Edmund G. Brown, Jr.
Governor

QUANTIFYING POLLUTANT EMISSIONS FROM OFFICE EQUIPMENT:

A CONCERN IN ENERGY EFFICIENT BUILDINGS

APPENDICES B–K

PIER COLLABORATIVE REPORT

California Environmental Protection Agency
AIR RESOURCES BOARD

November 2011
CEC-500-2011-046-APB-K

Prepared By
R. L. Maddalena,[1] T. E. McKone,[1,2] H. Destaillats,[1]
M. Rusell,[1] A. T. Hodgson,[1] and C. Perino[2]
[1] Lawrence Berkeley National Laboratory
[2] University of California, School of Public Health
Berkeley, CA 94720

Commission Contract No. # 500-02-023
Commission Work Authorization No: # 04-302

Prepared For:
Public Interest Energy Research (PIER)

California Energy Commission

Guido Franco
Program Area Lead
Energy-Related Environmental Research

Marla Mueller
Contract Manager

Linda Spiegel
Office Manager
Energy Generation Research

Laurie ten Hope
Deputy Director
ENERGY RESEARCH AND DEVELOPMENT DIVISION

Robert P. Oglesby
Executive Director

and

California Air Resources Board

Ryan Johnson
Contract Manager
Research Division

Peggy Jenkins
Manager
Indoor Exposure Assessment Section
Research Division

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Appendix B.

Quality Objectives

Appendix B. Quality Objectives

Quality assurance and quality control are critical to all aspects of this study. This appendix provides details on the project quality objectives and measurement quality objectives with an emphasis on actions taken to assure sample analysis quality.

B.1 Project Quality Objectives

There were separate quality objectives for Phases I and II. Given the screening nature of the Phase I 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. Phase II of the study looks at individual units focusing on factors that influence emissions such as computer aging so the need to provide sample that is representative of the current (or future) stock of office equipment in California households is not critical. However, as with Phase I, there was an effort to use a variety of units selected from major manufacturers. The study design in Phase II also provides initial estimates of variability across units and over time that can support development of a statically representative sampling plan in the future if a more detailed monitoring study is required.

B.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. The measurement performance for each analyte class was tracked 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.

B.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).

B.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.

B.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.

B.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. Operationally, the MDL can be estimated as a multiple (usually 3) of the standard deviation of low-level replicate measurements. 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.

B.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.

B.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.

B.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 period. 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 workload are also reported so the results can be “transformed” to make comparable with other studies if necessary.

B.3 Summary Results of Project Quality Assurance Measures

Table B.1 summarizes the quality assurance measures for all target chemicals in the project listed by chemical class and sorted in order of increasing boiling point. Appendix H lists the background concentration in the chambers during the Phase II experiments.

Table B.1. Overall summary of quality assurance measures

Chemical	CAS#	Chemical Class[a]	Analytical method used	MDL (ng)[b]	LOQ (ng)[b]	LOQ As chamber concentration[c] □g/m^3	LOQ As chamber concentration[c] ng/m^3	recovery[d]	Precision[e]
Phenol	108-95-2	alcohol	TD-GC/MS	0.53	1.68	0.56		N/A	15%
2-ethyl-1-hexanol	104-76-7	alcohol	TD-GC/MS	2.65	9.60	3.20		N/A	28%
Butylated Hydroxytoluene	128-37-0	alcohol	TD-GC/MS	0.48	1.54	0.51		N/A	19%
1-Hexadecanol	36653-82-4	alcohol	TD-GC/MS	1.26	4.01	1.34		N/A	
Formaldehyde	50-00-0	aldehyde	DNPH/HPLC	0.15	0.48	4.00		N/A	9%
Acetaldehyde	75-07-0	aldehyde	DNPH/HPLC	0.64	2.04	17.00		N/A	13%
Hexanal	66-25-1	aldehyde	TD-GC/MS	0.22	0.70	0.23		N/A	
Octanal	124-13-0	aldehyde	TD-GC/MS	1.92	6.10	2.03		N/A	
Benzaldehyde	100-52-7	aldehyde	TD-GC/MS	1.35	4.30	1.43		N/A	18%
Nonanal	124-19-6	aldehyde	TD-GC/MS	4.50	14.30	4.77		N/A	
Dodecane	112-40-3	alkane	TD-GC/MS	0.25	0.79	0.26		N/A	28%
Tridecane	629-50-5	alkane	TD-GC/MS	1.04	3.30	1.10		N/A	
Tetradecane	629-59-4	alkane	TD-GC/MS	0.42	1.35	0.45		N/A	17%
Pentadecane	629-62-9	alkane	TD-GC/MS	0.09	0.30	0.10		N/A	
Hexadecane	544-76-3	alkane	TD-GC/MS	0.42	1.34	0.45		N/A	17%
Benzene	71-43-2	aromatic	TD-GC/MS	0.73	2.31	0.77		N/A	13%
Toluene	108-88-3	aromatic	TD-GC/MS	0.13	0.40	0.13		N/A	18%
Ethylbenzene	100-41-4	aromatic	TD-GC/MS	0.21	0.67	0.22		N/A	18%
m/p-Xylene	108-38-3, 106-42-3	aromatic	TD-GC/MS	0.72	2.29	0.76		N/A	16%
o-Xylene	95-47-6	aromatic	TD-GC/MS	0.31	0.99	0.33		N/A	15%
Styrene	100-42-5	aromatic	TD-GC/MS	0.20	0.63	0.21		N/A	25%
Propyl-benzene	103-65-1	aromatic	TD-GC/MS	0.13	0.42	0.14		N/A	13%

Chemical	CAS#	Chemical Class[a]	Analytical method used	MDL (ng)[b]	LOQ (ng)[b]	LOQ As chamber concentration[c] □g/m^3	LOQ As chamber concentration[c] ng/m^3	recovery[d]	Precision[e]
1,3,5-trimethyl-benzene	108-67-8	aromatic	TD-GC/MS	0.11	0.36	0.12		N/A	12%
Benzene, (2-methylpropyl)-	538-93-2	aromatic	TD-GC/MS	0.20	0.65	0.22		N/A	16%
1,2,3-trimethyl-benzene	526-73-8	aromatic	TD-GC/MS	0.20	0.64	0.21		N/A	14%
Benzene, 1,3-diethyl-	141-93-5	aromatic	TD-GC/MS	0.31	0.75	0.25		N/A	15%
Butylbenzene	104-51-8	aromatic	TD-GC/MS	0.26	0.82	0.27		N/A	15%
Benzene, 1,2,3,5-tetramethyl-	527-53-7	aromatic	TD-GC/MS	0.40	0.78	0.26		N/A	18%
Benzene, 1,2,3,4-tetramethy	488-23-3	aromatic	TD-GC/MS	0.41	1.00	0.33		N/A	17%
TMPD-MIB	25265-77-4	ester	TD-GC/MS	0.03	0.10	0.03		N/A	
TMPD-DIB	6846-50-0	ester	TD-GC/MS	0.03	0.10	0.03		N/A	
Diethyl Phthalate	84-66-2	ester	TD-GC/MS	0.38	1.20	0.40		N/A	53%
Dibutyl phthalate	84-74-2	ester	TD-GC/MS	0.25	0.78	0.26		N/A	60%
acetone (2-propanone)	67-64-1	ketone	DNPH/HPLC	0.23	0.48	6.00		N/A	14%
Acetophenone	98-86-2	ketone	TD-GC/MS	0.83	2.65	0.88		N/A	16%
Hexamethylcyclotrisiloxane	541-05-9	misc.	TD-GC/MS	6.37	20.26	6.75		N/A	21%
Octamethylcyclotetrasiloxane	556-67-2	misc.	TD-GC/MS	1.89	6.02	2.01		N/A	32%
Decamethylcylopentasiloxane	541-02-6	misc.	TD-GC/MS	1.53	4.88	1.63		N/A	22%
Dodecamethylcyclohexasiloxane	540-97-6	misc.	TD-GC/MS	2.72	8.64	2.88		N/A	23%
Tetradecamethylcycloheptasiloxane	107-50-6	misc.	TD-GC/MS	1.04	3.30	1.10		N/A	19%
Hexadecamethylcyclooctasiloxane	556-68-3	misc.	TD-GC/MS	13.15	41.85	13.95		N/A	35%
Naphthalene	91-20-3	polyaromatic	TD-GC/MS, GC/IT/MS	0.57	1.80	0.60		N/A	21%
2-methyl-Naphthalene	91-57-6	polyaromatic	TD-GC/MS, GC/IT/MS	0.36	1.16	0.39		N/A	15%
1-methyl-Naphthalene	90-12-0	polyaromatic	TD-GC/MS, GC/IT/MS	0.35	1.12	0.37		N/A	14%
□-Pinene	7785-70-8	terpene	TD-GC/MS	0.82	2.60	0.87		N/A	
3-Carene	13466-78-9	terpene	TD-GC/MS	0.85	2.70	0.90		N/A	
□-Pinene	18172-67-3	terpene	TD-GC/MS	0.82	2.60	0.87		N/A	

Chemical	CAS#	Chemical Class[a]	Analytical method used	MDL (ng)[b]	LOQ (ng)[b]	LOQ As chamber concentration[c] □g/m^3	LOQ As chamber concentration[c] ng/m^3	recovery[d]	Precision[e]
d-Limonene	5989-27-5	terpene	TD-GC/MS	0.85	2.70	0.90		N/A	
tri(2-ethylhexyl) phosphate	78-42-2	OP	GC/NPD	1.97	6.25		0.45	272%	27%
triethyl phosphate	78-40-0	OP	GC/NPD	1.97	6.25		0.45	66%	66%
tri(2-butoxyethyl) phosphate	78-51-3	OP	GC/NPD	2.03	6.44		0.46	70%	
tri(n-butyl) phosphate	126-73-8	OP	GC/NPD	1.97	6.25		0.45	168%	20%
tri(2-chloroethyl) phosphate	115-96-8	OP	GC/NPD	2.09	6.65		0.47	226%	31%
triphenyl phosphate	101-02-0	OP	GC/NPD	1.97	6.25		0.45	129%	23%
2,4,4'-TriBDE	#17	BFR	GC/ECD, GC/IT/MS	0.79	2.50		0.18	97%	7%
2,4,4'-TriBDE	#28	BFR	GC/ECD, GC/IT/MS	0.79	2.50		0.18	108%	8%
2,2',4,4'-TetraBDE	#47	BFR	GC/ECD, GC/IT/MS	0.79	2.50		0.18	119%	11%
2,3',4,4'-TetraBDE	#66	BFR	GC/ECD, GC/IT/MS	0.79	2.50		0.18	103%	3%
2,3',4',6-TetraBDE	#71	BFR	GC/ECD, GC/IT/MS	0.79	2.50		0.18	109%	9%
2,2',3,4,4'-PentaBDE	#85	BFR	GC/ECD, GC/IT/MS	0.79	2.50		0.18	98%	1%
2,2',4,4',5-PentaBDE	#99	BFR	GC/ECD, GC/IT/MS	0.79	2.50		0.18	102%	4%
2,2',4,4',6-PentaBDE	#100	BFR	GC/ECD, GC/IT/MS	0.79	2.50		0.18	103%	17%
2,2',3,4,4',5'-HexaBDE	#138	BFR	GC/ECD, GC/IT/MS	0.79	2.50		0.18	88%	4%
2,2',4,4',5,5'-HexaBDE	#153	BFR	GC/ECD, GC/IT/MS	0.79	2.50		0.18	90%	8%
2,2',4,4',5,6'-HexaBDE	#154	BFR	GC/ECD, GC/IT/MS	0.79	2.50		0.18	87%	9%
2,2',3,4,4',5',6-HeptaBDE	#183	BFR	GC/ECD, GC/IT/MS	0.79	2.50		0.18	78%	19%
2,3,3',4,4',5,6-HeptaBDE	#190	BFR	GC/ECD, GC/IT/MS	0.79	2.50		0.18	71%	19%

Chemical	CAS#	Chemical Class[a]	Analytical method used	MDL (ng)[b]	LOQ (ng)[b]	LOQ As chamber concentration[c] □g/m^3	LOQ As chamber concentration[c] ng/m^3	recovery[d]	Precision[e]
DecaBDE	#209	BFR	GC/ECD, GC/IT/MS	7.84	24.90		1.78		
Acenapthylene	208-96-8	polyaromatic	GC/MS, GC/IT/MS	0.79	2.50		0.18	88%	8%
Acenapthene	83-32-9	polyaromatic	GC/MS, GC/IT/MS	0.79	2.50		0.18	107%	10%
Fluorene	86-73-7	polyaromatic	GC/MS, GC/IT/MS	0.79	2.50		0.18	90%	4%
Phenanthrene	85-01-8	polyaromatic	GC/MS, GC/IT/MS	0.79	2.50		0.18	110%	10%
Anthracene	120-12-7	polyaromatic	GC/MS, GC/IT/MS	0.79	2.50		0.18	110%	5%
Pyrene	129-00-0	polyaromatic	GC/MS, GC/IT/MS	0.79	2.50		0.18	124%	9%
Fluoranthene	206-44-0	polyaromatic	GC/MS, GC/IT/MS	0.79	2.50		0.18	119%	2%
Benz(a)anthracene	556-55-3	polyaromatic	GC/MS, GC/IT/MS	0.79	2.50		0.18	117%	12%
Chrysene	218-01-9	polyaromatic	GC/MS, GC/IT/MS	0.79	2.50		0.18	123%	13%
Benzo(b)fluoranthene	205-99-2	polyaromatic	GC/MS, GC/IT/MS	0.79	2.50		0.18	109%	9%
Benzo(k)fluoranthene	207-08-9	polyaromatic	GC/MS, GC/IT/MS	0.79	2.50		0.18	108%	8%
Benzo(a)pyrene	50-32-8	polyaromatic	GC/MS, GC/IT/MS	0.79	2.50		0.18	108%	15%
Dibenz(a,h)anthracene	53-70-1	polyaromatic	GC/MS, GC/IT/MS	0.79	2.50		0.18	118%	13%
Indeno(1,2,3-c,d)pyrene	193-39-5	polyaromatic	GC/MS, GC/IT/MS	0.79	2.50		0.18	115%	12%
Benzo(g,h,i)perylene	191-24-2	polyaromatic	GC/MS, GC/IT/MS	0.79	2.50		0.18	110%	11%

[a]Chemicals are sorted in order of increasing boiling point within each chemical class; [b]The minimum detection limit and the limit of quantification are reported in terms of the instrument and are calculated from replicate low level spikes (blue font), replicate background concentrations in the chamber(s) (green font), estimated based on the lowest calibration point (red font), or estimated as three times the "noise" or baseline response in the analysis, i.e., the MDL has a signal to noise ratio that is greater than one (black font); [c]The limit of quantification in terms of the chamber concentration are approximated using sample volumes of 3 liters for the VOCs, 60 liters for the low molecular weight aldehydes and 14 m^3 for the SVOCs; [d]No recovery experiments were performed for VOCs on thermodesorption tubes but repeat extraction of the thermodesorption tubes indicated complete removal of anlaytes; [e]Precision is reported as the percent relative difference between replicate measurements.

Appendix C.

Chamber Mass Balance Evaluation

Appendix C. Chamber Mass Balance Evaluation

A mass balance relationship was investigated to more accurately estimate device emission rates for analytes that potentially interact with chamber walls. For most pollutants, the emission rate can be estimated using only the air-exchange rate (ACH, h^{-1}), the background concentration, and the measured steady-state concentration. The time to steady-state in the emission chamber for these chemicals depends only on the ACH. The ACH is the ratio of the flow rate of air through the chamber (f, m^3/h) and the chamber volume (V, m^3), i.e., ACH = f/V, where the parameters can be determined from the chamber dimensions, the measured air flow through the chamber and/or a tracer gas decay measurements (described below). For example, in Phase II-experiments, the measured volume of the empty chamber is approximately 0.4 m^3 and the air flow through the chamber is controlled and measured using factory calibrated rotometers mounted in-line between the chamber exit and a rotary vane vacuum pump.

Although direct measurements can provide values for *V* and *f*, the results can be imprecise because (a) the flexible chamber walls do not always maintain a simple geometric shape, (b) there is an unknown air volume taken up in the chamber by the unit being tested, and (c) there can be changes in the flow measurement caused by variation in temperature and pressure during a given experiment and by the slight positive pressure in the chamber causing chamber leakage that is not recorded by the rotometer. Uncertainty in chamber characteristics can be further exacerbated by differences in the "apparent" volume of the chamber caused by interaction of individual chemicals with the chamber walls. Semi-volatile organic chemicals, reactive chemicals (ozone) and particles can interact with surfaces in ways that can influence the observed concentration in a test chamber. This influence is due to irreversible interactions or degradation on surfaces that increase the apparent loss rate in the chamber (increasing the apparent *ACH*), or by reversible partitioning between surfaces and the air flowing through the chamber thereby increasing the apparent volume of the chamber (and decreasing the apparent *ACH*). This section describes the process used to address this issue.

C.1 Estimating Air Exchange Rates with No Surface Interactions

For most of the chemicals tested in the chamber experiments, the air exchange rate is determined using a tracer gas method. In this method, the *ACH* is measured while the chamber is running, using uptake and removal rates of a tracer gas. CO_2 was used for all experiments in this study. The equation for the approach to steady-state for a non-reactive tracer gas without a background concentration in the chamber is

$$C_t = C_{ss} \times \left(1 - \exp^{-Qt}\right) \qquad \text{(C-1)}$$

where C_t (% CO_2) is the measured concentration in the chamber at time *t*, C_{ss} (% CO_2) is the maximum concentration attained by the tracer gas at steady-state in the chamber with the source on, *t* (h) is elapsed time after starting the source of tracer gas into the system and *Q* (h^{-1})

is the rate of removal of the chemical from the chamber, which for a non-reactive pollutant that does not strongly interact with surfaces is the *ACH* (h^{-1}) and is equal to f/V_a where f ($m^3\ h^{-1}$) is the flow rate through the chamber and V_a (m^3) is the volume of air in the chamber. The corresponding equation for removal or clearance of the tracer gas from the chamber after the source has been turned off is

$$C_t = C^* \times \exp^{-Q(t-t^*)} \qquad \text{(C-2)}$$

where t^* is the time that the source was turned off, C^* is the concentration when $t = t^*$ and the other variables are defined above.

