

# **INDOOR AIR EMISSIONS FROM OFFICE EQUIPMENT: TEST METHOD DEVELOPMENT AND POLLUTION PREVENTION OPPORTUNITIES**

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## Abstract

EPA's Air Pollution Prevention and Control Division (APPCD) and Research Triangle Institute (RTI) began a cooperative agreement in October 1993 to research pollution prevention approaches for reducing indoor air emissions from office equipment. The project included: (1) forming a group of technical advisors from industry and academia; (2) preparing a literature review and background report on the operation of, and emissions from, office equipment as well as pollution prevention opportunities; (3) developing and evaluating an *Emissions Testing Guidance Document for Dry-Process Photocopy Machines*; (4) identifying and evaluating pollution prevention options; and (5) preparing technical papers, presentations, and reports.

Because no standard test method exists to measure emissions from office equipment (e.g., ozone, volatile organic compounds, aldehydes/ketones, inorganic gases, and particles), it is difficult to compare data from different studies. Thus, the focus of this cooperative agreement was the development and evaluation of a large chamber test method for measuring emissions from dry-process photocopiers. The ultimate goal is to apply the method to better understand emissions from office equipment and to develop lower emitting machines. Challenges and complications encountered in developing and implementing the method include: heat generation which can cause large increases in chamber temperature; finite paper supplies for photocopiers which limit test duration; toner off-gassing between tests or toner carryover if different types of toner are tested; varying power requirements that may require changes in chamber electrical supply; and remote starting of the machines which is necessary to maintain chamber integrity.

The test method was evaluated in two phases. Phase I was a single laboratory evaluation of the method at RTI using four mid-range dry-process photocopiers. Phase I results indicated that the test method provided acceptable performance for characterizing emissions, adequately identified differences in emissions between machines both in compounds emitted and their emission rates, and was capable of measuring both intra- and inter-machine variability in emissions. For Phase I, the compounds with the highest emission rates from the four different machines tested were: ethylbenzene (28,000 µg/hour), *m,p*-xylenes (29,000 µg/hour), *o*-xylene (17,000 µg/hour), 2-ethyl-1-hexanol (14,000 µg/hour), and styrene (12,000 µg/hour). Although many of the same compounds were detected in emissions from each of the four photocopiers, the relative contribution of individual compounds varied considerably between machines, with differences greater than an order of magnitude for some compounds. The toners appear to be the primary source of organic emissions from the photocopiers.

Because all chambers may not produce similar results, Phase II was a four-laboratory round-robin evaluation of the method. A single dry-process photocopier was shipped to each of the four laboratories along with supplies (i.e., toner and paper). Phase II results demonstrate that the method was used successfully in the different chambers to measure emissions and that differences in chamber design and construction appeared to have had minimal effect.

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## **1.0 INTRODUCTION**

### **1.1 Background**

Several studies by the U.S. Environmental Protection Agency (EPA) have identified indoor air quality (IAQ) as one of the most important environmental risks to the Nation's health (U.S. EPA, 1987a and U.S. EPA, 1990). Major findings from long-term EPA studies of indoor air are (U.S. EPA's TEAM Studies):

- for many pollutants, indoor levels are 2 to 5 times higher than outdoors;
- in both rural and heavily industrialized areas, personal exposures and indoor concentrations exceed outdoor air concentrations for essentially all of the prevalent volatile organic compounds;
- after some activities, indoor air pollutant levels can be up to 1,000 times higher than outdoors; and
- in new nonresidential buildings, levels of volatile organic compounds can be as much as 100 times higher than outdoors.

People spend approximately 90 percent of their time in indoor environments, such as residences, public buildings, and offices. In the case of offices, the advent of electronic technologies has caused rapid changes. Photocopiers, printers, and fax machines have become prevalent in office settings, from home offices to large commercial or institutional settings, and can vary dramatically in size and numbers in use. Along with the technical and efficiency opportunities offered by these technologies comes the potential for increased pollution in the indoor environment. Researchers such as Wolkoff et al. (1992), National Institute for Occupational Safety and Health (NIOSH 1991), and Gallardo et al. (1994) have reported that the operation of office equipment can contribute to increased indoor air pollutant concentrations and has, in some cases, been associated with health complaints from exposed workers.

Traditionally, approaches for improving IAQ have generally focused on mitigation technologies, such as ventilation and air cleaning. These approaches do not prevent pollution--the pollution is simply transferred to another medium or outdoors. Depending on the source of indoor air pollution, another approach is to focus on source reduction, ensuring that pollutants do not enter the indoor environment in the first place. In the Pollution Prevention Act of 1990, Congress declared that pollution should be prevented or reduced at the source whenever feasible (EPA 1990). Source reduction may be accomplished by modifications to equipment, processes, and procedures; reformulations or redesign of products; substitution of raw materials; and improvements in use procedures.

The EPA's Air Pollution Prevention and Control Division (APPCD) of the National Risk Management Research Laboratory (NRMRL) is responsible for EPA's indoor environment engineering research. APPCD's Indoor Environment Management Branch (IEMB) applies

IEMB's expertise in IAQ (i.e., source characterization, ventilation, and microbials) to work cooperatively with EPA Program Offices, industry, consumers, and other researchers to identify and prevent pollutants from indoor sources (e.g., develop low emitting materials and products).

## **1.2 Approach**

During a 1993 IAQ/Pollution Prevention workshop, office equipment was identified by IEMB researchers and workshop participants as a source of indoor air emissions and as a technology that merited further research (Sarsony, 1993). In October 1993, Research Triangle Institute (RTI) and EPA's IEMB initiated a cooperative agreement to research pollution prevention approaches for reducing indoor air emissions from selected types of office equipment. The approach consisted of: (1) establishment of a group of technical advisors from industry and academia; (2) preparation of a literature review and a background report on the operation of, and emissions from, office equipment as well as pollution prevention opportunities; (3) development and extensive evaluation an Emissions Testing Guidance Document for Dry-Process Photocopy Machines; (4) identification and evaluation of selected pollution prevention options; and (5) preparation of technical papers, presentations, and reports. These activities are summarized in subsections below.

### ***1.2.1 Establishment of Technical Advisory Group***

In March 1994, a technical advisors planning meeting was convened to discuss the objectives and approach for this research and to get input on technical priorities. The technical advisors strongly recommended that a standard test method – that could be used to evaluate emissions from office equipment – be developed. It was felt that such a method was needed to evaluate different equipment types and to establish comparable baseline emission data that could then be used as a starting point for the development of specific pollution prevention approaches. The recommendations from the technical advisors meeting along with a list of attendees are included as Appendix A of this report.

### ***1.2.2 Literature Review***

Concurrently with the technical advisors meeting, a literature search was conducted to identify and review published information on office equipment design; indoor air emissions of ozone, particulates, and organics; and potential pollution prevention approaches for reducing these emissions (Hetes et al., 1995). A summary of the literature review is presented in Section 2 and serves as background for the remainder of the report.

As was conjectured by the small amount of data identified during the literature review, and confirmed by the technical advisors, much of the existing data on emissions from office equipment are proprietary. Additionally, the methods used for emissions testing are highly variable, and therefore, published data from different laboratories may not be comparable. These findings supported the need for an Emissions Testing Guidance Document both for the purposes of this cooperative agreement and for others conducting research on emissions from office equipment.

### ***1.2.3 Development and Evaluation of Emissions Testing Guidance***

The large chamber emissions testing development activities were conducted in two phases and comprised the majority of this project. Phase I activities required approximately 2 years and consisted of method development and evaluation at RTI. A subset of the technical advisors provided input and direction to this process. A summary of the Phase I testing methods and results are presented in Section 3. Phase II was a 1-year effort and consisted of a round-robin evaluation of the draft method (contained in Appendix B) at four laboratories. Section 4 presents the Phase II activities and results.

### ***1.2.4 Pollution Prevention Opportunities***

One of the primary goals of this research was to identify and evaluate pollution prevention opportunities for reducing emissions from office equipment. This was accomplished through literature reviews; discussions with the technical advisors; and laboratory testing of dry-process photocopiers, copy machine toner powder, and different types of printed circuit board laminate materials. Section 5 of this report includes discussions of some of the issues that were identified, but not tested, during this research and that have potential pollution prevention implications. Section 6 describes pollution prevention opportunities that were identified through the literature review and laboratory testing.

### ***1.2.5 Reporting***

The objectives of this report are to summarize the major activities that took place as part of this cooperative agreement and to present the results from the large chamber emissions test method development activities. Conclusions and recommendations from this research are presented in Section 7. Quality assurance activities were conducted throughout this research effort and are summarized in Section 8 and Appendix D. Readers interested in obtaining additional information on indoor air emissions from office equipment should refer to the sources contained in Appendix C.

## **2.0 BACKGROUND**

One of the first activities of this project was a literature review (Hetes et al., 1995). The review covered published information on the following types of office equipment:

- dry- and wet-process photoimaging machines (copiers, printers, and faxes);
- computers and computer terminals;
- spirit duplicators;
- mimeograph machines;
- digital duplicators;
- diazo (blueprint) machines; and
- impact (dot matrix) printers.

A summary of the report follows and provides background information useful for understanding the technical issues associated with test method development presented in Sections 3 and 4.

### **2.1 Introduction**

The office environment contains many types of equipment that emit indoor air pollutants. Emissions may occur as a result of equipment operation, offgassing from components, or episodic releases related to catastrophic failure of a unit. For equipment that does not use supplies (e.g., video display terminals), emissions are primarily from offgassing of residual organics. The source of these organics can either be construction materials (e.g., plastic casings) or components (e.g., cards used in manufacturing integrated circuit boards). Emissions resulting from offgassing decrease with time until they reach a point where they are negligible. It has been reported that over 300 hours of "on time" are required before a video display terminal's emissions reach a negligible level (Brooks et al., 1993).

Emissions from equipment that use supplies such as toner, ink, and paper (e.g., photocopiers, printers) result from both offgassing and operation. Emissions from offgassing will decrease with time as noted above; however, emissions from operation will remain fairly constant or may even increase between routine maintenance or as the equipment ages. For example, Selway et al. (1980) reported that ozone emissions from five tested photocopiers ranged from 16 to 131  $\mu\text{g}/\text{copy}$  before routine maintenance and were reduced to less than 1 to 4  $\mu\text{g}/\text{copy}$  after maintenance.

In general, published data on the emissions from office equipment are limited. However, increased levels of ozone, total volatile organic compounds (TVOC), and particulates have been observed in the presence of operating equipment (Etkin, 1992; Tsuchiya et al., 1988; Wolkoff et al., 1993). Furthermore, it has been reported that there is a significantly increased perception of headache; mucous irritation and dryness in the eyes, nose, and throat; and dry and tight facial skin among subjects exposed to office equipment (Wolkoff et al., 1992). Other researchers have also reported that emissions associated with normal operation of office equipment can contribute to

increased indoor air pollutant concentrations and have been associated with complaints from exposed workers.

Table 2-1 summarizes the published emission rates, IAQ impacts, and potential pollution prevention solutions associated with the equipment types that were evaluated as part of the literature review. The equipment is listed in priority order (highest priority at top) for evaluation as part of this RTI/EPA cooperative agreement. The criteria used to prioritize the equipment types include relatively high emissions (either as a unit or in total emissions), minimal design differences among manufacturers, easily understood processes, and the feasibility (both technical and economic) for pollution prevention measures. Certain types of equipment with limited applications can have high emission rates but may only affect IAQ in a limited area or in a few locations. Others may have much lower emission rates on a per unit basis but may be found throughout a building and therefore have a greater overall impact on IAQ. Therefore, the number of units in operation was considered when prioritizing equipment for test in this project.

As can be seen in Table 2-1, dry-process photocopiers were identified as a high priority for testing and investigation of pollution prevention options. Dry-process photocopiers are prevalent in most office environments and are a known source of ozone, volatile organic compounds (VOC), and particulate emissions. The size of photocopiers can range from small personal models to fairly large machines that can have relatively high emission rates.

Laser printers, which utilize a technology similar to that of dry-process photocopiers and have been shown to have similar emissions, were identified as a secondary priority for emission testing given that they are much smaller in terms of throughput and concomitant emission rates than photocopiers. Furthermore, NIOSH has recently completed an emissions test on four different models of laser printers. The report discussing the testing program and detailed results, "Methods for Characterizing Emissions From Laser Printers" (Gressel, 1996), can be obtained directly from NIOSH using the contact information in Appendix C of this report.

Wet-process photocopiers have been shown to be the major contributor to indoor air VOC levels in several studies and have significantly greater emissions than dry-process machines on a per unit basis (Hodgson and Daisey, 1989; Tsuchiya et al., 1988). However, wet-process machines constitute a small part of the photocopier market. Therefore, although wet-process machines have higher individual emission rates, dry-process photocopiers were considered to be a higher priority for this project based on the greater number of units in operation.

Computers, fax machines, and dot matrix printers have emissions generally related to outgassing from electronic components and basic construction materials. These emissions are highest for new machines and are thought to diminish rapidly with time. Therefore, although they may impact localized IAQ and are found in most office settings, their total combined impact on IAQ is likely to be less than dry-process photocopiers. However, based on the recommendations of the technical advisors on the project, a study was conducted as part of this project to evaluate off gassing emissions from printed circuit board laminates. The results of this study are summarized in Cornstubble and Whitaker (1998).

**Table 2-1. Summary of Office Equipment Literature Review**

Type of Equipment	Emissions	Emissions Rate/IAQ	Potential Options for Reduced Emissions	Summary of Prioritization
Dry-process photocopier machines	Hydrocarbons, respirable suspended particles, and ozone	Particulate: 1 ng/m <sup>3</sup> room concentration. <sup>a</sup> O <sub>3</sub> : peak production 131 µg/sheet <sup>b</sup> 0-1350 µg/min, avg. = 259 µg/min <sup>c</sup> 48-158 µg/copy <sup>d</sup> TVOC: 0.5-16.4 µg/sheet from paper <sup>e</sup>	Lower voltage, toner reformulation, transfer efficiency	Common product found in most office settings. Smaller units lower emission rates but more common, large production units often with dedicated HVAC systems
Laser printers	Hydrocarbons, respirable particulates, and ozone	Particulate: 0.0007-0.002 µg/page <sup>i</sup> ; 0.1-4 mg/m <sup>3</sup> room concentration <sup>e</sup> ; 0.0009-0.06 mg/min. <sup>i</sup> TVOC: 2.0-6.5 µg/sheet from paper <sup>e</sup> ; 0.08-0.26 mg/page <sup>i</sup>	Charged rollers	Common technology found in most office settings
Computer terminals	Ozone, electromagnetic fields (EMF), and offgassing VOCs	Little published data on EMFs, none on VOCs or ozone	Low-emitting materials and/or lower voltage	Thought to have relatively low emissions when compared to other sources that have operating emissions as well
Wet-process photocopier machines	Aliphatic hydrocarbons, VOCs and ozone	TVOC: 25 g/h, 0.241 g/copy observed high room concentration of 35 mg/m <sup>3</sup> <sup>f</sup>	Solvent reformulation, filters, decrease voltage	Obsolete technology, shrinking market share
Ink/bubble jet printers	Hydrocarbons, ozone	No published emissions rate data	Solvent reformulation	Used primarily for personal printers, home use
Spirit duplicators	Methanol	No published emissions rate data	Mineral spirits or photocopiers	Limited market, schools and institutions
Mimeograph printers	Hydrotreated heavy and light naphthenic distillates	No published emissions rate data	Replacement - photocopiers	Limited market, schools and institutions
Fax machines	Ozone and VOCs	No published emissions rate data	Charged rollers	Found in most office settings, rapidly changing technology may be integrated with copier/ printers
Blueprint machines (dyeline)	Ammonia, carbon monoxide, methanol, ethanol, trinitrofluorene, trichloroethane	1-40 ppm NH <sub>3</sub> in breathing zone of operator, average = 8.2 ppm <sup>g</sup>	CAD/alternative technologies	Older technology, losing market share to CAD/alternative technologies
Matrix printers	VOCs	TVOC: 0.7-1.0 µg/sheet from paper <sup>e</sup> No data on emissions from operation	Low-emitting materials	Used generally for personal printers, home use. Relatively low emission rates.
Plotters	VOCs, hazardous waste residuals	No published emissions rate data		Limited market share, sales around 250,000 a year worldwide <sup>h</sup>

<sup>a</sup> Schnell et al., 1992

<sup>b</sup> Greenfield, 1987.

<sup>c</sup> Hannsen and Anderson, 1986.

<sup>d</sup> Allen et al., 1978.

<sup>e</sup> Wolkoff et al., 1993.

<sup>f</sup> Tsuchiya et al., 1988.

<sup>g</sup> Tuskes et al., 1988.

<sup>h</sup> DeNucci, 1992.

<sup>i</sup> Gressel, 1996.

VOCs = volatile organic compounds

TVOCs = total volatile organic compounds

CAD = computer-aided design

As part of the literature review, other equipment that may have high individual emission rates was identified. This equipment include spirit duplicators, mimeograph machines, plotters digital duplicators and diazo (blueprint) machines. These types of equipment were not considered for further investigation in this project because they are rather specialized with a smaller number of units in operation. Furthermore, some of this equipment is no longer manufactured or is being replaced by alternative technologies. Therefore, this equipment, although significant in a limited number of settings, is believed to have lower total emissions and impact a smaller population than dry-process photocopiers. Section 2.2 summarizes the information in the literature review on photoimaging machines (Hetes et al., 1995).

## **2.2 Photoimaging Machines**

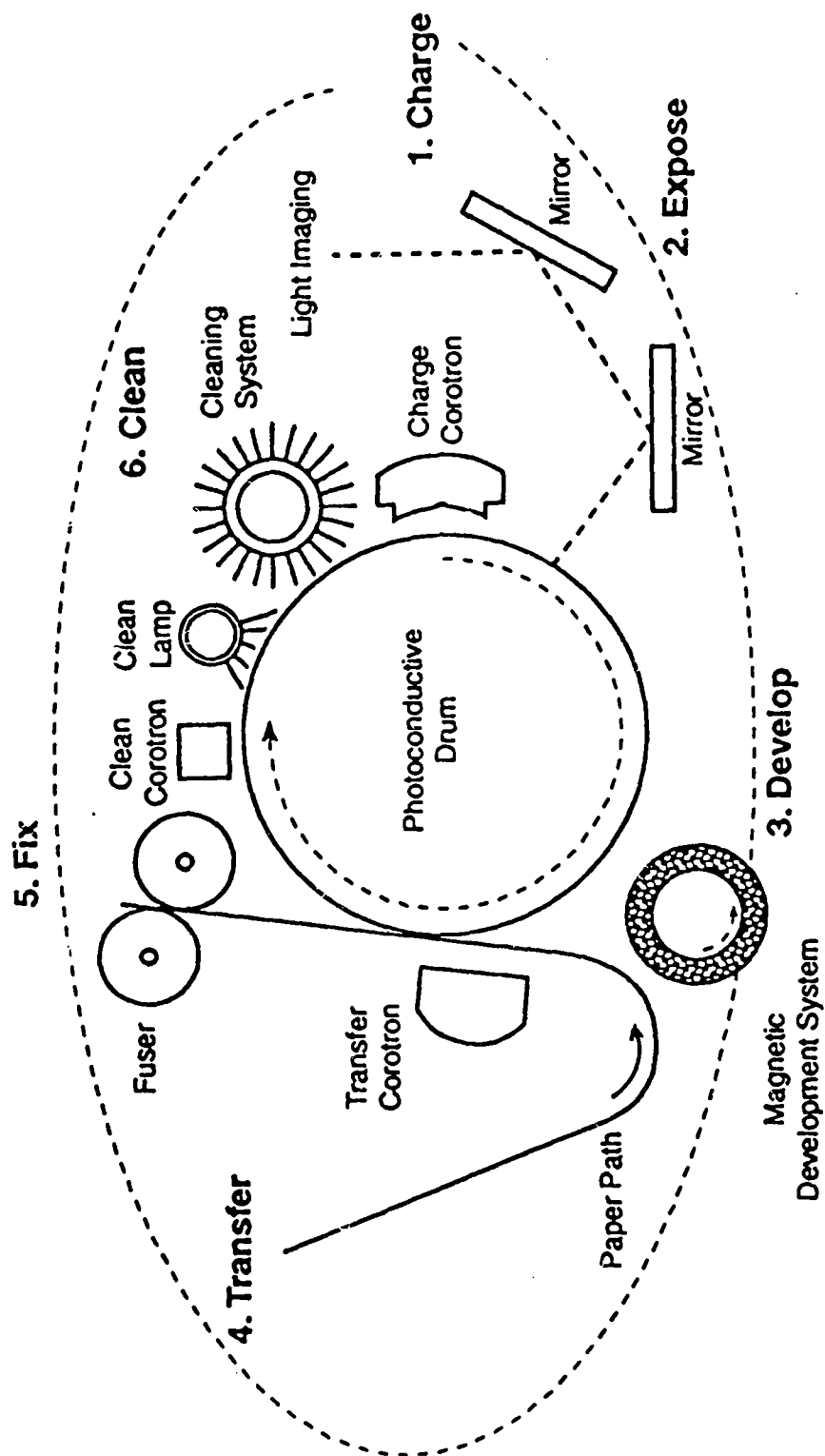
Dry-process photocopiers, one type of photoimaging machine, make up a majority of the photocopier market. The measurement of emissions from dry-process photocopiers was the focus of the test method development activities of this cooperative agreement. Therefore, summary information on photoimaging process design and operation, as well as selected emissions data, is presented here for background purposes.

### **2.2.1 Equipment Design and Operation**

Electrophotography is used in copiers, laser printers, and fax machines and is based on the electrostatic transfer of toner to and from a charged photoconductive surface. The basic steps in image processing are shown in Figure 2-1. They are: (1) charge, (2) expose, (3) develop, (4) transfer, (5) fuse, and (6) clean. This six-step process is repeated for each copy. The imaging process is depicted in Figure 2-2. The toner transfer process is depicted in Figure 2-3. The critical element of any photoimaging process is the photoconductive drum, which typically has a photoconductive coating such as selenium, cadmium sulfide, or zinc oxide. These materials have the unique property of holding an electrostatic charge in the dark and losing the charge when exposed to light, such as that reflected from the white areas of an original. Whether the drum is positively or negatively charged during this process depends on the type of photoconductive materials used. For the purposes of illustration, a positively charged selenium-based photoconductive material is described.

