamber air through each of two samplers mounted in parallel with flows controlled by a dedicated taper-tube rotometer for each sample line. Samples were 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 preferential flow paths from forming if the sorbent settled.

The extent of breakthrough was evaluated during two separate experiments by placing a second sampler cartridge containing XAD-4 in series with the primary sample cartridges. The primary cartridge was spiked on the leading face of the PUF with a known quantity of standard prior to use and run in parallel with a second sampler. The collection efficiency (*CE*) was calculated using equation 1 where C_2 and C_1 are the concentrations of analyte measured in the primary and backup sampler, respectively.

$$CE = 1 - (C_2/C_1) \qquad (1)$$

In addition, the combined mass extracted from the spiked cartridge and the backup cartridge, less the mass collected on the parallel sample cartridge, was used to estimate recoveries under actual experimental conditions. One of the breakthrough/recovery samples was analyzed and the second was extracted but archived for later analysis. Additional recovery experiments were run using spiked PUF plugs that were not deployed in sample cartridges.

The sorbent material was 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 the extracts were combined in a single concentration tube then concentrated under high purity N_2 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 autosample vial. After extraction, the samples were transferred along with chain of custody form to 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, it was not possible to estimate the fraction of peaks that were actually identified.

Organophosphate Analysis

The OP analytes are listed in Table 16 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 TCEP, 25 µL 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 4-point calibration curve. Standards were purchased from Sigma-Aldrich. Dilutions from the stock solution were prepared for each 2-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-um diameter and 0.25-um 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 1 minute, and then increased at 10 °C per minute to 120 °C; then increased by 30 °C per minute to a final temperature of 160 °C. The baseline output of the NPD was kept at approximately 30 milliamps for the analysis.

Table 16. Target Organophosphates in 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

Polycyclic Aromatic Hydrocarbon (PAH) Analysis

The PAH analytes are listed in Table 17 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 2-week period of analysis, and a full set of standards were run at least once on each day of analysis. All solutions are stored at –20 °C.

All PAH analyses were performed on a Hewlett Packard model 6890 GC equipped with a 5972 MS. A 30-m DB-17MS, (50%-Phenyl)-methylpolysiloxane fused silica capillary column, (0.25-mm ID and 0.25-um film thickness) was used for separation. The inlet and detector temperatures were 305 °C and 280 °C, respectively. The initial oven temperature was 65 °C, then ramped at 5 °C per minute to 280 °C, held for 20 minutes and then ramped at 10 °C per minute to 310 °C and held for 5 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.

Table 17. 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
Acenapthene	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

Polybrominated Diphenyl Ether (PBDE) Analysis

The PBDE congeners are listed in Table 18 along with the congener numbers and the GC retention times. A 2500 ng/mL stock solution of PBDE 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 µg/mL to 12.5 ng/mL. Dilutions from the stock solution were prepared for each 2-week period of analysis, and a full set of standards are 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 0.1um, is used for separation. The inlet temperature and detector were 305 °C and 340 °C, respectively. The initial oven temperature was 100 °C, then ramped at 20 °C per minute to 340 °C and held for 20 minutes.

Table 18. Target Polybrominated Diphenyl Ethers in 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

4.1.2.4 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 and organic carbon. The original proposal also includes an analysis of metals in the particle samples but the collected sample masses were too small to include metals analyses. Particle sampling methods used in Phase 1 are summarized below.

Particle number count

Ultrafine particle number concentrations (particles per cc) 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 >1µm), the particles that dominate measured number concentrations. Samples were typically collected for 1 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 aethalometer (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 to 10 minutes. For this study, the integration time was set to 5 minutes and the sampling rate at 3.3 lpm.

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 precleaned by baking in muffle furnace overnight at 500 °C. Following collection of particles, the filters were packaged along with several blank filters and shipped FedEx to Sunset Labs were they were used to determine elemental carbon and organic carbon content following method 5040, which is detailed in Appendix I.

Particle mass

Teflon 37 mm filters (Teflo®, Pall Corp.) were pre-weighed using a Cahn 21 Automatic Electrobalance and stored in petri dishes until use. Duplicate samples were collected in parallel by pulling chamber air through each filter at 20 lpm for 24 hours. The filters were re-weighed on at least two separate occasions both before deployment and after recovery. 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±3 C and RH = 30-40% for at least one weighing before 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 4 different filters on different days ranged from 0.01% to 0.1%.

4.1.2.5 Ozone

Ozone levels are evaluated continuously during operation of each of the equipment categories by employing an ultraviolet photometric detector (Model 400; API Inc.) calibrated prior to the beginning of the project.

4.2 Quality Objectives

4.2.1 Project Quality Objectives

Given the screening nature of the Phase 1 study, the validity of the results is dependent on how well the sample of computers or printers in each group are representative of office equipment currently used in California households. To address this issue, the research team developed an approach for selection of office equipment that used publicly available consumer journals and on-line reviews (see section 4.1.1.2 for further details).

4.2.2 Measurement Quality Objectives

Sample collection, processing and analysis all contribute to measurement uncertainty. This type of uncertainty can be controlled by adhering to a set of best laboratory practices. We tracked the measurement performance for each analyte class using standard data quality indicators (DQIs) including precision, bias, accuracy, sensitivity, representativeness, completeness and comparability. The working definition (taken from the EPA Guidance for Quality Assurance Project Plans, EPA QA/G-5, December 2002) and application of each of these DQIs to this project is discussed below.

4.2.2.1 Precision

Precision is a measure of agreement among repeated measurements of the same property under identical or substantially similar conditions. Precision is typically evaluated as a range, standard deviation or coefficient of variation from replicate measurements. We measured precision using a combination of duplicate instrumental analyses (i.e., replicate runs of the same extract on the same instrument), replicate matrix spikes (SVOCs) and analysis of co-located duplicate samples collected from the chamber experiments (VOCs and SVOCs).

4.2.2.2 Bias

Bias is a systematic or persistent distortion of a measurement process that causes errors in one direction. Bias was assessed in this study using matrix spikes with know compounds (SVOCs). The analytical labs at UCB and LBL also included standard quality control procedures that assessed method blanks, sample recovery and calibration standards, all of which provide indications of bias in different parts of the analytical stream. Another source of bias in the experiments was related to unknown chamber wall effects. This potential bias was not considered to be critical in Phase I due to the use of steady state conditions with the experiments. At steady state, the net gain/loss at the air/wall interface should not contribute significantly to measured concentrations in the chamber air.

4.2.2.3 Accuracy

Accuracy is the overall agreement of a measurement to a known value where the measurement combines random error (precision) and systematic error (bias) from both the sampling and analytical operations. Accuracy of the overall sample preparation and analysis scheme is best assessed using certified reference materials (CRMs). The broad spectrum of chemicals in this study and the lack of relevant CRMs made it necessary to use alternate methods to assess accuracy. We assessed accuracy for the SVOC analysis using blind matrix spikes. Ozone and particle number were determined using calibrated instruments. Accuracy for VOCs and aldehydes were assessed using matrix spikes. Accuracy was assessed by comparing the average measured value to the known spike amount in the matrix and precision and the relative standard deviation of the measurements was an indication of precision.

4.2.2.4 Sensitivity

Sensitivity is the capability of a method or instrument to discriminate between measurement responses representing different levels of the variable of interest. Sensitivity is typically given by the method detection limit (MDL), which is formally defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. The limit of quantitation (LOQ) can be estimated for all organic analytes as a multiple (usually 10) of the standard deviation of low level replicate measurements, blanks or low level matrix spikes. By these standard definitions, measurements below the MDL are not believable, measurements between the LOQ and the MDL are only semi-quantitative, and confidence in measurements above the LOQ is high. Formal estimates of the MDL and LOQ were not determined during Phase I of this study but qualitative estimates for VOCs were based on the past experience of the laboratory and for SVOCs were generally based on levels found in the blank chamber runs.

4.2.2.5 Representativeness

Representativeness is a qualitative term that expresses how well the data represent a characteristic of a population, parameter variations at a sampling point, a process condition, or an environmental condition. As indicated above, the representativeness of the sample of office equipment was addressed in part by adopting an approach for acquiring office equipment that was thought to be similar to how a consumer might purchase office equipment. In the chamber studies, representativeness of the samples was addressed by collecting multiple samples at different time points during different phases of the emissions experiment including before installation of OE in the chamber, with OE installed but not plugged in, with OE operating and after OE has been shut down and removed from the chamber. This design makes it possible to differentiate between background and emissions from the office equipment when the chamber and duty cycle conditions were highly artificial because of the screening nature of the study.

4.2.2.6 Completeness

Completeness is a measure of the amount of valid data that must be obtained from a measurement system in order to have sufficient confidence in any hypotheses based on these data. This DQI is not applicable to a controlled laboratory study where the amount of data or percentage of expected data points that are actually collected is usually high. Nevertheless, replicate samples were collected at most time points during the study for both VOC and SVOCs to make up for any samples that are contaminated or otherwise lost. Some of the duplicate samples were combined for the SVOCs to double the volume collected for a given time interval in the later experiment. Because of difficulties with the analysis, not all of SVOC samples were analyzed for the desktop and printer experiments. However, these samples have been extracted and archived for future analysis if necessary. For the metals analysis, the sample mass collected was not sufficient to analyze for metals.

4.2.2.7 Comparability

Comparability is a qualitative term that expresses the measure of confidence that applies when one data set is compared to another. The results from Phase I are reported as concentration in the chamber along with an indication of the method sensitivity as discussed above and for integrated samples the duration of sampling. Detailed chamber conditions were also tracked and reported including air exchange rate, temperature, relative humidity and chamber pressure at 1 min intervals. The number of units and work load are also reported so the results can be “transformed” to make comparable with other studies if necessary.

4.3 Screening Experiments: Results

4.3.1 Initial Laptop Experiment

An initial full-scale chamber experiment was run using laptop computers to optimize conditions and verify methods. The experiment used a convenience sample of 5 notebook computers of differing ages and from a range of manufacturers (Dell, Sony, Compaq, IBM and Apple). The chamber conditions and experimental timeline for the experiment is illustrated in Fig. 2. Stage *A* represents the empty chamber during its conditioning over several days and the determination of background levels for all target compounds made 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 compounds (VOC, Aldehydes, SVOCs and particulates) 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 the duration of the experiment.

The measured temperature (°C), percent relative humidity, pressure differential (Pa) and air exchange rate (h^{-1}) in the chamber (± 1 standard deviation) were 21.9 (±0.8), 36.5 (±6.6), 7.5 (±0.8) and 0.95 (±0.02), respectively, over the course of the experiment. The air exchange rate (ACH) was tracked continuously with a calibrated air-flow venturi on the inlet to the chamber during the laptop experiment.

Standard recovery analyses were run prior to the experiments with the notebook computers. These 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% (±7%) for naphthalene to a high of 124% (±8%). The PBDE target compounds also showed good recoveries ranging from a low of 71% (±10%) for BDE#190 to a high of 119% (±11%) for BDE#47. The exception for the PBDEs was the deca congener, BDE#209 where the recoveries from the spiked matrix were zero for all three replicates. Further investigation revealed that the BDE#209 was being lost in the GC and replacement of the inlet, seal and column alleviated the problem for the standards. However, the full recovery experiment was not repeated. For the target OP flame retardants, the results were not satisfactory with recoveries ranging from a low of 66% (±31%) for TEP to a high of 272% (±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 notebook experiment to include a hot methanol wash to remove polar nitrogen containing compounds prior to the laptop experiment.

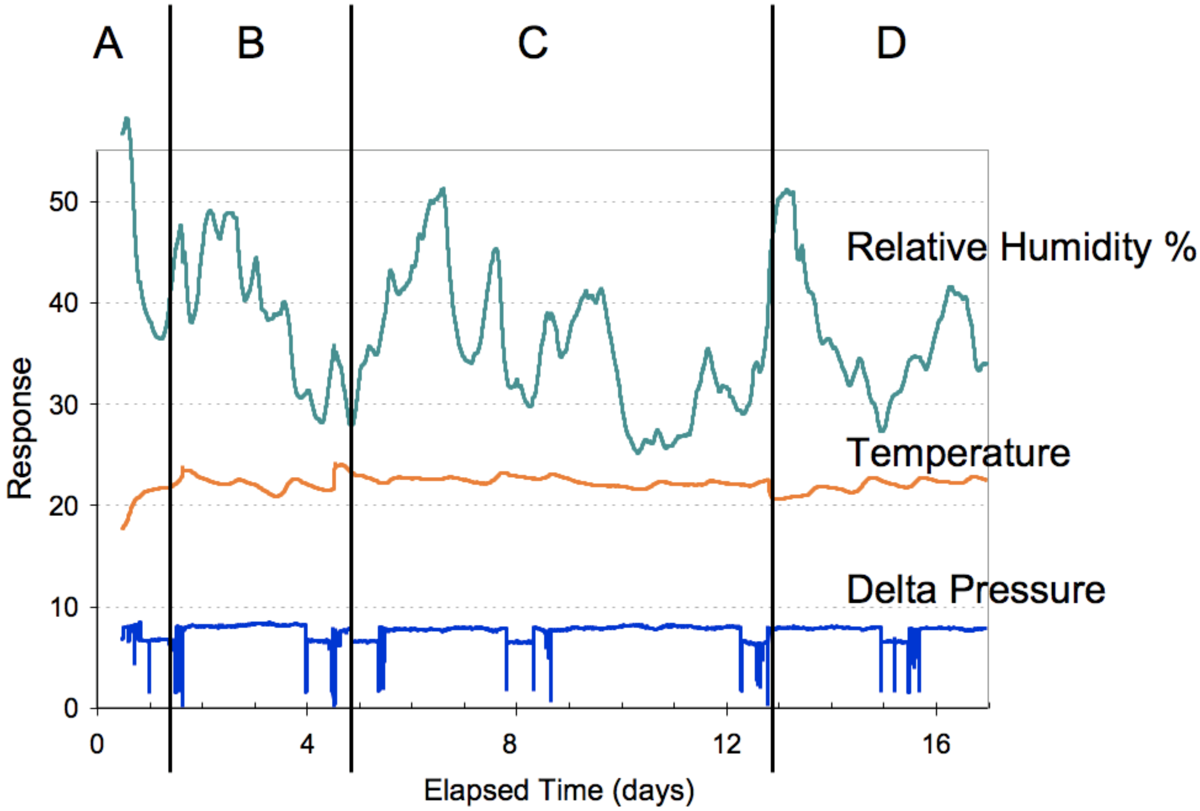

Figure 2: Chamber performance and experimental phases for laptop emission study. Delta Pressure shows that the internal pressure remained slightly elevated over ambient pressure where the periodic drop in pressure indicates a sampling event took place. The experimental phases identified by the verticle lines are A) pre-experiment conditioning of the chamber; B) chamber loaded with computers; C) computers running and D) chamber after computers were removed. Humidity was not controlled so the value roughly tracked changes in the ambient air conditions.