With a chemical such as CO_2 as a tracer gas, the background level in the chamber can alter the uptake and clearance curves because they do not start and end at zero. In this case, the overall concentration-versus-time curve is given by:

$$C_t = C_{ss} + \left(C^* - C_{ss}\right) \times \exp^{-Q(t-t^*)} \qquad \text{(C-3)}$$

The variables in this equation are assigned different values at each t^* point when the source is changed in a step-wise fashion. The values of these parameters are defined as follows. During the uptake phase in the chamber, C^* is the starting concentration when the source is turned on at $t=t^*$, which is generally the background concentration in the chamber, C_{ss} is the steady-state concentration that will be attained with the constant and continuous source of tracer gas turned (starting at $t = t^*$). During the clearance phase, t^* is now the time that the source is turned off, C^* is again defined as the concentration in the chamber when $t=t^*$ and C_{ss} is the steady state concentration in the chamber with no source. When the steady-state concentration is achieved during the uptake phase of the tracer gas experiment, then the rate constant, Q, is fit to the data by minimizing the sum of the square errors between measured CO_2 concentrations (expressed as % CO_2) and the value predicted by Eq. C-3 when Q is optimized. In other words, the model is fit to the measured data by changing Q. In some cases, as is illustrated in Figure C.1, both the steady-state concentration and the rate constant need to be optimized to fit Eq. C-3 to the measurements of the uptake and the clearance part of the concentration-time profile.

If the difference between the background and steady-state concentrations is great enough, the *ACH* can be estimated by plotting $\ln(C_t/C^*)$ against $(t-t^*)$. The slope of the line in the linear region before the curve approaches the background concentration is equal to $-ACH$ as illustrated in Figure C.2 using only the clearance data from the curve in Figure C.1. In this case the *ACH* value estimated using the simplified method is approximately 10% lower than the valued estimate from the more detailed model using both the uptake and clearance curves.

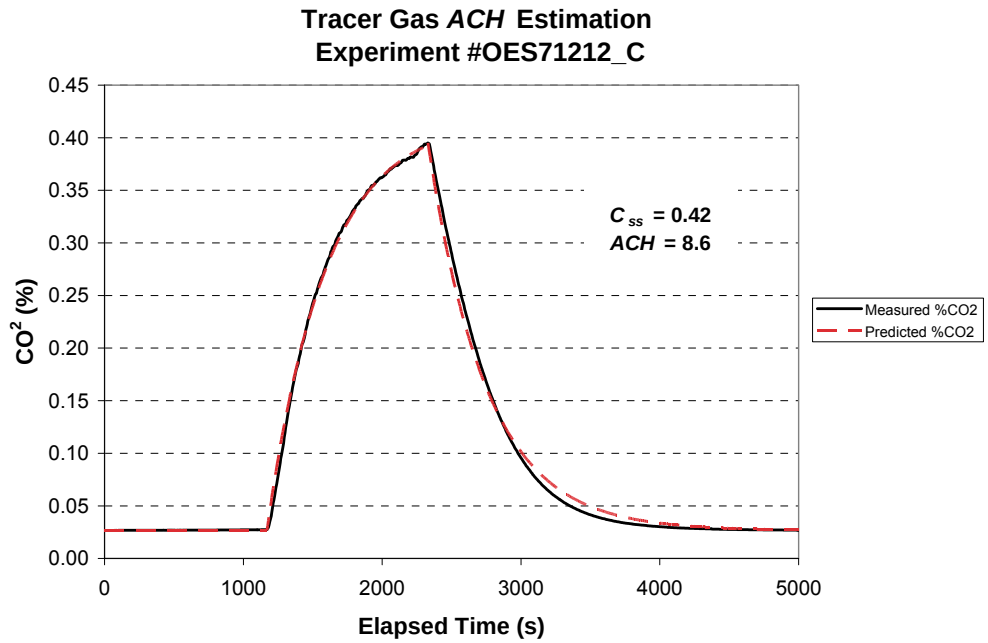


Figure C.1. An illustration of a tracer gas experiment to estimate ACH where dash line is Equation 4-3 optimized on C_{ss} and ACH by simultaneously minimizing the sum of the square errors between the measured and estimated % CO_2 for both the uptake and clearance phases.

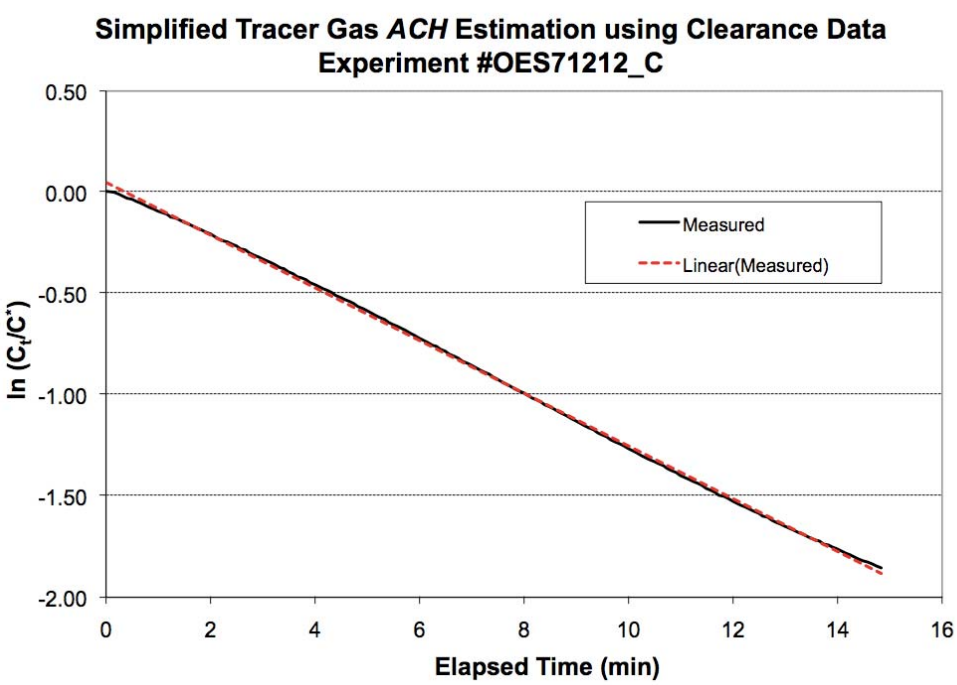


Figure C-2. If the difference between the background and steady-state concentrations is great enough, the *ACH* can be estimated by plotting ln(C_t/C*) against (t-t*). In this logarithm plot, the slope of the line in the linear region before the curve approaches the background concentration is equal to –*ACH.*

C.2 Estimating Clearance Rates with Surface Interactions

For pollutants that interact irreversibly with surfaces in the chamber (such as ozone and particulate matter) the observed clearance rate is actually faster than the *ACH*. In this case, one assumes that the overall clearance rate, *Q*, is constant and includes both the loss rate to the chamber surfaces and removal with air flowing out of the chamber. In this case, the rate constant is estimated from the clearance data for the specific pollutant after emission has ceased when real-time data is available (for example, after a printing device experiment is complete the measured ozone or particles are used to estimate clearance). This is illustrated in Figure C.3. In cases where one can assume a constant emission rate during a fixed period followed by no emissions, such as when a printer is warmed up and a print job of fixed duration is processed, then it is possible to use both the uptake and clearance data and apply Equation C.3 to estimate C_{ss} and the clearance rate constant but it is difficult to confirm that the emission is constant over the fixed durations so typically we use only the clearance data to estimate *Q*. The value of the clearance rate constant obtained in this way can be used in later experiments to estimate the emission factor for the unit being tested.

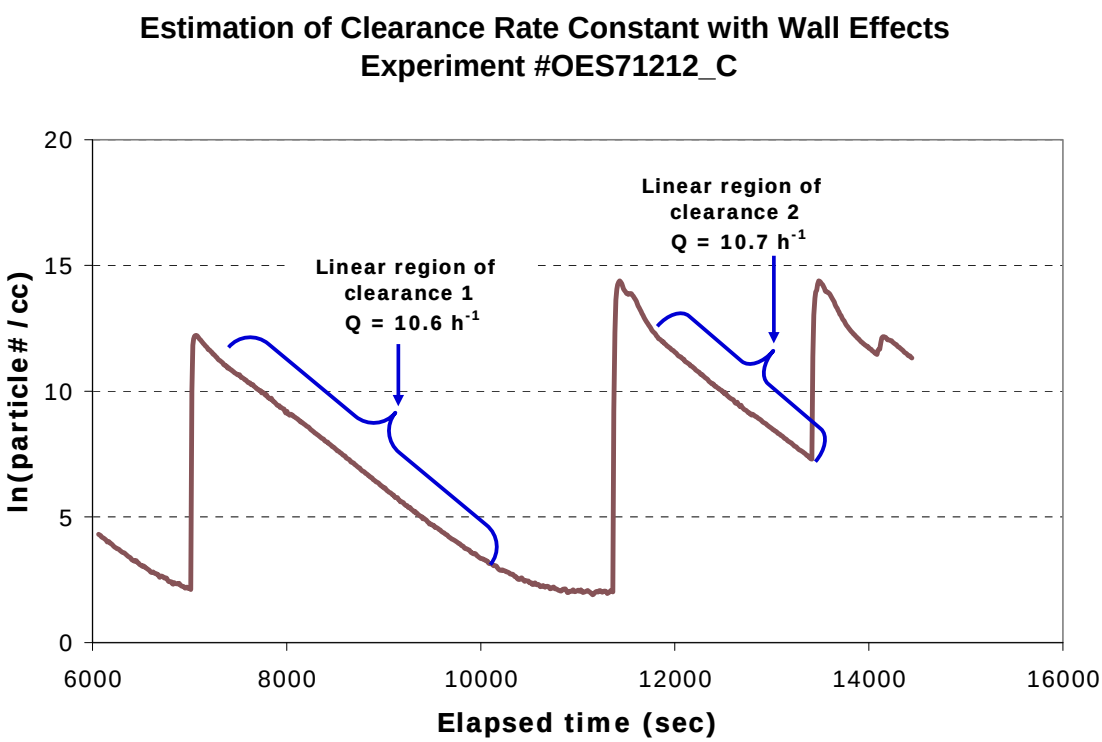


Figure C.3. Estimation of a clearance rate constant for aerosols that irreversibly react with surfaces in the test chamber. A similar approach is used with ozone where steady-state chamber concentrations are not reached during a given printing job for the printer experiments.

The more challenging case of surface effects occurs when the pollutant of interest partitions reversibly between the chamber air and chamber surfaces. This can happen for some of the semi-volatile organic chemicals and creates a situation where the measured concentration cannot be inferred to represent steady-state conditions unless a long-term experiment is run with a constant source. To check for this situation, one needs multiple measurements over time to assess whether the pollutant of interest is near steady-state (i.e., the measured concentration at different time points is relatively constant). This issue was addressed in both the room scale and the small chamber experiments by running them for extended periods (~200 air changes) to insure a steady-state concentration. But for some pollutants steady state cannot be reached in a reasonable amount of time.

When there is significant partitioning to chamber surfaces and the system does not reach steady-state during the experimental period, we assume that the mass transfer rate at the air/surface interface is fully reversible. In this case, the system behaves as if the chamber volume is much greater than the actual volume because the actual holding capacity of the chamber includes both the solubility in the air and the capacity of the surface to hold the chemical. With an abundance of experimental data, one can estimate the apparent chamber volume or rate constant for the specific chemical using Equation C-3. That is, use uptake and clearance curve data along with known flow rates (either measured or estimated from a CO_2 trace) to optimize Equation C-3 for C_{ss} and Q. One then uses the values obtained for C_{ss} and Q to estimate the apparent chamber volume, V^*. This approach is illustrated in Figure C-4, which shows results using unpublished data from an earlier study that employed a chamber that is similar in design to the small chamber used in Phase II.

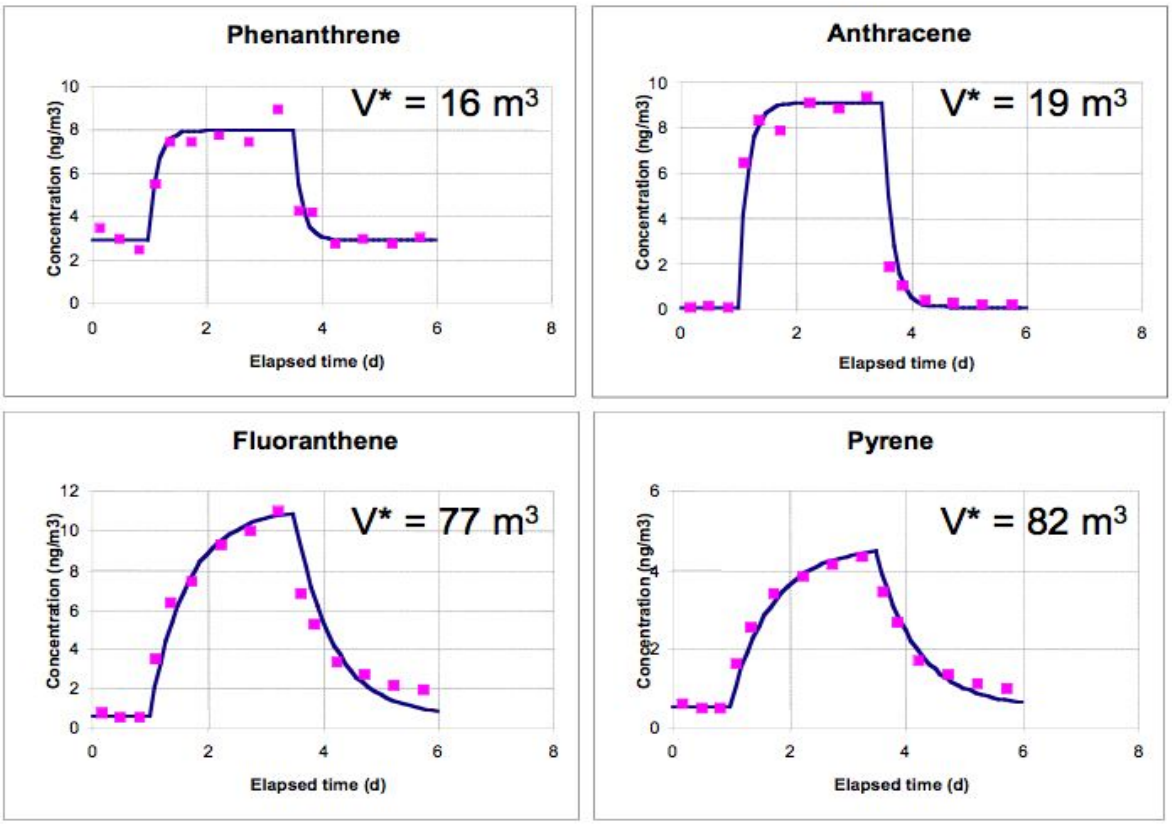


Figure C-4. Estimation of apparent chamber volume (V*) when chemical reversibly interacts with chamber surfaces. The four chemicals illustrated above were measured during the same experiment in a chamber similar to the one used for the small chamber study with an actual volume of 0.5 m^3.

Appendix D.

Particle Characterization During Phase I Experiments

Appendix D. Particle Characterization During Phase I Experiments

D.1 Particle Number Concentration Determination for Phase I Computer Experiments

Particle number concentration (particles per cc) were monitored either continuously or at designated intervals throughout the duration of each printer and computer screening experiment in Phase I using a P-Trak (TSI Inc.) condensation particle counter. This device allows for the detection of ultrafine particles (20 nm to >1 μm). Samples were typically collected for 1-2 hour using a one-minute averaging time for the computers and collected continuously for the duration of the study for the printer runs. Results for the printer runs are plotted in the body of the report and the data are not repeated here. The summary data for the laptop and desktop computer experiments are provided below.

Table D.1 Summary of particle number concentration data from phase I laptop computer experiment

Event	*Sampling Date*	*Average Particles (PN/cc)*	*Std Dev.*	*CV%*	*max*	*min*
computers off	1/6/2006	76	4.24	5.6%	82	67
computers off	1/9/2006	48	1.74	3.6%	51	43
door open to turn on computers	1/9/2006	2760				
computers on with door closed	1/9/2006	170	61.75	36.3%	313	96
computers on with door closed	1/10/2006	17	1.41	8.3%	20	15
computers on with door closed	1/13/2006	58	4.79	8.3%	64	46
computers on with door closed	1/17/2006	24	0.92	3.8%	26	22
outside chamber, in Rm 289	1/17/2006	3251	571.79	17.6%	4168	2170

Table D.2 Summary of particle number concentration from phase I desktop computer experiment

Event	Sampling Date	*Average Particles (PN/cc)*	max	min
computers off	**2/10/2006**	1348	82	67
computers off	2/13/2006	79	51	43
computers on with door closed	2/13/2006	82	313	96
computers on with door closed	2/14/2006	10	20	15
outside chamber, in Rm 289	2/14/2006	3054	4168	2170
(restart experiment with elevated ACH to control temperature)				
computers on with door closed	2/23/2006	56	75	29
computers on with door closed	2/27/2006	1	1	1
computers on with door closed	3/1/2006	4	2	7
outside chamber, in Rm 289	2/28/2006	765	1178	565

D.2 Particle Mass Determination of Printer Particle Emissions

Particles for mass determination were collected directly from the chamber onto 37 mm Teflon filters (Teflo®, Pall Corp.) at 19.6 lpm for 24 hours. No size selective inlets were used. Filters were pre-weighed using a Cahn 21 Automatic Electrobalance and stored in petri dishes until use. Duplicate samples were collected in parallel directly from the chamber on day two of the printer experiments. The filters were re-weighed on at least two separate occasions both before deployment and after recovery. 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. The duplicate samples differed by 7% and 17% for the large and medium laser printers, respectively. 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. Results are provided in the table below.