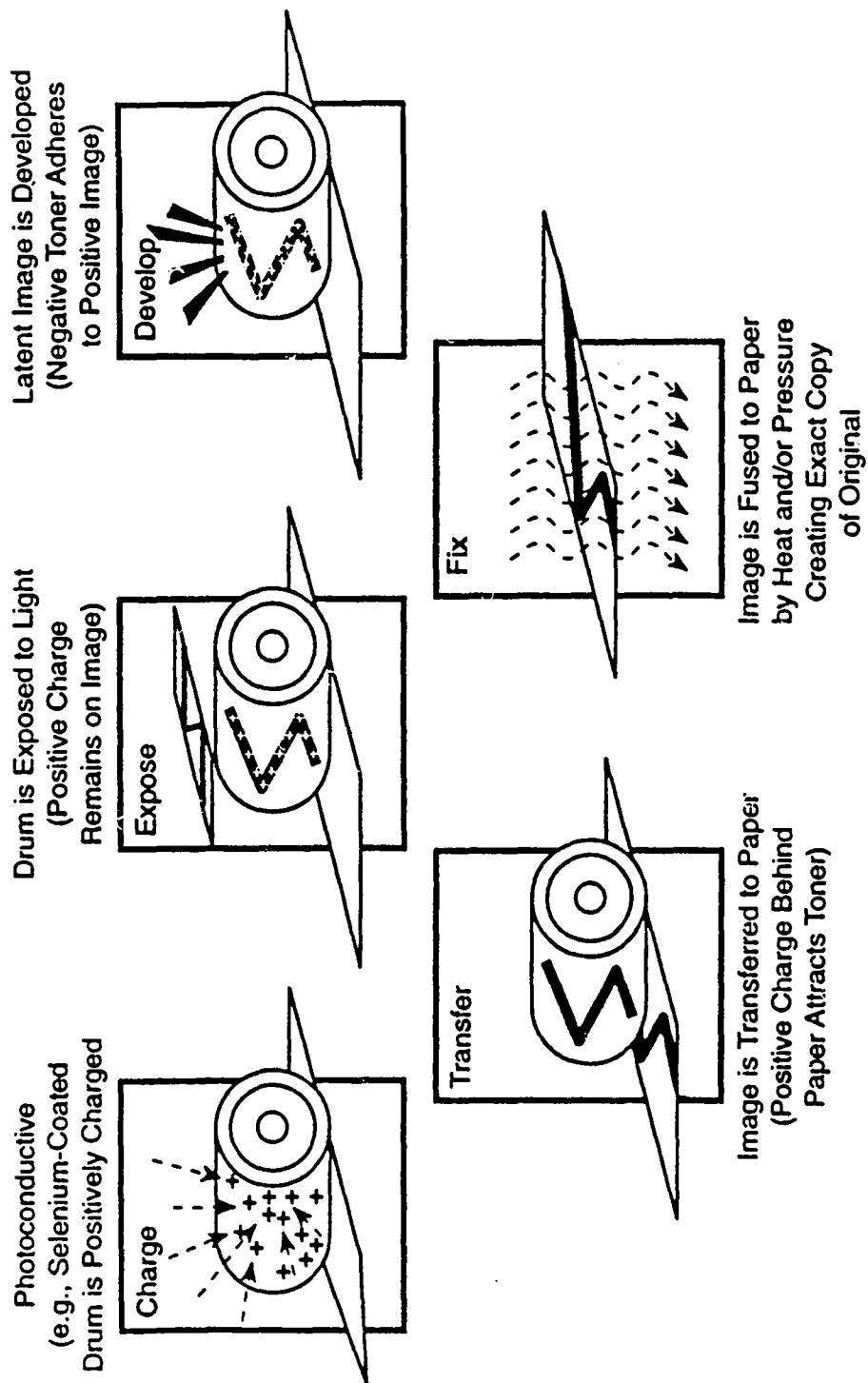
Charge: Charging the photoconductive drum is the first step in the process. In the charging step a uniform charge is imparted on the entire surface of the drum. In conventional laser print and photocopier designs, electrically charged corona wires are used to add a uniform primary charge across the surface of the photosensitive drum. Canon, Inc., has developed an alternative dry-process photoimaging system in which the corona wires are replaced with “charging” rollers. Unlike the corona wires, which are separated from the drum by a small distance, the charging rollers are pressed directly against the drum, requiring far lower voltages to generate the needed charge. This technology is now available in laser printers as well and has been shown by Canon, Inc. (1990) and Gressel (1996) to significantly reduce ozone emissions.





Source: Adapted from Maren, T., Dry Toner Fundamentals, Xerox Research Center, 8th Annual Toner and Developer Conference and Tutorial, September 1991, Diamond Research Company.

Figure 2-1. Six steps in the photoimaging process.



Source: Adapted from Maren, T., Dry Toner Fundamentals, Xerox Research Center, 8th Annual Toner and Developer Conference and Tutorial, September 1991, Diamond Research Company.

Figure 2-2. How photomaging transfers the image to paper.

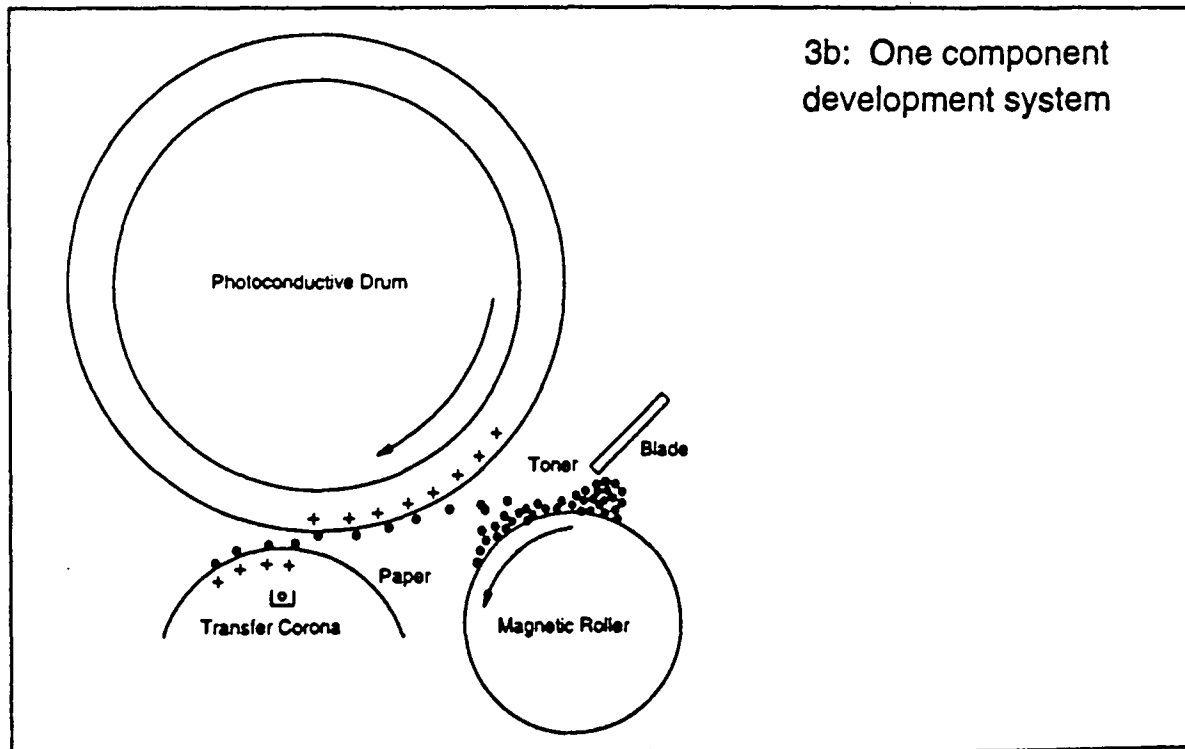
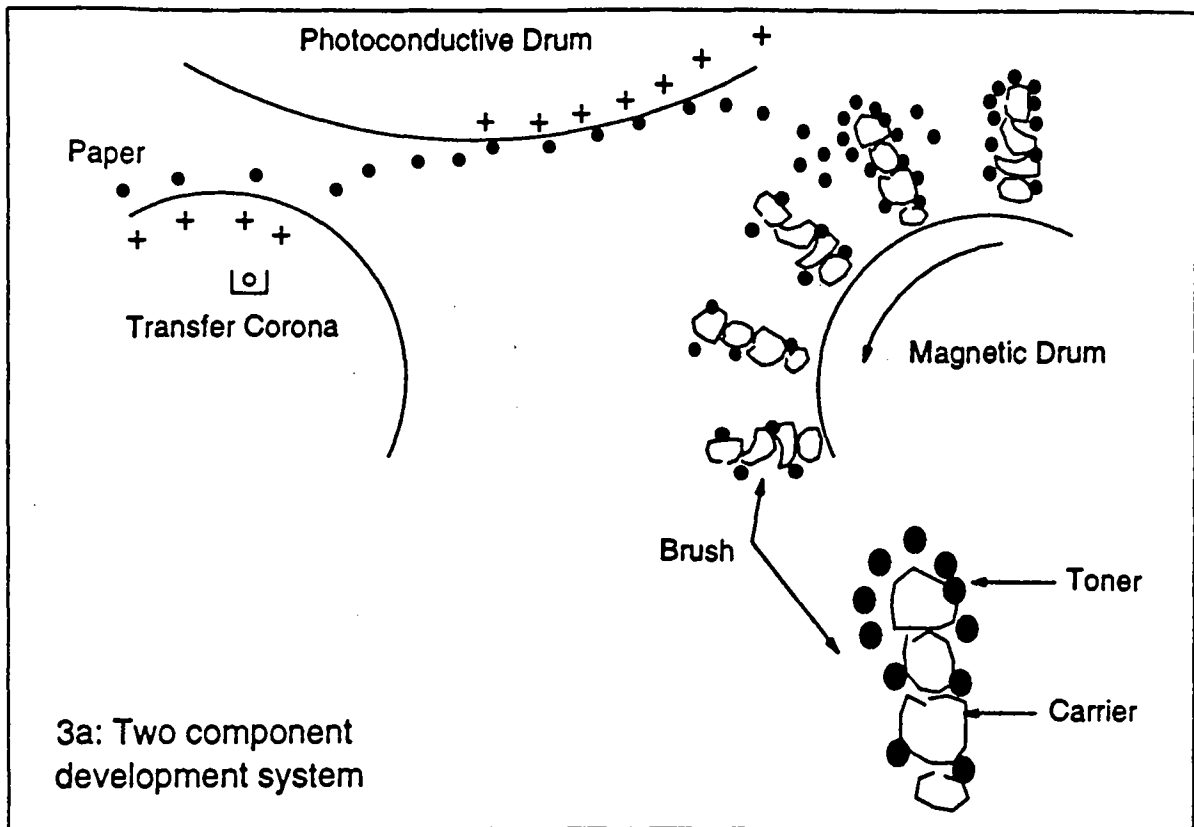


Figure 2-3. Schematic of toner transfer to and from photoconductive drum.

Expose: During the exposure step the image is reflected onto the surface of the drum. The original image (dark area) remains charged on the surface of the drum as the reflected white areas of the original lose their charge when exposed to the reflected light.

Develop: The image is developed when the negatively charged toner particles or aerosols are attracted to the positively charged areas of the image (see Figure 2-3). Developer makes the latent electrostatic image on the drum visible. Developers are broadly divided into dry and wet types. In general, the developer can consist of either one (toner alone) or two components (toner and carrier). There are several physical processes by which the toner is transferred to the charged image. The two-component developer (Figure 2-3a) consists of a carrier and a toner that are oppositely charged. A magnetic field is used to align the carrier (with attached toner) on a developing cylinder to form a “brush” that carries the toner closer to the photoconductive drum. The charged surface (image) on the drum then attracts the toner. A one-component system (Figure 2-3b) consists of toner alone, made up of a resin (color) and magnetic material. Again, a magnetic cylinder is used to align and uniformly collect the toner particles, which then are brought close to the drum and attracted to the charged image. A blade is sometimes used to ensure uniform coverage of toner on the magnetic drum.

Transfer: Once the image has been developed on the drum it must be transferred to the paper (see Figure 2-3). To transfer the image to the paper, a transfer corona wire applies a positive charge through the paper, which electrostatically attracts the negatively charged toner particles off the photo drum and onto the surface of the charged paper. In the Canon, Inc. process, a charged roller system is used to apply the positive charge to the paper. One charging roller sits on top of the photosensitive drum within the toner cartridge; the other charging roller (the transfer roller) is contained within the printer housing and sits under the photosensitive drum. The paper travels between the transfer roller and the photosensitive drum. The contact between the charging rollers and the photosensitive drum prevents the formation of electrical arcs. About 75 percent of the toner is transferred to the copy paper. The exact transfer efficiency depends on the environment during transfer and the kind of paper used (Canon, 1990).

Fixing (Fusing): Fusing refers to the process in which the toner that was transferred to the copy paper is permanently bound to the paper. There are essentially two kinds of fixing methods: heat fixing and pressure fixing (see Figure 2-2). In the heat fixing process, the paper passes through two drums, one of which is heated to a temperature of about 160 to 200 °C, which heats the other drum upon contact. The paper passes between the heated rollers and the toner is melted and pressed into the fibers of the paper, thus fixing the toner to the paper. In a wet-process system, the heat results in the volatilization of the carrier leaving the nonvolatile portion of the toner behind. In the pressure fixing method, the two rollers are in very firm contact with each other. The paper passes between these rollers and the toner is pressed firmly onto and into the paper, thus fixing the image. Some machines use a combination of heat and pressure.

Clean: Cleaning refers to the process in which any toner remaining on the surface of the photoconductive drum after transfer is cleaned off so that the next copy image will be clear and distinct. Cleaning is primarily a physical process in which a blade, brush, or web is wiped across the drum surface to remove residual toner particles and collect the waste toner. In some machines, a cleaning lamp may be used to remove the electrical charge from the drum prior to the application of the web, blade, or brush.

All photoimaging processes contain the six basic steps outlined above; however, features may differ with different equipment. For example, photocopiers use a high-intensity light source to reflect the image onto the surface of a photoconductive drum while laser printers and fax machines use a laser to impart the same charge on to the drum.

For dry-process photocopiers, the two-component developer described above consists of toner (mainly carbon, resin, and adhesive) and carrier (iron powder). The size of the toner particles typically range from 5 to 10  $\mu\text{m}$ , and the carrier particles range from 50 to 200  $\mu\text{m}$ . The one-component developer consists of toner alone, which is mainly resin and some magnetic material. The sizes of these particles are similar to the toner particles in the two-component system (about 10  $\mu\text{m}$ ). Toners are made primarily of styrene-based polyester resins with other ingredients added as stabilizers (e.g., salicylic acid chromium (III) chelate) and pigments (for color toner). Upon transfer of the toner to the charged paper, heat and pressure from the fuser rollers fuse the toner to the paper and set the copied or printed image. In general, higher fuser roller temperatures and smaller toner powder particle sizes are used in larger and faster photocopy machines to hasten the fusing process, though the chemical makeup of the toner powders may also be different. The temperature of the fuser rollers can be up to about 250 °C in the faster machines, as compared to 160 to 200 °C found in most machines.

### ***2.2.2 Published Indoor Air Emissions Data for Dry-process Photoimaging Machines***

Photoimaging machines and related supplies contribute to indoor air emissions. Emissions may result from operation and maintenance, equipment offgassing, or from processed paper. Types of emissions include organics, ozone, and particulates. The following sections summarize data in the literature on each of these emission types.

#### **2.2.2.1 Ozone**

Ozone is generated from the interaction of ultraviolet radiation with oxygen during electrostatic discharges and from reactions with nitrogen dioxide and hydrocarbons. The nitrogen dioxide and hydrocarbons may be produced in limited amounts from the source, may be found in the indoor air as a result of other indoor sources, or may result from infiltration of outdoor air. Ozone does not persist in the indoor environment because it quickly reacts and binds with materials in the surrounding environment. As a result, the indoor air concentration of ozone would be expected to decrease with distance from the source and with time. The electrically charged corona wires used to add a uniform primary charge across the surface of the photosensitive drum, and also to attract the toner from the drum to the paper surface, can

contribute to ozone production and emissions. High voltages are applied to the corona wires to attain the needed charge, and the associated electrical arcing results in the production of ozone.

Actual measurements of ozone emissions from photocopiers, typically using direct reading instruments sampling the outlet air, are variable. According to some studies, advanced dry-process photocopiers, even when recently serviced, can emit ozone at about 4 µg per copy (Etkin, 1992). Greenfield (1987) found that ozone production with extended use can peak at 131 µg per copy, with an average of around 40 µg/copy. By comparison, Allen et al. (1978) found that emissions ranged from 48 to 158 µg per copy and that photocopier emissions have been found to be dependent on copying rates, light intensity, and the maintenance status of the equipment. Hannsen and Anderson (1986) surveyed 69 types of photocopying machines, which were found to emit ozone at rates ranging from 0 to 1,350 µg/min, with a mean of 259 µg/min. Gressel (1996) evaluated ozone emissions from four different models of laser printers. Overall, their results indicated that ozone emissions from older printers with corona wires were high enough (0.005-0.06 mg/min) to cause concern in an indoor environment. On the other hand, newer printers with a charged roller system produced very little ozone (0.0008 mg/min).

Many copiers are equipped with ozone filters that allow the ozone to react with the filter media, thus reducing ozone emissions. These filters must be cleaned periodically to ensure proper removal of ozone because the filter media can be exhausted with time, reducing the effectiveness of ozone removal. Claridge (1983) presented data to indicate the effectiveness of servicing on reducing ozone production from photocopiers. As shown in Table 2-2, the amount of ozone produced per copy was greatly reduced following routine maintenance. Machines were serviced after about 64,000 copies had been made. Following servicing, the quantity of ozone gradually returned to preservicing levels after only 3,000 copies (Claridge, 1983).

**Table 2-2. Ozone Produced by Photocopiers Before and After Maintenance**

Machines	Emissions (µg/copy)	
	Before Service	After Service
IBM 6800	22	4
Xerox 3400	47	1
Kodak 100	16	1

Source: Claridge, 1983.

Etkin (1992) also reports that some researchers have downplayed the significance of indoor sources of ozone, demonstrating that in areas with high outdoor ozone levels, most indoor ozone actually originates from outdoors. Etkin's report notes that, in most office buildings, computer equipment, laser printers, and photocopying machines do not add significantly to indoor ozone levels. However, high densities of this equipment and/or inadequate fresh air supplies can lead to elevated ozone levels that may cause adverse health effects.

#### 2.2.2.2 Volatile Organic Compounds (VOCs)

NIOSH measured emissions of volatile organics from four different models of laser printers (Gressel, 1996). The generation rates (per page) of various volatile organics are reported in Table 2-3.

Wolkoff et al. (1993) have conducted one of the most comprehensive studies on emissions from finished products of selected office equipment. The study used both headspace analysis and chamber studies to quantify emissions from copied paper from office copiers and printers.

Results from Wolkoff et al. (1993) indicate that the VOCs in toner powders include solvent residues (e.g., benzene, toluene, xylene), monomers (styrene and acrylate esters), monomer impurities (ethyl, propyl, and isopropyl benzenes, and diphenyl butane isomers), coalescent agents (Texanol), monomer or polymer oxidation products (e.g., benzaldehyde), and polymer toner additive decomposition products. The more volatile components from toner powders dominate the emissions from paper. Xylenes and styrene were dominant in samples from processed paper from all machines tested, and acrylates were found to be minor components. Table 2-4 summarizes the major VOCs emitted from processed paper. Table 2-5 summarizes the TVOC emission rates from fresh copies from all machines evaluated. In general, emissions rates for matrix printers were lowest (0.7 to 1.0  $\mu\text{g}/\text{sheet}$ ) while there was wide variation in the rates from photocopied paper (0.5 to 16.4  $\mu\text{g}/\text{sheet}$ ). The authors estimated a styrene concentration of 12  $\mu\text{g}/\text{m}^3$  for 200 freshly processed copies in a 17- $\text{m}^3$  office. The air exchange rate used in this calculation was 0.25 air change per hour (ACH), and the emission rate used was 6  $\mu\text{g}/\text{m}^2/\text{h}$ .

#### 2.2.2.3 Particulates

Gressel (1996) used a TSI aerodynamic particle sizer to measure particulate emissions from four different models of laser printers. Particulate generation rates from the four printers were reported as being "well below 0.1  $\mu\text{g}/\text{min}$ ." However, particle generation from toner cartridge replacement or the effect of paper and/or paper type on particle generation were not considered.

**Table 2-3. Laser Printer Emission Rates of Various VOCs and TVOCs Reported as Toluene Equivalents (mg/page), Source: Gressel, 1996**

Printer	Printing Rate (pg/min)	Butanol	Toluene	Xylenes	Benzene*	Total VOCs
A	6.5	0.024 $\pm 0.0471$	ND	0.050 $\pm 0.0688$	ND	0.238 $\pm 0.318$
B	6.5	0.042 $\pm 0.0183$	ND	0.070 $\pm 0.0813$	ND	0.257 $\pm 0.163$
C	12.5	0.003 $\pm 0.00911$	0.006 $\pm 0.0107$	0.002 $\pm 0.00395$	0.002 $\pm 0.00532$	0.083 $\pm 0.131$
D	6.5	0.022 $\pm 0.0276$	0.003 $\pm 0.00666$	0.020 $\pm 0.0232$	ND	0.158 $\pm 0.158$

ND = Nondetected.

\*Benzene was quantified for printer C only; not identified as a major peak on the gas chromatograph for other printers.

**Table 2-4. VOC Emitted from Processed Paper (Listed According to GC Retention Time)**

	Photocopied						Laser Printed			Matrix Printed	
	A*	B	C	D	E	F	G	H	I	J	K
Benzene	x	x+	x+	x+	*+	*+	x	x+	x	x	x
1-Butanol	x+	x+		x	x+	x+	x+	x	x+		x
Toluene	x+	*+	x+	*+	x+		*+	x+	x+	*	x
Pyridine						x+					
1-Methyl-2-pentanone		x+		x+							
Hexanal	*	x	x	x	x	x	x	x	x	*	*
C <sub>4</sub> -Cyclohexane isomers			+	x+			+		+		
1-Butyl-ether		x+		+	x	+	x+	x+	x+	x	x
Ethyl benzene	*+	*+	*+	*+	*+	*+	*+	*+	*+	x	*
m- and p-Xylene	*+	x+	*+	*+	*+	*+	*+	*+	*+	x	*
o-Xylene	x+	x+	*+	x+	x+	x+	x+	x+	*+	x	x
Styrene	*+	*+	*+	*+	*+	*+	*+	*+	*+	*	*
1-Butyl acrylate		x+			*+		x+				
2-Phenylpropane	x	x+	x	x+	x+	x+	x+	x+	x+	x	x
3-Heptanol		x+									
1-Phenylpropane	x	x+	x+	x+	x+	x+	x+	x+	x+	x	x
Ethyl toluene isomers	x	x+	x+	x+	x+	x	x+	x+	x+	x	
3-Ethoxy-3-ethyl-4,4-dimethylpentane		*+								*	
1-Butyl methacrylate	x+						+				
Benzaldehyde	+			x+	x+	x+		x+	x+	x	x
Diethylbenzene isomers			x	x			x+	*+	x		x
2-Ethyl-1-hexanol				x+	+		+	x+	x+		x
2-Ethylhexylacetate			+	+				x+	+		
2,2-Azo-bis-isobutyronitrile	+	x+		x+					x+		
2-Ethylhexyl acrylate			x+	x+				x+	x+	x	x

x = detected in processed paper emissions, \* = four largest peaks, + = detected in toner powder.

\* Hexane, 1,1-dichloro-1-nitroethane, octene, pentanal, and trichloroethene were all observed in paper emissions.

Source: Wolkoff et al., 1993.



**Table 2-5. TVOC Emissions from Fresh Copies ( $\mu\text{g}/\text{copy sheet}$ )<sup>a</sup>, Source: Wolkoff et al., 1993.**

Photocopying Machines		Laser Printers		Matrix Printers	
A	1.6	G	6.5	J	0.7
B	16.4	H	2.6	K	1.0
C	0.5	I	2.0		
D	2.4				
E	6.1				
F	7.5				

<sup>a</sup> Emitted from fresh black copies during 16 hours.

Schnell et al. (1992) used a continuous tape-feed Aethalometer to measure the black carbon (BC) particulate emissions in an interior photocopier room in a six-story office/research building. The room's interior measurements were 20 ft x 15 ft x 10 ft (6x4.5x3m). The photocopier was a recent model (at the time of the study), designed for medium-volume office use. At the end of the copying run, which was 200 to 800 copies, the photocopier was turned off and an aethalometer continued to measure for 24 hours thereafter. The concentration of BC aerosol produced by the photocopier occasionally raised room levels to the  $1\text{-}\mu\text{g}/\text{m}^3$  level. This is equivalent to BC levels observed in urban areas under moderate vehicle traffic (Schnell et al., 1992). The concentration of finely dispersed, charged BC aerosol is reduced upon cessation of photocopying. In the room (under no-air-ventilation conditions), BC concentrations fell to background levels within 30 to 60 minutes.

The potential for particulate indoor air emissions is expected to increase over time between maintenance cycles. Typically, about 75 percent of the toner is transferred to the photoconductive drum. Toner particles that do not adhere to the drum become available for emission to the indoor air. As the photoconductive surface of the drum deteriorates, the toner transfer efficiency decreases. Although this decrease in efficiency increases the potential for indoor air emissions, there were no published data on the extent to which these unbound toner particles are emitted to the indoor environment.