Collection efficiency (breakthrough) of the SVOC sampling cartridges, recovery from field spikes, and trip blank cartridges were all evaluated during the notebook experiment. For the PAHs, the recovery of field spikes ranged from 74% to 102% with collection efficiencies generally near 100%. The one exception was acenaphthene for which the calculated collection efficiency was 54%. For PBDEs, the recovery of field spikes ranged from 60% to 143% except for a very high calculated recovery for PBDE#28 possibly due to elevated background in the sample media. The deca congener was also not detected in the spiked sample so it was not quantified in the remainder of the experiments. The collection efficiencies for the PBDEs were near 100% for all target chemicals except for PBDE#28, which possibly was due to elevated background. For the OP flame retardants, the collection efficiencies were near 100% but the recoveries still lacked precision even after changing the cleanup method to reduce background nitrogen containing compounds. The poor precision of the OP flame retardant recoveries indicated that either an additional sample cleanup step or a different detection method was required.

The next set of experiments were carried out without performing formal measurements of limits of detection (LOD) or the limits of quantification (LOQ) for the SVOCs. However, an approximate LOD was estimated for PAHs based on the previous experience of the laboratory. This LOD likely was near 0.2 ng/m^3 for the notebook computer experiment and 0.1 ng/m^3 for the remaining experiments where this decrease was due to a larger sample volume. An approximate LOD for PBDEs was estimated to be three times the baseline level. This LOD was about 5 ng/m^3 for the notebook computer experiment and 2.5 ng/m^3 for the remainder of the experiments. An approximate LOD for the OPs was estimated to be three times the standard deviation of the three measured values from spiked PUF. This LOD was about 30 ng/m^3 for the notebook computer experiment and 15 ng/m3 for the remaining experiments with TBEP excluded because of an interfering peak.

Results from the preliminary notebook experiment for PAHs are shown in Fig 3. Here there is a slight increase in total PAH 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.

Results for the PBDEs are provided in Fig 4 and show no discernable change in target chemical concentration with notebook computers installed and/or running. The measurements are well below our approximate LOD for PBDEs although the field spike recovery sample collected at time point *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.

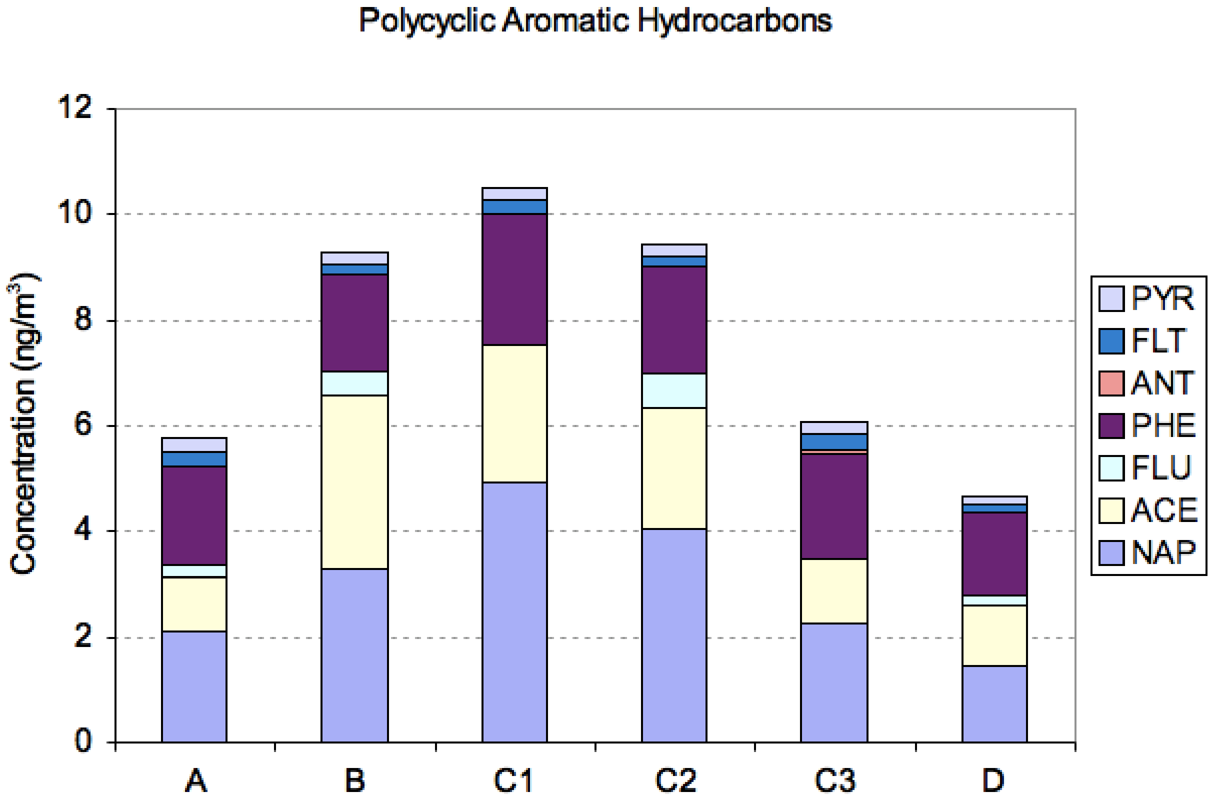

Figure 3: Results for PAHs emitted from laptop computers showing a small increase in naphthalene and acenaphthene levels. The ordinate axis labels identify the experimental phase illustrated in Fig. 2. Sample C1, C2 and C3 were collected at the start, midrange and end of the emission phase of the experiment indicated by the drop in pressure in Fig 2. Reported values are the average of two samples except for timepoint "D", which was collected in parallel with a field spike sample. The acronyms are defined as follows: NAP=Naphthalene, ACE=Acenapthene, FLU=Flurene, PHE=Phenanthrene, ANT=Anthracene, FLT=Fluranthene and PYR=Pyrene. No other target PAHs were detected.

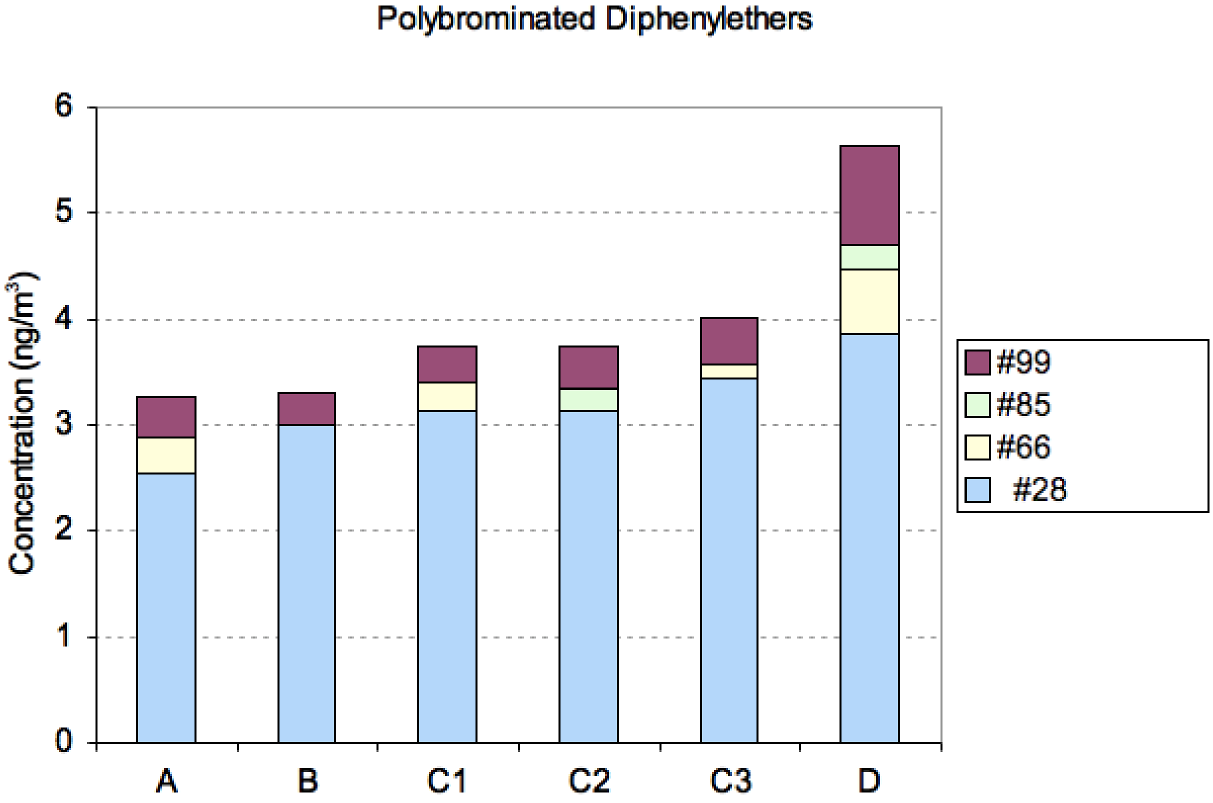

Figure 4: Results for PBDEs in notebook computer run showing no change to the concentration of target chemical measured in the chamber with and without notebooks installed and/or running. Reported values are the average of two samples except for timepoint "D", which was collected in parallel with a field spike sample. The acronyms are defined as follows: #28= 2,4,4'-TriBDE, #66= 2,3',4,4'-TetraBDE, #85= 2,2',3,4,4'-PentaBDE and #99= 2,2',4,4',5-PentaBDE. No other target congeners were detected.

The OP results are shown in Fig. 5. The results for TBEP were excluded due to interference in the chromatography. 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 were attributed to the TCEP but as seen in Fig 5, this compound was elevated prior to installing computers in the chamber. However, the elevated concentration of TCEP measured during time period A was due to only one of the parallel sampler. The second sample collected during that time period had no detectable levels.

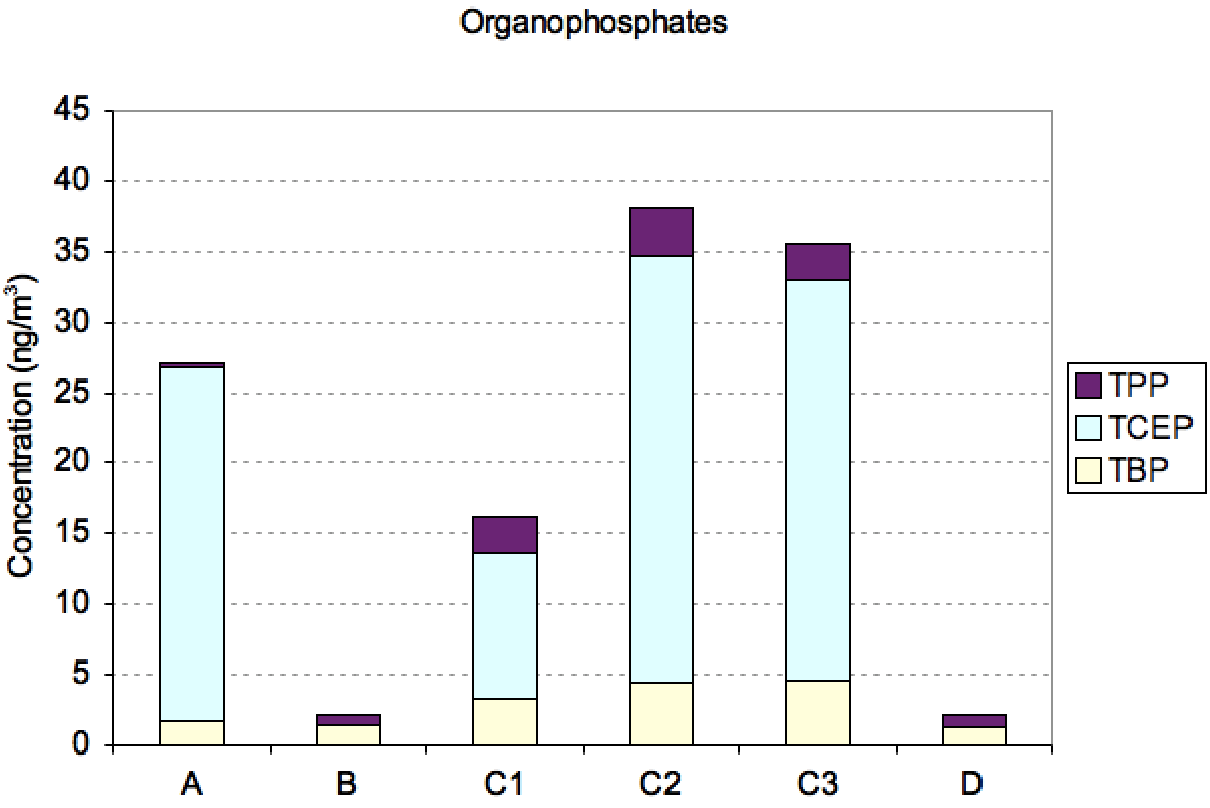

Figure 5: Results for OPs in notebook computer experiment. TBEP was excluded because of interfering peaks. TEHP was not detected. TEP was excluded because field blank concentrations were elevated. The acronyms are defined as follows: TEP=Triethyl phosphate, TBP=Tri(n-butyl) phosphate, TCEP=Tri(2-chloroethyl) phosphate, TPP=Triphenyl Phosphate, TBEP=Tri(2-butoxyethyl) phosphate and TEHP=Tri(2-ethylhexyl) phosphate.

The concentrations of the target volatile carbonyls measured in the experiment with the aged notebook computers were generally low relative to our limit of quantification with no discernable increase in chamber concentrations when the laptops were installed and/or running as illustrated in Figure 6. The results in Figure 6 represent the average of two samples collected in parallel with the coefficient of variation between the duplicates ranging from 1% to 67%. The low aldehyde concentrations were typical for all experiments. VOC results for the notebook experiment were also at or near the background concentrations in the empty chamber (results not shown).

Particle number concentration measured with the condensation particle counter and ozone measured continuously were both unchanged for the duration of the experiment. The air entering the chamber was filtered so background 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) ppm.

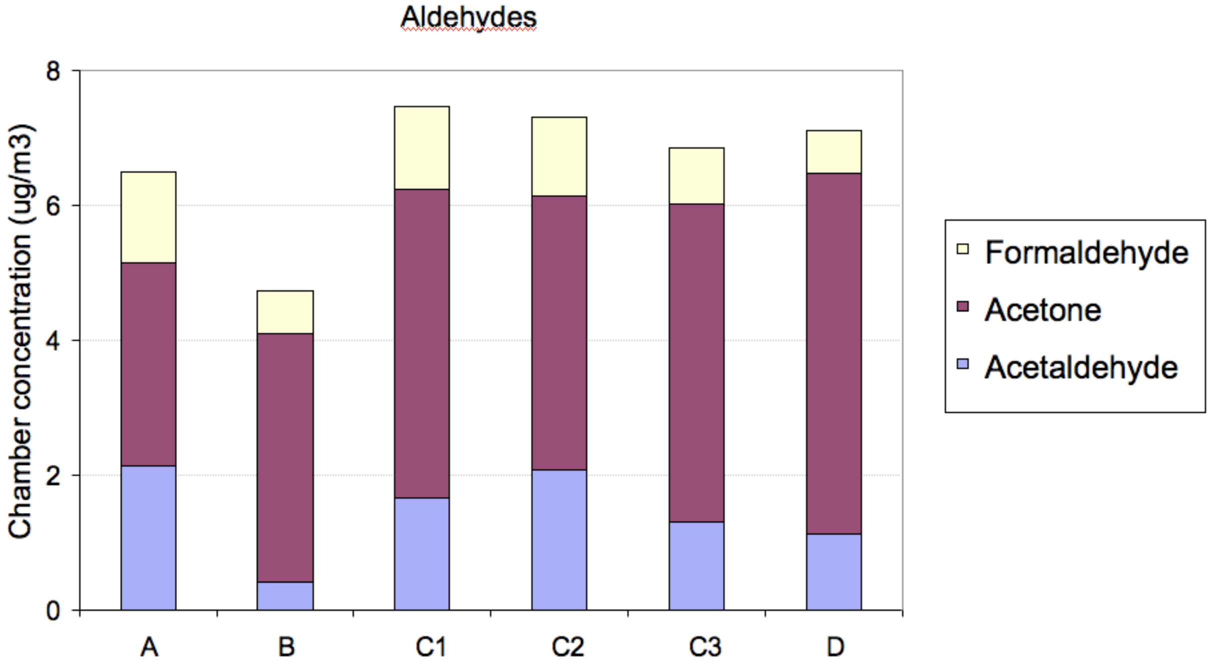

Figure 6: Results for volatile carbonyls during the preliminary notebook computer experiment showing no difference in concentrations for the primary aldehydes for the emission phase (Stages B and C) relative to the blank chamber (Stages A and D). Each bar represents the average of two parallel samples.