Table D.3 Particle mass results for phase I printer experiments

	filter mass (mg)	Filter and Particle mass (mg)	Particle mass (mg)	Sample Volume (m^3)	Conc. (µg/m3)
Large Laser Printers Day 2 Port A	6.140	6.214	0.074	28	2.64
Large Laser Printers Day 2 Port B	16.780	16.859	0.079	28	2.82
Medium Duty Laser Jets Day 2 Port A	10.167	10.200	0.033	28	1.18
Medium Duty Laser Jets Day 2 Port B	8.906	8.934	0.028	28	1.00

A subset of unused filters was weighed on several different occasions to evaluate measurement uncertainty and estimate the limit of detection for particle mass. The limit of quantification for particle mass is determined here as the 95% upper confidence limit on three times the standard deviation of replicate measurements for each of nine different filters. The measurements are shown below and the resulting LOQ for this study is 0.014 mg collected on the filter or a concentration of 0.5 μg/m^3. The percent coefficient of variation for weights collected on nine different filters measured on up to four different days ranged from 0.0% to 0.1% with a median value of 0.02%. The limit of particle mass determination estimated as the upper 95th percentile of the 10 determinations (three times the standard deviation of low level replicates) is 0.013 mg.

Table D.4 Evaluation of uncertainty and detection limit for particle mass determination

QA Samples	filter mass (mg)	3×STDEV
QA filter 1	6.141	
QA filter 1	6.139	0.0042
QA filter 2	15.690	
QA filter 2	15.688	0.0042
QA filter 3	13.421	
QA filter 3	13.417	0.0085
QA filter 4	4.171	
QA filter 4	4.167	0.0085
QA filter 5	9.757	
QA filter 5	9.760	0.0064
QA filter 6	3.413	
QA filter 6	3.412	
QA filter 6	3.411	
QA filter 6	3.421	
QA filter 6	3.416	0.012
QA filter 7	16.780	
QA filter 7	16.780	0.000
QA filter 8	9.740	
QA filter 8	9.742	
QA filter 8	9.739	0.0046
QA filter 9	12.482	
QA filter 9	12.492	
QA filter 9	12.483	
QA filter 9	12.492	
QA filter 9	12.491	0.015
QA filter 10	12.000	
QA filter 10	12.003	
QA filter 10	12.001	
QA filter 10	12.002	0.0039

D.3 Organic Carbon/Elemental Carbon Analysis of Printer Particle Emissions

Particles for EC/OC analysis were collected directly from the chamber onto quartz fiber filters (37 mm TissuQuartz®, Pall Corp.) at 19.6 lpm for 24 hours. Duplicate samples were collected in parallel through two different ports in the chamber (A and B). Particles for OC/EC determination were collected on day one of the experiment. Sample filters were packaged along with several blank filters and shipped overnight to Sunset Laboratories were they were used to determine elemental carbon and organic carbon content following NIOSH method 5040. The filters were cleaned prior to use per method 5040 by baking in a muffle furnace at 800 C for two hours. After cooling, the filters are carefully removed from furnace and transferred to labeled Petri dishes until use. The following table shows that the particles collected during the Phase I printer experiments were predominantly organic carbon.

Duplicate measurements ranged from 1% to 3% for the OC and TC determinations and between 12% and 27% for the lower EC determination.

D.5 Organic carbon (OC) / elemental carbon (EC) and total carbon (TC) results

Sample Identification	OC ($\mu g\ cm^{-2}$)	EC ($\mu g\ cm^{-2}$)	TC ($\mu g\ cm^{-2}$)	EC/TC ratio
Large Laser Printers Day 1 Port A	13.43 ± 0.87	0.28 ± 0.21	13.70 ± 0.99	0.02
Large Laser Printers Day 1 Port B	13.28 ± 0.86	0.24 ± 0.21	13.52 ± 0.98	0.02
Medium Duty LaserJet Day 1 Port A	10.34 ± 0.72	0.21 ± 0.21	10.55 ± 0.83	0.02
Medium Duty LaserJet Day 1 Port B	10.06 ± 0.70	0.16 ± 0.21	10.22 ± 0.81	0.02
Inkjet Printers Day 1 Port A	12.49 ± 0.82	1.19 ± 0.26	13.67 ± 0.98	0.09
Inkjet Printers Day 1 Port B	12.20 ± 0.81	1.06 ± 0.25	13.26 ± 0.96	0.08
Inkjet Printers Day 1 Port B (duplicate)	11.29 ± 0.76	0.76 ± 0.24	12.06 ± 0.90	0.06
Blank filter	0.56 ± 0.23	0.01 ± 0.20	0.58 ± 0.33	0.02
Blank filter	0.48 ± 0.22	0.04 ± 0.20	0.52 ± 0.33	0.07
Sucrose STD 52.58 µgTC	53.60 ± 2.88	0.13 ± 0.21	53.73 ± 2.99	0.00

Appendix E.

Bromine Screening Experiments Performed After Phase I

Appendix E. Bromine Screening Experiments Performed After Phase I

Presented in the table below are the results for the XRF assessment of bromine in several of the units tested during Phase I. Bromine response was primarily found in parts of the mouse for each unit tested but no clear pattern emerged to help with selection of units for testing in Phase II. Blank cells in the following table indicate no detectible levels of bromine. The highest bromine content was found in the computer peripherals, primarily the mouse but occasionally on parts of the monitors and on the top surface of two of the printers tested.

Table E.1 XRF assessment of bromine in several units tested during phase I

Unit/component or location	Br (ppm±stdev)
Compaq computer	
Element	
front of box on CD drive	621±11
front of box on main panel	56±8
Side panel on box - grey plastic material	
keyboard front (keys)	
keyboard back	113±8
mouse back	1149±17
side of mouse	
Samsung monitor used with Compaq computer	
upper edge	78±10
front top	90±9
lower edge	68±8
back	
back	
e-machine computer	
front panel on box	54±10
front panel on box	37±9
black plastic on side panel of box	58±9
side panel metallic material	
back of box metallic material	
back of keyboard	39±11
side of mouse	2302±22
back of mouse	652±15
side of mouse (same as above)	2326±23
side of mouse opposite of above	3380±31
side of speaker	68±9
back of speaker	47±10
monitor front edge	91±10
back of monitor	2095±23
back of monitor in second location	1784±22
electrical cables	

Table E.1 (continued)

Apple iMac	
front of computer	482±11
second location on front of computer	454±12
back of computer	126±8
second location on back of computer	208±8
back of keyboard	
back of mouse	3887±42
side of mouse	66±9
keyboard space bar	28±10
side of keyboard	302±9
Epson inkjet printer	
front	
back	
inside of printer	
Epson stylus inkjet printer	
front	
side	
Canon inkjet printer	
Top surface dark color	
top surface white	
top back dark color	
top back light color	
back of printer grey surface	
Lexmark inkjet printer/scanner	
top white surface	
top inside surface	155±11
paper tray	
front tray on inside of scanner area	5±2
bottom of printer	
HP LaserJet printer	
side	
front	
top	
HP LaserJet printer	
front	42±9
side	
top	966±16
back	69±10
back	

Appendix F.

Phase II SVOC Analytes and Analysis Methods

Appendix F. Phase II SVOC Analytes and Analysis Methods

This appendix summarizes analytical methods used in Phase II to determine target analyte concentrations for the SVOCs. Four classes of compounds were measured using three different analytical methods.

F.1 Polycyclic Aromatic Hydrocarbons (PAHs) and Phthalate Esters

PAHs (listed in following table) were measured using instrument conditions as described below.

Table F.1 List of target polycyclic aromatic hydrocarbons (PAHs)

Chemical
naphthalene
2-methylnaphthalene
1-methylnaphthalene
acenapthylene
acenaphthene
fluorene
phenanthrene
anthracene
fluoranthene
pyrene
benzo[a]anthracene
chrysene
benzo[b]Fluoranthene
benzo[k]fluoranthene
benzo[a]pyrene
perylene-d12
indeno[1,2,3-cd]pyrene
dibenz[a,h]anthracene
benzo[g,h,i]perylene

F.1.1 Gas chromatography conditions

The injection was made in a split/splitless mode with a ratio of 1:100 and a pressure pulse of 50 psi for 1.0 minute. The GC oven was held at 40°C for 1.0 min, followed by 15.0°C/min to 290°C, and hold for 1.0 min. The total run time was 18.67 minutes.

Table F.2 Gas chromatography conditions for phthalates and PAHs

Septa	BTO marathon
Liner	de-activated single taper with frit
Injection Temp.	300°C
Split/splitless	1:100, closed 1.0 min
Pulse	50 psi, 1.0 min
Carrier gas	He at 2.0 ml/min constant flow
Oven Temp.	40 °C, 1.00 min 15 °C/min to 290°C, hold 1.00 min.
Total run time	18.67 min.

F.1.2 Mass spectrometer conditions

The conditions for ion trap mass spectrometry used during Phase II are listed in the following table. Selective ion scanning was programmed to collect data for the analysis of PAHs.

Table F.3 Mass spectroscopy conditions for phthalates and PAHs

Ionization mode	Internal EI
Ion Trap Temp	200 °C
Transfer Line Temp.	280 °C
Manifold Temp.	80 °C
Emission current	20 μAmp
Multiplier Offset	0 V
Scan mode	Selective Ion Scanning (SIS)

A deuterated PAH analogue was used as an internal standard for each native PAH listed in the following table. Three deuterated PAHs (2-methylnaphthalene, *p*-terphenyl, and perylene) were used as recovery standards.

Table F.4 Retention times and mass ions for polycyclic aromatic hydrocarbons (PAHs)

PAH	*Retention time (min.)*	*m/z Quantitation Ion*
naphthalene	3.14	128
2-methylnaphthalene	4.24	141
1-methylnaphthalene	4.37	141
acenapthylene	5.52	152
acenaphthene	5.80	153
fluorene	6.58	165
phenanthrene	7.90	178
anthracene	8.04	178
fluoranthene	9.69	202
pyrene	9.98	202
p-terphenyl d14	10.49	244
benzo[a]anthracene	11.82	228
chrysene	11.86	228
benzo[b]fluoranthene	13.27	252
benzo[k]fluoranthene	13.31	252
benzo[a]pyrene	13.68	252
perylene d12	13.76	264
indeno[1,2,3-cd]pyrene	14.99	276
dibenz[a,h]anthracene	15.08	278
benzo[g,h,i]perylene	15.24	276

F.1.3 Brominated flame retardants (BFRs)

A selection of 10 polybrominated diphenyl ethers were measured. These are listed in the following table.

Table F.5 Target brominated flame retardants (BFRs)

Chemical	*Abbreviation*
2,2',4-Tribromodiphenylether	PBDE-17
2,4,4'-Tribromodiphenylether	PBDE-28
2,2',4,4'-Tetrabromodiphenylether	PBDE-47
2,3,4,4'-Tetrabromodiphenylether	PBDE-66
2,2',4,4',5-Pentabromodiphenylether	PBDE-99
2,2',4,4',6-Pentabromodiphenylether	PBDE-100
2,2',4,4',5,5'-Hexabromodiphenylether	PBDE-153
2,2',4,4',5,6'-Hexabromodiphenylether	PBDE-154
2,2',3,4,4',5',6-Heptabromodiphenylether	PBDE-183
Decabromodiphenylether	PBDE-209
^{13}C-Decabromodiphenylether	^{13}C-PBDE-209

F.1.4 Gas chromatography conditions

The injection was made in a splitless mode with a ratio of 1:100 and a pressure pulse of 45 psi for 1.5 minutes. The GC oven was held at 80°C for 1.5 min, followed by 12.5°C/min to 250°C, 25°C/min to 300°C, and hold at 300°C for 5.33 min. The total run time was 23.0 minutes.

Table F.6 Gas chromatography conditions for BFRs

Septa	BTO marathon
Liner	de-activated single taper with frit
Injection Temp.	270°C
Split/splitless	1:100, closed 1.5 min
Pulse	45 psi, 1.6 min
Carrier gas	He at 2.0 ml/min constant flow
Oven Temp.	80°C, 1.50 min
	12°C/min to 250°C, no hold
	25°C/min to 300°C, hold 5.33 min.
Total run time	23.00 min.

F.1.5 Mass spectrometer conditions

The conditions for ion trap mass spectrometry are listed in the next table. Following this is a table that lists the retention times and *m*/*z* ions used to measure the amount of BFRs. A suite of 17 deuterated PAHs were used as internal standards and an additional two deuterated PAHs were used as recovery standards. Decabrominated diphenyl ether was tracked using a carbon-13 labeled analogue.

Table F.7 Mass spectroscopy conditions for BFRs

Ionization mode	Internal EI
Ion Trap Temp	150°C
Transfer Line Temp.	280°C
Manifold Temp.	80°C
Emission current	20 μAmp
Multiplier Offset	+100V
Scan mode	Selective Ion Scanning (SIS)

Table F.8 Retention times and mass ions for brominated flame retardants (BFRs)

Congener	*Retention time (min.)*	*m/z Quantitation Ion*
PBDE-17	9.82	407
PBDE-28	10.11	407
PBDE-47	11.76	485, 325
PBDE-66	12.02	326, 485
PBDE-99	12.93	564, 403
PBDE-100	13.32	404, 564
PBDE-153	14.23	644, 483
PBDE-154	14.75	484, 643
PBDE-183	15.98	564, 723
PBDE-209	19.71	800, 959
^{13}C-PBDE-209	19.71	811, 971

F.2 Organophosphates

The organophosphate (OP) analytes are listed in the next table along with GC retention times. Standards were prepared by weighing an appropriate amount of each OP into a 10 mL volumetric cylinder and diluting to final volume with heptane. The resulting stock solutions are serially diluted to concentrations of 13.2, 33, 165, and 825 ng/mL providing a 4-point calibration curve. Standards are from Sigma-Aldrich. Dilutions from the stock solution are prepared for each 2-week period of analysis, and a full set of standards is run at least once on each day of analysis. All solutions are stored at –20°C. (note, this method is being modified to use an internal standard and relative response factors for quantification).

The inlet and detector temperatures are 250°C and 300°C, respectively. The initial oven temperature is held at 80°C for 1 minute, and then increased by 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 is maintained at approximately 30 milliamps for the analysis.

Table F.9 Retention times for organophosphates

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

Appendix G.

Particle Size Evaluation for a Subset of Printers in the Phase II Experiments

Appendix G. Particle Size Evaluation for a Subset of Printers in the Phase II Experiments

Size resolved particle number concentration data was collected for a subset of printer emissions experiments. The size resolved particle number concentration was measured using a Lasair model 1003 optical particle counter (OPC). The OPC measures particle number concentration in eight size fractions and was configured to report cumulative particle number concentration above 0.1, 0.2, 0.3, 0.4, 0.5, 0.7, 1.0 and 2.0 μm diameter with a maximum concentration of 1.4 x 10^4 cm^{-3}. The results in the following figures consistently show that the particles emitted from printers are predominantly less than 100 nm diameter. Only the > 0.1 μm cumulative channel is compared to the > 7 nm results from the condensation particle counter. The y-axis is displayed in log scale. The results show that the particles emitted during printing are between 7 nm and 100 nm.

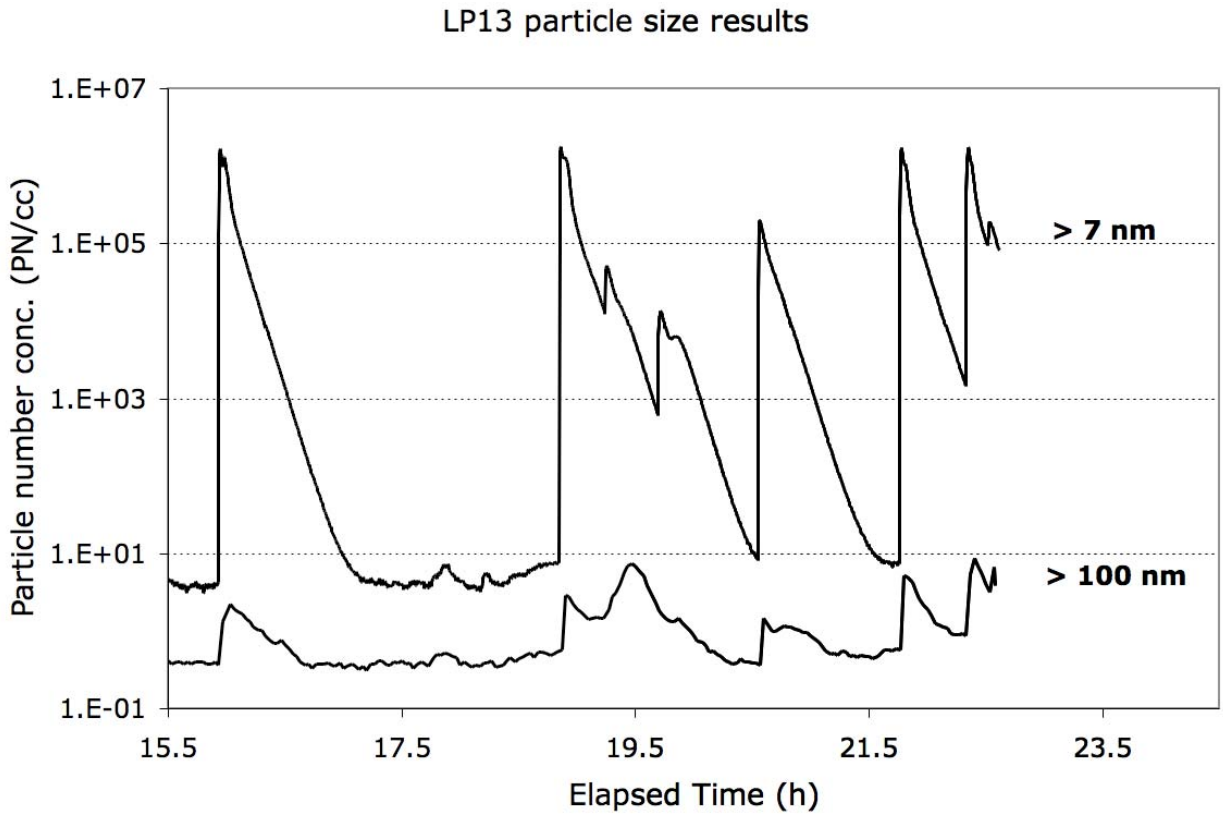


Figure G.1. The LJ13 printer was an older printer (production date March 1996) that was used in the initial work aimed at identifying relevant print cycles and experimental design for the base-line emission measurements but this printer was not included in the final set of printers that were tested because of problems with the paper feed mechanism that developed after this run was completed.