### 2.3 Summary

This literature review suggested that there is a general lack of published emissions data. Discussions with industry representatives indicated that much of the existing data on emissions from office equipment are proprietary. Furthermore, the methods currently being used for emissions testing both by researchers and by industry are variable. As a result, data from one study are not comparable to those from another using a different method. In addition, the test methods currently used often focus on measuring levels from equipment to determine if these levels exceed occupational limits as opposed to measuring pollutants present in the indoor air of a

typical office environment. Given these limitations, a high priority of this research was the development of a standard test method capable of providing emission rates for office equipment.

### **3.0 PHASE I: TEST METHOD DEVELOPMENT, EVALUATION, AND RESULTS**

The procedure that was used to develop the emission testing guidance consisted of: (1) forming an RTI/EPA/industry subcommittee; (2) obtaining and reviewing existing testing methodologies; (3) developing an outline of the major testing issues and objectives; (4) preparing a draft test method; and (5) reviewing and revising the method based on subcommittee member comments. The revised test method was then submitted to the entire group of technical advisors participating in this cooperative agreement for their input. The test methodology that resulted from this collaborative process was based on many discussions about balancing the desire for a specific and sophisticated method designed to establish minimum performance standards while still providing flexibility to accommodate different equipment types and emission test facilities.

#### **3.1 Discussion of Method**

The test method is detailed in Appendix B (Emissions Testing Guidance Document for Dry-Process Photocopy Machines), and a brief overview of the recommended chamber test conditions is presented here and summarized in Table 3-1.

The test method presented in the Emissions Testing Guidance Document uses flow-through dynamic chambers because they are generally applicable to all types of equipment and generally mimic typical use conditions found in an office. The chamber's linear dimensions should be a minimum of 1.4 times the dimensions of the equipment tested; e.g., the minimum size chamber for a machine measuring 1.5 by 1 by 0.5 m is 2.1 by 1.4 by 0.7 m. The value of 1.4 was selected based on the prior experience of manufacturers in chamber testing. Its primary basis is to allow for adequate space for servicing of equipment in the chamber, while also allowing for air movement.

Chamber temperature is maintained at 26-31°C by conditioning the inlet air. This temperature range is a practical compromise between typical office conditions (e.g., 23 °C) and temperatures that can be achieved when equipment that has a high thermal load is tested. Because photocopiers can produce large amounts of heat, up to 24,000 Btu/hr (25,322 kJ/hr), it may be difficult to maintain chamber temperatures below 26°C. An air exchange rate of  $2.0 \pm 15\%$  air changes per hour (ACH) on a once-through basis (i.e., non-recirculating) was specified for this method because it is a reasonable approximation of normal indoor conditions (approximately 1 ACH of outdoor air) and also addresses the need to dissipate heat that may be generated by equipment operation while still maintaining a temperature between 26 and 31°C. [Note that the American Society of Heating, Refrigerating and Air Conditioning Engineers (ASHRAE, 1989) has a standard which specifies an outdoor air requirement of 2.50 L/s·m<sup>2</sup> in duplicating and printing areas. The standard also specifies that the installed equipment must incorporate positive exhaust and control (as required) of undesirable contaminants.]

Relative humidity (RH) within the chamber is maintained between 30 and 35%. Initial experiments targeted 50% RH; however, at the high end of the temperature range (31°C), it was not possible to meet 50% RH. It was also anticipated that the amount of water needed to maintain

50% RH in the chamber might cause problems with water collection on the sorbent tubes during VOC analysis. A RH of 35% at 31°C represents a mass of water equivalent to 50% RH at 23°C.

**Table 3-1. Conditions for Chamber Testing**

Condition	Components Testing
Chamber Size	22.7 m <sup>3</sup>
Temperature	26 to 31 °C
% RH	30 to 35
Air Exchange Rate (ACH)	2.0 ± 0.2 h <sup>-1</sup>
Copier Operation Time	20 to 40 min
Sample Collection Time (integrated)	140 to 160 min
Loading (L)	1 Copier

The VOCs and aldehydes/ketones targeted for testing are shown in Table 3-2. VOCs were selected based on screening analysis of chamber air samples collected during copier emission tests. Replicate chamber air samples collected on a multisorbent tubes during each copier test were analyzed by full-scan Gas Chromatograph/Mass Spectrometer (GC/MS) followed by an electronic search of the National Institute of Health (NIH)/EPA Mass Spectral Data Base (MSDB), National Bureau of Standards (NBS) library, and the Registry of Mass Spectral Library (Wiley library) to identify the chemicals present. Manual verification was performed on each peak to confirm computer identifications and to identify compounds not found using the computer library search. Emission rates for these screening samples were estimated by comparison to a calibration standard for the chemical or to toluene. Compounds with estimated emission rates of about 400 µg/h and greater ( $\geq 2.5 \mu\text{g}/\text{m}^3$ ) were included in the target list. The target list for aldehydes/ketones reflects the individual compounds found in a commercially available calibration standard mix commonly used dinitrophenylhydrazine (DNPH) analysis. Methods for measuring chamber air concentrations of VOCs, aldehydes/ketones, ozone, and particles are summarized in Table 3-3.

The duration of the test was selected to ensure that chamber equilibrium is reached or that total emissions are measured. In general, 4 air changes are required to replace 99% of the air in the chamber used for this project since it is a single-pass system. Based on an ACH of 2.0, a 2 hour test is required for the chamber used in this study. Three alternative approaches could be used:

1. Operate the equipment for 2 hours continuously, at which time sampling could occur and, with the absence of wall effects, the chamber air concentration is assumed to be in equilibrium.

**Table 3-2. Organic Chemicals Targeted for Emissions Testing**

Chemical Class	Compounds	
VOCs	Toluene	$\alpha$ -Methyl styrene
	Benzaldehyde	<i>n</i> -Decane
	<i>n</i> -Butyl acetate	2-Ethyl-1-hexanol
	Ethylbenzene	$\alpha$ -Pinene
	<i>m,p</i> -Xylene	Limonene
	2-Heptanone	<i>n</i> -Nonanal
	Styrene	2,5-Dimethyl styrene
	<i>o</i> -Xylene	<i>n</i> -Undecane
	2-Butoxyethanol	<i>n</i> -Decanal
	Isopropyl benzene	<i>n</i> Dodecane
	<i>n</i> -Propyl benzene	BHT
Aldehydes/ketones	Formaldehyde	Methacrolein
	Acetaldehyde	Butyraldehyde
	Acetone	Benzaldehyde
	Acrolein	Valeraldehyde
	Propionaldehyde	<i>m</i> -Tolualdehyde
	Crotonaldehyde	<i>n</i> -Hexanal
	2-Butanone	

**Table 3-3. Methods for Measuring Chamber Air Concentrations of Target Analytes**

Analytes	Method
VOCs	VOCs in air samples (1 to 8 L) collected on multisorbent tubes. (Tenax/Ambrasorb/Charcoal tubes were used for Phase I. For Phase II, RTI used Tenax/Carboxen 1000 tubes.) Tubes analyzed by gas chromatography/mass spectrometry. Screening and quantitation samples collected and analyzed. Screening samples used to identify target VOCs. Quantitation samples used to measure air concentrations of target VOCs using a multipoint calibration.
Aldehydes/ketones	Aldehydes/ketones in air samples (36 L) collected on DNPH-coated silica gel cartridges. Cartridges solvent desorbed with acetonitrile. Extract analyzed by high performance liquid chromatography (HPLC). Concentrations in sample extracts measured using a multipoint calibration.
Ozone	Continuous monitoring of chamber air concentrations using a DASIBI model 1003-AH ozone monitor.
Particles	Continuous monitoring of chamber air concentrations using a particle measuring systems LAS-X optical particle counter.

2. Operate the equipment for a defined period of time, collecting an integrated sample from the start of operation until 2 hours (i.e., 4 air changes) after the equipment is turned off. In the absence of wall effects, this sample should represent about 99% of total emissions during operation for the chamber used in this study.
3. Take short-term periodic samples throughout the period of operation. This approach should be used when information on the time course of emissions is required. This option is useful to determine how emissions change with time of operation.

Note that some types of office equipment, such as photocopy machines and printers, can operate unattended only for a limited period of time due to a finite paper supply. If the equipment cannot operate continuously for the 2 hours required for the chamber to reach equilibrium plus the time required to collect a sample, then one of the following approaches must be used:

- Multiple machines must operate sequentially so that operation is continuous for the time period required (6 hours), or
- An integrated sample must be taken from the start of operation until 2 hours (4 air changes) after the cessation of operation.

For the machines evaluated in this study, 2000 copies were printed for each test, and an integrated sample was collected from the start of operation until 2 hours (i.e., 4 air changes) after the paper supply was exhausted. The paper supply of 2000 sheets was exhausted after 20 to 40 minutes, depending on the machine, resulting in a total sample collection time of 140 to 160 minutes.

### **3.2 Validation and Use of the Method**

After the test methodology was defined, it was evaluated using a two-phase process. Phase I was a single laboratory evaluation of the method in the RTI large chamber, and Phase II was a multilaboratory, or round-robin, evaluation. The following sections describe the Phase I activities and results. A similar discussion for Phase II is in Section 4.

The primary goal of the Phase I testing was to conduct a single laboratory evaluation of the test method for measuring emissions from dry-process photocopiers. Also, since the literature review indicated that little emission data for photocopiers were currently available in the published literature, a secondary goal of the effort was to develop emission rate data for dry-process photocopiers. It was also expected that results from the Phase I testing would be used to guide refinements in the test method prior to implementing the Phase II round-robin evaluation of the test method. Testing was to include measurements for VOCs, aldehydes and ketones, ozone, and particles. However, while the issue of particle emissions from photocopiers is important, it became apparent early in the project that a thorough evaluation of the particles would be beyond the scope of this study and, for this reason, particle measurements were not an emphasis of this project.

To meet the goals of the Phase I testing, four experimental objectives were defined.

1. Conduct a single laboratory evaluation of the large chamber test method using standard materials as sources for generating emissions inside the chamber. Precision and accuracy data for emission rate measurements were to be determined for the large chamber method based on these results. VOCs, aldehydes/ketones, and ozone were selected for evaluation in the large chamber at RTI since standard emitting sources for these chemical groups were easily available and could be shown to be reliable. Particles were omitted from this evaluation since methods for accurately evaluating them in the chamber is complex and would be difficult without potentially contaminating the chamber. A thorough evaluation of particles in the chamber would also require more effort than resources for this study could reasonably provide. Without particle recovery information, chamber validation for particles would not be possible and overall data accuracy would not be known. Because of these issues, evaluating particle emissions was limited to making some unvalidated initial measurements so some general conclusions might be possible, and the focus of the evaluation was centered on VOC, aldehyde/ketone, and ozone emissions.
2. Conduct triplicate tests on a single dry-process photocopier to identify emissions and quantify emission rates for VOCs, aldehydes/ketones, and ozone. During each test, a single time-integrated sample was collected to measure average chamber air concentrations over the test period. Results were used to determine precision of emission-rate measurements for the chamber test method during equipment operation.
3. Conduct tests on four dry-process photocopiers from different manufacturers to identify emissions and quantify emission rates for VOCs, aldehydes/ketones, and ozone. Tests were conducted using time-integrated samples to measure average chamber air concentrations over the test period. Results were used to identify the important emissions and to evaluate variability in emission rates between copiers.
4. Conduct emissions time-course tests on two dry-process photocopiers. During testing, samples were collected every 10 to 15 minutes to quantitate emission rates as a function of time. Results were used to evaluate changes in emission rates over time of copier operation and to determine if integrated samples were adequate.

Table 3-4 gives an overview of the experimental design that was used for Phase I testing. All testing was conducted in a 22.7 m<sup>3</sup> chamber at RTI designed for organic emissions testing. A description of the chamber is given in Table 3-5. Conditions for chamber testing are given in Table 3-1.

**Table 3-4. Experimental Design for Phase I Testing**

Type of Testing	Replicates	Purpose
<b>CHAMBER PERFORMANCE</b>		
Standard emitters for VOCs, aldehydes/ketones, ozone. Single time-integrated chamber air sample collected during chamber testing. Data generated over a 1-week period.	3	To generate precision and accuracy data for VOC, aldehyde/ketone, ozone emission rates for large chamber test method.
Standard emitter for VOCs. Single time-integrated chamber air sample collected during chamber testing.	1	To demonstrate ongoing recovery of known VOC emitters from the test chamber during the emissions testing.
Standard emitter for VOCs. Chamber air samples collected every 10 to 15 minutes during testing.	1	To demonstrate recovery of known VOC emitters from the chamber over short time intervals; used to judge method performance for time-course testing; to compare results from integrated and time-course samples.
<b>PHOTOCOPIERS</b>		
Photocopier 1. Single time-integrated chamber air sample collected during testing.	3	To identify VOCs emitted; to measure emission rates for VOCs, aldehydes/ketones, ozone, and particles in the full power and the idle mode; to evaluate precision of emission rate measurement for copiers in the full operation mode.
Photocopier 1. Single time-integrated chamber air sample collected during testing. Chamber air samples also collected every 10 to 15 minutes during test run.	1	To evaluate reproducibility of test method over an extended time period; to evaluate changes in emission rate over time of copier operation.
Photocopier 1. Single time-integrated chamber air sample collected during testing. All filters changed in copier.	1	To evaluate change in emissions as a result of changing operating conditions.
Photocopier 2. Single time-integrated chamber air sample collected during testing.	1	To identify VOCs emitted; to measure emission rates for VOCs, aldehydes/ketones, and particles in the full power and idle modes; to assess variability between copiers operated in the full power and idle modes.
Photocopier 3. Single time-integrated chamber air sample collected during testing.	1	To identify VOCs emitted; to measure emission rates for VOCs, aldehydes/ketones, and particles in the full power and idle modes; to assess variability between copiers operated in the full power and idle modes.
Photocopier 4. Single-time integrated chamber air sample collected during testing. Chamber air samples also collected every 10 to 15 minutes during test run.	1	To identify VOCs emitted; to measure emission rates for VOCs, aldehydes/ketones, and particles in the full power and idle modes; to assess variability between copiers operated in the full power and idle modes; to evaluate changes in copier emissions over operating time.



**Table 3-5. Description of RTI's Large Environmental Test Chamber**

Parameter	Description
Size	3.05 x 3.05 x 2.5 m (22.7m <sup>3</sup> ) or 10 x 10 x 8 ft. (800ft <sup>3</sup> )
Construction Materials	Ducts: Aluminum Ceiling/Walls: Aluminum Floor: Stainless Steel Gaskets: Viton
Air Supply System	Outside air passed through particulate filters then through Carasorb 200 filters for organics removal, followed by HEPA filtration and a final charcoal filter
Temperature Control	18 to 35°C ± 1°C (64 to 95° ± 2°F)
Humidity Control	40 to 70% Relative Humidity (RH) ±5%
Air Exchange Rate	0.2 air changes/h to 2 air changes/min
Sampling Ports	0.635 cm (0.25 inch) stainless steel Swagelok Adaptable to meet other requirements
Measurement Systems	Temperature/Humidity - General Eastman Model 850 Air Flow - Carrier Comfort Network Distributed Controller Data Acquisition - 386 PC

During Phase I, testing was conducted on four mid-range copiers (30-150 copies per minute). This type of copier was selected because the literature review (Hetes et al., 1995) indicated that these types of copiers are prevalent in the office environment. The process used to select the specific copier models for testing included a review of the Buyers Laboratory Copier Specification Guide (BLI, 1995) to identify mid-range copiers using different toner types, developing systems, fusing mechanisms, and photoconductive drum surface materials. Characteristics of the four copiers selected for testing are given in Table 3-6.

**Table 3-6. Copiers Tested**

Copier ID	1	2	3	4
Toner Type	dry, dual-component	dry, dual-component	dry, mono-component	dry, dual-component
Development	magnetic brush	magnetic brush	magnetic roller	magnetic brush
Fusing	heat/pressure	heat/pressure	hot roller	heat/pressure
Photoconductor	organic drum	organic belt	amorphous silica drum	organic drum
Toner Condition	used	new	new	used
Condition	used~50,000 copies	new	new <100 copies	used ~76,000 copies
Copies per Minute	50	85	50	50

### 3.3 Chamber Evaluation

#### 3.3.1 Procedure

As a first step in evaluating the large chamber test method, a recovery study was conducted to evaluate the accuracy and precision of the emission rate measurements. This was accomplished by introducing selected VOCs, formaldehyde, and ozone into the chamber at known rates. Procedures for generating and introducing these chemicals into the chamber air are outlined in Table 3-7. Chamber air samples were then collected and analyzed for pollutant concentrations using procedures identical to those used during the emission tests with photocopiers. The measured amount of pollutant emitted during each test was calculated as

$$E_m = C_c \times V_c \times A_c \times T_s \quad (1)$$

where

$E_m$	=	the measured amount of target pollutant emitted during each test in $\mu\text{g}$ .
$C_c$	=	the measured chamber air concentration in $\mu\text{g}/\text{m}^3$ .
$V_c$	=	the chamber volume in $\text{m}^3$ .
$A_c$	=	the air exchange rate in $\text{h}^{-1}$ .
$T_s$	=	the sample collection time in h.

**Table 3-7. Methods for Generating Standards with Known Emissions**

Chemical Class	Method
VOCs	<p>Cylinder containing toluene and chloroform or n-decane prepared</p> <ul style="list-style-type: none"><li>• 10 L volume metered into chamber at a rate of 1.0 LPM. Samples collected over 2 hr 10 min period to give an integrated chamber air concentration of <math>\sim 10\mu\text{g}/\text{m}^3</math>.</li><li>• 10 L volume metered into chamber at a rate of 0.25 LPM over 40 min. Time point samples collected for T = 0-10, 10-20, 20-30, 30-45, 45-60, 60-75, 75-90, 90-105, 105-120, and 120-160 min.</li></ul>
Aldehydes/Ketones	<p>Aqueous solution of formaldehyde (<math>\sim 53\mu\text{g}/\text{mL}</math>) delivered to chamber with HPLC pump, vaporized by passing through <math>350^\circ\text{C}</math> heated tubing at rate of 2.1 mL/min for 30 min, samples collected over a 2 hr 30 min period.</p>
Ozone	<p>Generator producing <math>\sim 75\text{--}90\text{ ppm O}_3</math> at 1 LPM attached to chamber for 2 hr period. Monitored increase and decrease of chamber concentration.</p>

Percent recovery of the emitted pollutant was used to evaluate accuracy of the emissions test method. Percent recovery (%R) was calculated as

$$\%R = E_{\text{am}}/E_{\text{as}} \times 100 \quad (2)$$

where  $E_{\text{am}}$  is the amount measured during the recovery test in  $\mu\text{g}$ , and  $E_{\text{as}}$  is the amount that was introduced into the chamber during the test in  $\mu\text{g}$ .

Recovery tests using integrated samples collected over the test period were conducted in triplicate for the VOCs, formaldehyde, and ozone. For these recovery tests, precision of the emission rate measurement was evaluated as percent relative standard deviation (%RSD) of the replicate tests.

For the VOCs, the recovery test was repeated midway through the Phase I testing to demonstrate ongoing performance of the large chamber. A time-course recovery study was also conducted to evaluate the recovery of VOCs from the chamber over time. For this latter test, both time-point samples and an integrated sample for the entire test period were collected to allow a comparison of data generated by both collection schemes.

### 3.3.2 Results

Results of the VOC recovery tests are summarized in Table 3-8. Data for the time-course recovery study are given in Figures 3-1 and 3-2 which are plots of chamber air concentration vs. time for chloroform and toluene, respectively. The figures show both the concentrations measured during testing and the theoretical concentration given the known emission source under the chamber test conditions.

In general, the results show good accuracy and precision for the chamber evaluation. Observations from the results follow.

- For the triplicate recovery tests using time integrated samples (Test 1 to 3, Table 3-8), both accuracy and precision of the test method was good for both chloroform and toluene.
- The repeat test for the time-integrated recovery study (Test 4, Table 3-8) again showed good recovery for both chloroform and toluene demonstrating that acceptable performance of the emission test method continued throughout Phase 1 testing.
- Results for the time course study (Test 5, Table 3-8) showed good recovery for toluene for both the time-point and the integrated sample. However, for chloroform, calculated recovery using data from the time-point samples showed good recovery, but the integrated sample showed poor recovery. Poor recovery using the integrated sample was due to a problem during analysis, not poor recovery from the chamber. Excess water collected on the time-integrated sample suppressed the signal from the MS during analysis to give a low measured chamber air concentration for chloroform.
- Plots of the data for the time-point samples (Figures 3-1 and 3-2) showed good agreement between the measured and the theoretical concentrations for all time points except the point at 37.5 minutes. Given the good agreement for the other time points, it is likely that the lower measured concentration at this point may be due to an inaccuracy for sample collection or analysis.

Results for the recovery test for formaldehyde and ozone are given in Table 3-9. Data again showed reasonable accuracy and precision of the large chamber test method for these two pollutants. A plot of the ozone concentration data over time compared to the theoretical values is given in Figure 3-3. Recovery of ozone is on the low side possibly due to reactions with the chamber surfaces or due to comparison to the relatively crude method of using Dräger tubes for determining generator concentrations.

**Table 3-8. Chamber Recovery Test Results - VOCs**

Chemical	Date	Measured Mass (µg)	Theoretical Mass (µg)	% Recovery
Chloroform				
Test 1	5/22/95	2,700	3,000	90
Test 2	5/23/95	2,900	3,000	97
Test 3	5/25/95	2,600	3,000	87
			Mean	91 (6.2) <sup>a</sup>
Test 4	9/1/95	3,100	3,000	103
Test 5	9/14/95			
Integrated sample		1,500	2,600	58 <sup>b</sup> (52) <sup>b,c</sup>
Time-point sample		2,200	2,600	85 (73) <sup>c</sup>
Toluene				
Test 1	5/22/95	2,400	2,100	114
Test 2	5/23/95	2,500	2,100	119
Test 3	5/25/95	2,500 (2.1) <sup>a</sup>	2,100	119
			Mean	118 (2.1) <sup>a</sup>
Test 4	9/1/95	2,400	2,100	114
Test 5	9/14/95			
Integrated sample		2,000	1,800	111 (95) <sup>c</sup>
Time-point sample		2,100	1,800	117 (99) <sup>c</sup>

<sup>a</sup> %RSD of replicate chamber air samples.

<sup>b</sup> Water in sample suppressed signal for chloroform to give low calculated emission.

<sup>c</sup> Release rate from cylinder changed slightly over 40-minute release period. Recovery given in parentheses calculated using the higher release rate. Change in release rate at the start was probably due to pressure buildup in the valve.