4.3.2 Desktop Experiment

The full desktop emission experiment was conducted with five new or recently purchased computers with flat screen LCD monitors. All units were installed with keyboard and mouse. Speakers were installed where available. Details on the units are provided in Table 19.

The chamber conditions and experimental timeline for the desktop experiment is illustrated in Fig. 7. The experimental stages are as described for the preliminary laptop study where stage *A* represents the empty chamber prior to loading computers, stage *B* represents the chamber with computers installed but not running, stage *C#* is the actual emissions phase of the study with all computers running at full load 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.

Table 19. Desktop computer specifications

Manufacturer	**Compaq**	**eMachines**	**Apple**	**Micron**	**Dell**
Model	SR1721NX	T3304	iMac	D915GXODYD	OptiPlex GX280
Serial Number	MXK5500HPN	CCA5C 100 02363	826-7421-A	40624230001	
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	32 x 64 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	10/100/1000BASE-T Ethernet;	10/100/1000 Mbits/sec	

		(RJ-45 port)	AirPort Extreme; Bluetooth 2.0 + EDR		
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 Samsung SyncMaster 730b	15 inch eMachine 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

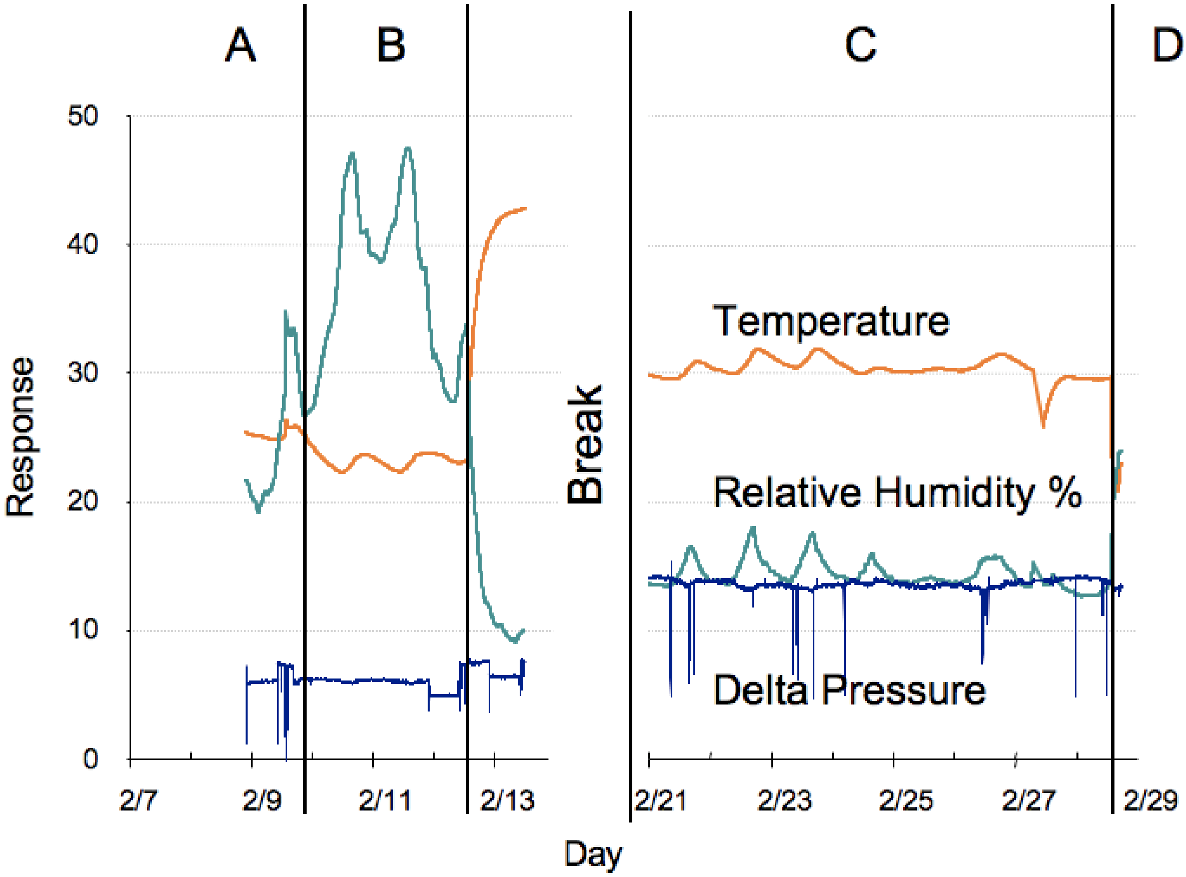

Figure 7: Experimental timeline and chamber conditions for Desktop experiment. The break between stage *B* and *C* was due to modifications to the chamber conditions that were needed to compensate for the heat load from the desktop computers and monitors. The Stage D sample was collected prior to the start of the printer experiments 8 days after the computers were removed from the chamber.

There was a break between stage *B* and *C* in the desktop run because of problems with heat buildup in the chamber. Given the heat output (see power usage in Table 19) when the computers were running it was necessary to run a chiller on the input air and to increase the air exchange rate as illustrated in Figure 7. This 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, we tracked the air changes by periodically injecting CO_2 into the chamber as a tracer gas for decay curve calculation. The chilled air input also reduced the relative humidity in the chamber and the higher air exchange rate increased the pressure slightly in stages *C#* and *D*. The chamber conditions prior to the use of the chiller on the air inlet were 23.7 (± 1.0), 33.7 (± 8.1), 6.0 (±0.7) and 0.98 (±0.01) for temperature (Celcius), percent relative humidity, pressure differential (Pa) and air exchange rate (h^{-1}), respectively. After the chiller was installed the temperature (Celcius), percent relative humidity, pressure differential (Pa) and air exchange rate (h^{-1}) were 30.1 (±1.5), 14.5 (±1.5), 13.6 (±0.6) and 1.4 (±0.03), respectively. The higher pressure differential was due to the higher air exchange rate used and the lower relative humidity was due to a combination of the higher temperature and the use of chilled air in the inlet line.

Although the relative humidity during the emissions phase of the desktop experiments was below the intended target range for the experiments, we do not expect this to have a significant impact on the screening level measurements. Wolkoff (1998) studied the influence of several environmental factors on emission and found no change in the emissions of measured VOCs from PVC material with changes in relative humidity. 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 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. Samples were collected for SVOC analysis at multiple time points including several QA samples as was done with the notebook experiment but only three time points were analyzed to represent stages *B, C* (day 7) and *D*. In addition, the parallel samples were combined after extraction to increase the integrated air volume to 28.8 m^3 to improve detection limits. No changes were needed to the other sample collection methods.

The concentrations of PAHs in the chamber air are illustrated in Fig. 8 for the three experimental stages. 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 were not detected. Increased chamber temperature during the emissions phase of the experiment may have increased the amount of material volatized 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 for several hours which would be expected to reduce the amount of chemical sorbed to walls so this contribution is expected to be negligible.

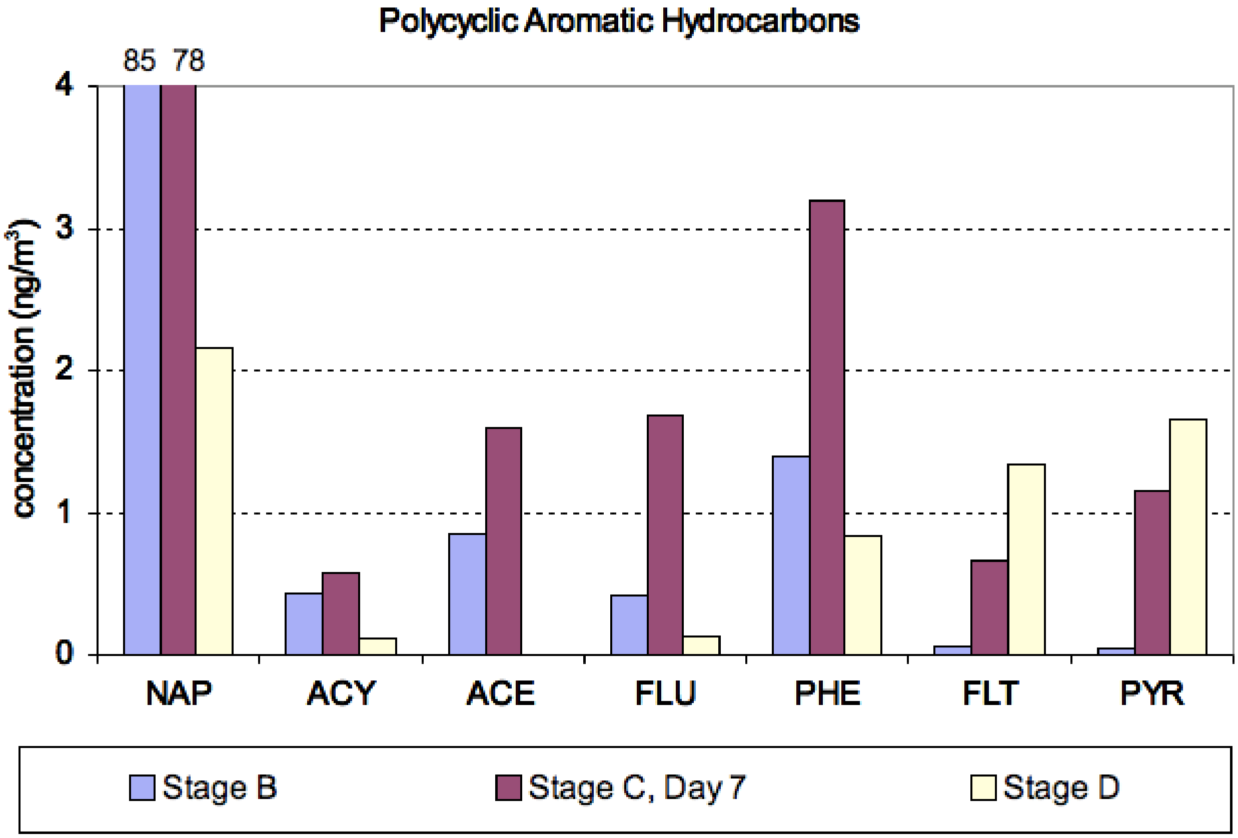

Figure 8: Results for PAHs from Desktop computer experiment. The Stage *C* sample was collected after 7 days of continuous operation of the computers and the stage *D* sample was collected 8 days after computers had been removed from the chamber. Anthracene and PAHs heavier than Pyrene were not detected.

The results are illustrated for the PBDEs in Fig. 9 and for OPs in Fig. 10. The PBDE results show no measurable difference between the blank chamber and the chamber with computers loaded and/or running and the values are well below the operational LOD for this experiment. The OP results do 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 LOD.

Two of the lighter phthalate esters (diethyl- and dibutyl-phthalate) were quantified with the VOC method for which samples were collected on Tenax cartridges. The results are presented in Fig. 11. The two phthalate esters did not show the same pattern as the other VOCs, indicating that interaction with the chamber walls may be a factor that affects gas-phase concentrations. In the case of DEP, concentrations were only slightly higher than background levels. For DBP, there was a buildup with concentrations approaching steady state around 200-250 ng/m3. Concentrations decayed slowly after the computers had been removed indicating desorption from the wall of the chamber. Post-experiment blanks collected more than a week after the end of the experiment still showed measurable concentrations of DBP.

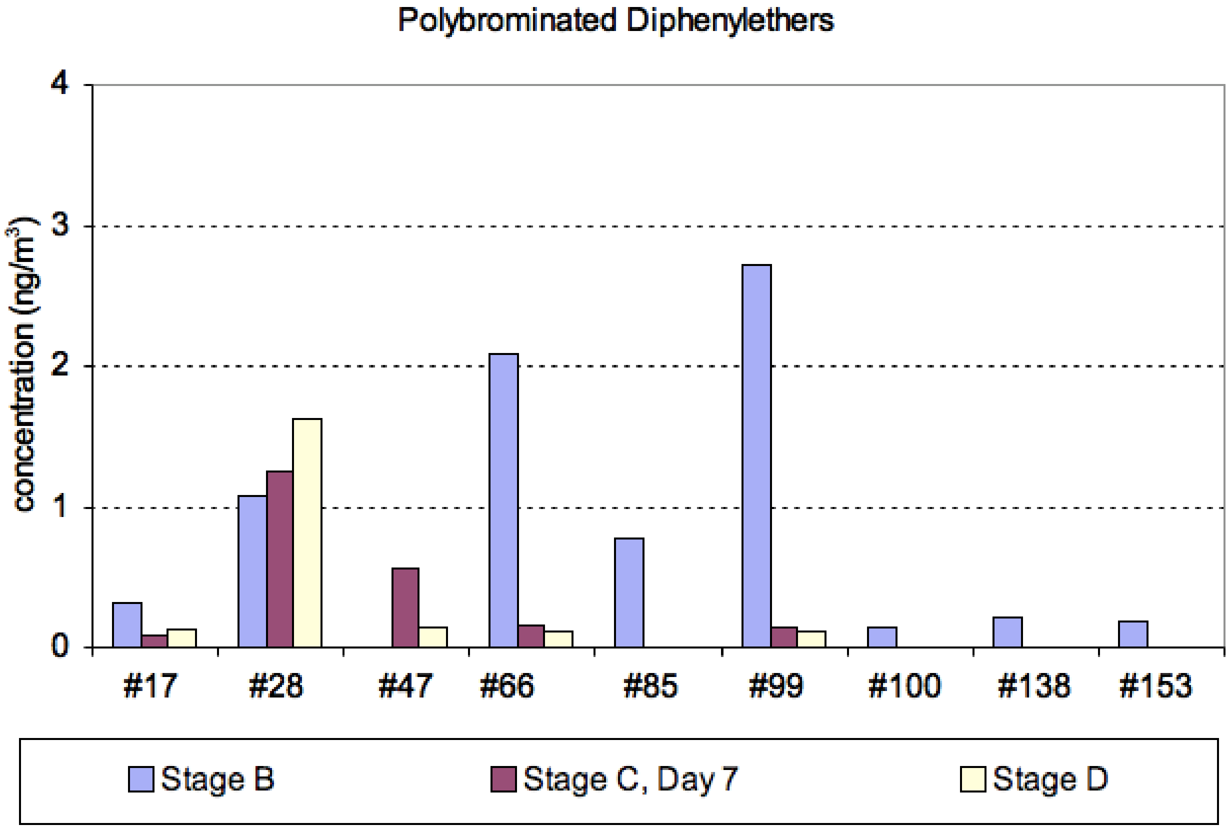

Figure 9: Results for PBDEs in the desktop computer experiment show no change in the levels of target chemical measured in the chamber during Stage C relative to the blank chamber, Stages B and D. Congeners #71, #154, #183, #190 were not detected. Congener #209 was not included in the analysis.