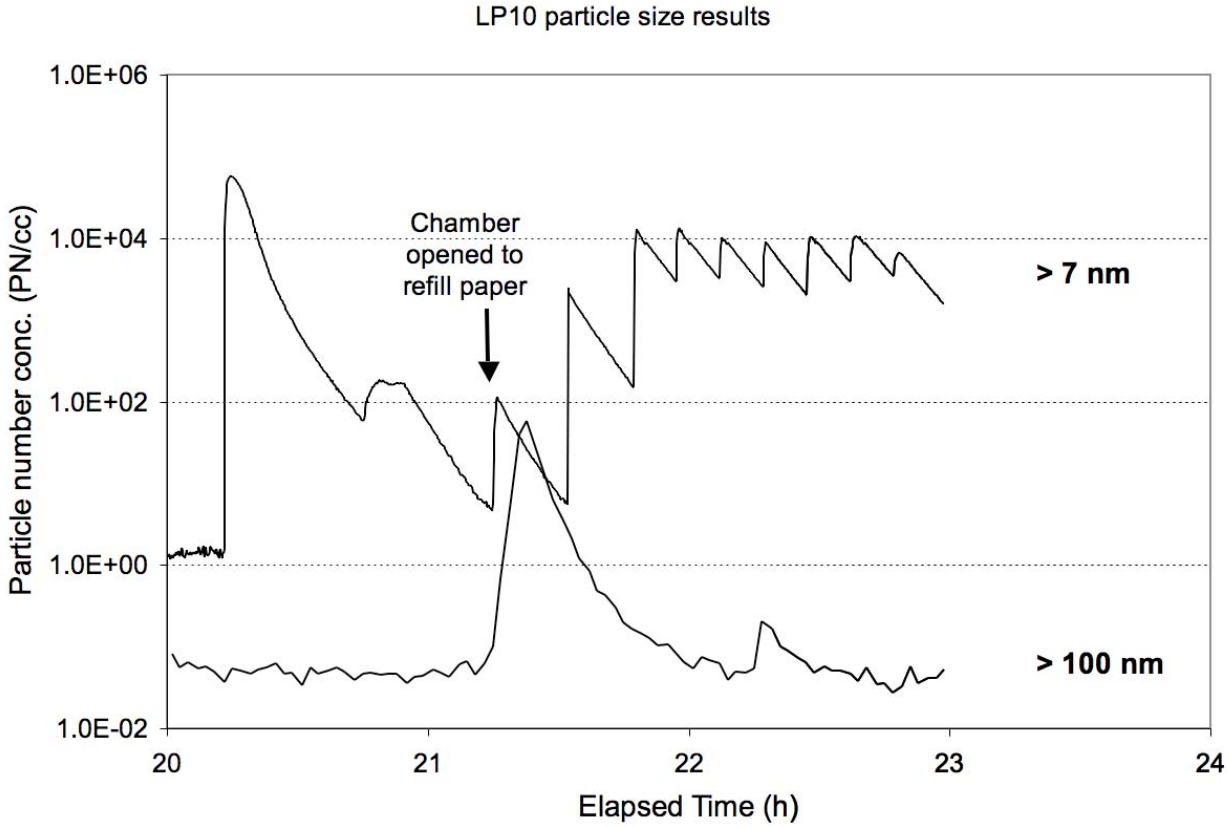


Figure G.2. The increase in particle number concentration for the > 100 nm size fraction shown in this figure occurred when the chamber door was opened to refill the paper tray.

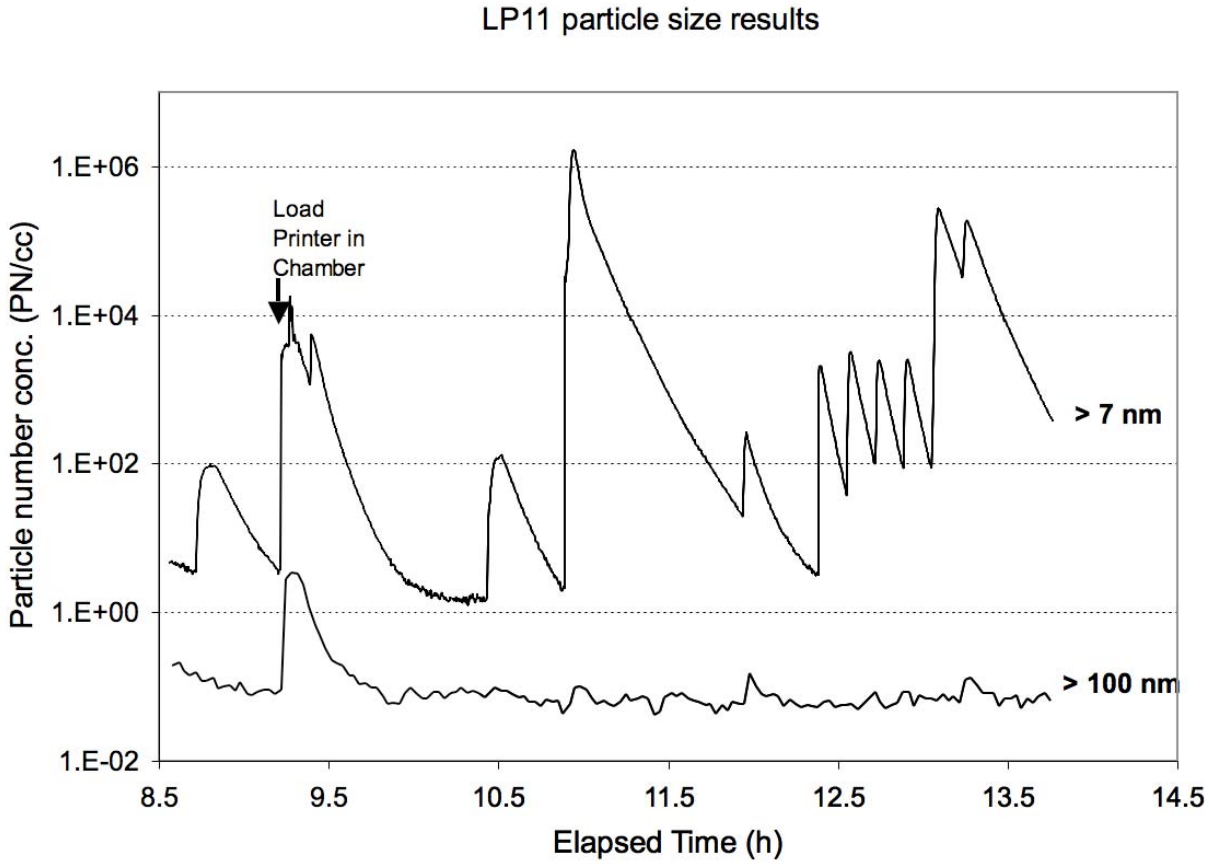


Figure G.3. In this case, the elevated particle number concentration for the > 100 nm size fraction occurred when the printer was initially loaded in the chamber. The remainder of the trace shows insignificant particle number concentrations for particles greater than 100 nm in diameter.

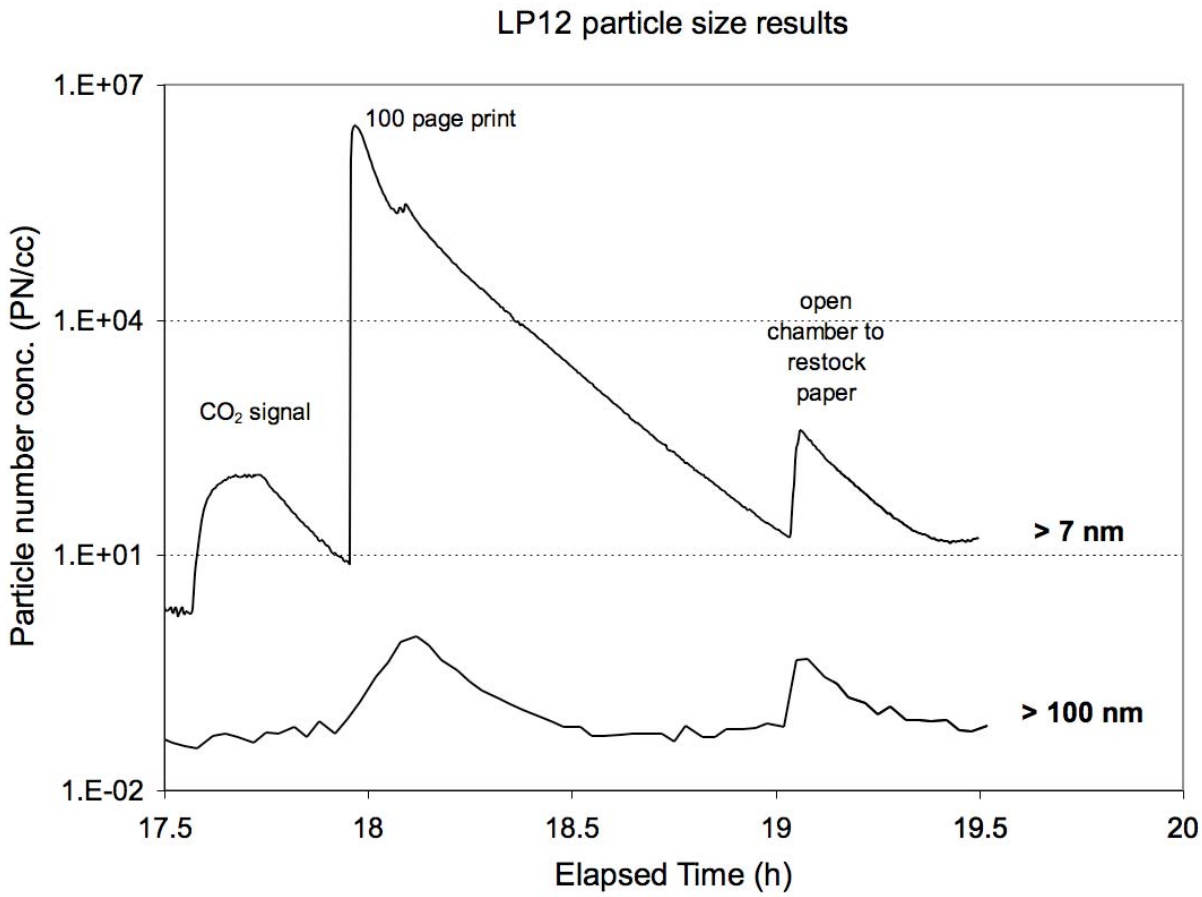


Figure G.4. The initial increase in particle number concentration for the > 7 nm fraction is associated with the CO_2 source that was used to measure ACH in the chamber. There is a slight increase in particles greater than 100 nm in diameter during the 100 page print job but at the maximum concentration, the number of particle in the fine fraction were only ~ 1 particle/cc compared to > 2×10^5 particles/cc in the ultra-fine fraction.

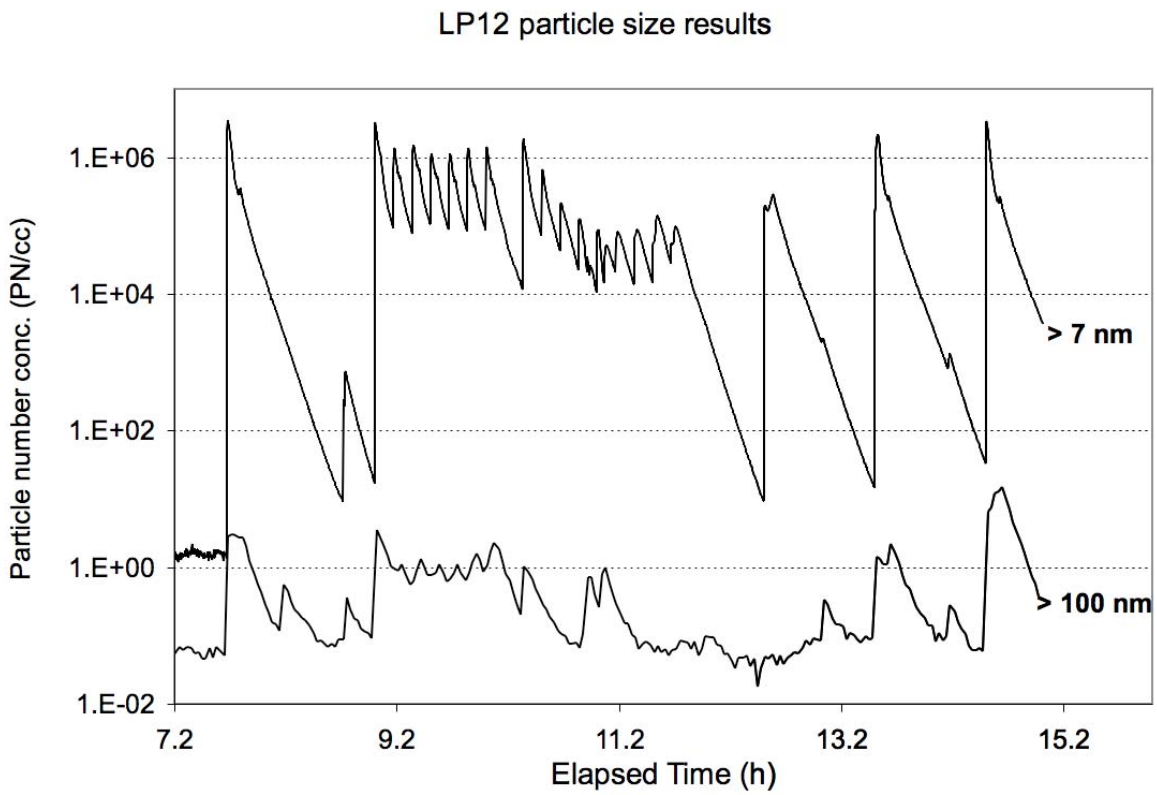


Figure G.5. Same printer as in Figure J.4, but including a series of print jobs with different page counts.

Appendix H.

Background Concentrations in the Small Chamber During Phase II Experiments

Appendix H. Background Concentrations in the Small Chamber During Phase II Experiments

Background concentrations (with no device present) were measured in the 395-L chamber for all VOC and SVOC analytes during both the computer and printer experiments. The results of these measurements are provided in the following tables.

Background Concentrations During Phase II Computer Experiments (µg/m^3)			
	average	stdev	(n=)
Benzene	0.56	0.16	11
Hexamethylcyclotrisiloxane	1.90	1.15	11
Octamethylcyclotetrasiloxane	0.35	0.17	11
Decamethylcylopentasiloxane	0.58	0.65	11
Dodecamethylcyclohexasiloxane	0.71	0.29	11
Tetradecamethylcycloheptasiloxane	0.24	0.16	11
Hexadecamethylcyclooctasiloxane	0.56	0.34	11
Toluene	1.15	0.56	11
Ethylbenzene	0.24	0.13	11
m/p-Xylene	0.64	0.33	11
o-Xylene	0.26	0.13	11
Styrene	0.09	0.06	11
Propylbenzene,	0.05	0.03	11
1,3,5-Trimethyl-benzene	0.06	0.03	11
2-Methylpropylbenzene	0.02	0.01	11
1,2,3-Trimethyl-benzene	0.10	0.12	11
Benzaldehyde	1.26	0.53	11
1,3-Diethyl-benzene	0.01	0.01	9
Butyl-benzene	0.02	0.01	11
2-Ethyl-1-hexanol	0.67	0.96	11
1,2,3,4-Tetramethylbenzene	0.01	0.01	10
1,2,3,5-Tetramethylbenzene	0.02	0.01	11
Dodecane	0.19	0.17	11
Acetophenone	0.94	0.52	11
Phenol	0.62	0.30	11
Naphthalene	0.05	0.03	11
Tetradecane	0.12	0.07	10
2-Methyl-naphthalene	0.01	0.01	10
1-Methyl-naphthalene	0.01	0.01	11
Hexadecane	0.13	0.09	11
ButylatedHydroxytoluene	0.02	0.01	11
Diethylphthalate	0.24	0.48	11
Dibutylphthalate	0.15	0.24	11

Background During Phase II Printer Experiments (μg/m^3)

	Average	stdev	n=
Benzene	0.58	0.34	6
Hexamethylcyclotrisiloxane	2.71	0.95	6
Octamethylcyclotetrasiloxane	0.43	0.12	6
Decamethylcyclopentasiloxane	0.18	0.07	6
Toluene	0.12	0.04	6
Ethylbenzene	0.01	0.01	6
m/p-Xylene	0.02	0.01	6
o-Xylene	0.00		6
Styrene	0.02	0.01	6
Propyl-benzene,	0.00		6
1,3,5-trimethyl-benzene	0.00		6
(2-methylpropyl)-benzene	0.00		6
1,2,3-trimethyl-benzene	0.01	0.02	6
Benzaldehyde	0.11	0.02	6
1,3-diethyl-benzene	0.00		6
Butyl-benzene	0.00		6
2-Ethyl-1-Hexanol	0.20	0.12	6
1,2,3,4-tetramethyl-benzene	0.00		6
1,2,3,5-tetramethyl-benzene	0.00		6
Dodecane	0.15	0.25	6
Acetophenone	0.09	0.03	6
Phenol	0.10	0.03	6
Naphthalene	0.01	0.02	6
Tetradecane	0.04	0.05	6
2-methyl-naphthalene	0.00		6
1-Methyl-naphthalene	0.00		6
Hexadecane	0.02	0.01	6
Butylated Hydroxytoluene	0.01	0.01	6
Diethyl Phthalate	0.05	0.07	6
Dibutyl phthalate	0.02	0.01	6
Hexanal	0.12	0.07	6
α-Pinene	0.00		6
β-Pinene	0.00		6
3-Carene	0.00		6
Dimethyl methylphosphonate	0.00		6
D-Limonene	0.00		6
Octanal	0.79	0.61	6
Nonanal	2.00	1.43	6
Tridecane	0.28	0.33	6
Pentadecane	0.03	0.03	6
TMPD-MIB	0.00	0.01	6
TMPD-DIB as Texanol	0.02	0.03	6
1-Hexadecanol	0.15		6

Appendix I.