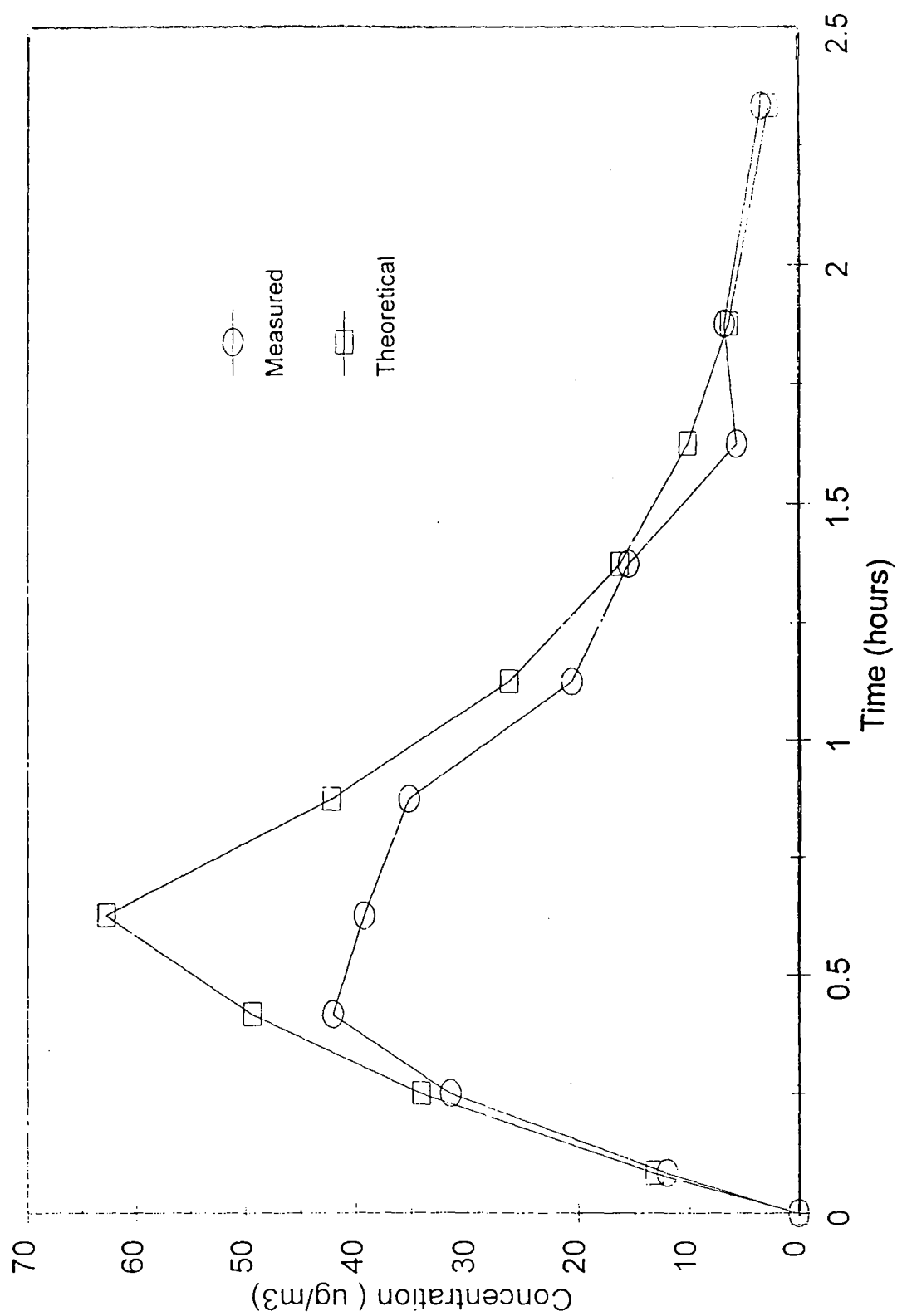


Figure 3-1. Recovery from chamber chloroform.

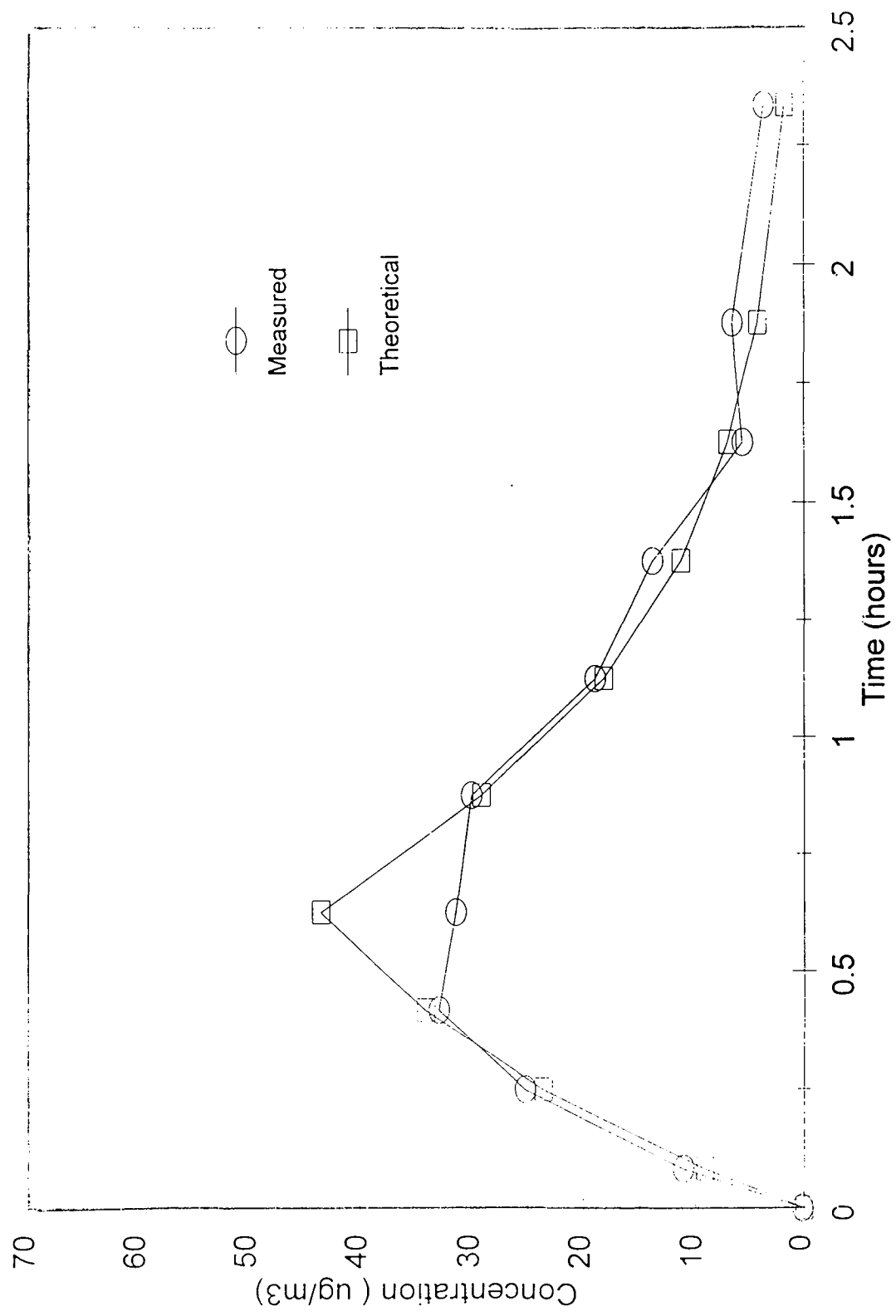


Figure 3-2. Recovery from chamber toluene.

**Table 3-9. Chamber Recovery Test Results - Formaldehyde and Ozone**

Compound	Measured Emission Rate (µg/h)					Theoretical Emission	% Rec. Rate(µg/h)
	Test 1	Test 2	Test 3	Mean	% RSD		
Formaldehyde	5800	5900	6100	6000	2.0	6400	93
Ozone (peak conc.)	6700	6600	5600	6300	9.4	8800 <sup>a</sup>	72

<sup>a</sup> Based on Dräger tube measurements.

### 3.4 Photocopier Test Results

#### 3.4.1 Sample Collection and Emission Rate Calculations

Large chamber emission tests were performed on four dry-process photocopiers from different manufacturers. As described in Table 3-4, five experimental objectives were defined:

1. Evaluate precision of the emission rate measurements for one copier in the idle and full operation modes using a fixed set of operating conditions;
2. Evaluate the variability of emission rate measurements between copiers from different manufacturers;
3. Evaluate the variability of emission rate measurements for one copier using different operating conditions;
4. Evaluate the change in emission rates as a function of copier operating time; and
5. Evaluate the practical aspects of test method implementation.

To address these experimental objectives, a total of nine separate emissions tests were conducted. For each test, the same basic sequence of operations was performed as outlined in Table 3-10. The copiers tested and specific conditions for each test are given in Table 3-11. For each test, concentrations of VOCs, aldehydes/ketones, and ozone were measured in the chamber air. Particles were measured for a subset of the nine photocopier tests. However, since experiments were not conducted to determine the recovery of particles from the chamber, little emphasis was placed on these results. This was not to say that the results were not important, just that a full evaluation of the particle measurements/validation was beyond the scope of this study. Figure 3-4 shows a typical particle trace of photocopier 1 during an emissions test and Figure 3-5 shows the particle size distribution during the same test.



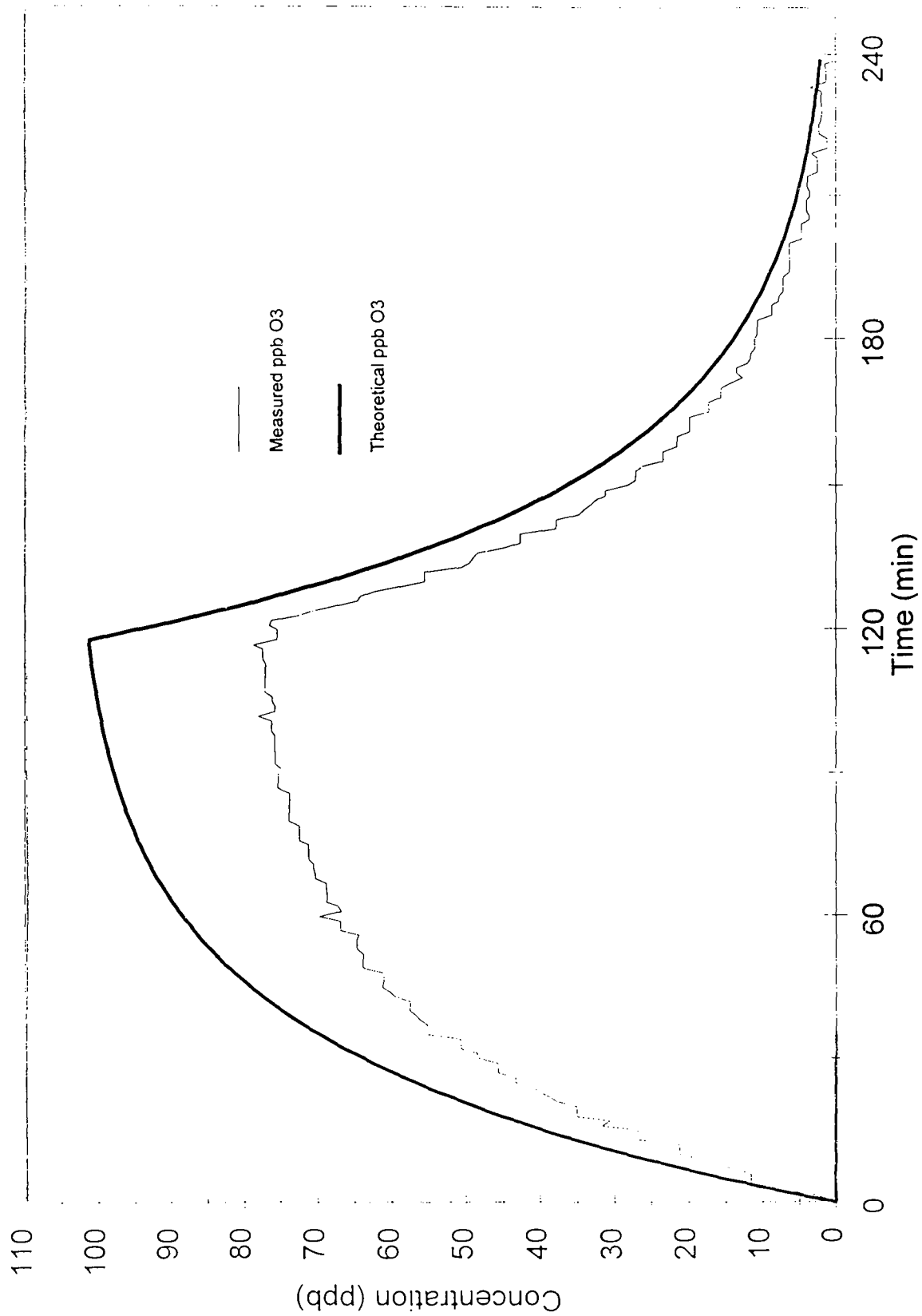


Figure 3-3. Chamber recovery  
ozone - recovery test 3.

**Table 3-10. Copier Testing Procedure for Phase I (refer to Appendix B for details)**

- 
1. Background air samples collected from empty chamber.
  2. Copier placed in chamber.
  3. Service representative checked copier and assisted in setting up remote start capability.
  4. Paper loaded in copier, copier powered up, equilibrated overnight.
  5. Air samples collected during copier powered up but idle.
  6. Air samples collected during full copier operation
    - 2,000 copies/30-40 minute operation time
    - For integrated sample, sample collection started when copier started printing; collection continued for 2 hours (4 air changes after copying process ended)
    - For time-point samples, sample collected for T = 0-10, 10-20, 20-30, 30-45, 45-60, 60-75, 75-90, 90-105, 105-120, and 120-160 minutes after copier began printing.
  7. Carbon monoxide release made during copier operation to accurately determine air exchange rate.
-

Table 3-11. Conditions for Copier Testing

Copier	1	1	1	1	1	1	1	1	1	2	3	4
Test	1	2	3	4	5	6	7	8	9			
Date	5/1/95	5/4/95	5/5/95	5/8/95	9/19/95	9/21/95	4/25/95	8/30/95	8/28/95			
Toner Type	dry, dual	dry, dual	dry, dual	dry, dual	dry, dual	dry, dual	dry, dual	dry, mono	dry, dual			
Development	magnetic brush	magnetic brush	magnetic brush	magnetic brush	magnetic brush	magnetic brush	magnetic brush	magnetic roller	magnetic brush			
Fusing	heat/pressure	heat/pressure	heat/pressure	heat/pressure	heat/pressure	heat/pressure	heat/pressure	hot roller	heat/pressure			
Photoconductor	organic drum	organic drum	organic drum	organic drum	organic drum	organic drum	organic drum	amorphous silica drum	organic drum			
Toner Lot	1-1	1-2	1-2	1-2	1-2	1-2	2-1	3-1	4-1			
Toner Condition	used	new	new	new	used	used	new	new	used			
Copier Condition	used ~50,000 copies	used ~51,000 copies	used ~53,000 copies	used ~55,000 copies	used ~57,000 copies	filters replaced ~59,000 copies	new	new <100 copies	used ~76,000 copies			
Run Time (min)	19.17	37.85	37.78	37.72	37.55	37.58	22.98	39.90	37.12			
# Pages	999	2,000	2,000	2,000	2,000	1,998	1,929	1,998	1,998			
ACH	1.86	1.82	1.82	1.91	1.79	1.87	1.86	1.89	1.85			
Chamber T (°C)												
Idle (avg)	26.2	26.5	26.3	26.8	26.2	26.6	26.9	26.9	26.4			
Max	27.8	29.0	28.7	29.5	28.3	29.4	31.1	29.1	28.1			
Change	1.6	2.5	2.4	2.7	2.1	2.8	4.2	2.2	1.7			
Chamber RH (%)												
Idle (avg)	32.6	32.7	32.6	32.8	27.2	31.5	32.7	31.1	31.6			
Max	39.1	45.3	44.0	42.3	47.9	40.6	36.6	46.4	51.7			
Change	6.5	12.6	11.4	9.5	20.7	9.1	3.9	15.3	20.1			
Sampling	Integrated	Integrated	Integrated	Integrated	Time-Course, Integrated	Integrated	Integrated	Integrated	Time Course, Integrated			

ACH = air changes per hour  
T = temperature  
RH = relative humidity

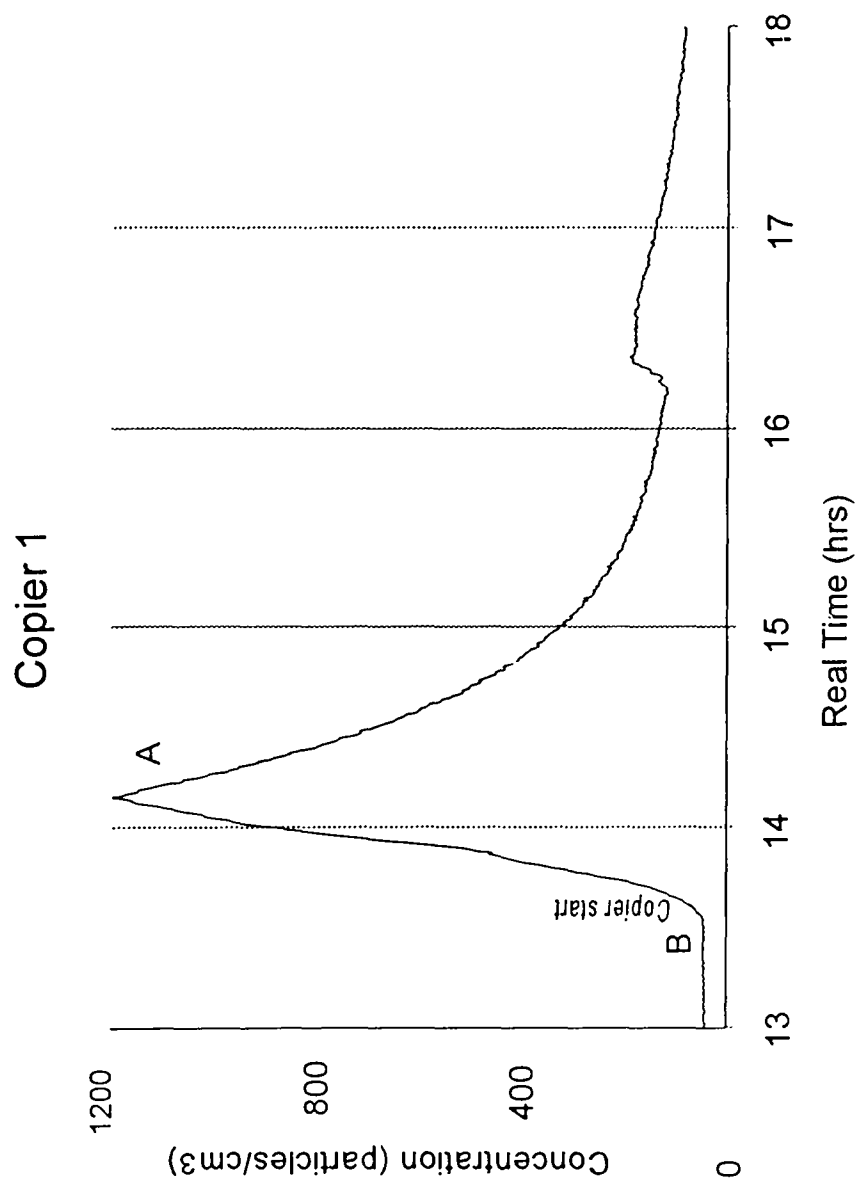


Figure 3-4. Copier 1, particle concentration during test run.

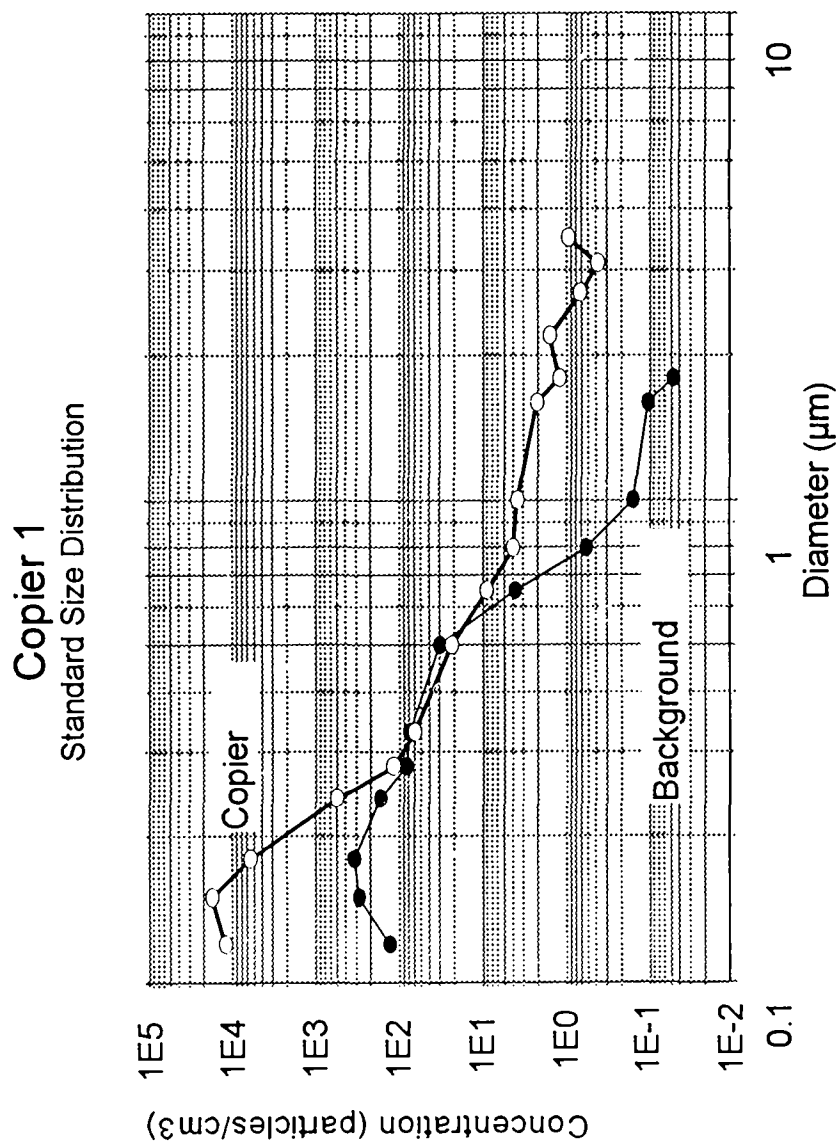


Figure 3-5. Copier 1, particle size distribution during test run.

For VOCs and aldehydes/ketones, chamber air samples were collected then analyzed for the target chemicals. As outlined in Table 3-10, a chamber air sample was collected prior to placing the copier in the chamber. A second chamber air sample was collected after the copier was placed in the chamber and was powered up but was not printing. This sample was collected to provide data on the equilibrium chamber air concentration in the idle mode and was taken after the copier had equilibrated in the chamber overnight. Finally, a third chamber air sample was collected from the time the copier started printing until 2 hours (4 chamber air changes) after printing was completed. This sample provided data on the average time-integrated chamber air concentration over the test period. For the chamber used for this study, 4 air changes are required to replace 99% of the air in since it is a single-pass system.

The emission rate ( $ER_i$ ) in the idle mode was calculated assuming steady-state conditions after the copier had been idling in the chamber overnight.

$$ER_i = [(C_i - C_b) \times V_c \times A_c] / n \quad (3)$$

where,

$ER_i$	=	emission rate in the idle mode in $\mu\text{g/h} \cdot \text{copier}$
$C_i$	=	chamber air concentration in the idle mode in $\mu\text{g}/\text{m}^3$
$C_b$	=	background chamber air concentration in $\mu\text{g}/\text{m}^3$
$V_c$	=	chamber volume in $\text{m}^3$
$A_c$	=	chamber air exchange rate in $\text{h}^{-1}$
$n$	=	number of copiers in chamber.

The emission rate of VOCs attributed to printing ( $ER_c$ ) was calculated using a simple mass balance equation and applying the following assumptions:

1. There is no reversible or irreversible adsorption of the target organics in the chamber during the testing period. This was demonstrated to be true through chamber recovery tests.
2. The chamber air is well-mixed. This was demonstrated for each test through the release and measurement of CO in the chamber air during testing.
3. The chemicals in the chamber are in the vapor phase and uniformly distributed in the chamber air. This is a property of VOCs.
4. The steady state emissions measured in the idle mode remain constant during the copying mode. Any changes are considered to result from copying, therefore by definition, a change will be attributed to printing.