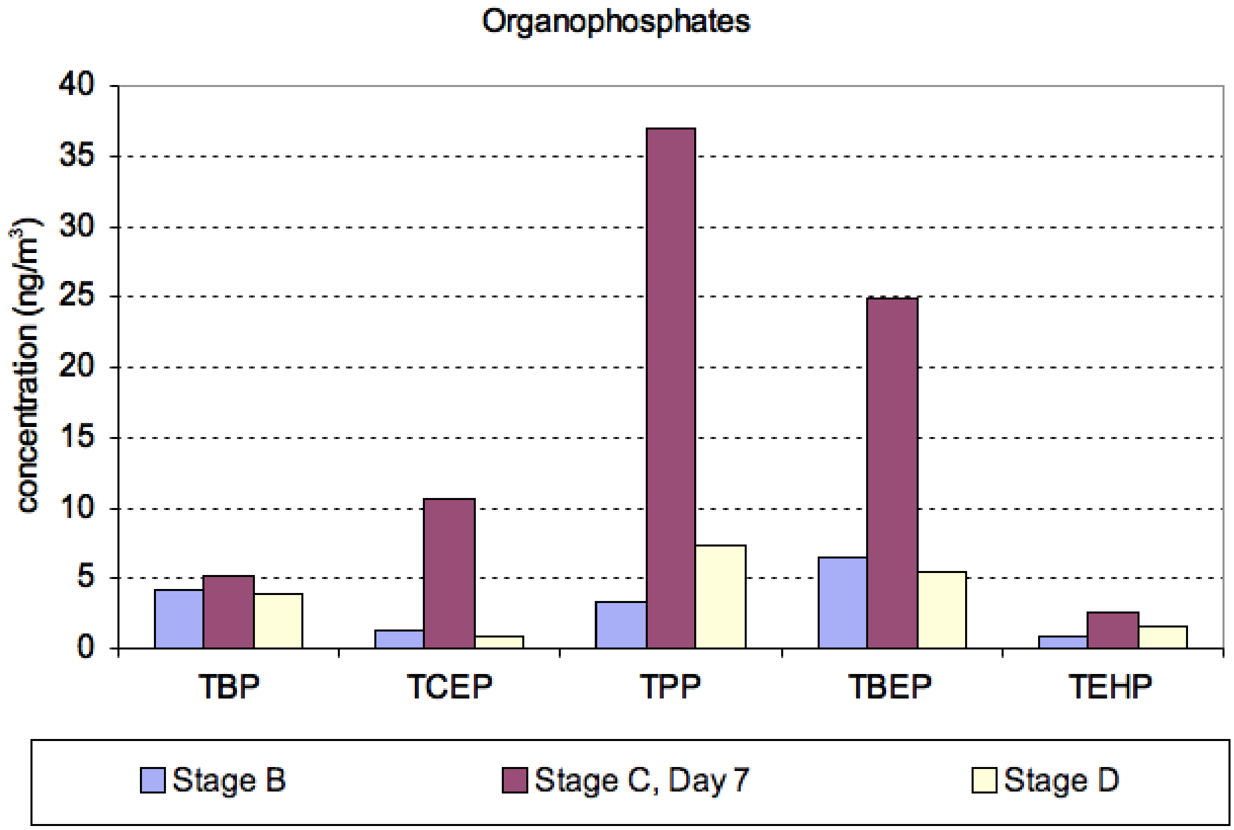

Figure 10: Results for OPs showing a slight elevation in the concentration of several of the target chemicals during operation (Stage C) relative to the blank chamber (Stages B and D). TEP was not detected.

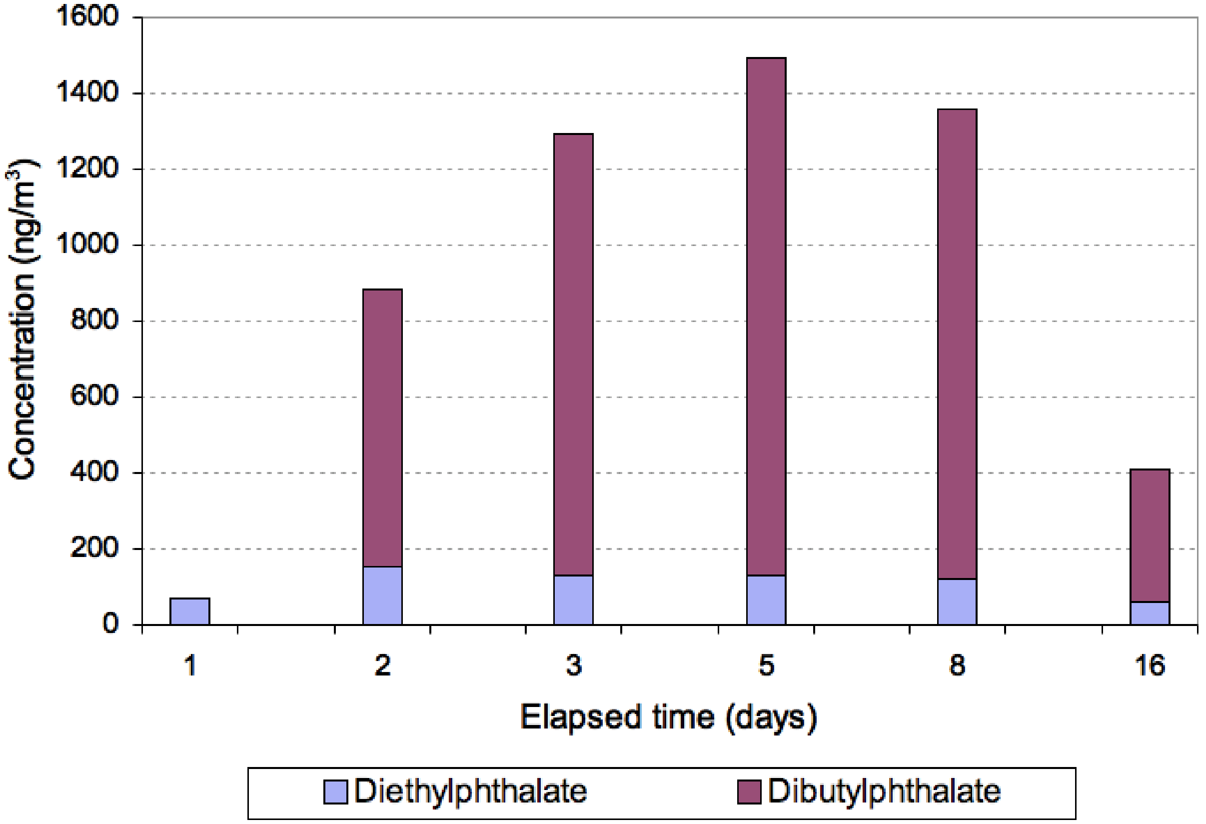

Figure 11: Concentration of two phthalate esters showing possible chamber wall effects for these higher molecular weight compounds. Computers were removed from chamber on day 8. The results are the average of two samples with CVs ranging from a high of 107% (day 2) to a low of 2%.

Results for the VOCs that were positively identified in this experiment are illustrated in Fig. 12. These represent ~ 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 Fig. 12 show an initial increase in chamber concentrations after the computers were installed followed by a steady decline over the duration of the experiment. The results in Fig 12 were converted to approximate emission rates as reported in Table 20 assuming there are no significant net wall effects for the lighter VOCs using Equation 2. With the emission phase lasting over several days the VOC concentrations have reached steady state where there may be interaction with chamber walls but the net effect on concentration is likely to be negligible.

$$ER = \lambda CV/n \qquad (2)$$

where ER is the emission rate per computer (ug/h), λ is the air change rate in the chamber (h^{-1}), C is the chamber concentration for the VOC (ug/m^3), V is the chamber volume (m^3) and n is the number of computers in the chamber during the experiment.

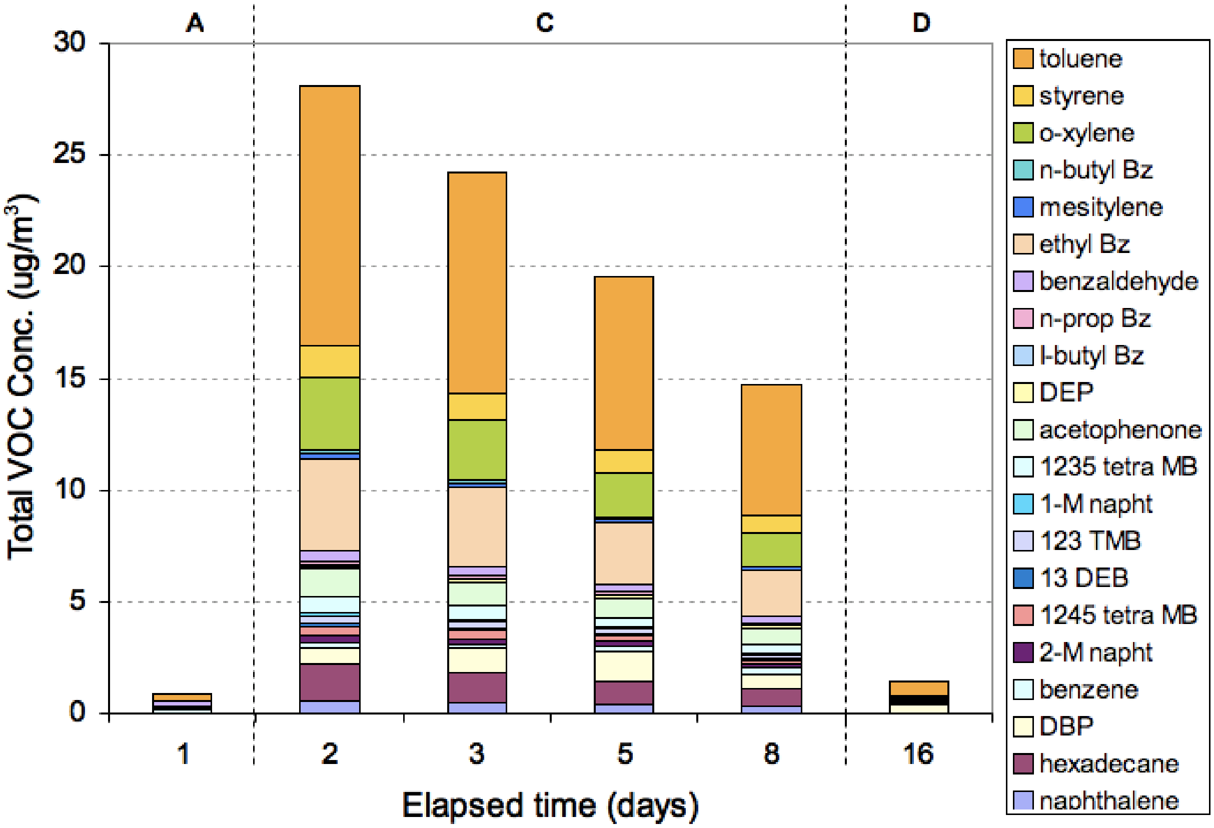

Figure 12: Results for identified VOCs showing an initial elevation of concentrations with computers running (stage C). No measurements were made during stage B. The concentrations of many VOCs steadily declined over time while the computers were running. The results represent the average of two samples collected in parallel. Actual values used to construct this figure are presented in Table 20.

Table 20. Average chamber concentration (μg/m^3) of VOCs

Chemical	*Stage A*	*Stage C1*	*Stage C2*	*Stage C3*	*Stage C4*	*Stage D*
naphthalene	0.005	0.125	0.104	0.084	0.065	0.004
hexadecane	0.000	0.414	0.341	0.264	0.203	0.000
DBP	0.000	0.140	0.222	0.261	0.119	0.067
benzene	0.025	0.063	0.032	0.057	0.077	0.024
2-M naphthalene	0.000	0.067	0.055	0.044	0.035	0.000
1245 tetra MB	0.000	0.068	0.060	0.047	0.035	0.000
13 DEB	0.000	0.028	0.024	0.016	0.011	0.000
123 TMB	0.000	0.085	0.070	0.051	0.034	0.000
1-M naphthalene	0.000	0.027	0.024	0.020	0.016	0.000
1235 tetra MB	0.000	0.194	0.172	0.106	0.103	0.000
acetophenone	0.022	0.243	0.201	0.176	0.148	0.011
DEP	0.013	0.027	0.024	0.023	0.022	0.011
i-butyl benzene	0.000	0.006	0.005	0.008	0.004	0.000
n-prop benzene	0.000	0.049	0.039	0.027	0.021	0.000
benzaldehyde	0.042	0.093	0.081	0.072	0.060	0.016
ethyl benzene	0.004	0.948	0.814	0.635	0.488	0.008
mesitylene	0.000	0.065	0.052	0.036	0.026	0.000
n-butyl benzene	0.000	0.026	0.023	0.017	0.012	0.000
o-xylene	0.004	0.778	0.643	0.483	0.354	0.005
styrene	0.004	0.350	0.305	0.240	0.184	0.008
toluene	0.063	2.699	2.276	1.803	1.358	0.150

Table 21. Average emission rates (ug/h/unit) (± standard deviation)

Chemical	*First day*	*Last day*
toluene	69.95 (±1.34)	35.20 (±0.16)
ethylbenzene	24.41 (±0.3)	12.55 (±0.11)
o-xylene	19.50 (±0.0.25)	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)
dibuthylphthalate	4.38 (±0.4.7)	3.7 (±5.2)
naphtalene	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)
diethylphtalate	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)**

Concentrations of volatile carbonyl compounds during computer operation were not elevated over background concentrations. Measured particle levels in the chamber during the desktop experiment were similar to levels during the preliminary desktop experiment with measurements typically less than 100 particles/cc. Ozone levels measured continuously in the chamber showed no difference with and without computers or with the computers operating.

4.3.3 Printer Experiments

The three printer emission experiments were conducted in series starting with 3 medium output laser technology printers followed by two high output laser technology printers and then 5 inkjet technology printers. A typical experimental timeline is illustrated in Fig. 13. The chamber was allowed to equilibrate for 72 hours between runs. Each printer group was installed in the chamber and allowed to equilibrate at least 24 hours before printing. The printers were then run using repeating print jobs sequentially for each printer in the chamber over a period of approximately 6 hours active printing followed by ~ 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 before installing the next group of printers.