Printer-Specific Emissions Rates for VOCs

Appendix I. Printer-Specific Emissions Rates for VOCs

The following tables provide details on the measured baseline emission rates for each chemical and printer tested. The pages printed during determination of active print emission rates are also listed for each printer. For the idle phase, the emission rate is in micrograms of chemical per hour while the active phase emission rate is in micrograms per hour of active printing. This value can be converted to emission from a printing event or emission per page printed using the print speed published in each printers specifications. For example, printer *LP12* has a print speed of up to 21 pages per minute so the active phase emission rate would be divided by (21 pages/minute × 60 minutes/hour) to convert to emission per page printed.

Unit-specific printer emission rates (µg/h/unit) during idle or active periods

Pages printed	100			150		
Printer:	**LP06**			**LP07**		
	Idle (pre-print)	Active print	Stdev (active)	Idle (pre-print)	Active print	Stdev (active)
Benzene						
Cyclotrisiloxane, hexamethyl-	10.28	143.22	57.99	9.06	175.95	14.37
Toluene	0.40	11.97	0.38	0.22	4.17	0.31
Hexanal	9.11	698.09	9.28	3.20	511.45	14.78
Ethylbenzene	0.15	24.05	0.78	0.09	16.71	0.25
p-Xylene	0.15	21.23	0.09	0.15	15.69	0.07
1R-.alpha.-Pinene	0.43	6.88	0.32			
o-Xylene	0.05	28.59	0.89	0.11	20.34	0.34
Styrene	0.41	90.32	3.90	0.20	53.07	1.98
Cyclotetrasiloxane, octamethyl-	2.67	60.34	6.79	2.43	50.95	4.74
Benzene, propyl-						
3-Carene	0.00	8.52	1.34			
Benzene, (2-methylpropyl)-						
D-Limonene	0.16	8.54	0.92	0.00	5.24	0.52
Benzene, 1,2,3-trimethyl-						
Benzaldehyde	1.96	170.88	2.84	2.04	108.11	3.30
Octanal	3.05	107.09	13.78	2.16	91.20	2.37
Benzene, 1,3-diethyl-						
Benzene, butyl-						
Cyclopentasiloxane, decamethyl-	2.73	80.41	10.91	1.81	57.65	9.07
1-Hexanol, 2-ethyl-	0.68	35.06	5.53	0.61	33.58	1.35
Nonanal	5.09	115.89	50.26	3.56	216.27	1.95
Dodecane	0.59	74.68	2.74	0.34	31.53	0.01
Acetophenone	1.75	111.60	0.28	1.66	69.58	3.32
Phenol	4.69	135.64	21.15	3.59	108.81	14.05
Tridecane	0.94	179.86	11.83	0.51	98.84	3.00
Tetradecane	3.15	1130.8	94.49	2.41	749.16	44.65
Pentadecane	0.97	538.73	52.88	0.78	387.17	24.74
Texol_01						
Hexadecane	0.23	56.75	6.33	0.17	45.83	2.66
Butylated hydroxytoluene				0.04	1.57	0.19
TXIB	0.28	12.04	3.43			
Diethyl Phthalate				0.32	5.09	0.02
1-Hexadecanol	0.00	8.29	0.47			
Dibutyl phthalate	0.43	7.34	0.50	0.25	7.01	1.13

continued

Pages printed	150			100		
Printer:	**LP08**			**LP09**		
	Idle (pre-print)	Active print	Stdev (active)	Idle (pre-print)	Active print	Stdev (active)
Benzene	0.95	4.36	3.04	1.12	6.91	1.84
Cyclotrisiloxane, hexamethyl-	20.84	6.29	1.77	10.92	212.66	65.10
Toluene	0.24	229.58	22.87	1.04	11.45	3.50
Hexanal	1.01	75.90	9.94	0.00	170.55	42.47
Ethylbenzene	0.27	216.46	20.36			
p-Xylene	0.35	382.10	36.27			
1R-.alpha.-Pinene						
o-Xylene	0.33	170.14	16.11			
Styrene	0.35	23.10	8.40			
Cyclotetrasiloxane, octamethyl-	3.23	7.79	0.78	2.14	37.53	10.04
Benzene, propyl-	0.08	7.34	0.66			
3-Carene						
Benzene, (2-methylpropyl)-						
D-Limonene						
Benzene, 1,2,3-trimethyl-	0.41	135.19	10.50			
Benzaldehyde	1.15	98.26	3.83	0.68	15.72	3.70
Octanal	1.46	21.07	4.98			
Benzene, 1,3-diethyl-						
Benzene, butyl-						
Cyclopentasiloxane, decamethyl-	1.22	89.22	16.87	3.16	37.91	6.85
1-Hexanol, 2-ethyl-	0.20	209.72	11.61	0.98	40.03	5.08
Nonanal	1.54	35.64	2.77	1.08	247.34	42.20
Dodecane	0.45	82.28	6.78	0.00	6.85	1.15
Acetophenone	0.95	42.27	9.01	0.52	9.11	2.13
Phenol	1.51	98.74	4.60	1.21	27.92	8.34
Tridecane	0.44	590.84	21.81	0.00	34.99	6.14
Tetradecane	0.62	252.45	11.47	0.00	217.06	46.22
Pentadecane	0.38	8.31	2.17	0.00	85.04	18.75
Texol_01	0.23	20.99	1.27			
Hexadecane				0.00	9.15	2.79
Butylated hydroxytoluene				0.00	17.10	4.80
TXIB						
Diethyl Phthalate						
1-Hexadecanol						
Dibutyl phthalate						

continued

Pages printed	200			100		
Printer:	**LP10**			**LP11**		
	Idle (pre-print)	Active print	Stdev (active)	Idle (pre-print)	Active print	Stdev (active)
Benzene						
Cyclotrisiloxane, hexamethyl-	10.67	33.65	8.51	8.70	66.04	5.05
Toluene	0.69	59.80	0.33	0.92	2.66	2.40
Hexanal	2.83	125.44	4.30	2.59	306.34	5.01
Ethylbenzene	0.36	132.15	2.84	0.29	5.84	0.57
p-Xylene	0.35	103.37	2.15	0.33	19.93	0.25
1R-.alpha.-Pinene	0.00	2.65	0.05	0.05	8.69	0.26
o-Xylene	0.14	81.45	1.89	0.09	12.65	0.40
Styrene	0.36	146.89	2.99	0.82	36.26	2.70
Cyclotetrasiloxane, octamethyl-	1.77	12.26	0.85	3.23	71.46	4.13
Benzene, propyl-				0.03	5.78	0.32
3-Carene						
Benzene, (2-methylpropyl)-				0.00	4.84	0.06
D-Limonene	1.54	234.54	6.05	0.29	27.83	0.97
Benzene, 1,2,3-trimethyl-						
Benzaldehyde	0.39	82.08	1.23	1.11	56.62	1.25
Octanal	1.53	123.02	1.32	16.05	107.69	85.10
Benzene, 1,3-diethyl-				0.18	96.73	3.61
Benzene, butyl-				0.09	6.68	0.03
Cyclopentasiloxane, decamethyl-	0.52	21.24	0.11	3.00	115.31	5.90
1-Hexanol, 2-ethyl-	0.22	25.79	1.01			
Nonanal	2.42	345.04	8.14			
Dodecane	0.26	47.07	0.25	0.00	26.87	0.61
Acetophenone	0.35	42.47	1.10	0.61	6.51	0.37
Phenol	1.56	30.74	2.30	1.15	35.55	5.14
Tridecane	0.45	5.60	2.60			
Tetradecane	0.31	291.64	13.87	1.38	484.87	24.76
Pentadecane	0.17	115.50	5.79	0.84	189.60	13.70
Texol_01	0.00	9.43	0.66			
Hexadecane	0.07	17.33	1.00	0.27	31.35	2.23
Butylated hydroxytoluene						
TXIB	0.08	6.39	0.57	0.86	18.51	2.48
Diethyl Phthalate	0.14	2.31	0.17			
1-Hexadecanol	0.00	2.77	1.39			
Dibutyl phthalate						

continued

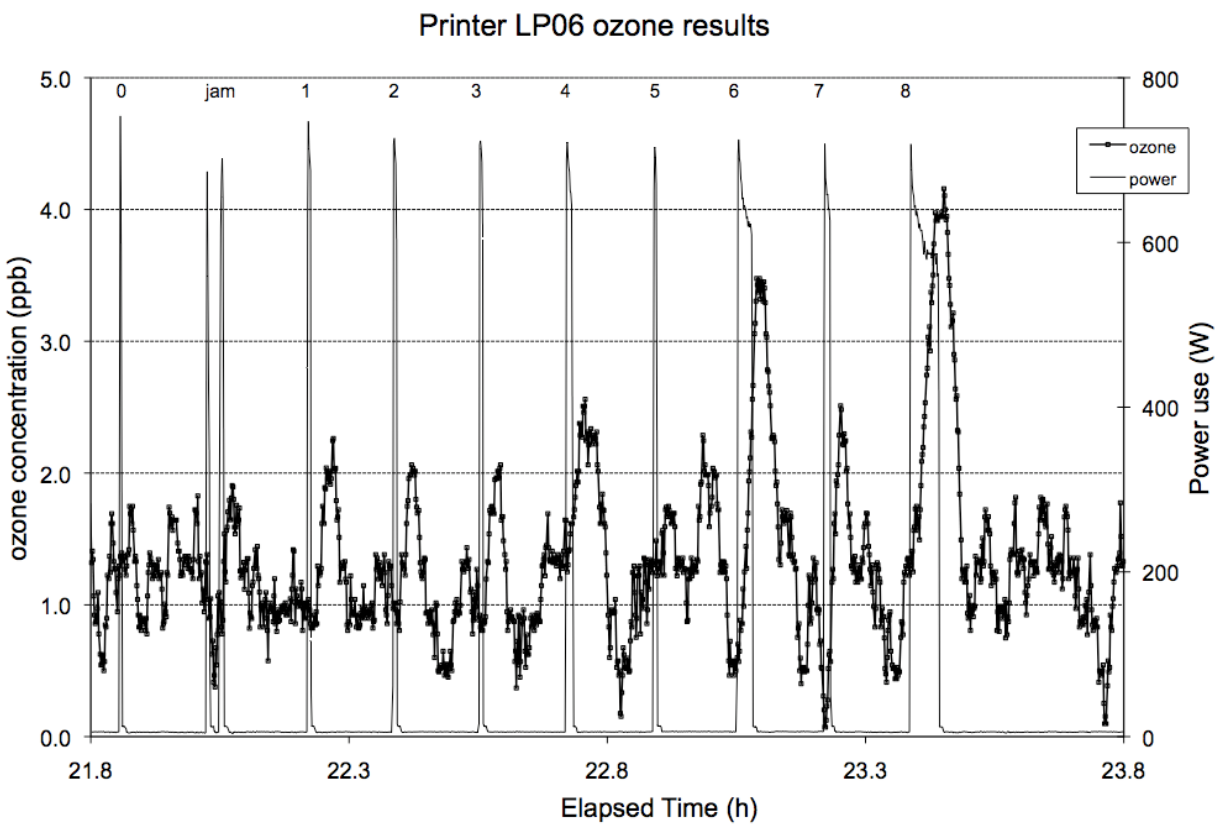
Pages printed	100			38		
Printer:	**LP12**			**IJ06**		
	Idle (pre-print)	Active print	Stdev (active)	Idle (pre-print)	Active print	Stdev (active)
Benzene						
Cyclotrisiloxane, hexamethyl-						
Toluene	30.37	312.94	43.08	12.27	29.22	10.58
Hexanal	3.93	70.75	0.17	0.38	0.30	0.30
Ethylbenzene	2.88	513.63	8.65	1.31	2.99	1.03
p-Xylene	0.59	27.33	0.67	0.11	0.00	0.08
1R-.alpha.-Pinene	1.38	70.86	1.43			
o-Xylene						
Styrene	0.63	37.89	0.84			
Cyclotetrasiloxane, octamethyl-	1.96	130.20	3.30	1.36	1.24	0.35
Benzene, propyl-	20.78	577.54	2.06	2.23	4.57	1.31
3-Carene						
Benzene, (2-methylpropyl)-						
D-Limonene						
Benzene, 1,2,3-trimethyl-						
Benzaldehyde						
Octanal	1.06	64.97	0.12	1.24	1.75	0.51
Benzene, 1,3-diethyl-	21.11	248.31	69.86			
Benzene, butyl-	0.77	112.52	2.78			
Cyclopentasiloxane, decamethyl-						
1-Hexanol, 2-ethyl-	6.67	390.07	6.28	0.87	1.87	0.56
Nonanal	3.22	55.81	11.76	2.26	2.11	0.04
Dodecane						
Acetophenone	0.00	29.45	0.48			
Phenol	0.47	12.57	0.71	1.93	2.18	0.57
Tridecane	0.52	9.56	0.54	3.12	3.19	0.89
Tetradecane	0.00	15.62	0.32			
Pentadecane	1.28	596.72	36.57	1.51	1.09	0.26
Texol_01	0.49	198.23	12.47	2.41	1.73	0.28
Hexadecane						
Butylated hydroxytoluene	0.12	31.25	1.43	2.40	1.74	0.40
TXIB						
Diethyl Phthalate						
1-Hexadecanol						
Dibutyl phthalate						

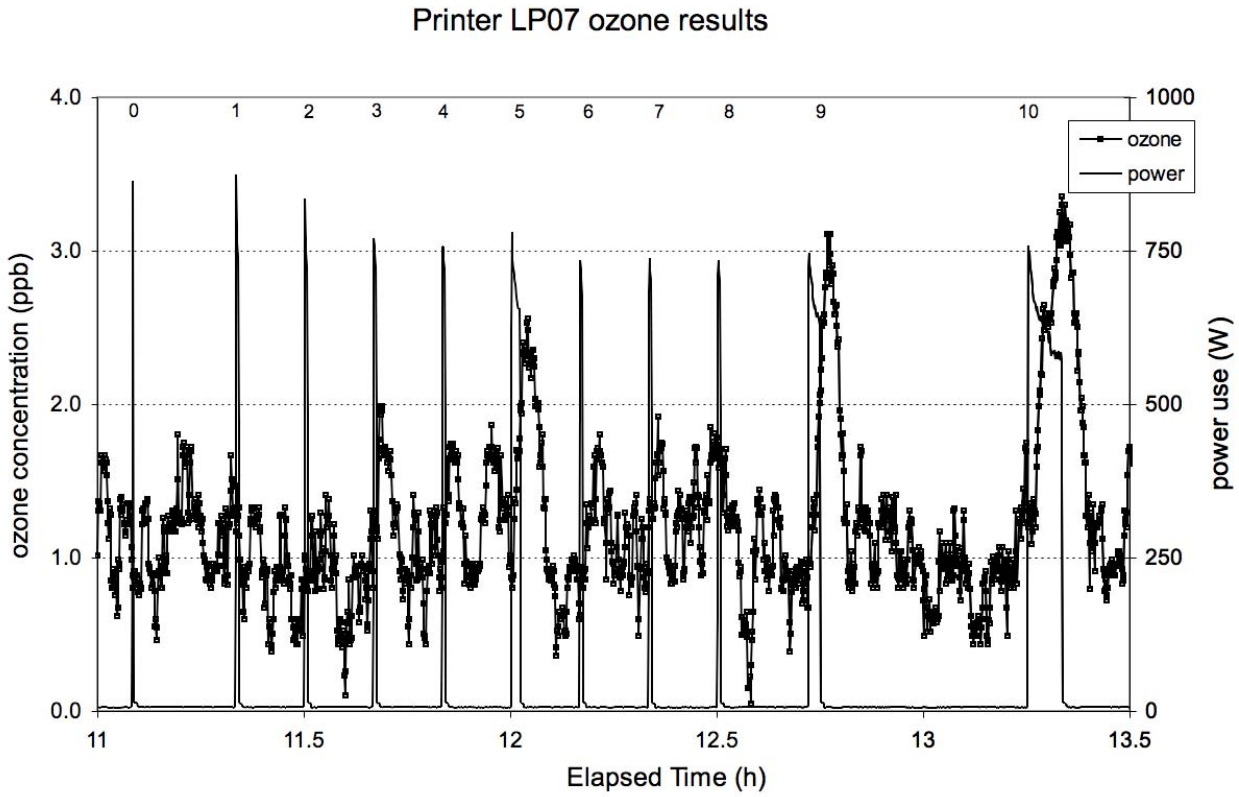
Appendix J.