After 4 air changes, 99% of the chamber air was exhausted from the chamber. Since chamber air samples were collected from the time the copier started until the time that 4 air changes had been achieved after copying had stopped, 99% of the VOCs emitted during testing were exhausted from the chamber during the sample collection period. Under these conditions:

$$ER_c = M_t / (T_p \times n) \quad (4)$$

where,

$ER_c$	=	emission rate attributed to printing in $\mu\text{g/h} \cdot \text{copier}$
$M_t$	=	total net mass of VOC measured in the chamber air in $\mu\text{g}$
$T_p$	=	time the copier was printing in h

$$M_i = (C_p - C_i) \times T_{av} \quad (5)$$

where

$$\begin{aligned} C_p &= \text{measures time-integrated chamber air concentration measured during the chamber test in } \mu\text{g/m}^3 \\ C_i &= \text{chamber air concentration measured during idle mode in } \mu\text{g/m}^3 \\ T_{av} &= \text{total volume of air that passed through the chamber during testing in m}^3. \end{aligned}$$

Here we have taken the approach that the concentration of VOCs in the chamber air attributed to printing can be estimated by correcting the total concentration measured during the chamber copying experiment by the concentration measured during the chamber idle experiment.

$$T_{av} = V_c \times A_c \times T_c \quad (6)$$

where

$$\begin{aligned} V_c &= \text{chamber volume in m}^3 \\ A_c &= \text{chamber air exchange rate in h}^{-1} \\ T_c &= \text{time the sample was collected for in h.} \end{aligned}$$

Equations 4, 5, and 6 are then combined, resulting in the following equation:

$$ER_c = [(C_p - C_i) \times V_c \times A_c \times T_c] / (T_p \times n) \quad (7)$$

In two tests, chamber air samples for VOC analysis were also collected at shorter time intervals (10 to 15 minutes) throughout the test period. Average emission rates for each time interval were calculated using the chamber air concentration at that time interval as

$$ER_t = (\Delta C_i / \Delta T_i + A_c C_i) \times V_c / n \quad (8)$$

where,

$$\begin{aligned} ER_t &= \text{emission rate for time interval t in } \mu\text{g/h} \cdot \text{copier} \\ \Delta C_i &= \text{change in chamber air concentration for time interval t in } \mu\text{g/m}^3 \\ \Delta T_i &= \text{length of time interval T in hours} \\ C_i &= \text{average measured chamber air concentration for time interval t in } \mu\text{g/m}^3 \end{aligned}$$

For ozone, chamber air concentrations were measured over the test period using real time instruments. Here, these chemicals emission rates were calculated as

$$ER_o = [(C_e \times A_c \times V_c) / (1 - e^{-A_c T_p})] / n \quad (9)$$

where

$$\begin{aligned} ER_o &= \text{emission rate for ozone in } \mu\text{g/h} \cdot \text{copier} \\ C_e &= \text{equilibrium chamber air concentration in } \mu\text{g/m}^3 \end{aligned}$$

### 3.4.2 Precision of Emission Rate Measurements

Precision of the emission rate measurements in the idle and print modes was evaluated by conducting triplicate large chamber tests on copier 1 using a single set of operating conditions. Precision was evaluated as % RSD of the triplicate emission rate measurements. Precision data for the replicate large chamber emissions tests are provided in Table 3-12 (VOCs) and Table 3-13 (aldehydes/ketones and ozone). Results are provided for the average emission rate measurements and their %RSD for the triplicate tests in both the idle and the print modes. Results for the print mode generally show excellent precision (RSD < 10% in many cases) for the emission rate measurements. The exceptions were for those compounds where measured emission rates were low (i.e., 2-butoxyethanol and *n*-decanal in the print mode, ethylbenzene and the xylenes in the idle mode) or the background level for either the method blank or the chamber background samples were relatively high (i.e., acetone and acetaldehyde) compared to the chamber air concentrations measured during emission testing.

### 3.4.3 Between Copier Variability of Emission Rate Measurements

Large chamber emissions tests were conducted at RTI on four different dry-process photocopiers. For each of these tests, estimated emission rates were calculated based on results from integrated chamber air samples collected over the entire test period (as outlined in Table 3-10). Results of these tests are given in Tables 3-14 to 3-20, and Figure 3-6 as follows.

- Table 3-14 -- VOCs during idle in  $\mu\text{g/h} \cdot \text{copier}$ ,
- Table 3-15 -- VOCs during operation in  $\mu\text{g/h} \cdot \text{copier}$ ,
- Table 3-16 -- VOCs during operation in ng/page,
- Table 3-17 -- Aldehydes/ketones during idle in  $\mu\text{g/h} \cdot \text{copier}$ ,
- Table 3-18 -- Aldehydes/ketones during operation in  $\mu\text{g/h} \cdot \text{copier}$ ,
- Table 3-19 -- Aldehydes/ketones during operation in ng/page,
- Table 3-20 -- Ozone during operation in  $\mu\text{g/h} \cdot \text{copier}$ , and
- Figure 3-6 -- Continuous ozone concentrations in ppb.

Note that tables 3-16 and 3-19 report the results in ng/page, not  $\mu\text{g/h} \cdot \text{copier}$ . Consequently, emission rates that have low per copier values may have high per page values and vice versa, depending on the copy feed rate or speed of the copier (see Table 3-11).

Overall results tend to show varied emission rates between the different copiers, although most of the same chemicals were emitted from all four copiers. Tests were conducted over a 5-month period, and the recovery tests during that period showed acceptable performance (Table 3-8). Therefore, differences in measured emission rates should be considered to be a result of differences between copiers and not a result of changing test performance.



**Table 3-12. VOC Emission Rate Precision Data for Triplicate Large Chamber Tests of Copier 1 <sup>a, b</sup>**

Chemical	Idle		Print	
	Average Emission Rate (µg/h • copier)	% RSD	Average Emission Rate (µg/h • copier)	% RSD
Toluene	-- <sup>c</sup>	--	760	14
<i>n</i> -Butyl Acetate	--	--	50	13
Ethylbenzene	180	38	27,000	6
<i>m,p</i> -Xylene	160	38	29,000	6
2-Heptanone	--	--	--	--
Styrene	44	23	9,900	4
<i>o</i> -Xylene	88	28	17,000	4
2-Butoxyethanol	--	--	67	141
Isopropyl benzene	--	--	400	3
Benzaldehyde	NT <sup>d</sup>	--	NT	--
$\alpha$ -Pinene	NT	--	NT	--
<i>n</i> -Propyl benzene	--	--	790	1
$\alpha$ -Methyl styrene	13	9	1,100	7
<i>n</i> -Decane	12	15	450	13
2-Ethyl-1-hexanol	33	15	230	11
Limonene	--	--	220	23
<i>n</i> -Nonanal	--	--	1,100	13
2,5-Dimethyl styrene	--	--	--	--
<i>n</i> -Undecane	36	10	2,000	8
<i>n</i> -Decanal	--	--	130	52
<i>n</i> -Dodecane	54	18	960	8
BHT	--	--	--	--

<sup>a</sup> Data generated for Copier 1, tests 2, 3, and 4. (See Table 3-11)

<sup>b</sup> Values are based on three runs

<sup>c</sup> Less than 10 µg/h • copier

<sup>d</sup> NT = Not tested

**Table 3-13. Aldehyde/Ketone and Ozone Emission Rate Precision Data for Triplicate Large Chamber Tests of Copier 1 <sup>a, b</sup>**

Chemical	Idle		Print	
	Average Emission Rate (µg/h • copier)	% RSD	Average Emission Rate (µg/h • copier)	% RSD
Formaldehyde	-- <sup>c</sup>	--	<500 <sup>d</sup>	--
Acetaldehyde	140	36	710 <sup>d</sup>	27
Acetone	--	--	2,000 <sup>d</sup>	45
Acrolein	--	--	--	--
Propionaldehyde	--	--	--	--
Crotonaldehyde	--	--	--	--
2-Butanone	--	--	--	--
Methacrolein	--	--	--	--
Butyraldehyde	--	--	160	5.4
Benzaldehyde	--	--	1,800	11
Valeraldehyde	--	--	540	10
<i>m</i> -Tolualdehyde	--	--	--	--
<i>n</i> -Hexanal	--	--	210	17
Ozone	NC <sup>e</sup>	NC	3,000	7.1

<sup>a</sup> Data generated during Copier 1, Tests 2, 3, and 4 (see Table 3-11)

<sup>b</sup> Values are based on three runs

<sup>c</sup> Less than 10 µg/h • copier

<sup>d</sup> High background on cartridges or in chamber

<sup>e</sup> NC = Not calculated

**Table 3-14. Estimated VOC Emission Rates ( $\mu\text{g/h} \cdot \text{copier}$ ) Dry-Process Photocopiers--Idle**

Chemical	Emission Rate ( $\mu\text{g/hr} \cdot \text{copier}$ )			
	Copier 1 Test 2-4 (average)	Copier 2 Test 7	Copier 3 Test 8	Copier 4 Test 9
Toluene	-- <sup>a</sup>	--	390	74
<i>n</i> -Butyl Acetate	--	140	--	--
Ethylbenzene	180	--	10	--
<i>m,p</i> -Xylene	160	48	--	23
2-Heptanone	--	460	--	--
Styrene	44	220	49	47
<i>o</i> -Xylene	88	--	--	14
2-Butoxyethanol	--	--	--	--
Isopropyl benzene	--	--	--	--
Benzaldehyde	NT <sup>b</sup>	NT <sup>b</sup>	--	--
$\alpha$ -Pinene	NT <sup>b</sup>	NT <sup>b</sup>	--	--
<i>n</i> -Propyl benzene	--	--	--	--
$\alpha$ -Methyl styrene	13	10	17	--
<i>n</i> -Decane	12	--	24	--
2-Ethyl-1-hexanol	33	150	82	--
Limonene	--	130	11	93
<i>n</i> -Nonanal	--	40	120	--
2,5-Dimethyl styrene	--	--	--	--
<i>n</i> -Undecane	36	--	49	--
<i>n</i> -Decanal	--	--	--	--
<i>n</i> -Dodecane	54	--	35	--
BHT	--	70	--	--

NT = Not tested

<sup>a</sup> Less than 10  $\mu\text{g/h} \cdot \text{copier}$

**Table 3-15. Estimated VOC Emission Rates (µg/h • copier) Dry-Process Photocopiers-- During Operation**

Chemical	Emission Rate (µg/hr • copier)			
	Copier 1 Test 2-4 (average)	Copier 2 Test 7	Copier 3 Test 8	Copier 4 Test 9
Toluene	760	290	220	110
<i>n</i> -Butyl Acetate	50	110	-- <sup>a</sup>	--
Ethylbenzene	28,000	2,400	<50	360
<i>m,p</i> -Xylene	29,000	6,100	100	510
2-Heptanone	--	--	--	--
Styrene	9,900	12,000	300	3,000
<i>o</i> -Xylene	17,000	4,500	--	850
2-Butoxyethanol	70	1,400	--	500
Isopropyl benzene	400	3,000	--	660
Benzaldehyde	NT	NT	--	6,200
α-Pinene	NT	NT	--	70
<i>n</i> -Propyl benzene	790	2,100	--	460
α-Methyl styrene	330	60	--	--
<i>n</i> -Decane	450	--	62	320
2-Ethyl-1-hexanol	230	14,000	130	5,600
Limonene	220	1,100	--	200
<i>n</i> -Nonanal	1,100	3,600	2,000	3,900
2,5-Dimethyl styrene	--	--	--	--
<i>n</i> -Undecane	2,000	70	103	62
<i>n</i> -Decanal	130	500	380	224
<i>n</i> -Dodecane	960	120	75	82
BHT	--	--	170	--

NT = Not tested

<sup>a</sup>Less than 50 µg/h • copier.

**Table 3-16. Estimated VOC Emission Rates (ng/page) Dry-Process Photocopiers--During Operation**

Chemical	Emission Rate (ng/page)			
	Copier 1 Test 2-4 (average)	Copier 2 Test 7	Copier 3 Test 8	Copier 4 Test 9
Toluene	240	58	73	34
<i>n</i> -Butyl Acetate	-- <sup>a</sup>	20	--	--
Ethylbenzene	8,800	480	--	110
<i>m,p</i> -Xylene	9,100	1,200	30	158
2-Heptanone	--	--	--	--
Styrene	3,100	2,400	100	930
<i>o</i> -Xylene	5,300	890	--	260
2-Butoxyethanol	20	280	--	150
Isopropyl benzene	130	600	--	200
Benzaldehyde	NT	NT	--	1,900
$\alpha$ -Pinene	NT	NT	--	20
<i>n</i> -Propyl benzene	250	420	--	140
$\alpha$ -Methyl styrene	100	10	--	--
<i>n</i> -Decane	140	--	--	100
2-Ethyl-1-hexanol	70	2,800	43	1,700
Limonene	70	220	--	60
<i>n</i> -Nonanal	340	700	670	1,200
2,5-Dimethyl styrene	--	--	--	--
<i>n</i> -Undecane	630	15	34	20
<i>n</i> -Decanal	40	100	130	70
<i>n</i> -Dodecane	300	25	25	25
BHT	--	--	57	--

NT = Not tested

<sup>a</sup> Less than 17 ng/page

**Table 3-17. Estimated Aldehyde/Ketone Emission Rates ( $\mu\text{g/h} \cdot \text{copier}$ ) Dry-Process Photocopiers--Idle**

Chemical	Emission Rate ( $\mu\text{g/hr} \cdot \text{copier}$ )			
	Copier 1 Test 2-4 (average)	Copier 2 Test 7	Copier 3 Test 8	Copier 4 Test 9
Formaldehyde	-- <sup>a</sup>	--	1,100	--
Acetaldehyde	140	--	--	--
Acetone	--	220	2,200	--
Acrolein	--	--	--	--
Propionaldehyde	--	--	--	--
Crotonaldehyde	--	--	--	--
2-Butanone	--	--	--	--
Methacrolein	--	--	--	--
Butyraldehyde	--	--	--	--
Benzaldehyde	--	--	--	--
Valeraldehyde	--	--	--	--
<i>m</i> -Tolualdehyde	--	--	--	--
<i>n</i> -Hexanal	--	--	--	--

<sup>a</sup>Less than 100  $\mu\text{g/h} \cdot \text{copier}$

**Table 3-18. Estimated Aldehyde/Ketone Emission Rates ( $\mu\text{g/h} \cdot \text{copier}$ ) Dry-Process Photocopiers--During Operation**

Chemical	Emission Rate ( $\mu\text{g/h} \cdot \text{copier}$ )			
	Copier 1 Test 2-4	Copier 2 Test 7	Copier 3 Test 8	Copier 4 Test 9
Formaldehyde <sup>a</sup>	<500 <sup>a</sup>	2600	2200	<500 <sup>a</sup>
Acetaldehyde <sup>a</sup>	710	960	1200	<500 <sup>a</sup>
Acetone	2000	<500	2800	-- <sup>b</sup>
Acrolein	--	--	--	--
Propionaldehyde	--	160	260	150
Crotonaldehyde	--	--	100	--
2-Butanone	--	380	190	210
Methacrolein	--	--	--	--
Butyraldehyde	160	840	--	--
Benzaldehyde	1800	2600	--	3800
Valeraldehyde	540	--	250	270
<i>m</i> -Tolualdehyde	--	--	--	--
<i>n</i> -Hexanal	210	1200	440	100

<sup>a</sup> background contamination on cartridge and in chamber increased detection limit.

<sup>b</sup> less than 100  $\mu\text{g/hr} \cdot \text{copier}$

**Table 3-19. Estimated Aldehyde/Ketone Emission Rates (ng/page) Dry-Process Photocopiers--During Operation**

Chemical	Emission Rate (ng/page)			
	Copier 1 Test 2-4	Copier 2 Test 7	Copier 3 Test 8	Copier 4 Test 9
Formaldehyde <sup>a</sup>	<150 <sup>a</sup>	520	740	<150
Acetaldehyde <sup>a</sup>	220	700	390	<150
Acetone <sup>a</sup>	630	<500	940	-- <sup>b</sup>
Acrolein	--	--	--	--
Propionaldehyde	--	33	88	48
Crotonaldehyde	--	--	34	--
2-Butanone	--	76	63	66
Methacrolein	--	--	--	--
Butyraldehyde	54	170	--	--
Benzaldehyde	570	530	--	1,200
Valeraldehyde	170	--	82	83
<i>m</i> -Tolualdehyde	--	--	--	--
<i>n</i> -Hexanal	69	240	150	39

<sup>a</sup>Background contamination on cartridge and in chamber increased detection limit

<sup>b</sup>Less than 30 ng/page

**Table 3-20. Estimated Ozone Emission Rates (µg/h · copier) Dry-Process Photocopiers--During Operation**

Copier	Emission Rate (µg/hr · copier)
1	3,000
2	4,700
3	7,900
4	1,300



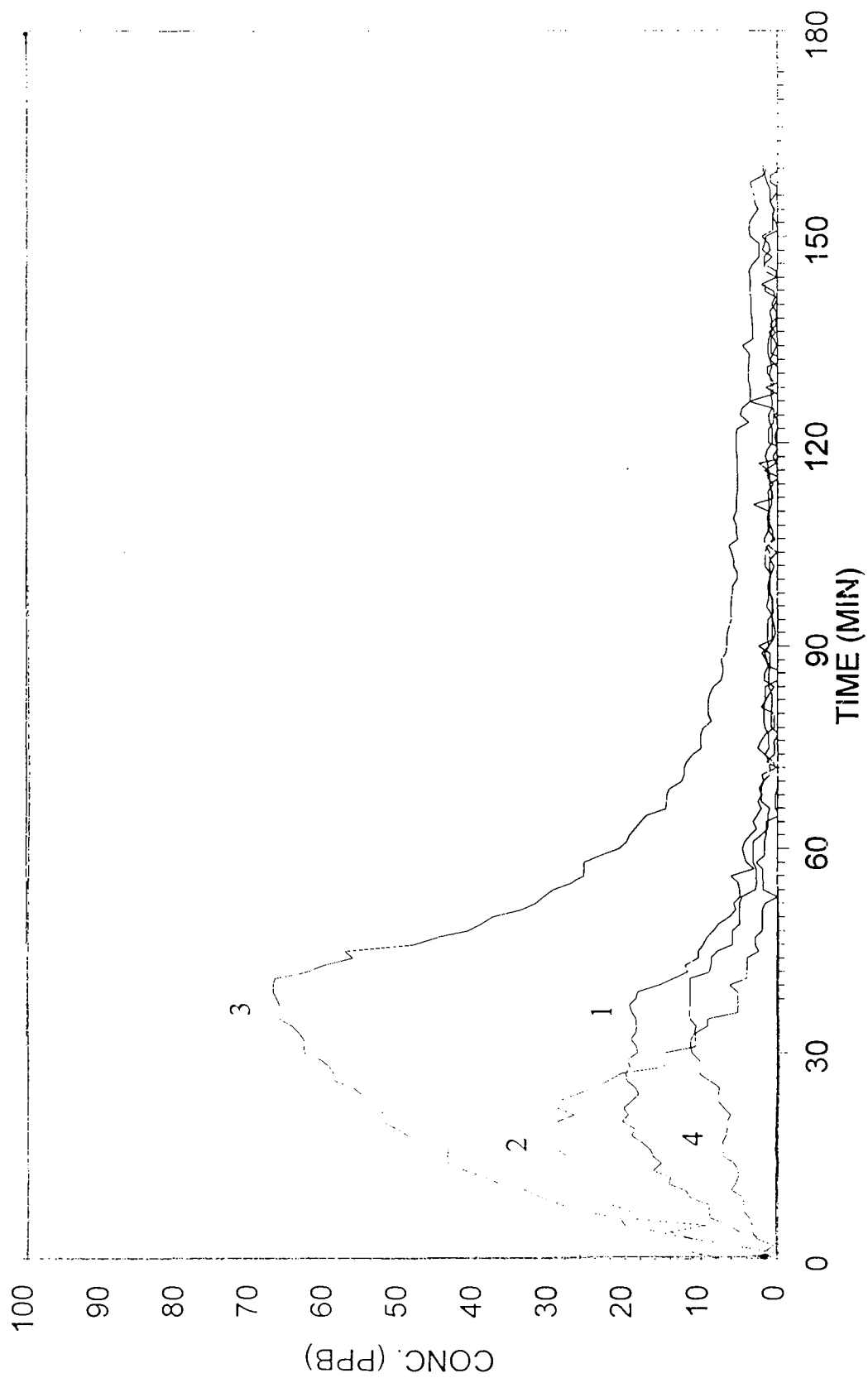


Figure 3-6. Ozone results  
copiers 1, 2, 3, and 4.

The following observations can be made from the results:

- In most cases, emission rates of individual compounds in the idle mode were low ( $<500 \mu\text{g/h}$ ) as shown in Tables 3-14 and 3-17. Two exceptions were relatively high measured emission rates for formaldehyde and acetone from copier 3 (Table 3-17). Copier 3 was the only copier with a monocomponent toner. It is possible that differences in toner type could be responsible for elevated emission rates for these two chemicals in the idle mode.
- In almost all cases, higher emission rates of individual compounds were measured in the print mode compared to the idle mode. This result suggests that the most important impacts on IAQ will occur during printing; as a corollary, pollution prevention strategies should focus on the print operation. Exceptions to this general observation were measured emission rates for toluene from copier 3 (Tables 3-14, 3-15); butyl acetate, 2-heptanone, and BHT from copier 2 (Tables 3-14, 3-15); and acetone from copier 2 (Tables 3-17, 3-18). In all of these cases, the emission rates in both the print and idle modes were relatively low. Two additional exceptions were emission rates for formaldehyde and acetone from copier 3 as discussed above.
- As indicated by Table 3-15, three of the four copiers (1, 2, and 4) showed relatively high emission rates for styrene (3,000 to 12,000  $\mu\text{g/h} \cdot \text{copier}$ ). All three of these copiers used dual-component toners, which contain styrene polymers as a base. On the other hand, copier 3, which uses a monocomponent toner, showed a much lower emission rate for styrene (300  $\mu\text{g/h} \cdot \text{copier}$ ).
- For the VOCs, Table 3-15 shows lowest emission rates were measured for copier 3 (the copier with the monocomponent toner). Copier 1 had the highest emission rates for the aromatic hydrocarbons. Copier 2 also had high emission rates for several of the aromatic hydrocarbons and for several polar VOCs, including 2-ethyl-1-hexanol and *n*-nonanal. Copier 4 showed high emission rates for several polar VOCs, including benzaldehyde, 2-ethyl-1-hexanol, and *n*-nonanal. It is hypothesized that differences in emission rates for VOCs from different copiers may be due to differences in the chemical composition of the toners.
- Generally, emission rates for the individual aldehydes/ketones in the print mode were lower than for the individual VOCs (comparing Tables 3-15 and 3-18). However, relatively high emission rates ( $>1000 \mu\text{g/h} \cdot \text{copier}$ ) were measured for formaldehyde from copiers 2 and 3; acetaldehyde from copier 3; acetone from copiers 1 and 3; benzaldehyde from copiers 1, 2, and 4; and *n*-hexanal from copier 2. Although the paper supply could be considered a source for aldehydes/ketones, the same lot of paper was used throughout testing; consequently, differences in emission rates between copiers are probably not due to the paper supply. As for the VOCs, differences in emission rates may be due to differences in toners.

- Tables 3-16 and 3-19 show the emission rates per page for VOCs and aldehydes/ketones, respectively. Generally, the trends for the emission rate per page were similar to the emission rates per copier per hour for the individual compounds. Exceptions to this trend include styrene (copier 1 had highest per page emissions; copier 2 had highest per hour emission rates), formaldehyde (copier 3 had highest per page emissions; copier 2 had highest per hour emission rates), and acetaldehyde (copier 2 had highest per page emissions; copier 3 had highest per hour emission rates).
- For ozone, as indicated in Table 3-20, substantial differences in emission rates were seen between the four copiers, ranging from a low of 1,300  $\mu\text{g}/\text{h} \cdot \text{copier}$  for copier 4 to 7,900  $\mu\text{g}/\text{h} \cdot \text{copier}$  for copier 3. It should be noted that copier 4 is advertised as a low ozone emitting copier. Results confirm that this machine resulted in lower ozone emissions during copier operation than the other three copiers.
- As indicated previously, limited particulate data were collected for two of the four machines tested. Preliminary results showed that operation of Copier 1 increased particle levels to approximately 30 times chamber background levels for particles smaller than 0.2  $\mu\text{m}$  in diameter.