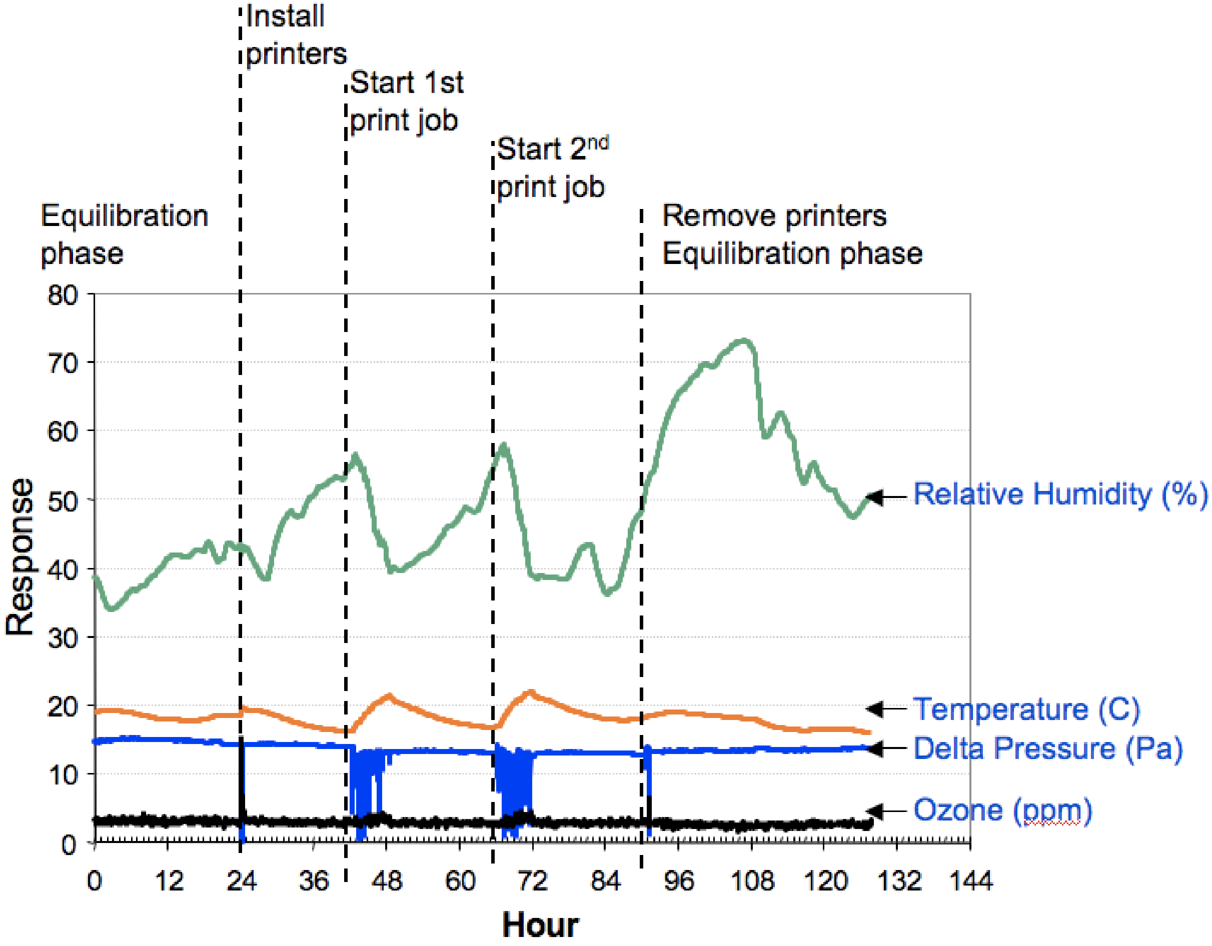

Figure 13: Chamber conditions during the medium output laser printer emissions experiment. The experimental phases are listed across top of figure. This cycle was repeated for both the high output laser printers and the inkjet printers.

A summary of the chamber conditions during the ~ 72 hour period while each printer group was installed in the chamber is provided in Table 22. Fresh toner and ink cartridges were installed prior to the experiments and all printers were operated in black and white mode only. Details on the printers in each category are listed in Table 23.

Table 22. Chamber conditions (± standard deviation) during printer experiments

	Number of printers	*Relative humidity*	*Temperature*	*Delta pressure*	*Air exchange rate*
High output laser technology printers(1)	2	48.6 (±5.3)	18.3 (±.5)	13.3 (±1.1)	1.4 (±0.03)
Medium output laser printers (1)	3	45.8 (± 6.0)	18.7 (± 1.4)	13.3 (± 1.3)	1.4 (±0.03)
Inkjet printers (2)	5				1.4 (±0.03)

(1) Based on 4 complete days of data starting when printers are loaded into chamber.
(2) Inkjet conditions based on only two days due to chamber malfunction on second day of print cycle.

Table 23. Printer specifications

High output laser technology	HP4200	HP4000			
Print speed(ppm)	33	45			
Print resolution (dpi)	1200	1200			
Recommended monthly duty cycle (pages)	150,000	200,000			
Power usage (watts)					
active	580	680			
standby	21	13			
Tone cartridge					
Paper type					
Medium output laser printers	HP LaserJet 1160Le	Brother HL-5170DN	HP LaserJet 3015		
Print speed(ppm)	20	21	15		
Print resolution (dpi)	1200	600-1200	1200		
Recommended monthly duty cycle (pages)	10,000	20,000	7,000		
Power usage (watts)					
active	345	460	260		
standby	6	75	7		
Tone cartridge					
Paper type					
Inkjet printers	LexMark X75	Epson Stylus C60	Epson 777i	HP 932C	HP 2175
Print speed(ppm)	11	12	8	9	18
Print resolution (dpi)	2400X1200	2880X720	2880X720	600X600	1200X1200
Recommended monthly duty cycle (pages)	3000	1,000-9,999	1,000-9,999	1,000-9,999	2000
Power usage (watts)					
active	14	17	15	25	75
standby	5			4	4
Ink cartridge					
Paper type					

The SVOC samplers were collected in parallel over the full 24 hour cycle (6 hours printing + 18 hours idle). Of the 4 SVOC samples collected for each printer group, only one was analyzed. The results for PAHs, PBDEs, and OPs are illustrated in Figs. 14, 15 and 16, respectively. The blank chamber results reported in these figures is the average (± 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 LOD. The elevated level of TCEP in figure 16 may be significant but difficulties with interfering peaks in the OP analysis make the results uncertain.

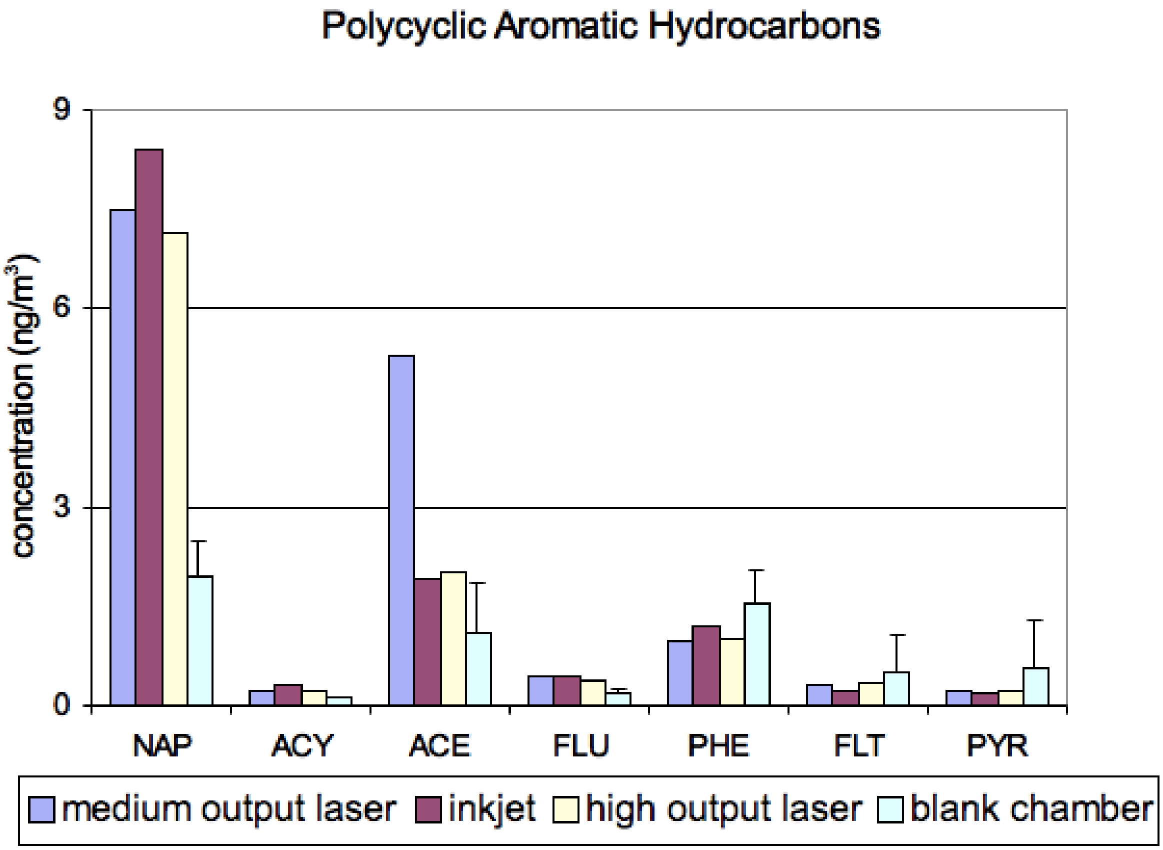

Figure 14: Results for PAH measurements while printers were operating. Samples were integrated over 24 hours. The blank chamber results are the average of all experiments (n=4).

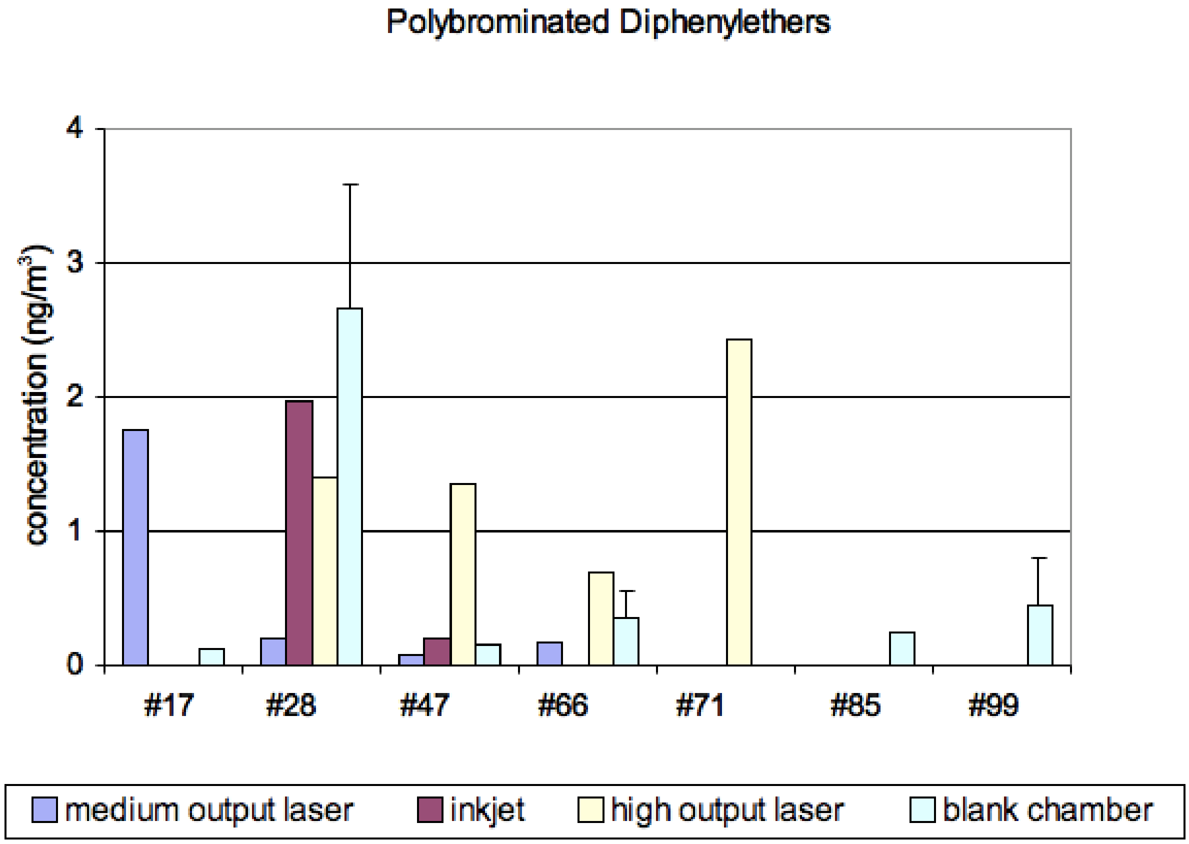

Figure 15: Results for PBDE measurements while printers were operating. Samples were integrated over 24 hours. The blank chamber results are the average of all experiments (n=4).

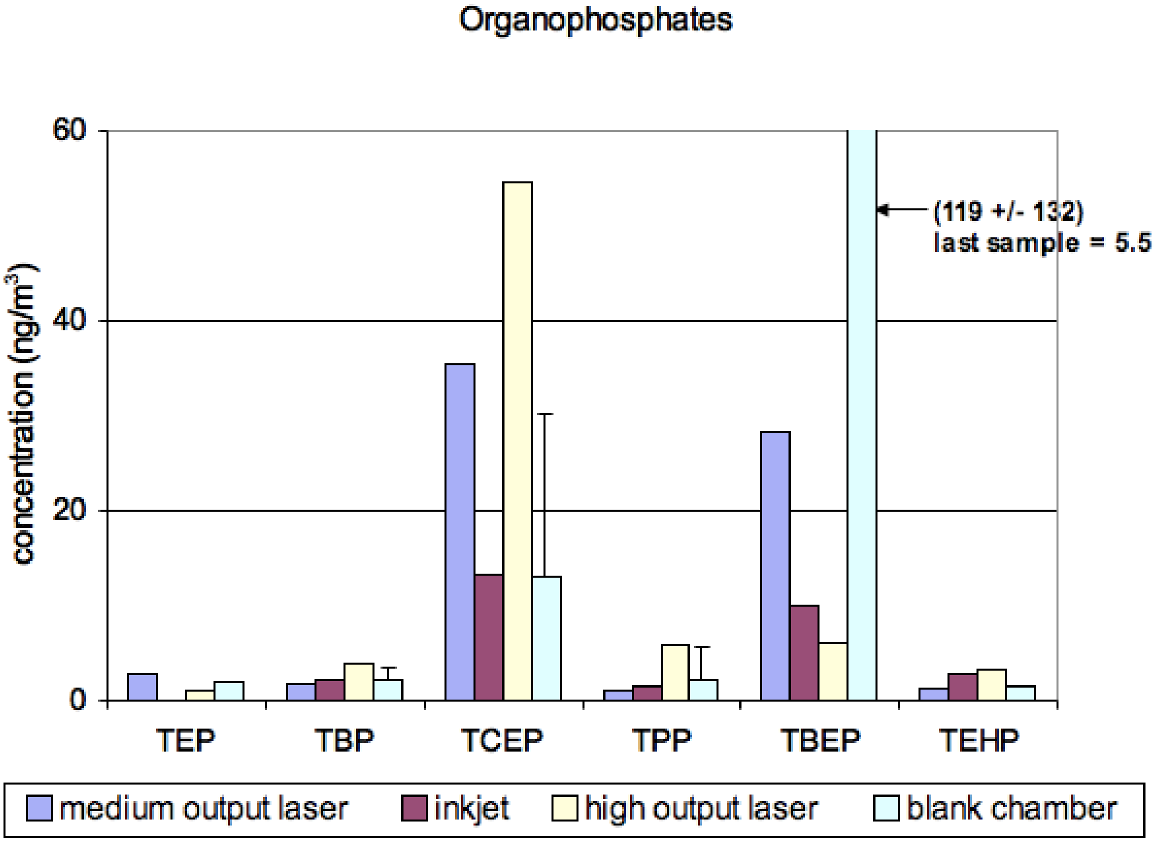

Figure 16: Results for OP measurements while printers were operating. Samples were integrated over 24 hours. The blank chamber results are the average of all experiments (n=4).