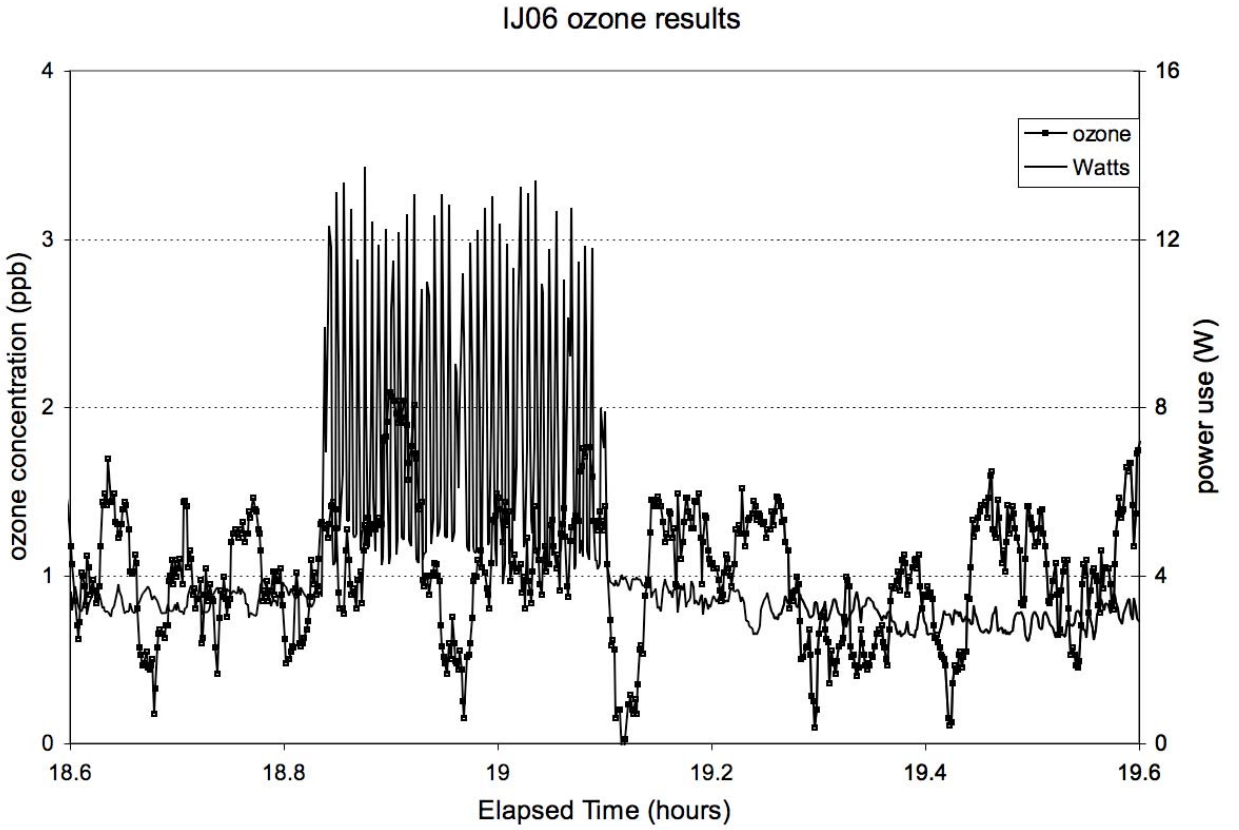
Ozone Emission Data for Individual Printers in Phase II Experiments

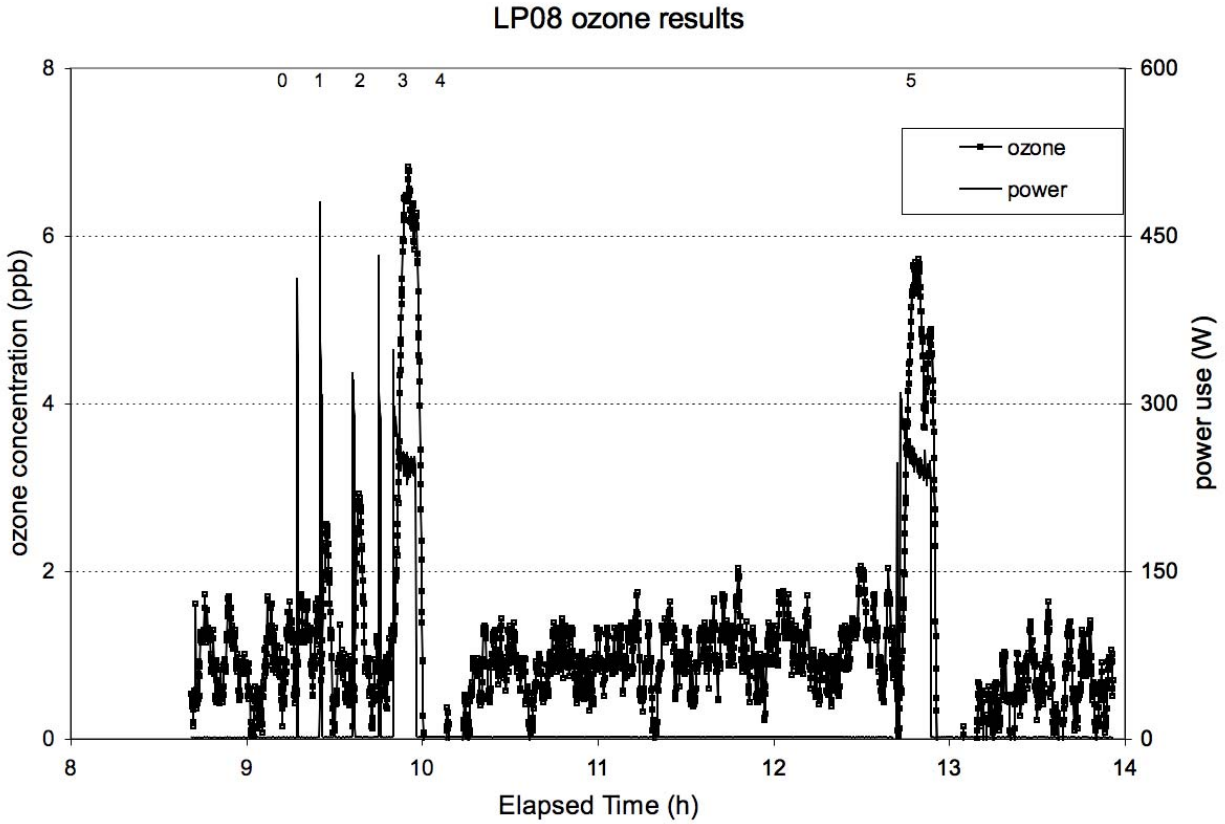
Appendix J. Ozone Emission Data for Individual Printers in Phase II Experiments

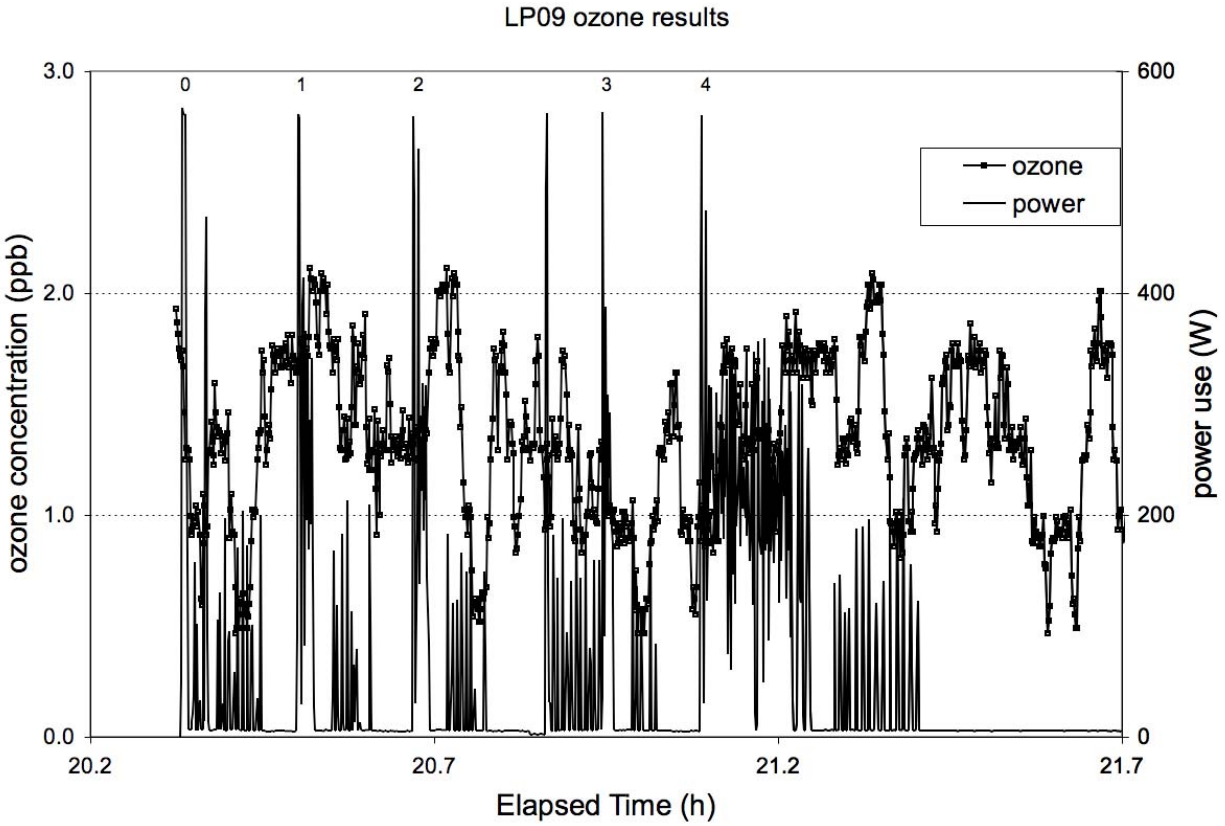
The following figures show the ozone concentration measured in the chamber during the baseline printer emissions experiments. The numbers shown across the top of each figure coincide with the print job number listed in the detailed particle emission tables for each printer in Appendix K. For a given printer and print job, ozone emissions were characterized as non-detect if the concentration during printing was indistinguishable from the baseline, trace if the concentration during printing was distinguishable but was less than three times the background in the chamber, and an emission rate was calculated if the concentration during printing was greater than three times the background ozone concentration. The figures are presented in the same order in Appendix K.

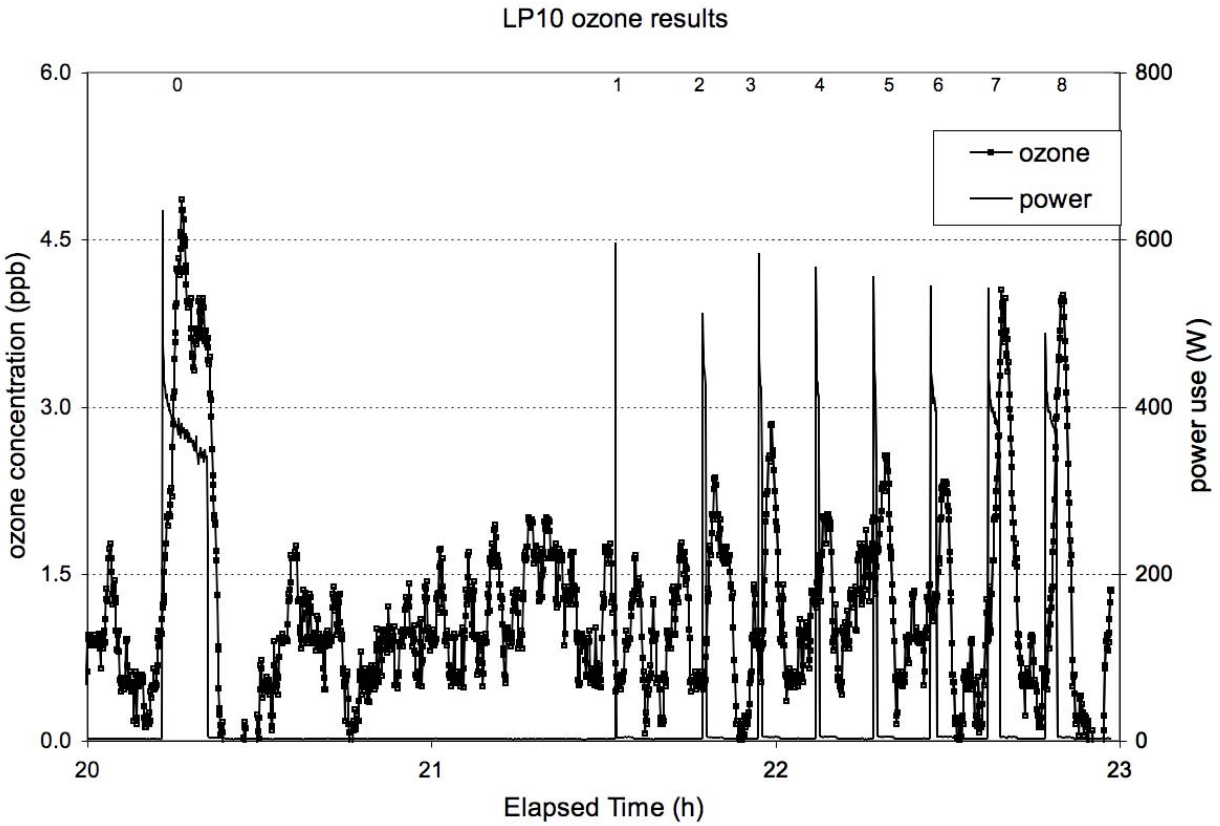


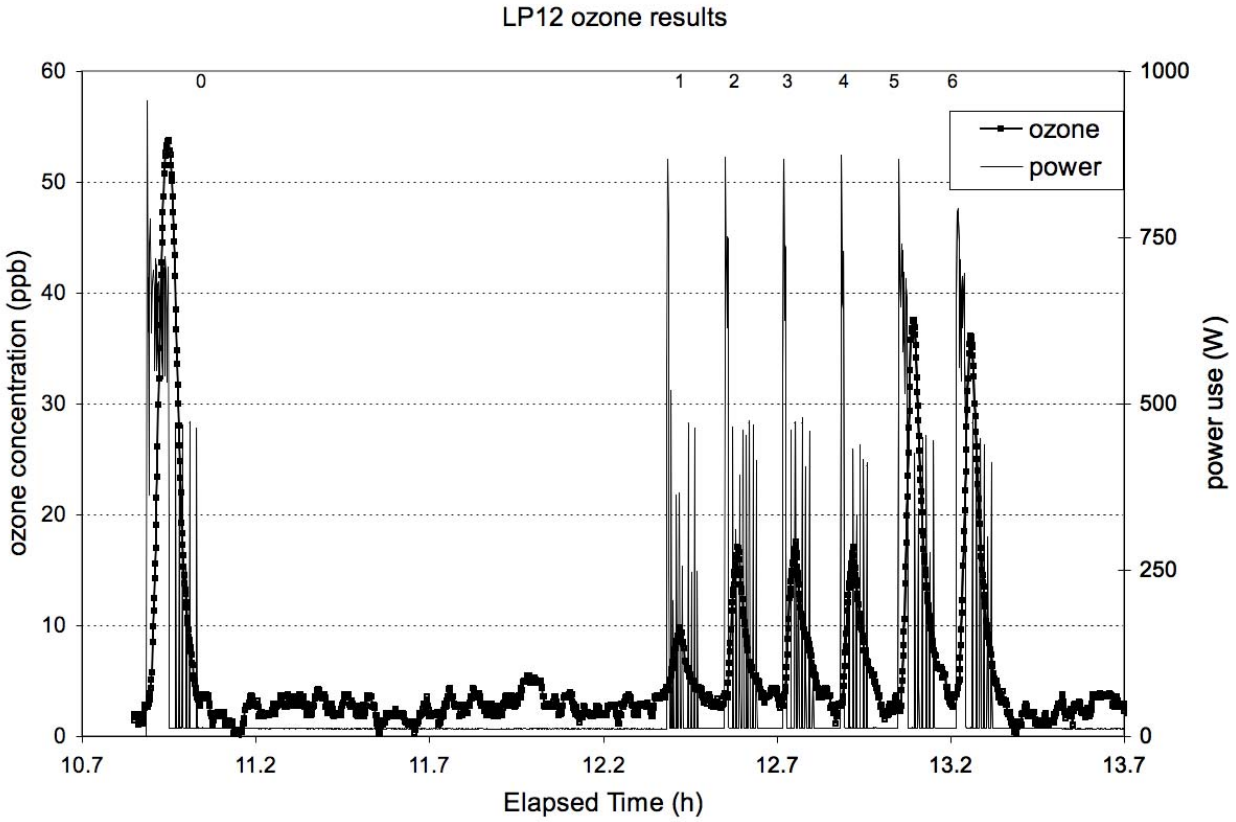

Printer LP07 ozone results
ozone concentration (ppb)
power use (W)
Elapsed Time (h)
ozone
power
0
1
2
3
4
5
6
7
8
9
10
4.0
3.0
2.0
1.0
0.0
1000
750
500
250
0
11
11.5
12
12.5
13
13.5


IJ06 ozone results
ozone concentration (ppb)
power use (W)
Elapsed Time (hours)
ozone
Watts
4
3
2
1
0
16
12
8
4
0
18.6
18.8
19
19.2
19.4
19.6


LP08 ozone results
0
1
2
3
4
5
ozone
power
ozone concentration (ppb)
power use (W)
Elapsed Time (h)
8
6
4
2
0
600
450
300
150
0
8
9
10
11
12
13
14


LP09 ozone results
0
1
2
3
4
ozone
power
ozone concentration (ppb)
power use (W)
Elapsed Time (h)
3.0
2.0
1.0
0.0
600
400
200
0
20.2
20.7
21.2
21.7


LP10 ozone results
ozone concentration (ppb)
power use (W)
Elapsed Time (h)
ozone
power
0
1
2
3
4
5
6
7
8
6.0
4.5
3.0
1.5
0.0
800
600
400
200
0
20
21
22
23


LP12 ozone results
ozone concentration (ppb)
power use (W)
Elapsed Time (h)
ozone
power
0
1
2
3
4
5
6
60
50
40
30
20
10
0
1000
750
500
250
0
10.7
11.2
11.7
12.2
12.7
13.2
13.7