#### **3.4.4      *Within Copier Variability of Emission Rate Measurements***

Multiple large chamber emission tests (Tests 1 through 6, Table 3-11) were conducted on copier 1 in order to determine within-copier variability over a number of runs. VOC emission rates for these tests are presented in Tables 3-21 and 3-22 for the print and idle modes, respectively. As shown in Table 3-11, the tests were conducted at two different times and used several different toner lots. Tests 1, 2, 3, and 4 were conducted during an initial 8-day period. Tests 5 and 6 were conducted approximately 4 months later. Test 1 utilized a toner cartridge that was shipped with the copier and had only enough toner to complete 999 copies before it was empty. A new toner cartridge was installed for Tests 2, 3, and 4. Tests 5 and 6 used the same toner cartridge as Tests 2, 3, and 4; however Tests 5 and 6 were conducted 4 months after installing the toner cartridge. No special storage precautions were taken during this time period - the toner was left in the copier and the copier stored at room temperature during the 4-month period. Since the tests were conducted and samples analyzed during two time periods approximately 4 months apart, a duplicate multisorbent cartridge that had been collected during Test 4 and stored in a freezer was analyzed with the second set of samples to verify that the analytical system was performing consistently. These results are also shown in Table 3-21. (Note that previous experience at RTI has shown that control samples on multisorbent tubes yield consistent results after as much as 1 year in the freezer.) Just prior to performing Test 6, all photocopier particle and charcoal filters were replaced by the manufacturer's service technician.

**Table 3-21. Comparison of Intra-Machine (Copier 1) Variability in Emissions  
( $\mu\text{g/h} \cdot \text{copier}$ ) During Replicate Runs--During Operation**

Chemical	Emission Rate ( $\mu\text{g/h} \cdot \text{copier}$ )					
	New Toner			Old Toner		
	Test 2-4 Mean	Test 2-4 % RSD	Test 4	Test 1	Test 5	Test 6
Test Date	4/95		4/95	4/95	9/95	9/95
Analysis Date	4/95		9/95	9/95	9/95	9/95
Toluene	760	14	560	600	760	26,000
Butyl Acetate	50	13	- <sup>a</sup>	-	-	-
Ethylbenzene	27,000	6	31,000	18,000	18,000	21,000
<i>m,p</i> -Xylene	29,000	6	33,000	20,000	19,000	21,000
2-Heptanone	-	-	-	-	-	-
Styrene	9,000	4	9,900	6,600	5,500	6,300
<i>o</i> -Xylene	17,000	4	18,000	13,000	10,000	12,000
2-Butoxyethanol	67	141	-	-	-	-
Isopropyl benzene	400	3	410	270	220	240
Benzaldehyde	NT <sup>b</sup>	-	2,500	1,500	1,200	1,400
$\alpha$ -Pinene	NT	-	81	91	-	-
Propyl benzene	790	1	740	590	400	440
$\alpha$ -Methyl styrene	1,100	7	1,100	1,300	600	650
<i>n</i> -Decane	450	1	300	480	94	-
2-Ethyl-1-hexanol	230	11	90	98	110	52
Limonene	220	23	250	280	74	-
<i>n</i> -Nonanal	1,100	13	3,000	1,300	770	1,400
2,5-Dimethyl styrene	-	-	-	-	-	-
<i>n</i> -Undecane	2,000	8	1,900	1,900	530	-
<i>n</i> -Decanal	130	52	100	-	-	-
<i>n</i> -Dodecane	960	8	870	950	260	77
BHT	-	-	-	-	-	-

<sup>a</sup> Less than 50  $\mu\text{g/h} \cdot \text{copier}$

<sup>b</sup> Not Tested

Test 1: toner had run out (old toner) during test run.

Test 2-4: toner cartridge replaced and triplicate runs made, average of these three runs and %RSD presented.

Test 4: original test 4 run in 4/95, duplicate sample was analyzed in 9/95 to evaluate analytical differences between runs.

Test 5: same toner cartridge used in test 2-4 (time-series test also run).

Test 6: same toner cartridge used in test 2-4 all filters replaced.

**Table 3-22. Comparison of Intra Machine (Copier 1) Variability in Emissions ( $\mu\text{g/h} \cdot \text{copier}$ ) During Replicate Runs--Idle**

Chemical	Emission Rate ( $\mu\text{g/h} \cdot \text{copier}$ )			
	New Toner		Old Toner	
	Test 2-4 Mean	Test 2-4 % RSD	Test 5 Old filters	Test 6 New Filters
Test Date 4/95				
Toluene	- <sup>a</sup>	-	-	180
Butyl Acetate	-	-	-	-
Ethylbenzene	180	38	34	120
<i>m,p</i> -Xylenc	160	38	30	120
2-Heptanone	-	-	-	-
Styrene	44	23	13	-
<i>o</i> -Xylene	88	28	18	-
2-Butoxyethanol	-	-	12	-
Isopropyl benzene	-	-	-	-
Benzaldehyde	NT <sup>b</sup>	-	-	-
$\alpha$ -Pinene	NT	-	-	-
Propyl benzene	-	-	-	-
$\alpha$ -Methyl styrene	13	9	-	-
<i>n</i> -Decane	12	15	-	-
2-Ethyl-1-hexanol	33	15	-	-
Limonene	-	-	-	12
<i>n</i> -Nonanal	-	-	-	39
2,5-Dimethyl styrene	-	-	-	-
<i>n</i> -Undecane	36	10	-	13
<i>n</i> -Decanal	-	-	-	-
<i>n</i> -Dodecane	54	18	-	-
BHT	-	-	-	-

<sup>a</sup>Less than 50  $\mu\text{g/h} \cdot \text{copier}$

<sup>b</sup>Not tested

Test 1: toner had run out (old toner) during test run.

Test 2-4: toner cartridge replaced and triplicate runs made, average of these three runs and RSD.

Test 5: same toner cartridge used in test 2-4 (time-series test run).

Test 6: same toner cartridge used in test 2-4 all filters replaced.

As seen in Table 3-21, a comparison of results for the tests conducted when the toner cartridge was “new” (Tests 2 - 4) compared to tests conducted with the “old toner” 4 months later (Tests 5 and 6) showed consistently higher emission rates associated with the “new” toner. For the aromatic hydrocarbons such as ethylbenzene, *m*-,*p*-, and *o*-xylenes, and styrene, the emission rates with “new” toner were approximately 50% higher than the emission rates with the “old toner.” The same trend was also seen with benzaldehyde. For the other VOCs (most of which had low emission rates), no noticeable trend was observed. The multisobent cartridge collected and frozen during Test 4 and later analyzed during the second round showed results comparable to those measured during the first analysis. This indicates that the differences between the tests are real and not due to analytical response. For Tests 2, 3, and 4, conducted during the same time period and with the same “new” toner, the results are very consistent, as shown by the generally low %RSD values. This indicates that the photocopier test results are reproducible if the proper variables are controlled. These results indicate that offgassing of the toner during storage can impact the emissions.

Replacement of the filters (Test 6 compared to Test 5) seemed to have little effect on the emissions with the exception of toluene. Toluene substantially increased after the change out of the filters. This may be due to adhesives used to hold the filters in place. Most of the filters have a peel and apply backing to attach the filters to the copier. This may also be the reason for the presence of toluene during the idle period for Test 6 (Table 3-22).

#### ***3.4.5 Emission Rates as a Function of Copier Operation Time***

During the chamber emissions tests with copiers 1 and 4 (Test 5 and 9, Table 3-11), chamber air samples for VOC determinations were collected at short-time intervals throughout the test period to evaluate the change in emission rate over time. For these tests, samples were collected at T = 0-10, 10-20, 20-30, 30-45, 45-60, 60-75, 75-90, 90-105, 105-120, and 120-160 minutes after the copier started printing. A time-integrated sample over the entire test period (T = 0-160 minutes) was also collected for comparison.

Chamber air concentration measured during these tests are shown in Figures 3-7 to 3-14 as follows for selected compounds:

- Figure 3-7 -- Copier 1: Styrene
- Figure 3-8 -- Copier 1: *m,p*-Xylene
- Figure 3-9 -- Copier 1: *o*-Xylene
- Figure 3-10 -- Copier 1: Ethylbenzene
- Figure 3-11 -- Copier 4: Styrene
- Figure 3-12 -- Copier 4: Benzaldehyde
- Figure 3-13 -- Copier 4: 2-Ethyl-1-hexanol
- Figure 3-14 -- Copier 4: *o*-Xylene.

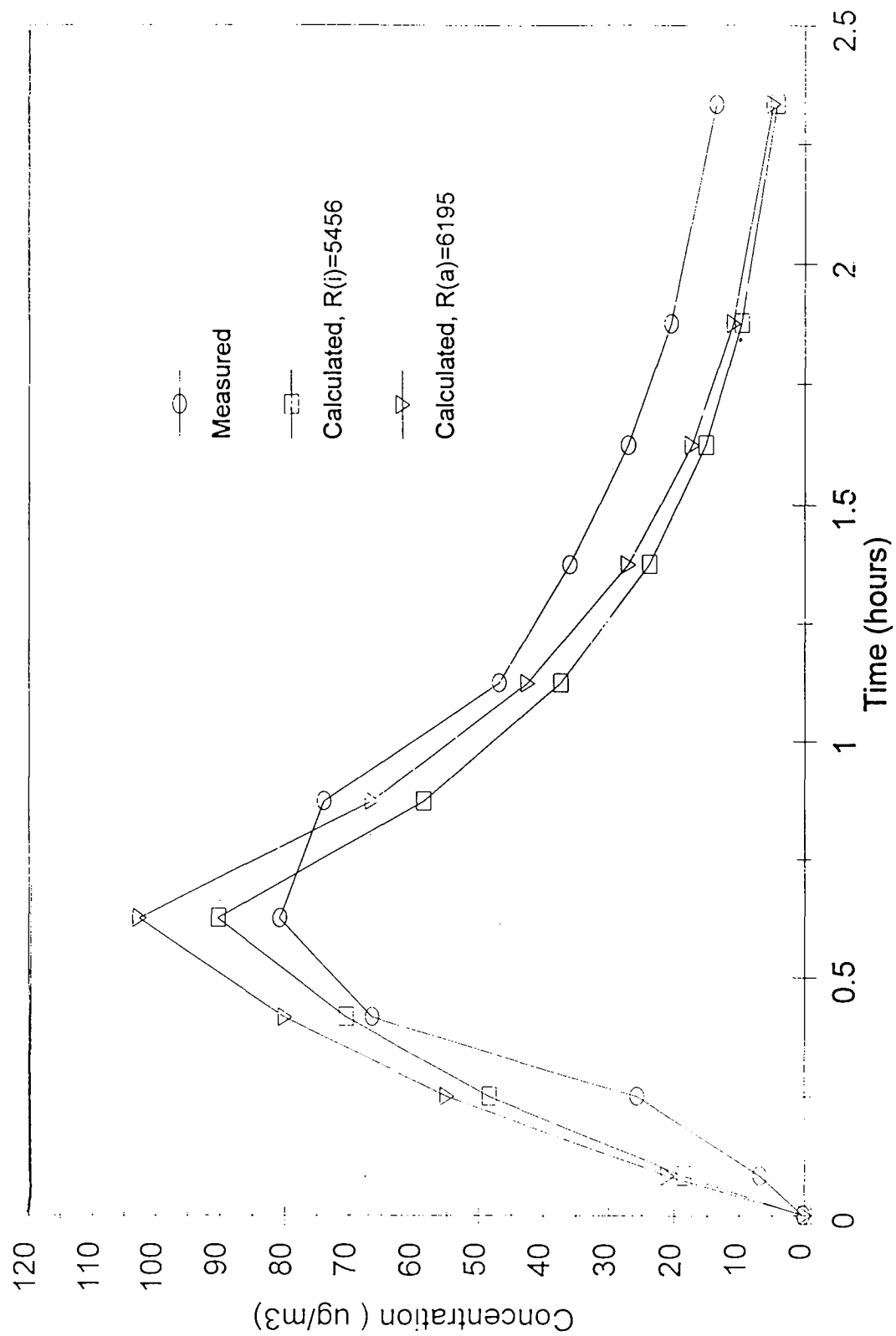


Figure 3-7. Copier 1  
styrene concentrations.

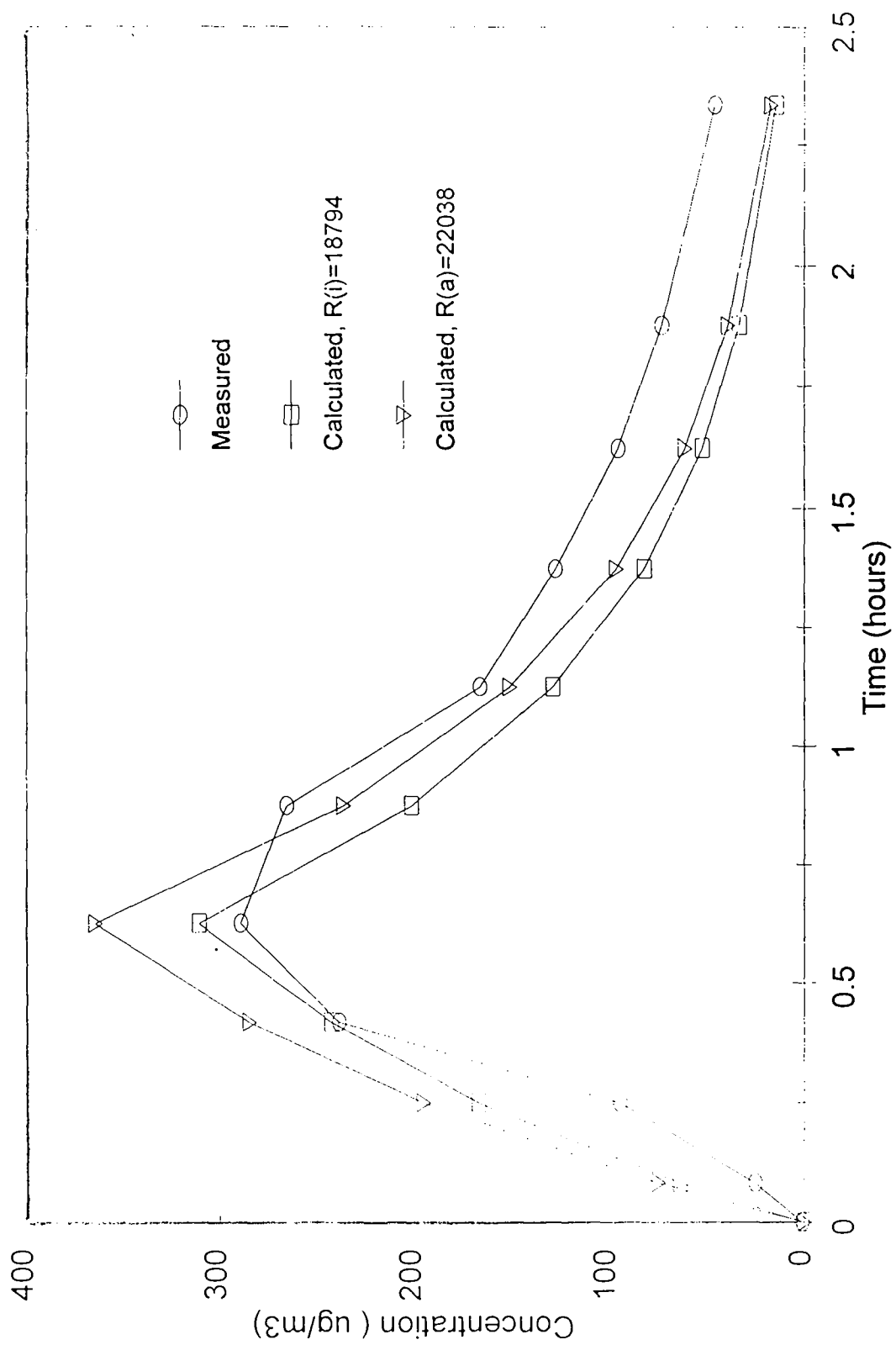
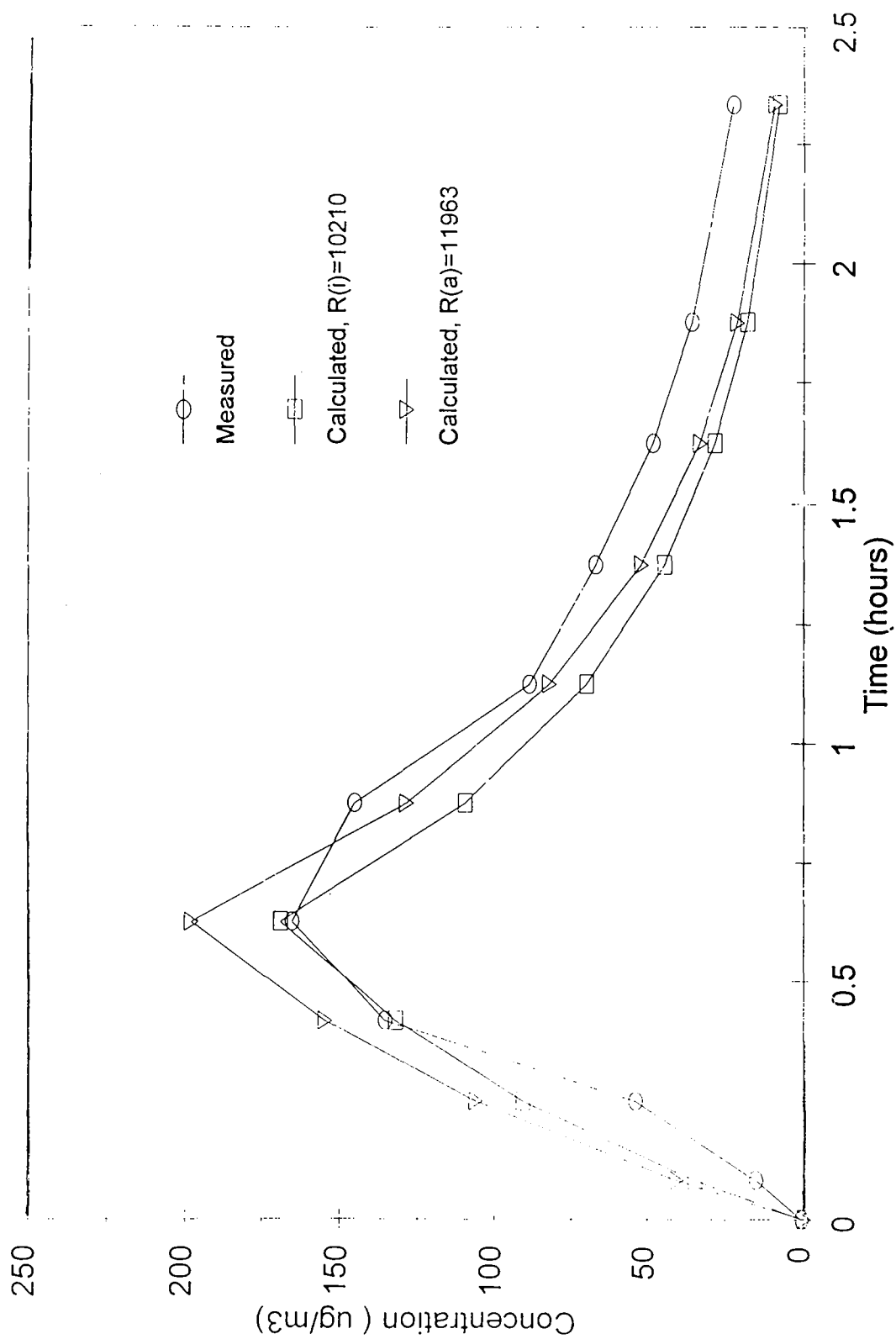
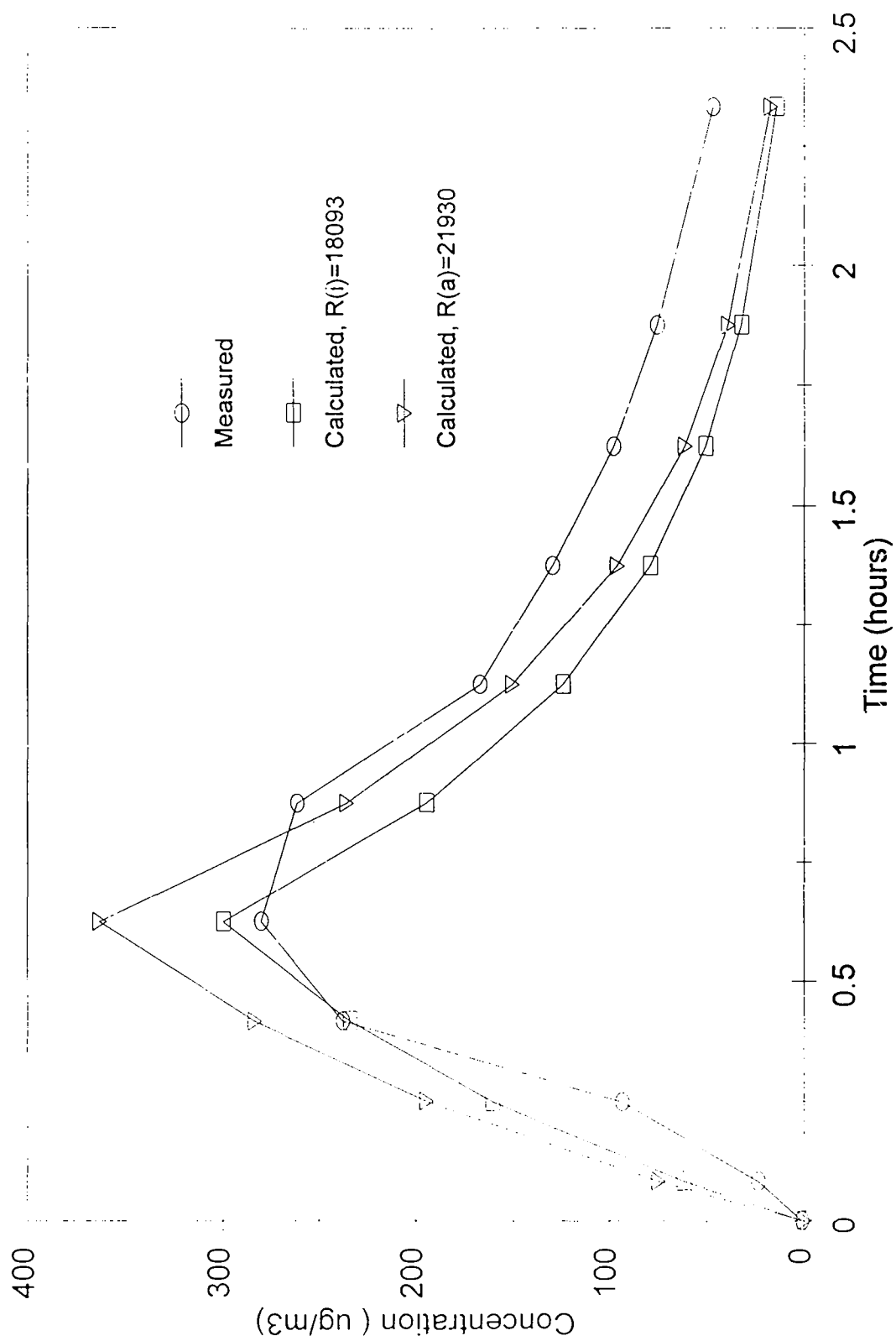


Figure 3-8. Copier 1  
m,p-xylene concentrations.