VOC samples were collected during both the active and idle phases of each 24 hour emission experiment. Results for the high output laser, medium output laser units and inkjet printers are illustrated in Figs. 17, 18 and 19, respectively. As with the computers, there appeared to be an 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 and hexadecane (7% each). The medium duty laser printers were primarily toluene (26%) o-xylene (15%), styrene (13%), ethyl benzene (11%) and benzaldehyde (7%). The InkJet printers did not result in elevated VOCs.

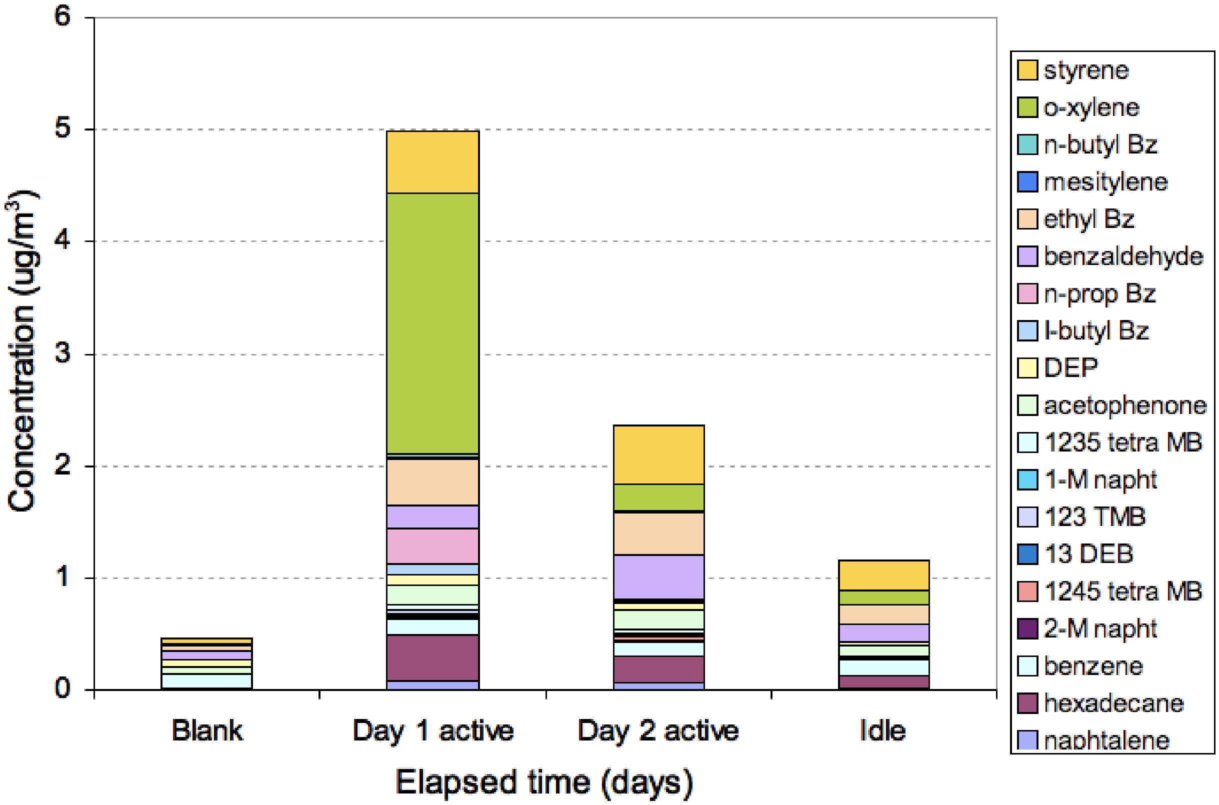

Figure 17: VOC concentrations (ng/m3) during the experiment with two high output laser printers. Included are results for the blank chamber without printers installed, two consecutive active printing periods and the idle period after the second day's print job. Dibutyl phthalate and toluene concentrations in the samples were similar to those in the blank chamber.

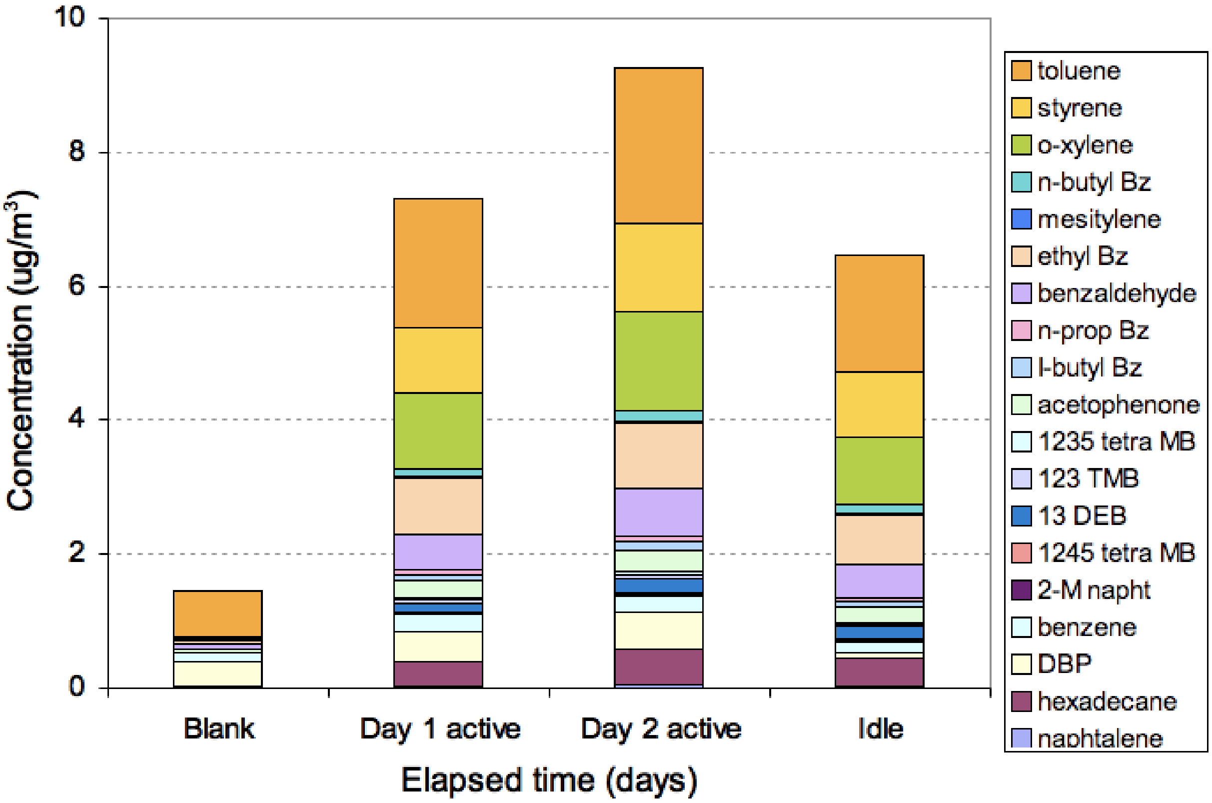

Figure 18: VOC concentrations (ng/m3) during the experiment with three medium output laser printer. Included are results for the blank chamber without printers installed, two consecutive active printing periods and the idle period after the second day's print job. 1 methylnaphthalene and diethyl phthalate were were similar to those in the blank chamber.

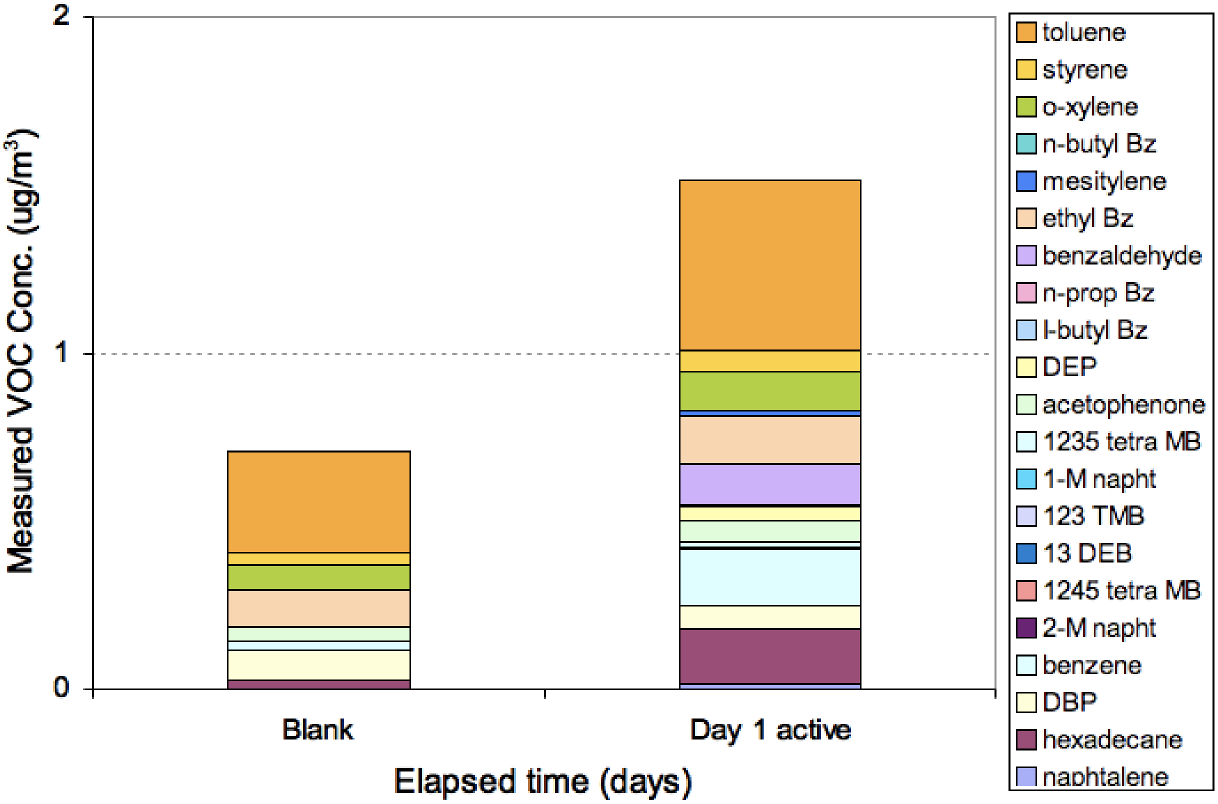

Figure 19: VOC concentrations (ng/m3) during the experiment with five inkjet printer. Included are the results for the blank chamber without printers installed and the first day of active printing. The experiment was terminated early due to a chamber malfunction.

There was no increase in the concentrations of volatile carbonyls for any of the printer experiments.

The particle count concentrations collected continuously during and after printing for each day and averaged over one minute time steps are presented for the High Output Laser, Medium Output Laser and InkJet printers in Figs. 20 – 22. Only one day of data was collected for the InkJet printers (Fig. 22) but the results for the InkJet printers did not show a significant increase in the particle count concentration. The spikes that are evident for the InkJet experiment are caused by room air entering the chamber when the paper was being loaded in the printers. Both the high and medium output laser technology printers did result in significant increases in particle concentration during printer operation. Notably high particle 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 one (Fig. 20) 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 experimane with the medium output laser printers. This was caused by a need to change the batteries in the P-Trak instrument.

Particle mass concentration during the two laser technology printer experiments was consistently around 1 ug/m^3 for the medium output units and 3 ug/m^3 for the high output units (blank chamber measurements were not collected for particle mass). Continuous measurements with an aethelometer did not detect an increase in black carbon over background. The OC/EC analysis of the particles did show that particle mass on filters was primarily organic carbon. Ozone levels remained at background concentrations for all three printer experiments.

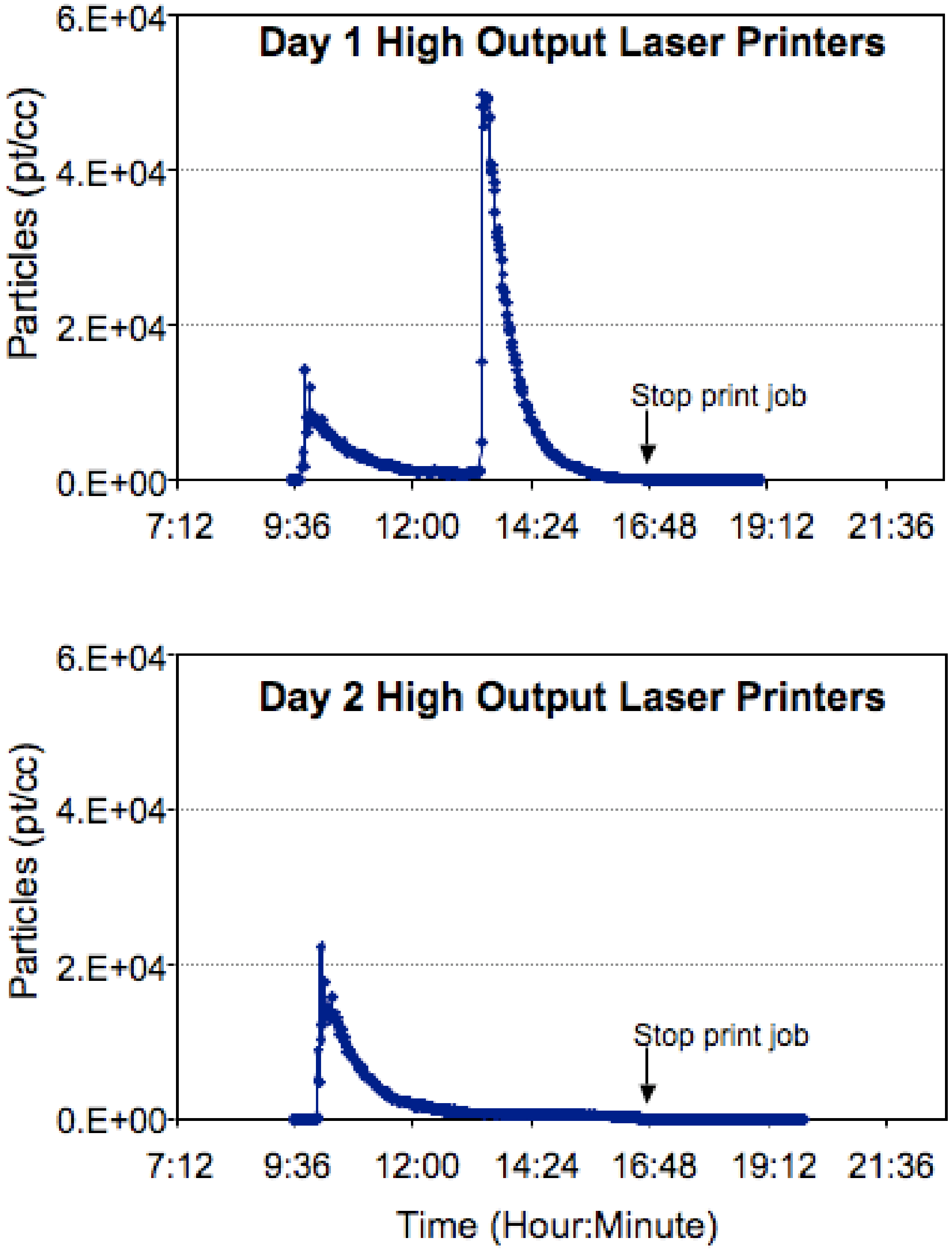

Figure 20: Particle concentration for day 1 and day 2 of experiment with two high-output laser printers. The initial spike in particle counts on both days occurred immediately after cold startup of the printers.