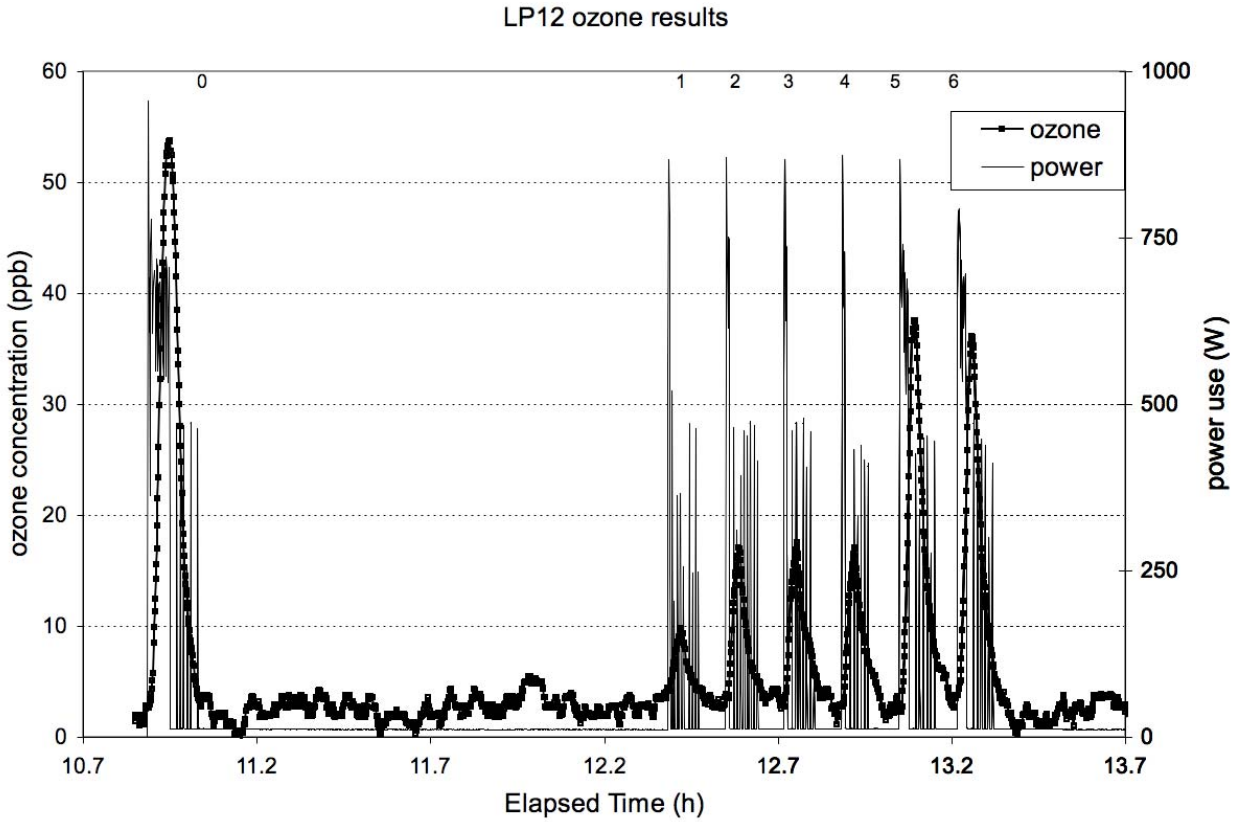


Table J.1 Summary of ozone emissions from printers

Printer	Ozone removal rate in chamber h^{-1}	Emission rate μg/h active printing
LP06	n/a	Trace
HP07	n/a	Trace
IJ06	n/a	N.D.
LP08	n/a	Trace
LP09	n/a	N.D.
LP10	n/a	Trace
LP11	32.6 ± 5	583 ± 111
LP12	23 ± 0.4	1750 ± 92

Appendix K.

Detailed Particle Emission Data for Individual Printers in Phase II Experiments

Appendix K. Detailed Particle Emission Data for Individual Printers in Phase II Experiments

The following tables and figures summarize the particle number concentration (particles greater than 7 nm in diameter) measurements collected during each baseline emission experiment for printers. Each experiment consisted of several print jobs with differing page counts. Emission rates were estimated for each print job and summary statistics were calculated for all prints excluding cold-start prints. The figures include a plot of the power usage and particle number concentration during the experiment. The individual print jobs in the table are identified by number across the top of each figure.

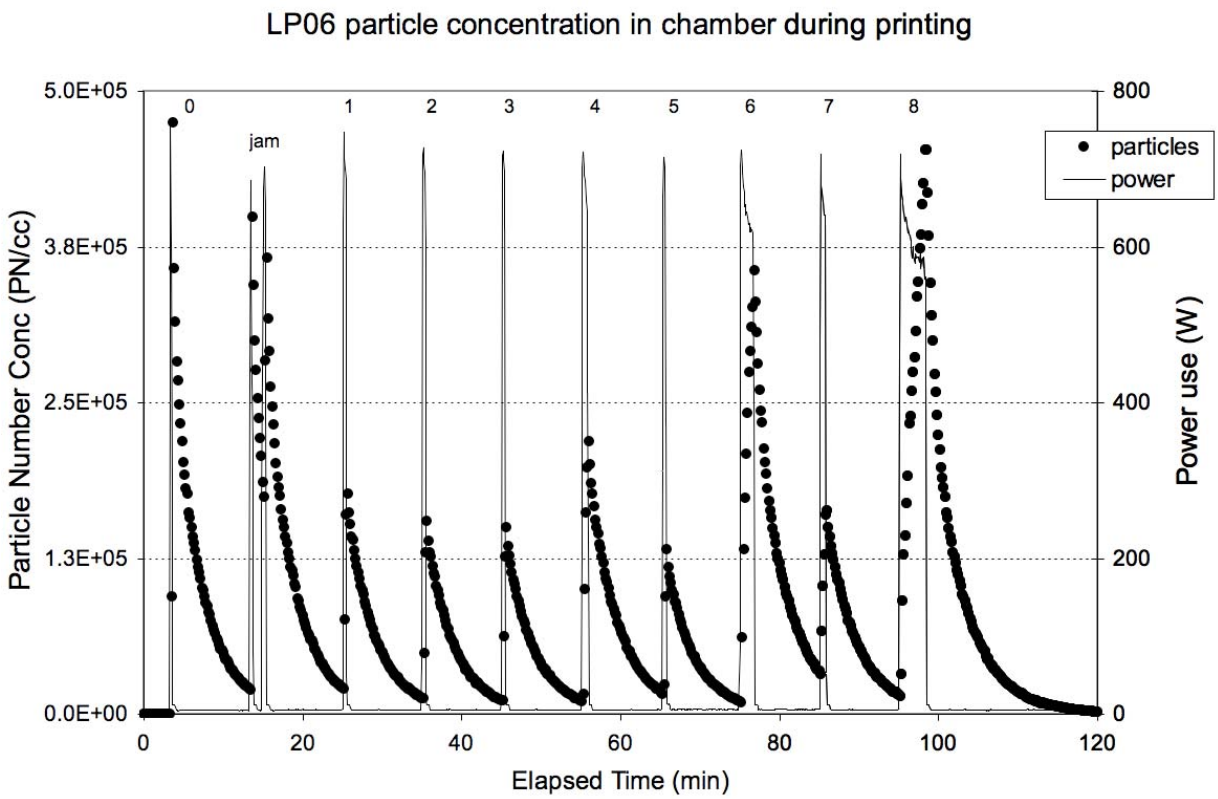
The method detection limit for the particle emission estimates was determined from the background emission rates during times when the chamber was empty and purged prior to or between prints. Slight variation in the particle number concentration (particles/cc) detected by the analyzer is magnified when the concentration is scaled up to the volume of the chamber. For example, at very low particle concentrations in the chamber, a change of 1 PN/cc during a 10 second time step is not unusual. When this change in concentrations is extrapolated to the full chamber volume, the apparent change in particle inventory in the chamber is on the order of 4×10^5 particles. If this increase or decrease in concentration due to instrument noise is transformed to an apparent emission then the temporal variation in background emission rates due to instrument noise in the experimental system can be used as an indicator of the MDL and LOQ as defined in Appendix II and summarized below.

Particle number concentration data collected during times when the chamber was completely purged and no particle emissions were present were used to calculate the MDL and LOQ. Ten consecutive particle number concentrations were used to estimate the apparent emission rate for each ten second time-step. The standard deviation of these emissions rates was multiplied by 3 to estimate the MDL and by 10 to estimate the LOQ for the experimental system. Several different experiments and different regions of experiments were used. The resulting MDL for emission rates is approximately 5×10^4 PN/second and the LOQ is ~ 1×10^5 PN/second.

Values between the MDL and the LOQ are flagged with a single asterisk (*) and values below the MDL are flagged with a double asterisk (**) in the following tables. Summary statistics are calculated using all values excluding cold-start print jobs.

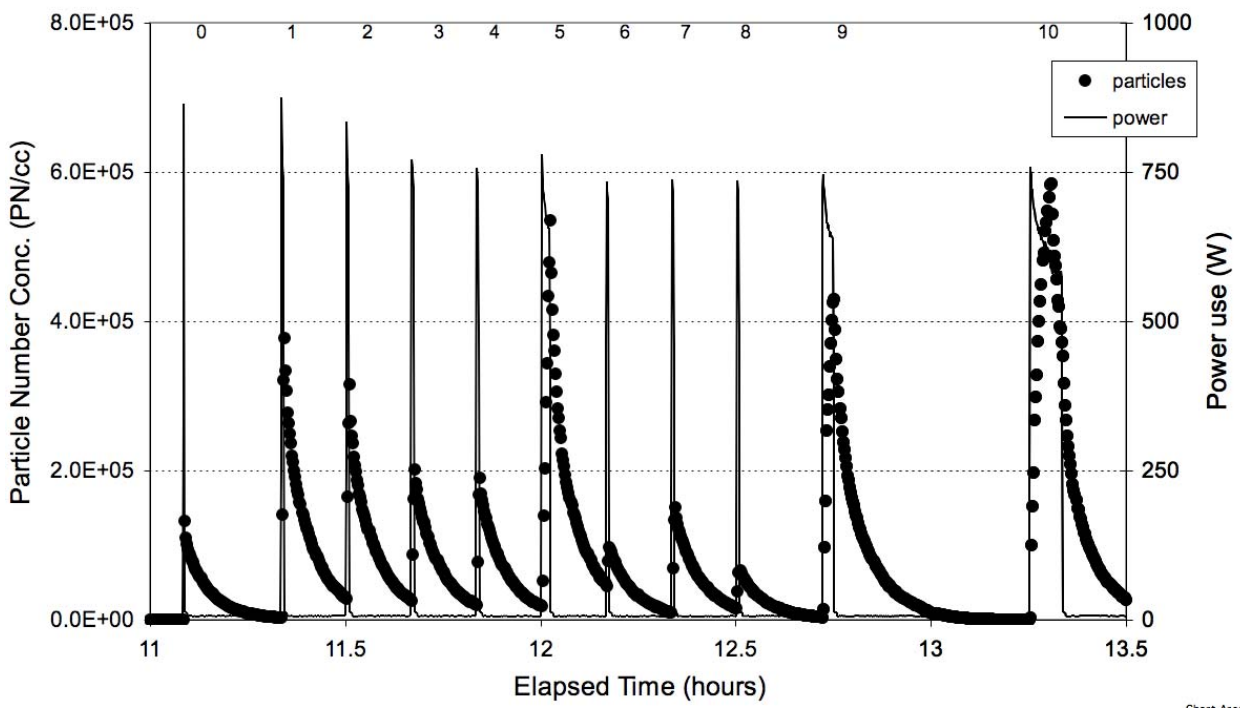
Summary of Results for LP06

Print number - type	pages	duration (s)	PN/s	PN/page	PN/print
0 – cold print	1	19	9.69E+09	1.84E+11	1.84E+11
1 – warm print	10	32	2.26E+09	7.23E+09	7.23E+10
2 – warm print	10	32	2.03E+09	6.51E+09	6.51E+10
3 – warm print	10	32	2.02E+09	6.45E+09	6.45E+10
4 – warm print	20	50	1.86E+09	4.66E+09	9.32E+10
5 – warm print	10	32	1.67E+09	5.33E+09	5.33E+10
6 – warm print	50	110	1.79E+09	3.93E+09	1.97E+11
7 – warm print	20	50	1.23E+09	3.09E+09	6.17E+10
8 – warm print	100	213	1.36E+09	2.90E+09	2.90E+11
		Average of warm prints	1.78E+09	5.01E+09	1.12E+11
		stdev	3.E+08	2.E+09	9.E+10
		%CV	19%	33%	76%

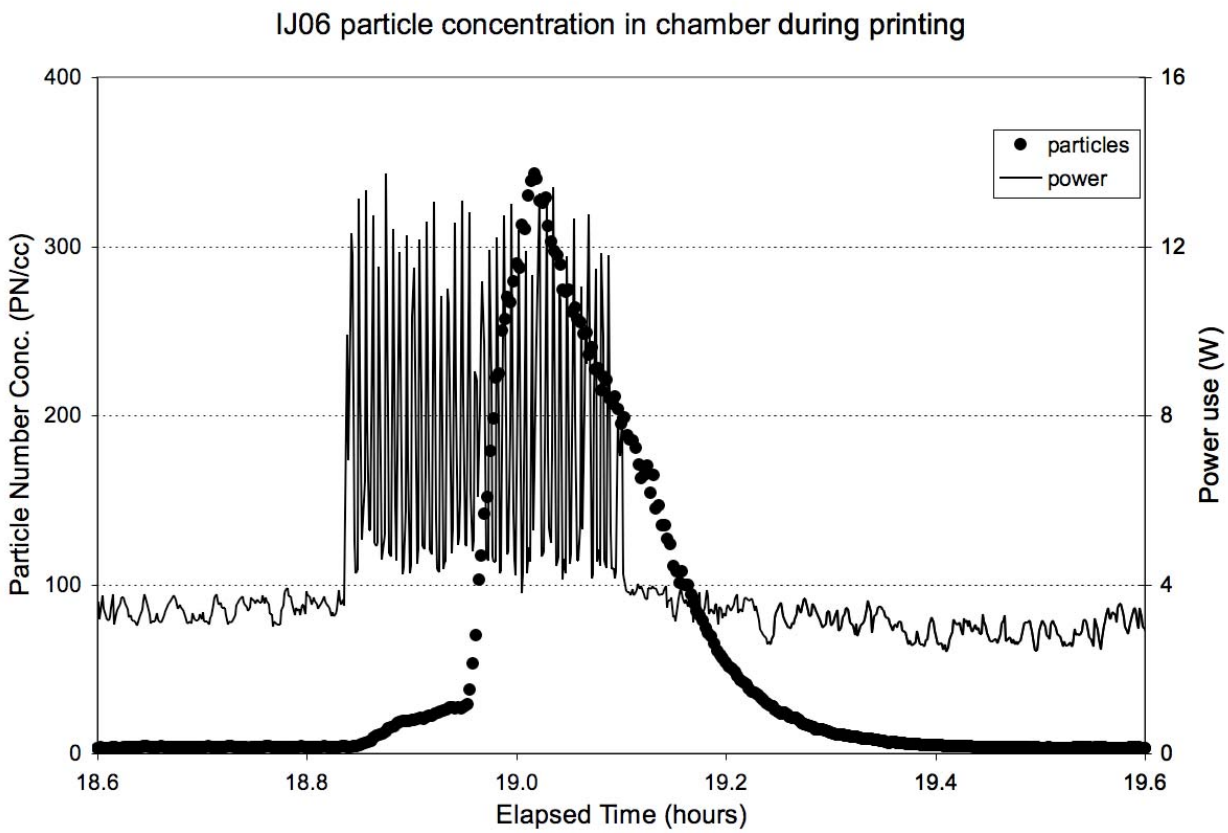


Summary of Results for LP07					
Print number - type	pages	duration (s)	PN/s	PN/page	PN/print
0 – cold print	1	14	5.32E+09	1.01E+11	1.01E+11
1 – warm print	10	32	5.29E+09	1.69E+10	1.69E+11
2 – warm print	10	32	4.12E+09	1.32E+10	1.32E+11
3 – warm print	10	32	2.50E+09	7.99E+09	7.99E+10
4 – warm print	10	32	2.42E+09	7.76E+09	7.76E+10
5 – warm print	37	88	3.02E+09	7.18E+09	2.66E+11
6 – warm print	10	32	7.87E+08	2.52E+09	2.52E+10
7 – warm print	10	32	2.00E+09	6.40E+09	6.40E+10
8 – warm print	10	32	7.46E+08	2.39E+09	2.39E+10
9 – warm print	50	110	1.96E+09	4.31E+09	2.15E+11
10 – warm print	150	311	1.77E+09	3.68E+09	5.51E+11
		average	2.46E+09	7.23E+09	1.60E+11
		stdev	1.E+09	5.E+09	2.E+11
		%CV	57%	65%	99%

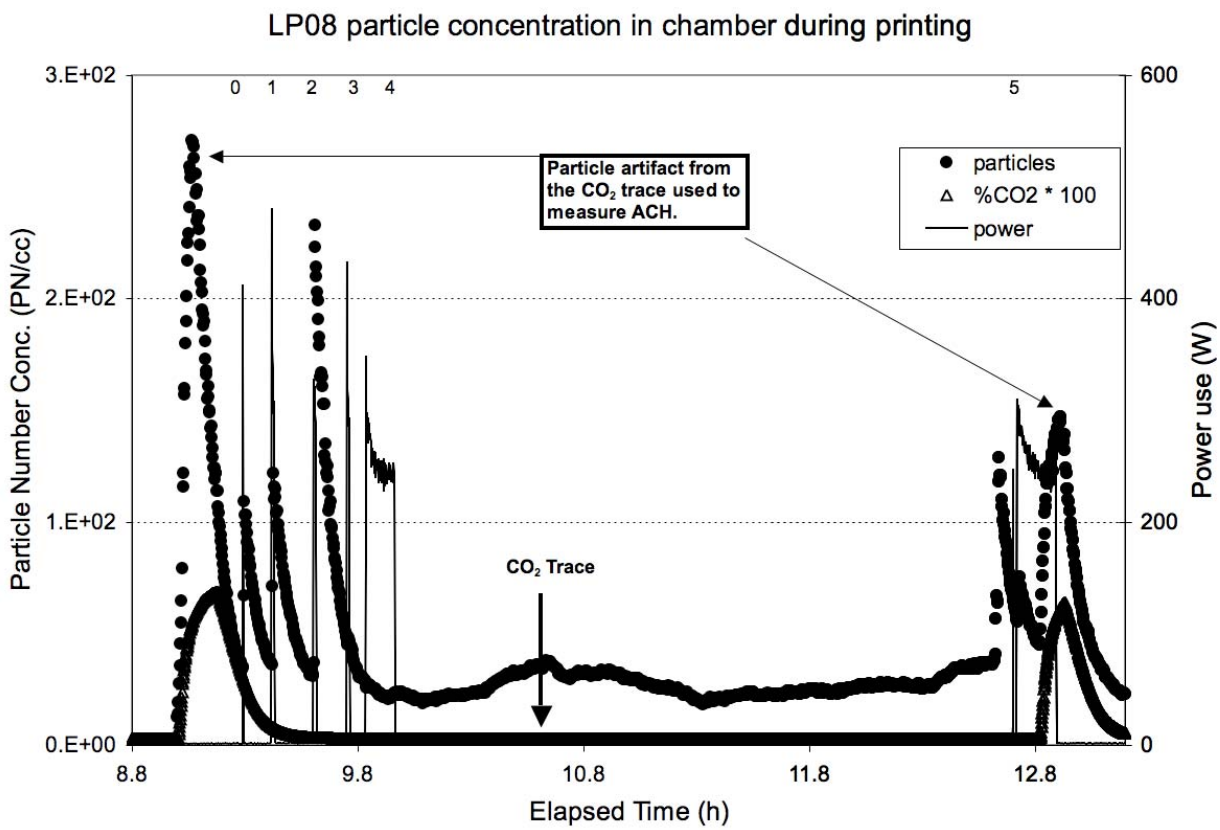
LP07 particle concentration in chamber during printing