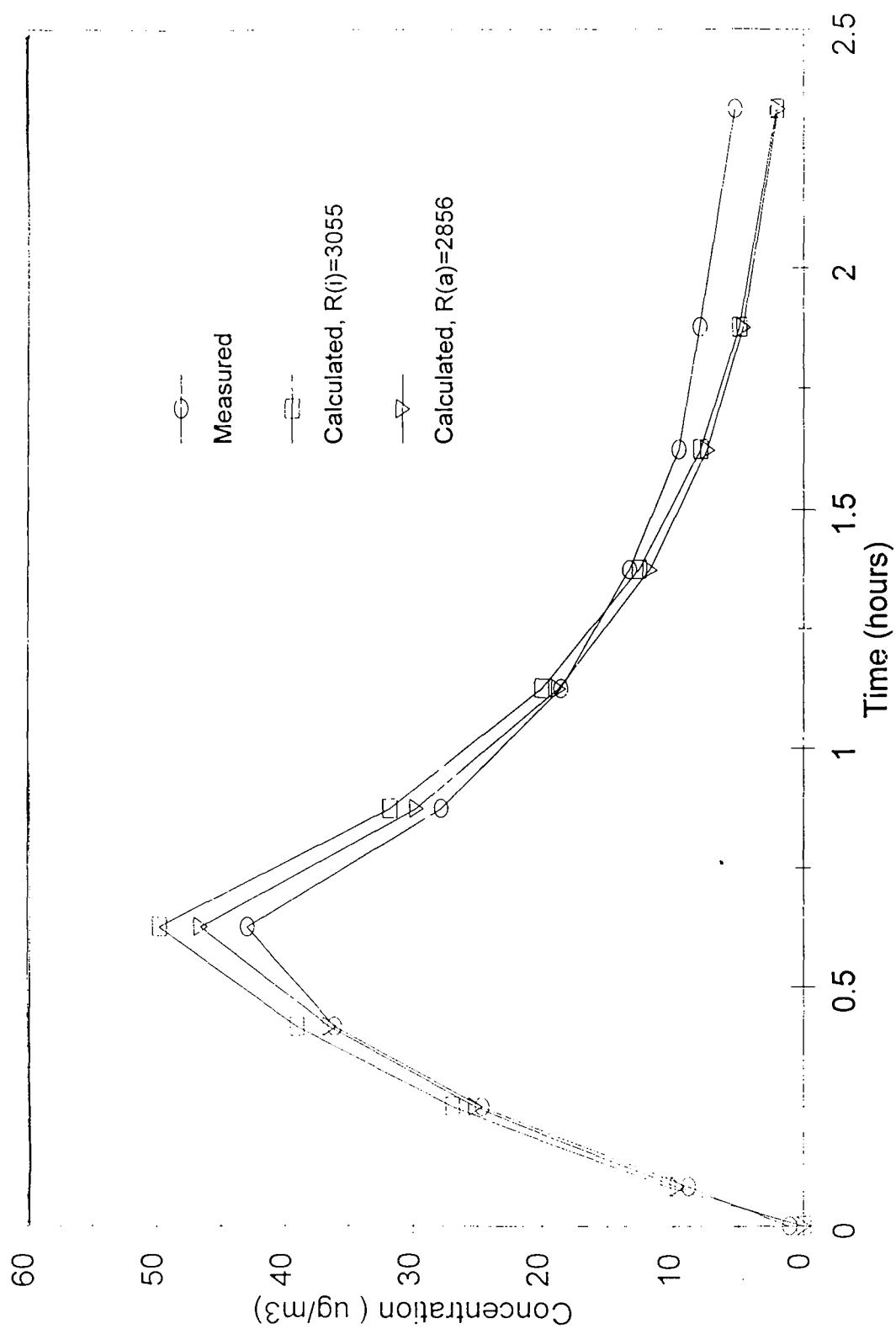




**Figure 3-9. Copier 1  
o-xylene concentrations.**



**Copier 3-10. Copier 1  
ethylbenzene concentrations.**



**Figure 3-11. Copier 4  
styrene concentrations.**

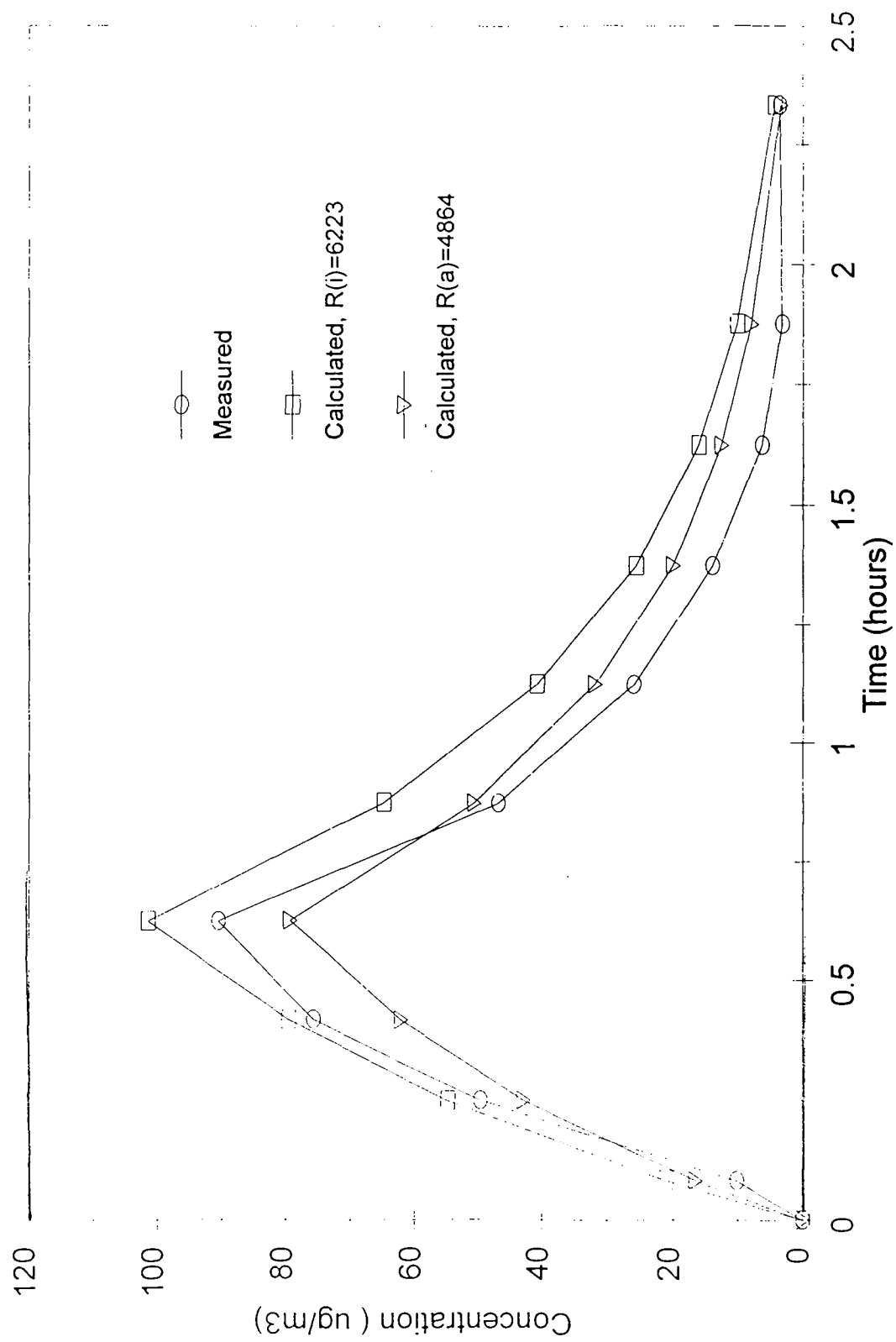


Figure 3-12. Copier 4  
benzaldehyde concentrations.

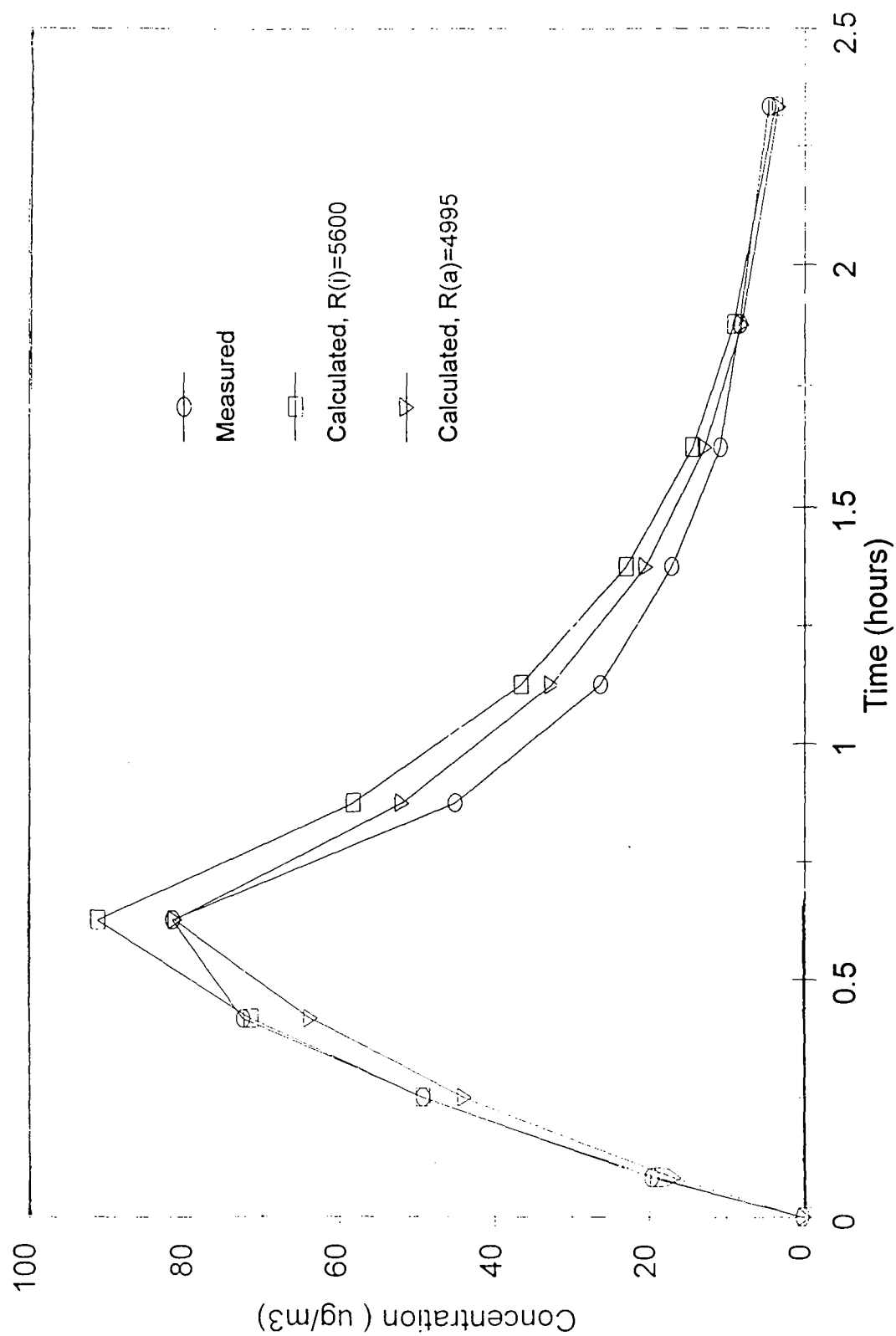


Figure 3-13. Copier 4  
2-ethyl-1-hexanol concentrations.

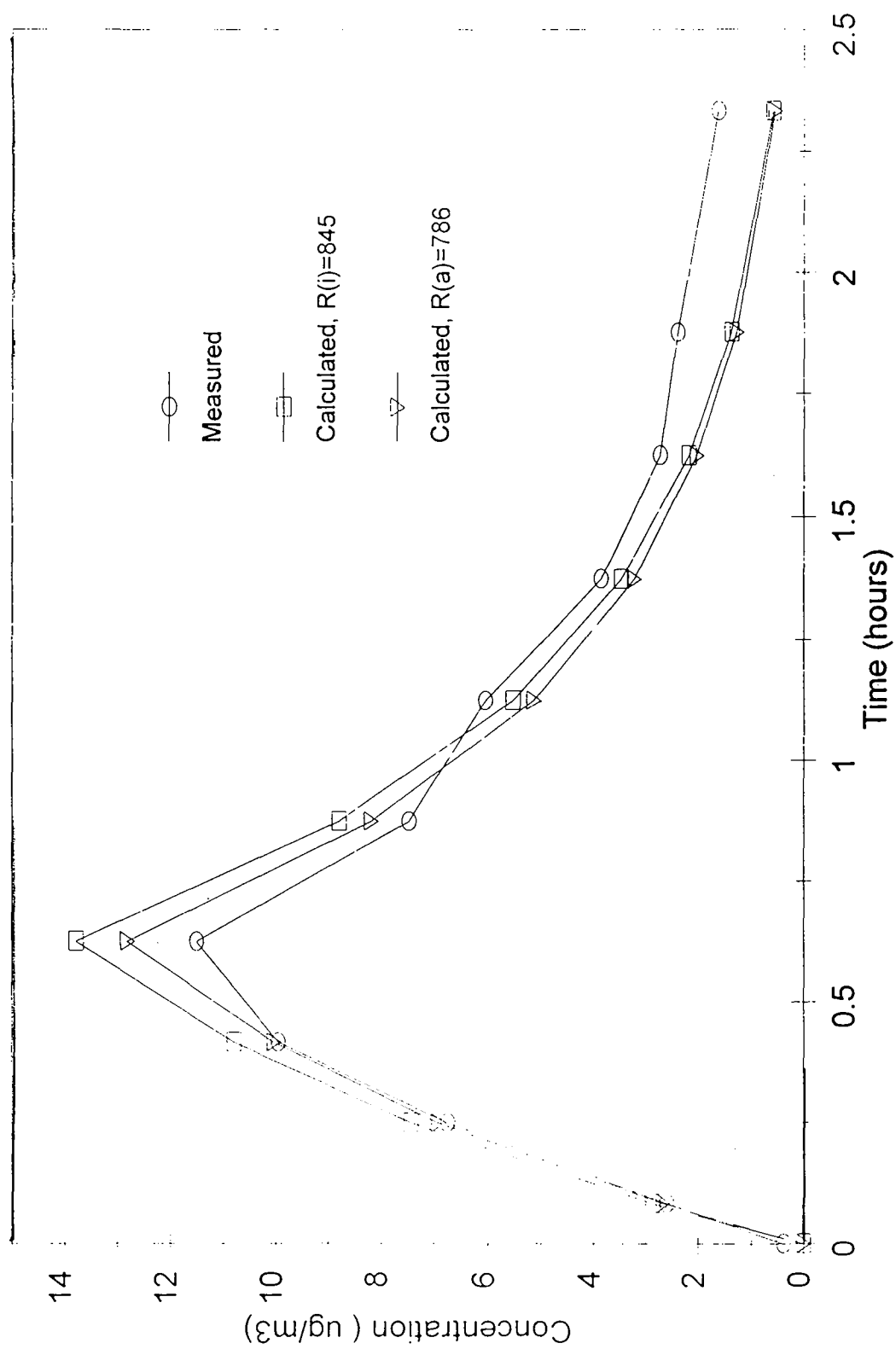


Figure 3-14. Copier 4  
o-xylene concentrations.

In each figure, the average measured chamber air concentration is plotted for each time period at the midpoint for that time period, e.g., the concentration for T=10-20 minutes (0.17-0.33 hours) is plotted at the T=15 minutes (0.25 hours) point. For comparison, the theoretical concentrations at the same time point calculated using the emission rate generated for the time-integrated sample (R(I)) and the average emission rate generated for the time-point samples (R(a)) are also given. The area under the curve for the measured concentrations and the concentrations calculated using R(a) should be equal.

For copier 4, plots for all four VOCs (Figures 3-11 to 3-14) show good agreement between the measured concentrations and the theoretical concentrations. Differences between the measured and the theoretical concentrations are usually less than 10 percent, well within the expected precision of the analytical methods. These results suggest that emission rates are constant over time while the copier is printing and that emissions drop to zero or close to zero once printing is stopped. Results for copier 1 show a different trend, although the data are consistent for the four VOCs shown. Data for copier 1 shows lower measured concentrations compared to the theoretical concentration during the first two time periods. Higher concentrations than theoretical are measured during the later time periods. The lower-than-expected concentration at the start of the test suggests that emission rates are not constant over time; essentially the emission rates at the start of printing are lower and then increase with time.

The higher than expected concentrations after printing has stopped suggest that the copier is still emitting VOCs after the printing has stopped. The same trend of higher-than-expected chamber air concentrations after copying stops would be seen if VOCs were reversibly absorbed to the chamber surfaces; however, plots of VOC concentration over time for the recovery tests (Figures 3-1 and 3-2) indicate that this is not occurring.

To further evaluate the data, emission rates were calculated for selected VOCs for each time period. These data are given in Table 3-23 for copier 1 and in Table 3-24 for copier 4. These data are displayed graphically for styrene in Figure 3-15 and for ethylbenzene in Figure 3-16. These data for emission rates show the same trends as described above for chamber air concentrations. For copier 4, the emission rates are fairly constant during the period when copies are being made, then drop substantially when copying stops.

For copier 1, on the other hand, the emission rates at the first time point (0-10 min) were substantially lower than for the other time points when the copier is operating. It should be noted that only a single sample was collected and analyzed at this time point; thus, this difference could be due to analytical variability. However, the differences in emission rates for this time point compared to the other time points is greater than what would be considered normal analytical variability. These results suggest that, for copier 1, emission rates are not constant over time but increase with time after copying starts. Data for copier 1 also show that VOCs are still emitting after copying stops. This is most apparent for the first time point (T = 52.5 min) after the copier is turned off.

**Table 3-23. Estimated Emission Rates as a Function of Time - Copier 1**

Chemical Time (min)	Emission Rate ( $\mu\text{g/h} \cdot \text{copier}$ )										
	Copier on					Copier off					
	0-10	10-20	20-30	30-45	Integrated Sample	40-60	60-75	75-90	90- 105	105- 120	120- 160
Toluene	480	350	370	260	440	56	18	30	11	31	-10
Ethylbenzene	9000	18000	22000	19000	22000	4900	730	1600	1100	1600	480
<i>m,p</i> -Xylene	9000	18000	22000	20000	22000	4900	730	1600	1100	1600	480
<i>o</i> -Xylene	5200	10000	13000	11000	12000	2300	120	720	390	720	230
Styrene	2500	5100	6200	5500	6200	1400	240	460	330	480	180
2-Ethyl-1-hexanol	42	100	120	48	100	53	13	12	1	10	3
Isopropyl benzene	110	220	280	240	240	44	9	12	9	12	1
Benzaldehyde	0	600	1500	1600	780	20	340	190	68	32	120
$\alpha$ -Pinene	27	43	16	16	53	16	16	16	16	9	11
Limonene	0	75	120	46	48	1	0.2	18	0	0	0
Propylbenzene	210	400	500	430	450	74	11	25	15	27	8



**Table 3-24. Estimated Emission Rates as a Function of Time - Copier 4**

Chemical Time (min)	Emission Rate ( $\mu\text{g/h} \cdot \text{copier}$ )									
	Copier on				Copier off					
	0-10	10-20	20-30	Integrated	45-60	60-75	75-90	90-105	105-120	120-160
Toluene	150	36	46	130	60	42	24	38	34	22
Ethylbenzene	240	280	290	340	26	33	35	23	27	10
<i>m,p</i> -Xylene	360	430	430	470	22	39	24	22	39	4.0
<i>o</i> -Xylene	680	770	700	790	17	42	33	33	46	11
Styrene	2500	2900	2600	2900	18	77	99	100	160	43
2-Ethyl-1-hexanol	5500	5700	5100	5000	620	170	5	46	150	10
Isopropyl benzene	540	600	530	610	4	28	23	30	43	12
Benzaldehyde	4500	6600	5800	4900	960	400	320	230	8	170
$\alpha$ -Pinene	170	5	18	66	75	25	16	12	11	34
Limonene	47	56	140	139	40	28	14	2	15	30
Propylbenzene	400	440	410	430	9	14	12	14	23	5

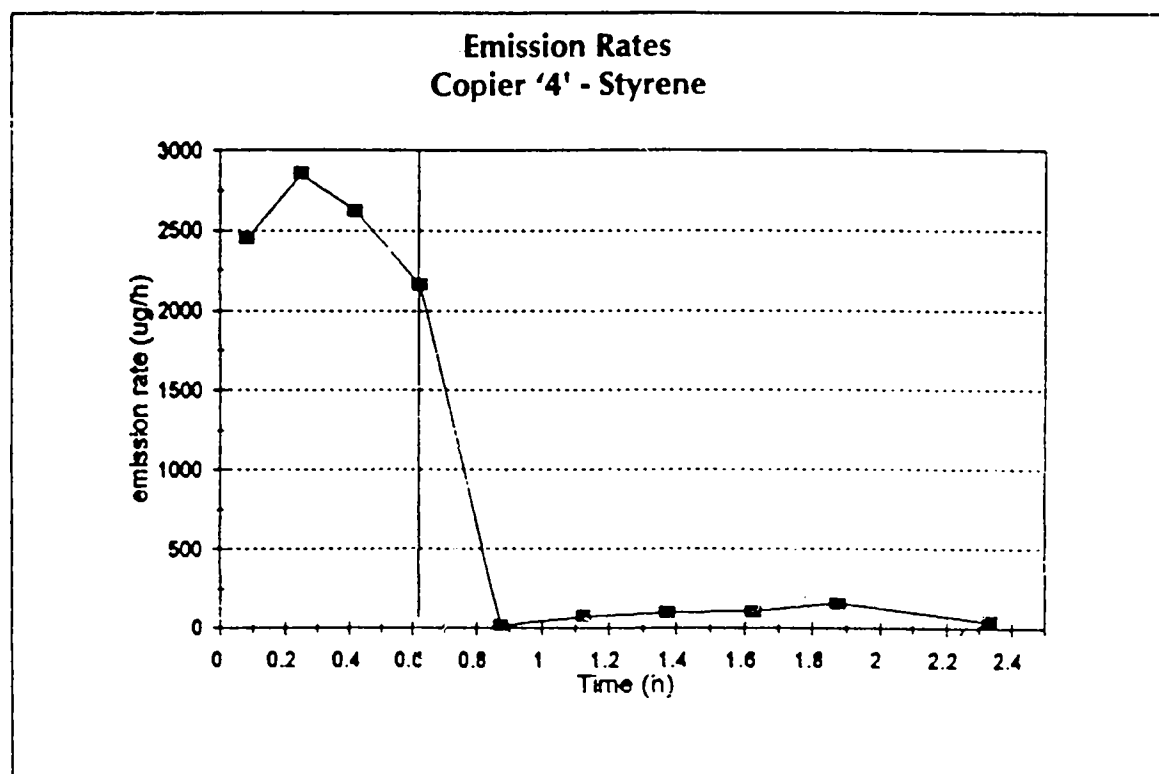
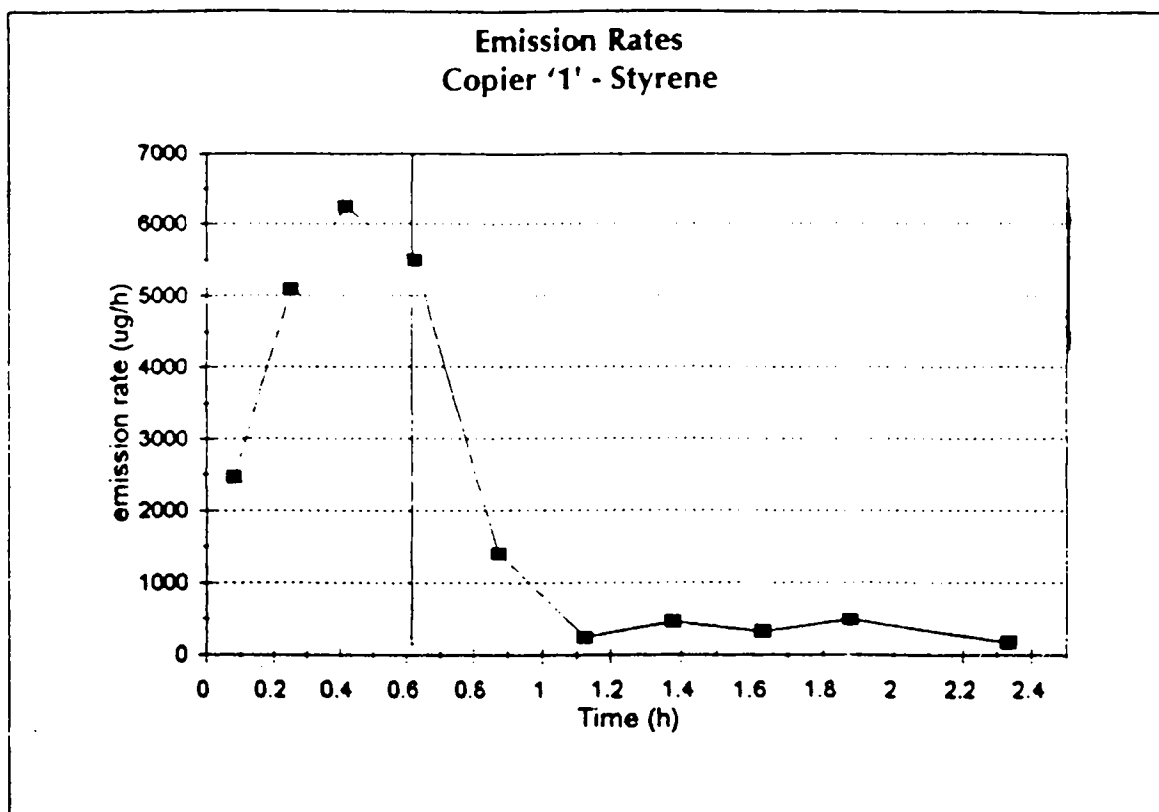