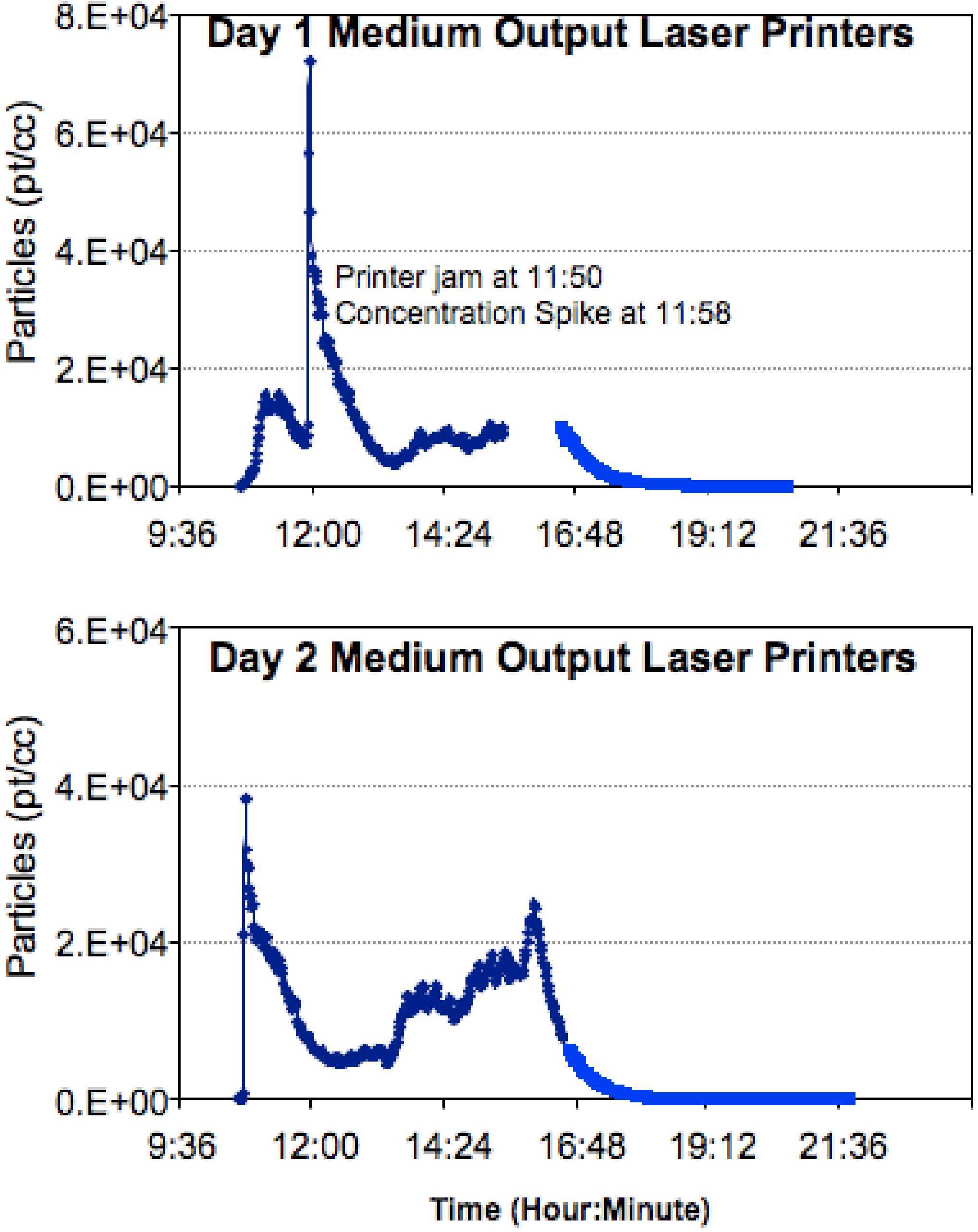

Figure 21: Particle count concentrations for days 1 and 2 of the experiment with three medium output laser printers. The break in the data for day one occurred due to a short shutdown of the particle counting instrument.

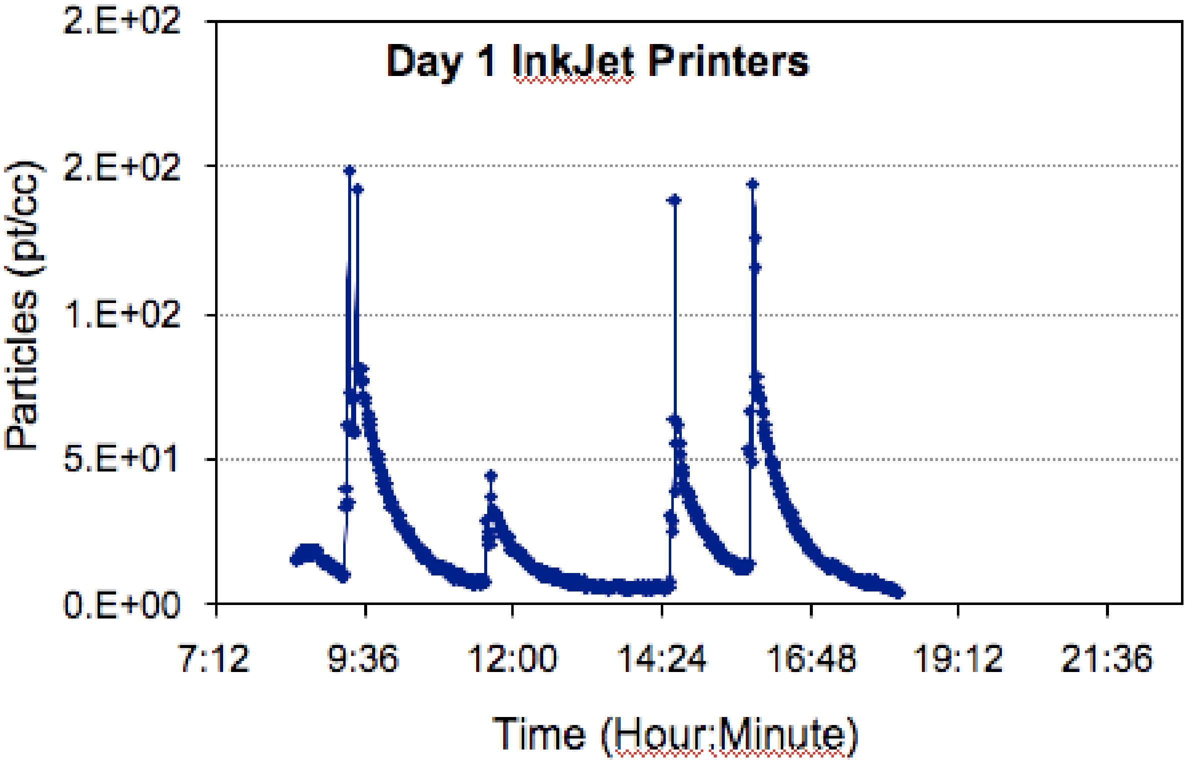

Figure 22: Particle count concentrations for day one of the experiment with five InkJet printers. The particle count concentratiosn are near background and the spikes are due to opening of the chamber door to reload paper in the printers.

5 RECOMMENDATIONS FOR PHASE II EXPERIMENTS

Phase I experiments focused on composite samples of desktop computers and printing devices run over extended periods to identify potentially important emissions. We measured a suite of SVOCs, VOCs, ozone and particles that were selected based on published results. The experiments were run in a highly controlled experimental chamber system.

In the original proposal for this project, Phase II research was designed to build on lessons learned form Phase I. In this section we provide an updated project plan for Phase II based on the results and lessons learned in Phase I. As conceived in the proposal, Phase II provides more detailed measurements for individual office equipment components and addresses questions that could not be resolved using Phase I screening results.

5.1 Overview and Primary Objectives

In general, the results from Phase I indicate that chemical emissions are low for all units tested but this observation applies only to the target chemicals selected for Phase-I quantification and applies in the context of the experimental system used in the screening analysis. In addition, these results have not been assessed in reference to any health specific standards. Given these findings, the project team's two recommendations for Phase II include experiments to confirm or refute the findings of low emissions both in the clean atmosphere used in Phase I and in a more natural atmosphere containing particulates that may influence the movement of chemicals.

Phase-I results also show that the target chemicals only represent a fraction of the total VOCs detected during the chemical analyses. The results for the SVOCs also appeared to only identify a fraction of the chemicals present in the extract although 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 is to identify significant unknowns in the emissions stream.

Another key finding of the Phase-I experiments is that fine-particle emissions during laser printing was elevated and episodic, particularly during initiation of the printing each day. The inkjet printing had low emissions of both aerosols and gas-phase chemicals although these results have not been compared to reported reference concentrations and health specific endpoints. This element of the Phase-I results leads to a fourth recommendation for Phase II experiments to characterize both the composition/size distribution of particle emissions from laser technology printing devices and to identify the potential causes of these episodic emission events.

Building on findings from Phase I the research team recommends several modifications to the work plan for Phase II including changes in the number and duration of individual component experiments along with some additional tasks. These recommendations are summarized in Table 24 and are described in greater detail in the following sections.

Table 24. Summary of recommended goals for Phase II experiments

Recommended goal	Approach	Reason
Confirm/refute low chemical emissions (in an artificially clean atmosphere)	Use individual units in small controlled chambers to repeat results from composite runs performed in Phase I	Finding low emissions is an important result that generally agrees with most but not all published studies
Confirm/refute low chemical emission (in a natural atmosphere)	As above but in presence of controlled levels of atmospheric aerosols.	Air in the controlled experimental chamber was artificially low in aerosol, which may influence transport of SVOC and low volatility chemicals like the highly brominated flame retardants away from source
Evaluate previously unidentified chemicals in emissions stream	Use GC/MS to systematically identify peaks (VOCs and SVOCs) in extracts from emissions phase	Chemicals selected from published literature as target compounds for this study appear to represent only a fraction of the total emission stream.
Characterize particle emissions from laser printers	Using smaller environmental chambers and individual printers, track size resolved particle emission profile and where feasible, the chemical composition of particles during different print cycles.	Identification of cause of elevated particle emissions may provide insight into ways to reduce emissions

Working in the context of the original proposal for Phase II experiments, we provide here a description of how research the remaining Phase-II tasks will be carried out to meet both the preliminary research goals from the original proposal and the focused research goals listed in Table 24. The primary objectives from the original proposal are listed below along with an explanation of how the Phase I study met these objectives and/or how our recommendations for the Phase II study are expected to meet the stated objective.

1. <u>Identify and quantify the chamber concentrations of air pollutants of interest emitted by major categories of distributed office equipment.</u> This objective was

satisfied through the screening experiments conducted during Phase I of the study and the results led to the recommendations listed in Table 24.

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. This information was originally included to allow comparison of machines to determine if some are substantially better than their peers with respect to their emissions of pollutants. However, the findings from Phase I indicate low emissions among each major category. Therefore, the new expected outcome from this objective is to confirm/refute our original findings of low emissions.
3. Characterize the effects of ageing and use on emissions for individual machines spanning several categories. These longitudinal studies were originally included to document changes in emissions as machines age and provide guidance about new versus used device emissions. An additional goal is to understand variability both among different machines and over time with the same unit.
4. Evaluate the importance of operational factors that can be manipulated to reduce pollutant emissions from office machines. Detailed studies will aim to identify best practices for reducing emissions and diagnose factors that lead to unusually high emissions. Phase I experiments found episodic emissions in some printer categories but low emissions for computers. The detailed experiments with individual units will track a number of operational factors particularly for the printing devices but also during the experiments with the computers and these results are expected to address this objective.
5. Explore the potential relationship between energy consumption and pollutant emissions for machines performing equivalent tasks. These measurements will be performed during the experiments planned for Phase II and the results may identify “win-win” situations in which low energy consumption machines have lower pollutant emissions.

5.2 Phase II Measurements of Emissions and Energy Use for Individual Components

In Task 4, we will focus 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. By incorporating aerosols in the air stream we can explore other factors that might contribute to emissions such as the potential for ambient aerosols to transport some SVOCs. The Project Advisory Committee (PAC) considered the lack of aerosols in the air as a possible reason for the low emissions of SVOCs, particularly the brominated flame retardants. The goal of Task 4a is to develop mass-balance models that can be applied to the observed temporal concentration patterns in the chambers to more accurately estimate device emission rates. The product of this effort will be a spreadsheet mass-balance model that describes the sorption re-emission patterns of SVOCs on chamber surfaces. Task 5 will be dedicated to the quantitation of volatile and semivolatile organic compound and particle emissions along with measures of energy use for the individual printing devices. The primary focus of Task 5 is to develop a better understanding of the particle emissions (size distribution and composition) from printing devices. Task 6 will begin to identify factors that contribute to elevated emissions of particles and to identify measures that can be taken to reduce these emissions. Task 6 will build on evidence from Task 5 but focus on a wider range of factors that might influence emissions. In Tasks 4 and 5 each device will be tested using the operating cycle for the group developed in Phase I with some modifications for the printers to explore the influence of duty cycle on emissions. We will measure the effect of ageing and use on emissions for a subset of the individual units.

Table 25 provides a summary of the revised list of experiments planned for Tasks 4 through 6 of Phase II. Included in this summary are the projected total numbers of devices to be tested in each subtask. ARB staff will be consulted about the selection of specific devices and variables for testing throughout Tasks 4 through 6. Task 7 will include a complete reporting of Phase II results and the synthesis of findings from the entire study. This will include a final project report, presentations at scientific meetings and in a manuscript for an archival journal.

5.2.1 Task 4. Individual Computer Systems

Task 4 will focus on the measurement of volatile and semivolatile organic chemical emissions from individual computer systems and their components. Testing of individual computer systems in Task 4 will be conducted in a custom-designed and constructed test chamber. The test chamber that will be used in Phase II was developed for earlier work at UC Berkeley to study the mass transfer of airborne pollutants in a system containing vegetation. The chamber will be re-assembled and adapted for use with the office equipment.