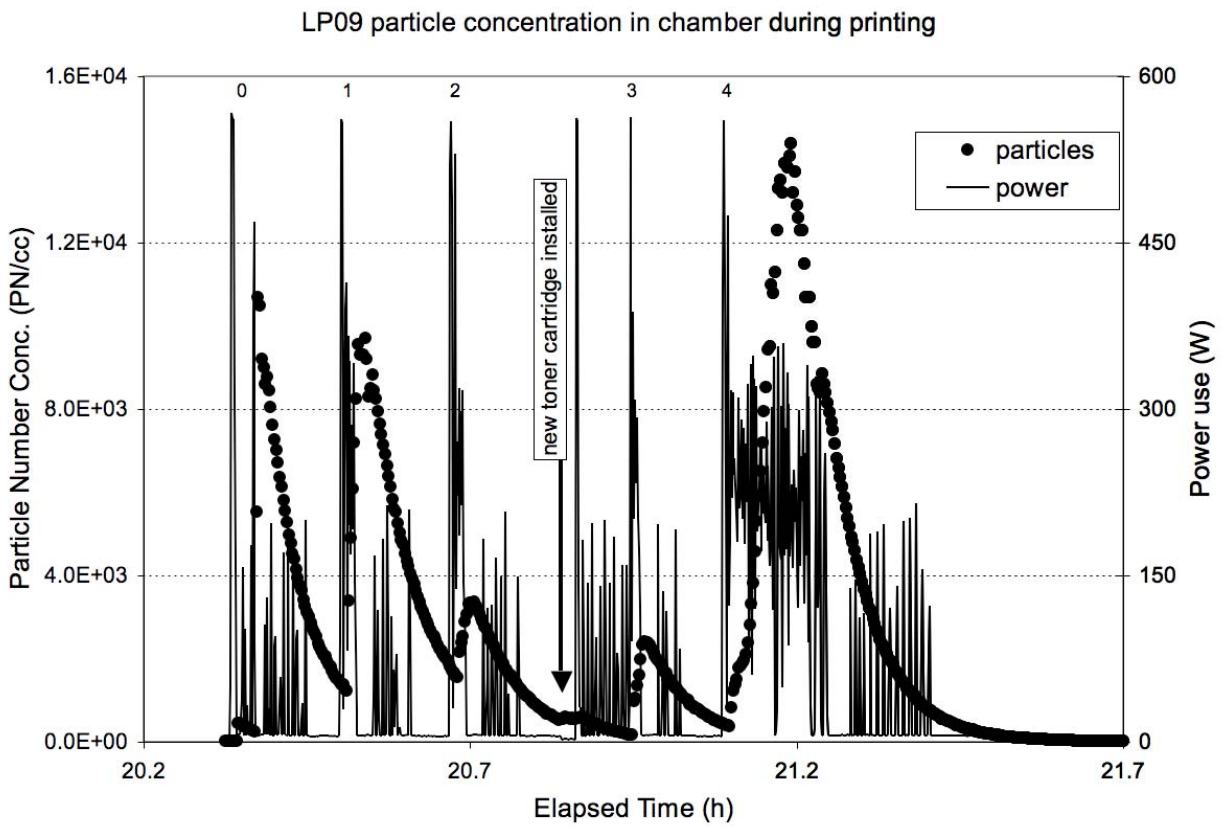
Summary of Results for IJ06					
Print number - type	pages	duration (s)	PN/s	PN/page	PN/print
0 – cold print	38	885	3.41E+05	7.93E+06	3.01E+08



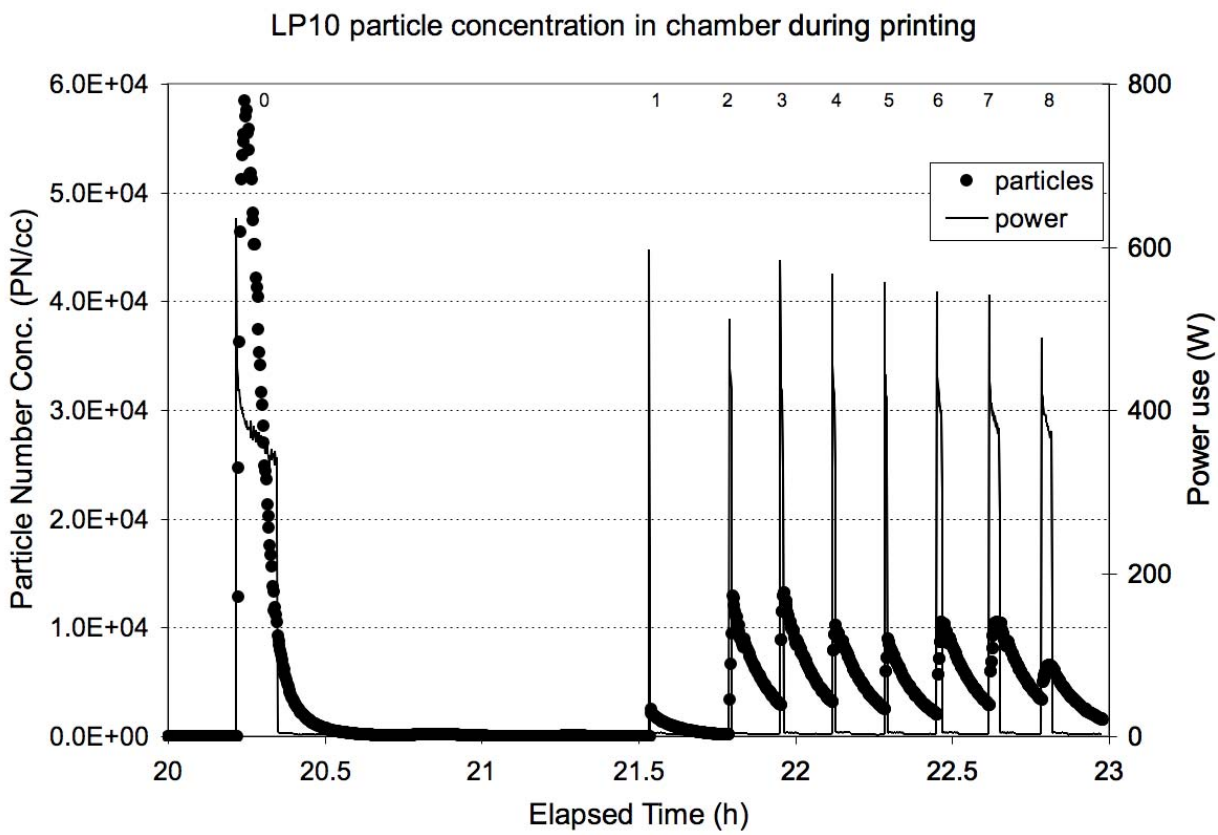
Summary of Results for LP08					
Print number - type	pages	duration (s)	PN/s	PN/page	PN/print
0 – cold print	1	9	1.55E+06	1.39E+07	1.39E+07
1 – warm print	10	48	7.17E+05	3.44E+06	3.44E+07
2 – warm print	10	50	1.65E+06	8.24E+06	8.24E+07
3 – warm print	10	48	1.70E+04**	8.16E+04**	8.16E+05**
4 – warm print	110	470	1.95E+04**	8.32E+04**	9.35E+05**
5 – warm print	150	640	8.70E+04*	3.71E+05*	5.57E+07*
		average	4.97E+05	2.44E+06	3.48E+07
		stdev	7.E+05	4.E+06	4.E+07
		%CV	142%	145%	101%



Summary of Results for LP09					
Print number - type	pages	duration (s)	PN/s	PN/page	PN/print
0 – cold print	1	76	1.46E+08	1.11E+10	1.11E+10
1 – warm print	10	93	4.62E+07	4.30E+08	4.30E+09
2 – warm print	10	93	1.19E+07	1.10E+08	1.10E+09
3 – warm print	10	68	1.16E+07	7.91E+07	7.91E+08
4 – warm print	100	585	1.97E+07	1.15E+08	1.15E+10
		average	2.23E+07	1.84E+08	4.43E+09
		stdev	2.E+07	2.E+08	5.E+09
		%CV	73%	90%	113%

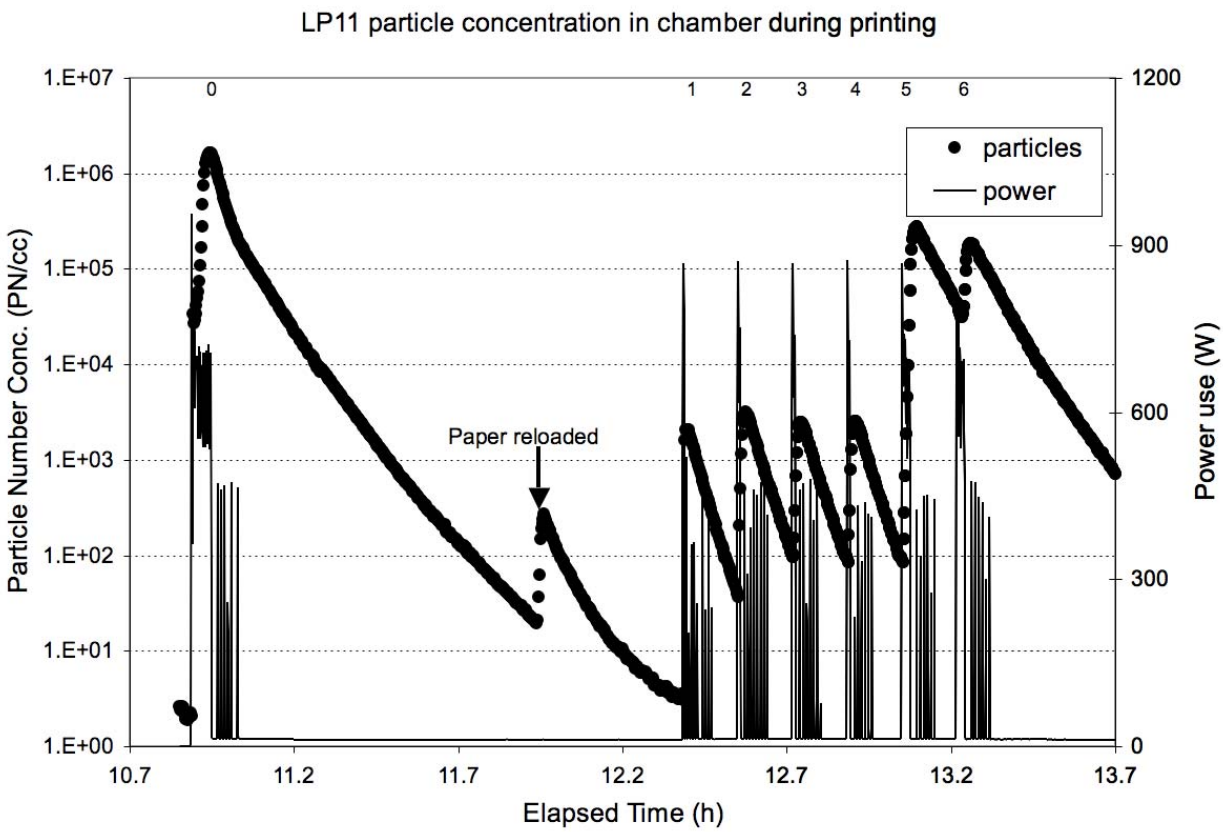


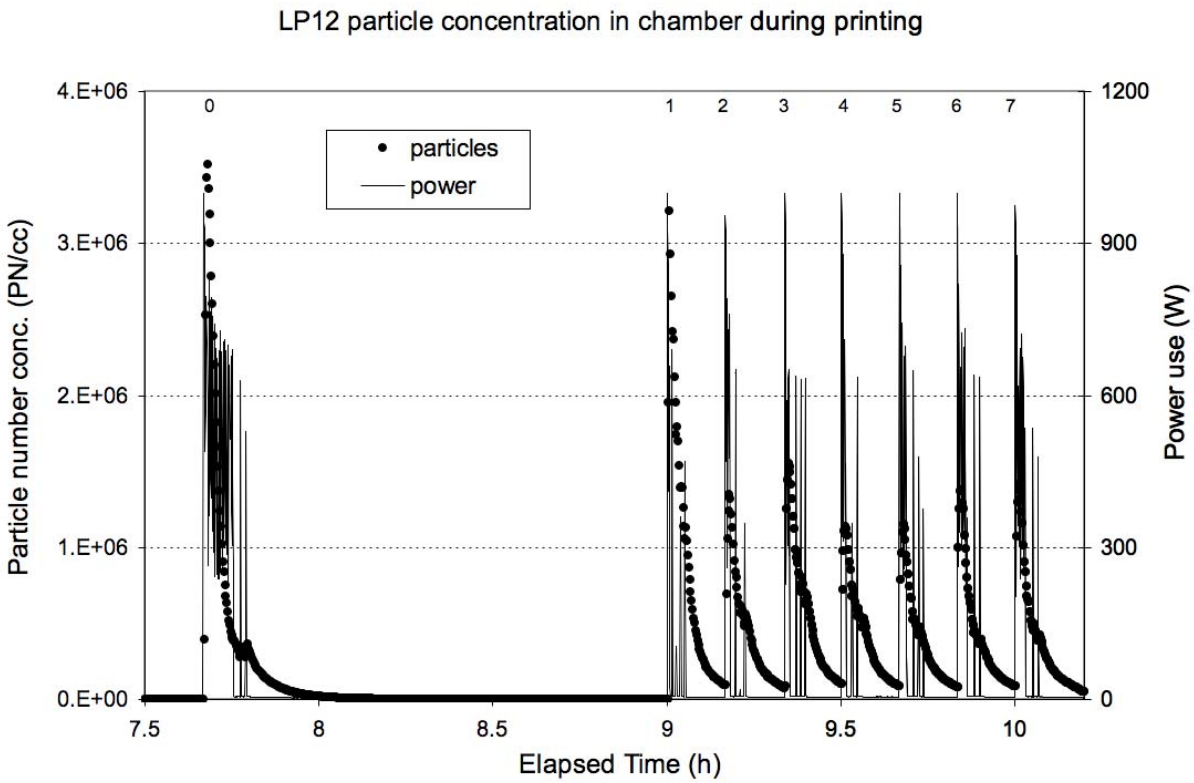
Summary of Results for HP LaserJet 1160 Le S/N CNG1PO1877					
Print number - type	pages	duration (s)	PN/s	PN/page	PN/print
0 – cold print	200	480	4.69E+07	1.13E+08	2.25E+10
1 – cold print	1	10	4.41E+07	4.41E+08	4.41E+08
2 – warm print	10	38	1.34E+08	5.08E+08	5.08E+09
3 – warm print	10	36	1.14E+08	4.10E+08	4.10E+09
4 – warm print	10	38	7.64E+07	2.90E+08	2.90E+09
5 – warm print	10	37	6.95E+07	2.57E+08	2.57E+09
6 – warm print	20	67	5.36E+07	1.80E+08	4.79E+09
7 – warm print	40	128	3.33E+07	1.06E+08	4.26E+09
8 – warm print	40	127	1.56E+07	4.96E+07	1.98E+09
		average	6.79E+07	2.39E+08	6.02E+09
		stdev	4.E+07	2.E+08	7.E+09
		%CV	59%	67%	112%



Summary of Results for LP11

Print number - type	pages	duration (s)	PN/s	PN/page	PN/print
0 – cold print	100	225	3.74E+09	8.41E+09	8.41E+11
1 – cold print	1	20	4.24E+07	8.48E+08	8.48E+08
2 – warm print	10	36	1.85E+07	6.65E+07	6.65E+08
3 – warm print	10	37	2.03E+07	7.51E+07	7.51E+08
4 – warm print	10	36	2.11E+07	7.59E+07	7.59E+08
5 – warm print	40	97	1.04E+09	2.52E+09	1.01E+11
6 – warm print	40	97	7.65E+08	1.86E+09	7.42E+10
		average	3.18E+08	9.07E+08	2.97E+10
		stdev	5.E+08	1.E+09	5.E+10
		%CV	145%	117%	154%



Summary of Results for LP12

Print number - type	pages	duration (s)	PN/s	PN/page	PN/print
0 – cold print	100	316	3.71E+10	1.48E+10	1.48E+12
1 – cold print	1	27	6.61E+10	1.79E+12	1.79E+12
2 – warm print	10	55	1.09E+10	6.01E+10	6.01E+11
3 – warm print	10	55	1.30E+10	7.17E+10	7.17E+11
4 – warm print	10	50	9.22E+09	4.61E+10	4.61E+11
5 – warm print	20	77	5.25E+09	2.02E+10	4.04E+11
6 – warm print	30	105	3.88E+09	1.49E+10	2.98E+11
7 – warm print	30	105	3.76E+09	1.45E+10	2.89E+11
		average	1.19E+10	3.46E+10	6.08E+11
		stdev	1.E+10	2.E+10	4.E+11
		%CV	98%	70%	69%