5.2.1.1 Selection of test computer systems

The first two of the five sub-tasks listed for Task 4 will support the selection of computer systems for testing. Rather than follow the selection criteria used in Phase I, i.e. to include one unit from each of five leading manufacturers, this phase will target units that are expected to contain elevated levels of bromine and/or other organic chemicals of interest. We will identify these units using a combination of surface wipe samples and XRF analysis for bromine levels. The XRF analysis will use a portable XRF instrument calibrated for bromine content. The method was developed by the Hazardous Materials Laboratory, California Department of Toxic Substances Control and presented at recent Indoor Air (Petreas et. al. 2006) and American Chemical Society conferences (Li et.al., 2006). The method has been validated by comparing XRF results to analytical chemistry results and the correlation ranged between 0.61 and 0.89 depending on sample matrix (Petreas et. al. 2006). The computers used here will be selected from those used during Phase I of the study and supplemented with new units as needed. Since we are primarily concerned about material emissions, these computers will represent current base-level technology but will not include the most expensive features or memory/processor speed upgrades. For new computers, units will be ordered directly from the manufacturer or from leading distributors. We will confirm that the units are newly produced (i.e. not long-stocked units) and that the casing materials are similar to those used for other models within the product line. Specific models will be selected in consultation with ARB staff. Purchasing and delivery of the computers will be coordinated to accommodate the sampling schedule.

Table 25. Updated Experimental Matrix for Phase II.

Task	Devices	Experiments/Variables	Total Experiments	Proposed Analytes
4	Multiple computer and printer systems	X-ray fluorescence and wipes of surfaces	2 experiments with multiple units	Bromine content to help identify units for further study
4	Empty chamber with known emissions source	Develop a positive control to confirm detection of known sources and explore wall interactions	4 (est.)	VOCs and SVOCs using different analytical methods
4	3 computer systems originally tested in Phase I (picked as candidates for Phase II)	Determine SVOC on surface wipes and temporal patterns of emissions	3 experiment with each unit (9 total)	SVOCs to help identify units for further study and provide insight into unknowns
4	2 additional computer systems identified from previous experiments	Confirm/refute Phase-I results in small chamber and measure device variability	2	VOCs and SVOCs
4	Same computer systems as above plus 2 new units	Measure Influence of particles on long-term SVOC emission measurements	2	
5	3 medium output laser technology printers or multifunction devices	Detailed analysis of emissions as a function of print cycle	6 (est.)	O_3; $PM_{2.5}$ mass, $PM_{2.5}$ BC; Particle number, size resolved particle analysis, 2 additional analytical methods*
5	3 additional printers or multifunction devices	Individual device variability after aging	9 including replicate runs for QA	
6	Printers, computer components;	Non-OEM printing supplies, recycled paper, varied tasks, extended ageing, etc.	10	

*Additional analyses may include EC/OC, PM metals, speciated VOCs, or speciated analysis for subgroup of SVOCs (e.g. PBDEs, OFRs, PAH, carbonyls, etc).

5.2.1.2 Test chamber design and operation

All of the tasks in Phase II will be completed using a smaller (~ 1 m^3) environmental chamber designed to provide a controlled well-mixed environment 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. The modification, testing, and calibration of the emission chamber will be the first major activities of Phase II. The chamber is a cylindrical design constructed with Teflon coated aluminum top, bottom and frame and wrapped in a transparent Teflon film. Chamber materials were selected to minimize the interaction of pollutants with the chamber walls (Maddalena et.al., 2002). The chamber is a continuous stirred flow through design. The chamber will be housed in the climate-controlled chamber used in Phase I and the system will initially use the same conditioned air supply as was used in the earlier experiments. The flow rate of air will be selected to achieve approximately 2.5 to 5 air changes per hour depending primarily on the amount of heat generated by the operating unit. Switching valves and multiple sample ports will be used to provide continuous flow while collecting samples. Pollutant concentrations will be measured either continuously (e.g. for ozone, particle count and particle size distributions) or by collecting integrated air samples (VOCs, SVOCs, particle mass) and chamber conditions (T, RH and delta_P) will be logged continuously and the experiments will be conducted in the dark to prevent photodegradation of pollutants of interest. The small chamber was selected for use in Phase II to accommodate the measurement of emissions from single units but also to provide a system where a “positive control” can be developed using controlled releases of several pollutants of interest.

5.2.1.3 Wall effects and positive control for SVOC contaminants

Sorption of SVOCs onto chamber surfaces can influence the results when relating emission rates to chamber concentrations. In the third sub-task of Task 4, we will investigate wall effects by measuring concentrations over time using a constant SVOC source with a known emission rate. A steady state SVOC source will be constructed using polyurethane foam plugs spiked with excess chemical in a closed container with a controlled stream of air passing through it. The source container will be placed in an oven held slightly above room temperature. Temperature of the container and the flow rate will be used to adjust the levels of contaminant in the source stream that is introduced into the exposure chamber. Measured concentrations at the chamber outlet with the steady state source at the chamber inlet will be used to construct and validate sorption models to characterize individual analyte behavior in the chamber. These results also represent a positive control to demonstrate that emissions can be measured so the finding of low emission rates in Phase I can be confirmed. The validated models will in turn allow for quantitative estimation of total mass emission rates of individual devices during experiments.

5.2.1.4 Identify unknowns and confirm Phase I emissions measurements with small chambers

In order to confirm results from Phase I, it is critical that we carefully evaluate emissions from individual units in a highly controlled system to replicate the observation of low levels of emissions. The fourth subtask of Task 4 is directed at identifying previously unknown compounds in the VOC and SVOC emissions stream where these unknowns are found at levels comparable or greater than the original target analytes based on instrument response. Preliminary screening of unknown analytes using a library search of mass spectra will be used to identify compounds of potential interest to the ARB (e.g., toxic air contaminants and Proposition 65 substances) for confirmation and quantification using known standards. The chamber described in Section 5.2.1.2 will be used to house an individual computer with monitor and peripherals. The chamber design will provide for full capture of the entire chamber air volume during sampling to improve experimental detection limits. Formal LOQ values will be developed for the SVOCs and a newly acquired Varian Ion Trap GC/MS will be used for all chemical classes to improve our detection limits and our ability to identify unknown analytes.

5.2.1.5 Confirm Phase I results and explore impact of particles on SVOC emissions measurements

The last subtask of Task 4 follows the original proposal’s description of an effort to measure the temporal pattern of computer system emissions from the time the equipment was first removed from the box until emissions reach approximately stable levels. Results from Phase I and prior studies suggest that emissions from many new consumer devices and materials decrease sharply over the first month and reach approximately stable levels within one to three months (e.g., Carlsson et al., 2000; Kemmlein et al., 2003). Given our findings from Phase I of low emissions for organic compounds and the rapid decline in those levels, the temporal patterns of emissions are of much less interest to the overall findings of this effort. However, confirming the low emission levels is very important so we recommend modifying the original task to focus on repeating the emissions measurements using previously identified units (Section 5.2.1.1). Two of our original computer systems and/or two new computer systems (including monitor, keyboard, mouse and speakers) will be used.

When new computers are used, purchasing of the systems will be offset in time to allow for them to be tested in the same chamber at the same age. Upon receipt, the system will be loaded with the duty cycle control software, all executables comprising the operating duty cycle developed for Phase I, and any other software required for the duty cycle. The systems will then be placed into the test chamber within 1 week of removal from the OEM-shipping box. The system will be operated continuously and pollutant measurements will be conducted over a period of three or more days. Specific analytes will be selected in consultation with ARB staff and the PAC based on Phase I experimental results and on identification of unknowns during the early stage of Phase II. Energy use will be measured throughout the duty cycle, during sleep mode for each component and when each component of the system is powered “off”.

To further verify earlier results, emissions will be measured from two additional complete computers or computer components that will be purchased new and handled as described above. These computers will be operated on the same duty cycle in an auxiliary climate controlled room between experiments.

Members of the PAC have recommended that ambient aerosols might contribute to the transport of low volatility chemicals of interest such as the highly brominated flame retardants (i.e., PBDE-209) so the final set of experiments will include a number of phases where aerosols are introduced into the chamber and collected to explore potential changes in transport of the very low volatility organic compounds. A nebulizer will be used to generate a constant level of well-defined ammonium sulfate aerosol in the 20 m^3 chamber housing the smaller experimental chamber to provide a source air containing a known level of aerosols. Particles will be measured in the source air and in the air exiting the chamber to explore the influence of particles on the transport of pollutants away from the office equipment. We will also collect dust material from the surfaces and internal compartment of equipment following experiments to explore potential uptake of contaminants into the dust phase that could potentially be released into houses after extended use.

5.2.2 Task 4a. Analysis of Surface Chamber Effects

It is likely that the losses of some compounds to chamber surfaces could be substantial. This makes in necessary to quantify sorption rates and equilibrium partitioning for some SVOCs interacting with chamber surfaces. The goal of this task is to employ mass balance models to the observed temporal concentration patterns in the chambers to more accurately estimate device emission rates. The goal of this added task is to develop mass-balance models that can be applied to the observed temporal concentration patterns in the chambers to more accurately estimate device emission rates. This effort will be initiated at the start Task 4 and will be completed by the end of Task 5. The product of this effort will be a spreadsheet mass-balance model that describes the sorption re-emission patterns of SVOCs on chamber surfaces.

5.2.3 Task 5. Individual Printers

The primary object of the Phase-II expanded study of printing devices is to characterize the composition of aerosols released during printing and to explore the factors that lead to the episodic high levels of particles being generated.

In this task, three different printers will be tested individually in the emission chamber. Before working in the emission chamber, the printers will be operated over a range of duty cycles with continuous monitoring of fine particles in different areas of the printer to identify the potential source. The printers will then be installed in the chamber to identify conditions that lead to significant increases in particle emissions. The group-level results from Phase I will guide the selection of individual printers with our primary interest in the medium duty laser technology units.

Three additional printers will be included when they are new and at two ages (~6 and 12 months). Between tests, the printers will be “aged” by placing them in situations that reflect office use where they will be used at levels approaching at least one-half (e.g., 40-90%) of the manufacturer’s recommended capacity. A logbook will be attached to each device to record all maintenance activities including re-supply of ink cartridges or toner. Users will also be asked to track the approximate number of pages printed, e.g. by recording of the number of paper reams that are consumed. Alternatively, the printers will be aged by running a specified duty cycle on a daily basis for the necessary period of time.

Specific analytes for the individual printer experiments will be determined based on Phase I results. We expect these will include ozone, PM mass, particle count concentration, size resolved particle counts, and a screening measurement to identify chemicals of potential interest to the California Air Resources Board from the Phase I experiments; other possibilities are elemental/organic carbon, PM metals, carbonyls, or classes of SVOCs. Particle number concentrations will be measured with a condensation particle counter (i.e., P-TRAK) to detect emissions of ultrafine particles. The energy use will be measured from each device throughout the operating cycle, during sleep mode, and when powered "off".

5.2.4 Task 6. Mitigation of Emissions and Exposures

In Task 6, we will investigate other variables that may affect device energy use and emissions, e.g., use of non-OEM (original equipment manufacturer) printing supplies, use of recycled paper, varied types of operation, or the effects of heavy-use and/or extended aging. The major goal of this task will be to identify measures that operators can take to reduce emissions. Task 6 will therefore focus on an experimental matrix of individual devices and conditions that resulted in the highest observed emissions in earlier experiments. Individual units will be tested under varying operating conditions and varying use scenarios (e.g. intermittent versus extended continuous printing, printing text versus pictures, Black and White versus color, cold start printing versus warm, etc.). A subset of experiments will be dedicated specifically to evaluating potential emissions and exposure mitigation strategies. These may include servicing of older printers, installing new toner or ink cartridges, etc. Additional experiments may be conducted to quantify the effect of additional printer variables such as the use of non-OEM toner or recycled inkjet-printer cartridges and recycled versus virgin paper. Individual computer system components could also be tested during this Task. Effort is budgeted for 9 – 10 experiments lasting 1-3 days each using the small test chamber and measurement techniques used in previous tasks. Decisions about the specific experiments to be conducted during this phase will be made in consultation with ARB staff. More experiments may be feasible if funds remain from earlier tasks.

5.3 Revised Project Schedule and Time Frame for Advisory Input

Once the experiments were completed for Phase I, we realized that the time schedule for the Task 4 and Task 5 experiments as originally proposed is longer than will actually be needed. In this section, we provide a revised project schedule based on what we learned in Phase I. The principal revision to the schedule is the reduction in time needed to complete the Task 5 and Task 6 experiments. We also amended this to show the expected performance period for Task 4a, Analysis of Surface Chamber Effects.

The revision of the experimental schedule for Phase II also made it necessary to reconsider the timeframe for Phase II advisor input. In the revised project schedule, we have added an additional meeting with ARB and the PAC set for April 2007 to coincide with completion of the Task 4 experiments, the midterm of the Task-5 experiments and the early phases of the Task 6 experiments. This is a point at which we recognized that outside input is important.

Task 1. Literature Review
Task 2. Screening Experiments for Device Groups
Task 3. Phase I Reporting
Task 4. Individual Computer Systems
Task 4a Analysis of Surface Chamber Effects
Task 5. Individual Printers
Task 6. Mitigation of Emissions and Exposures
Task 7. Synthesis and Final Reporting

YEAR 1 (July 2005 through June 2006)

	Month	1	2	3	4	5	6	7	8	9	10	11	12	
Task														
1		■	■	■	■	■	■							
2				■	■	■	■	■	■	■				
3										■	■	■	■	
4														
4a														
5														
6														
7														
		m		p			p			p			i	

YEAR 2 (July 2006 through June 2007)

	Month	1	2	3	4	5	6	7	8	9	10	11	12	
Task														
1														
2														
3		■	■											
4				■	■	■	■	■	■					
4a							■	■	■					
5								■	■	■	■	■		
6											■	■	■	
7														
		m		p			p			p	m		p	

YEAR 3 (July 2007 through June 2008)

	Month	1	2	3	4	5	6	7	8	9	10	11	12	
Task														
1														
2														
3														
4														
4a														
5														
6		■	■	■										
7		■	■	■	■	■	■	■	■	■	■	■		
		m		p		d						f		

p = Progress report

i = Deliver interim report
d = Deliver draft final report
f = Deliver final report
m = Meeting with ARB staff and Project Advisory Board

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7 GLOSSARY OF TERMS, ABBREVIATIONS, AND SYMBOLS

General abbreviations

BFR	Brominated flame retardants
GCMS	Gas chromatography – Mass spectrometry
HPLC	High performance liquid chromatography
OPFR	Organophosphate flame retardants
PM	Particulate matter
SVOC	Semivolatile organic chemicals
LVOC	Low volatility organic compounds
TVOC	Total volatile organic chemicals
VOC	Volatile organic chemicals

Brominated Flame Retardants

BB 1-209	Brominated biphenyl congeners 1-209
BDE 1-209	Brominated diphenyl ether congeners 1-209
BTBPE	1,2-Bis(2,4,6-tribromophenoxy)ethane
TBBPA	Tetrabromo bisphenol A

Organophosphate Flame Retardants

BDP	Bisphenyl A bis (diphenyl phosphate)
DOPP	Di-n-octylphenyl phosphate
IPPDPP	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
TNBP	Tri(n-butyl) phosphate
TPP	Triphenyl phosphate

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 phtalate
DPP	Dipropyl phtalate

Perfluoroalkyl sulfonamides

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