Figure 3-15. Plots of emission rate vs. time for styrene.  
(Verticle line indicates copying stopped)

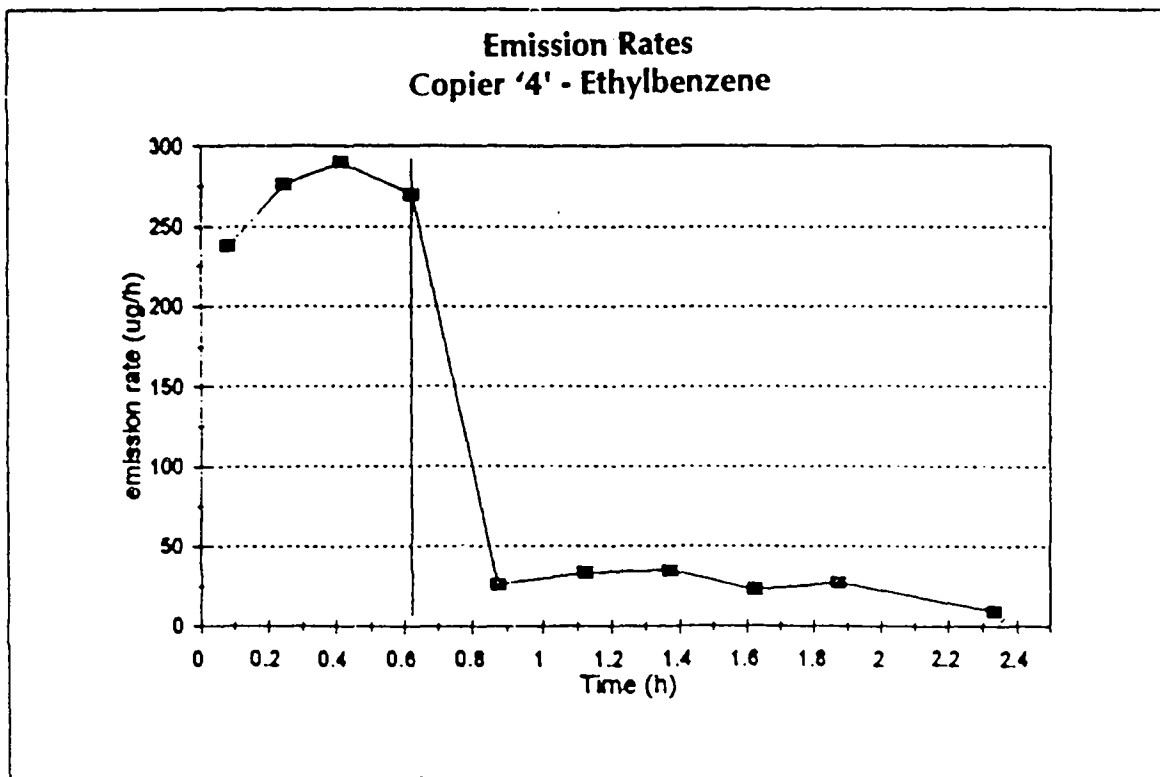
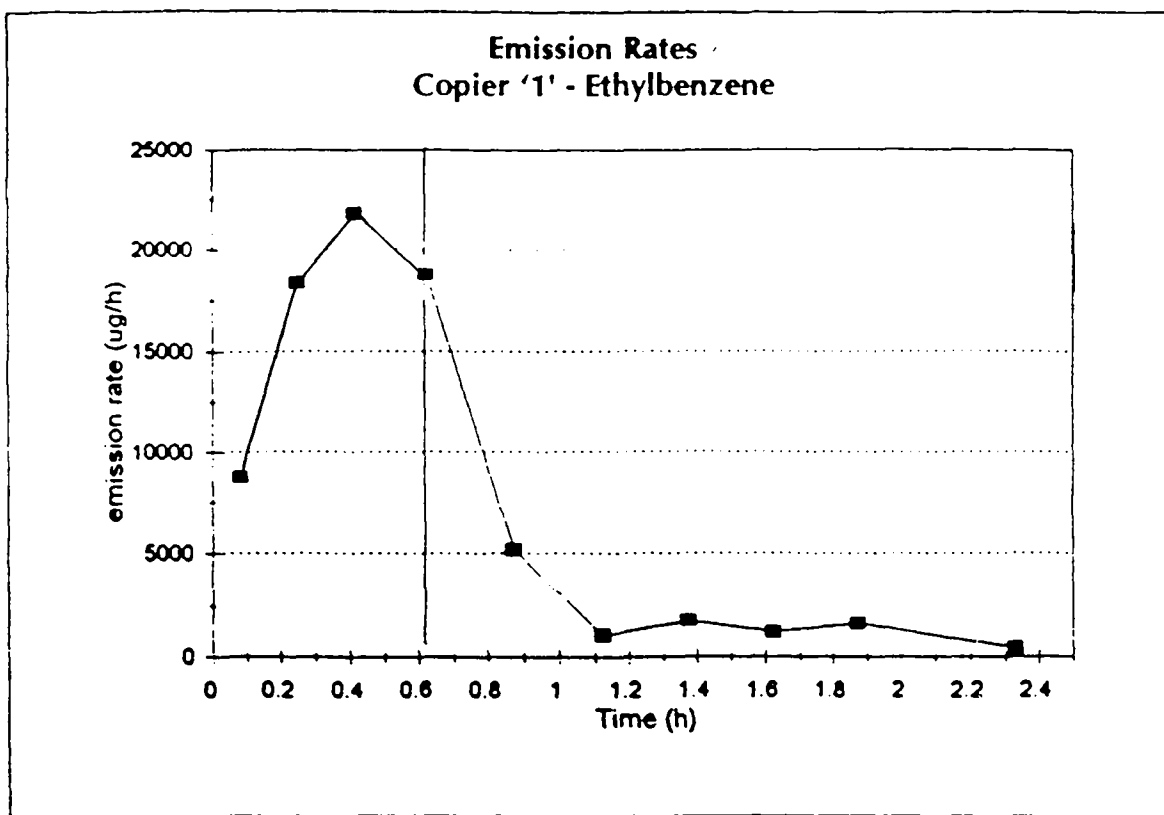


Figure 16. Plots of emission rate vs. time for ethylbenzene.  
(Verticle line indicates copying stopped)

### 3.4.6

### *Practical Aspects of Test Implementation*

Throughout the course of Phase I, several issues arose concerning the practical aspects for conducting the large chamber emissions tests for photocopiers. A listing of these issues and their resolution during this study are given in Table 3-25.

#### 3.4.6.1 Toner Aging/Headspace Analysis

In addition to the issues listed on Table 3-25, another issue related to toner lot and age and the effect on emissions was identified. Specifically, variability of data was observed for a single copier tested multiple times under the same chamber conditions during Phase I. This occurred both during a changeover to a new toner lot and when extended periods of time (1-3 months) had elapsed between tests using the same toner lot. It was necessary to resolve this issue before any round-robin testing could be conducted for Phase II. To do this, different toner lots were evaluated both by chamber testing and by a headspace analysis method. Headspace tests were conducted on samples from six different toner lots, but all manufactured by the same company for use with Copier 1, defined as follows:

- Toner 1— old toner from previous copier 1 runs (Lot 1-2),
- Toner 2— new toner cartridge for copier 1 (Lot 1-4),
- Toner 3— new toner cartridge for copier 1 (Lot 1-3),
- Toner 4— new toner cartridge for copier 1 (Lot 1-5, A & B),
- Toner 5— new toner cartridge for copier 1 (Lot 1-7, A), and
- Toner 6— old toner sampled from existing RTI copier; age unknown, (Lot 1-8).

For each test, 50 mg of toner was placed in a 28.3 mL container and allowed to equilibrate for 1.5 hours at which time a 1 mL headspace gas sample was withdrawn using a gas-tight syringe. An injection was made into a flash evaporation system and purged onto a multisorbent cartridge. The multisorbent cartridge was analyzed by GC-Flame Ionization Detector (FID). Tests were conducted at 100 °C for all toner samples (the bottom of the fusing temperature range for all the copiers tested) and at 35 °C and 200 °C for some of the samples. In all tests, the four major peaks from the chamber tests (ethylbenzene; *m*-,*p*-xylene; *o*-xylene; and styrene) were quantified. As a check on the analysis, duplicate samples were taken from one toner cartridge (toner 5, Lot 1-7A) and single samples were taken from two separate cartridges from the same lot (toner 4, Lot 1-5A and 1-5B). The results from these tests are presented in Table 3-26. As can be seen from the data:

- increased temperature resulted in increased equilibrium headspace concentrations;

**Table 3-25. Practical Considerations for Copier Testing Issues and Resolutions**

Issue	Resolution
<ul style="list-style-type: none"><li>• Maintaining Chamber Temperature with Added Head Load</li></ul>	<ul style="list-style-type: none"><li>• Increased Acceptable Test Range</li><li>• Increased Allowed Air Exchange Rate</li><li>• Decreased Supply Air Temperature</li></ul>
<ul style="list-style-type: none"><li>• Remote Operation of Copier<ul style="list-style-type: none"><li>- Hardware Issues (start/Stop, Reset Switches)</li><li>- Software Issues</li></ul></li></ul>	<ul style="list-style-type: none"><li>• Removed Keyboard or Jumpered Start Switch and extended cables to allow operation outside Chamber</li><li>• Reprogrammed Features</li></ul>
<ul style="list-style-type: none"><li>• Paper Capacity<ul style="list-style-type: none"><li>- Infeed</li><li>- Outfeed</li></ul></li></ul>	<ul style="list-style-type: none"><li>• Required High Capacity Paper Tray</li><li>• Outfeed Trays were Inadequate so a “Catch Basket” was used</li></ul>
<ul style="list-style-type: none"><li>• Power Requirements</li></ul>	<ul style="list-style-type: none"><li>• Capability of 110V and 220V necessary</li></ul>
<ul style="list-style-type: none"><li>• Humidity</li></ul>	<ul style="list-style-type: none"><li>• Supplied Humidity at Mass Equivalent to 23 °C, 50%RH</li></ul>

- large differences were observed between the headspace concentrations of different toner lots having the same manufacturer's specifications;
- the ratio of the headspace concentration results of toner 1 (old toner) to toner 2 (new toner) is similar to the ratio of copier emissions data for runs (using old toner) to runs using new toner (See Table 3-21).

#### 3.4.6.2 Toner Carryover

Following the headspace tests, additional chamber tests were run sequentially using the same copier but different lots of toner. It became apparent that the residual toner in the toner delivery system of the copier needed to be depleted and replenished with fresh toner when changing cartridges or when a period of a week or so elapsed between tests using the same lot. Without the depletion/replenishment, toner from a new cartridge would be diluted by the residual toner in the delivery system. A procedure for performing this depletion/replenishment was developed for the round-robin testing and was included in the Emission Testing Guidance Document for Dry-process Photocopiers (Appendix B). It should be noted that the specific method for toner depletion/replenishment is dependent on the particular copier being tested, and therefore each copier must be evaluated individually.

#### 3.4.6.3 Vent Gas Sampling

Because the large chamber emissions measurement method developed during this cooperative agreement requires specialized facilities and is relatively expensive to perform, preliminary investigations were conducted to evaluate an option for rapid-screening of copier organic emissions: copier vent gas analysis. Preliminary results from the vent gas sampling and analysis appeared to indicate that a correlation existed between the vent gas concentrations and the chamber data for the one copier that was evaluated. However, because each copier is designed differently, with a different number of vents and different vent flow rates, a single screening method that could be used for all copiers is highly unlikely.

**Table 3-26. Results of Toner Headspace Experiments**

	Concentration in Headspace (ng/mL)			
	ethyl-benzene	<i>m, p</i> -xylene	o-xylene	styrene
Tests at 100°C				
Toner 1 (Lot 1-2)	490	510	250	64
Toner 2 (Lot 1-4)	710	770	350	79
Toner 3 (Lot1-3)	960	960	450	110
Toner 4A (Lot 1-5A)	150	430	140	23
Toner 4B (Lot 1-5B)	130	410	140	21
Toner 5A (Lot 1-7A)	120	380	120	18
Toner 5B, duplicate (Lot 1-7A)	120	400	120	18
Toner 6 (Lot 1-8)	450	510	230	120
Tests at 200°C				
Toner 1 (Lot 1-2)	720	950	460	190
Toner 2 (Lot 1-4)	1100	1300	670	240
Tests at 35°C				
Toner 2 (Lot 1-4)	94	110	60	N/A
Toner 2, duplicate (Lot 1-4)	110	130	60	N/A

NA = not available

## **4.0 PHASE II: ROUND-ROBIN EVALUATION AND RESULTS**

The primary goal of Phase II testing was to evaluate the method outlined in the guidance document (Appendix B) for measuring emissions of VOCs, aldehydes/ketones, and ozone from dry-process photocopiers. The usefulness of the method was determined by comparing the results from four laboratories in a round-robin test. The following major activities were part of the Phase II testing:

- conducted round-robin testing using the same photocopier (copier 1) under identical conditions at four test laboratories using procedures developed and revised in Phase I;
- reviewed data from the round-robin testing to determine if the data were comparable between laboratories and if the method is useful for accomplishing the objectives; and
- summarized and reported on emissions results from all laboratories.

The following sections summarize the materials and procedures followed for the round-robin testing.

### **4.1 Materials and Methods**

Four U.S. laboratories participated in the round-robin tests. To minimize the variability due to the copier, a single photocopier, whose emissions had already been measured at RTI, was sent to the other three laboratories for the round-robin testing program and returned to RTI for a final test. The copier was transported via a commercial office products shipping firm to all locations. Upon arrival at each location, a field technician representing the manufacturer inspected, set up, and tested the copier to ensure that it was performing properly.

A representative from RTI traveled to each of the test facilities to perform a release of standard emissions sources in the participating test chambers to evaluate performance. A single lot of toner and a single lot of copier paper were used by all participating laboratories in the round-robin copier test. The same standard test pattern image (representing 15% coverage) was used for all tests (Appendix B, pages B-17 and B-18). The RTI representative also helped with the toner depletion/replenishment and remote start aspects of the copier tests as discussed in Section 3.3.6.2 and Appendix B. Personnel at each chamber facility were responsible for the chamber operation and sample collection. Each laboratory was responsible for providing sample cartridges for samples to be analyzed at the laboratory; however, RTI provided sample cartridges for replicate samples to be analyzed at RTI. Specific instructions were provided to participating laboratories when necessary to explain collection of toner samples and VOC and aldehydes/ketones sampling. The RTI representative observed at least one copier test at each facility to promote consistency between laboratories. Descriptions of the participating laboratories' test chambers are provided in Table 4-1. Particle measurements were attempted by three of the labs using gravimetric and/or particle counters; however, results were inconclusive.



A total of seven separate emission tests were conducted at the four participating facilities. (At one facility, the copier was tested three times to evaluate the precision at a facility other than RTI.) For each test, concentrations of VOCs, aldehydes/ketones, and ozone were measured in the chamber air. For each test, the same sequence of operations was performed:

- Step 1. Service representative checked copier and assisted in setting up remote start capability;
- Step 2. Toner depletion/replenishment was conducted on copier;
- Step 3. Background air samples collected from empty chamber;
- Step 4. Copier placed in chamber;
- Step 5. Copier powered up, paper loaded in copier, remote start tested, and equilibrated overnight;
- Step 6. Chamber air samples collected during copier idle period;
- Step 7. Chamber air samples collected during full copier operation (1,998 copies, ~38 minute operation time, total sample collection time of ~ 158 minutes) and samples collected for 4 air changes after copy process ends; and
- Step 8. Air exchange rate accurately determined through CO or other method during test.

**Table 4-1. Descriptions of Test Chambers Used in Round-robin Testing**

Lab	Chamber Dim. (m x m x m)	Chamber Vol. (m <sup>3</sup> )	Construction Materials	Air System	Air Exchange Rate (h <sup>-1</sup> )
Lab 1	3 x 3 x 2.5	22.7	aluminum walls, stainless steel floor, viton door seals	single pass	1.88
Lab 2	5.1 x 2.15 x 2.34	25.7	aluminum walls, stainless and galvanized steel floor	single pass	1.75
Lab 3	4.7 x 3 x 2.3	35.4	Marlite walls, ceiling, and vinyl floors	recirc.	0.904
Lab 4	4 x 2.8 x 2.6	29.1	stainless steel	single pass	1.62

#### **4.1.1 Chamber Dosing and Recovery Experiments**

Chamber dosing and recoveries were determined by introducing selected VOCs, formaldehyde, and ozone into the chamber at known rates (See Table 3-7). Chamber air samples were collected and analyzed for pollutant concentrations using procedures identical to those used during the Phase I emission tests with photocopiers. Percent recovery of the emitted pollutant was used to evaluate the accuracy of the emission test method and to ensure consistency between the different test chambers.

#### ***4.1.2 Chamber Air Samples During Emissions Tests***

The chamber designs allowed for continuous operation of the copier being tested and sampling of chamber air without opening the chamber during the test. Sampling points for the chamber air had to be representative of the chamber concentrations. A duplicate set of VOC and aldehyde samples were collected for analysis at RTI by the participating laboratory using cartridges and pumps supplied by RTI.

Methods used for collection and analysis of VOCs included various multisorbent tubes and Tenax cartridges. Each participating laboratory was allowed to use either type method as long as adequate performance could be demonstrated. For each method, the sample volumes collected for analysis and sampling time were determined by the flow rate and analytical sensitivity required.

Although other methods could have been used, all laboratories used the silica gel/2,4-DNPH method for monitoring formaldehyde and other low molecular weight aldehydes/ketones (Winberry, 1988). Using this method, aldehydes/ketones were collected by passing chamber air through cartridges containing silica gel impregnated with DNPH. Formaldehyde, as well as other aldehydes and ketones, react with the DNPH and are collected on the cartridge material. With the DNPH method, care had to be taken to address the potential interference of ozone. Potassium iodide-coated denuders or commercially available potassium iodide scrubbers were placed upstream of the DNPH cartridge to remove ozone.

For VOCs and aldehydes/ketones, chamber air samples were collected and analyzed for the target chemicals. As outlined in the steps listed above, a chamber air sample was collected prior to placing the copier in the chamber. A second chamber air sample was collected after the copier was placed in the chamber, powered up (but not printing), and equilibrated overnight in the chamber. This sample provided data on the equilibrium chamber air concentration in the idle mode. Finally, a third chamber air sample was collected from the time the copier started printing until 4 chamber air changes after printing was completed (approximately 2 hours). This sample provided data on the average time-integrated chamber air concentration over the test period.

Each laboratory stored collected samples in a manner consistent with their usual handling practices. For RTI, this consisted of storing the VOC cartridges in sealed glass tubes inside friction-sealed steel cans in a freezer maintained at -10 °C. The DNPH cartridges were stored in sealed polypropylene jars supplied by the manufacturer in a refrigerator maintained at 4 °C. These storage methods were recommended to the other participating laboratories.

For the two laboratories performing particle mass measurements (Laboratories 2 and 3), chamber air was passed through a particle size selective device (impactor) at a constant and specified flow rate. Particles less than 10 µm were collected on a preweighed filter. The mass of the collected particles was determined gravimetrically using an analytical balance. At the third lab (Laboratory 4), measurements using a real time particle counter were attempted.

#### **4.1.3 Toner Samples for Headspace Analysis**

Toner samples of 50 mg from each toner cartridge used were collected by the testing laboratory and sent to RTI for headspace analysis. These samples were collected so that the chemical consistency of the different toner cartridges from the same lot could be compared. The toner samples were collected by the participating laboratory immediately following each copier emission test. RTI provided a sampling kit complete with detailed sampling instructions to each laboratory prior to testing. Headspace analysis procedures were the same as those used during Phase I testing (see Section 3.4.6.1) except that the temperature during Phase II testing was 150°C.

### **4.2 Results**

In general, the results (calculated using the equations presented in Section 3) show good accuracy and precision for the round-robin chamber tests. The results demonstrate that the method can be used successfully by other laboratories to measure VOCs, ozone, and aldehydes/ketones from dry-process photocopiers. Particle measurements provided poor data for these purposes and results are inconclusive.

#### **4.2.1 Chamber Dosing and Recovery Experiments**

Results of the VOC, aldehyde, and ozone recovery tests are summarized in Table 4-2. These emission rate values are the result of the release of the standard emission sources. The emission rates measured during the release at each laboratory, the theoretical emission rates, and the calculated percent recoveries of the sources are presented. These recovery tests were conducted using the same chamber conditions as when the copier was tested. General recoveries for toluene and n-decane are very good for Laboratories 1, 2, and 4. Likewise, recoveries for formaldehyde for Laboratories 1 and 4 are also greater than 90%. Results from the recovery tests confirmed the bias observed at Lab 3 and are discussed in Section 4.2.2. The reason for the low recovery of formaldehyde at laboratory 2 is unknown. However, it may be due to the complicated system required for formaldehyde delivery at this location or, there could have been an unobserved (due to the fact that one could not see into this chamber) malfunction of the system. Ozone recoveries vary from 25 to 86%.

Due to the limited time schedule at each test facility, time was not allotted for each laboratory to analyze recovery data and optimize recovery conditions or take corrective action before testing the copier. Each laboratory was expected to have already performed basic recovery evaluations prior to this study. Also, part of this study was to evaluate the effects of different chambers relative to the test method. The recovery data were used to evaluate the copier results after each laboratory's data were reported. Once reported to RTI, data were reviewed at RTI for calculation errors and analytical bias. Participating labs were notified of problems and allowed to make justified corrections before the data were included in this report.

**Table 4-2. Chamber Recoveries Based on Standard Emission Sources (µg/hour • copier)**

Chemical	Theoretical	Lab 1		Lab 2		Lab 3		Lab 4	
		Measured	% Recovery	Measured	% Recovery	Measured	% Recovery	Measured	% Recovery
Samples Analyzed at Each Laboratory									
Toluene	12000	13000	108	14000	117	17000	142	10000	83
Decane	14000	14000	100	- <sup>a</sup>	-	20000	143	13000	93
Formaldehyde	6400	6000	94	3700	58	23000	359	6900	108
Ozone	8300	5500	62	4800	55	2200	25	7600	86
Samples Analyzed at RTI									
Toluene	12000	13000	108	15000	125	- <sup>b</sup>	-	15000	125
Decane	14000	14000	100	- <sup>a</sup>	-	- <sup>b</sup>	-	15000	107
Formaldehyde	6400	6000	94	2600	41	5400	84	7000	109

<sup>a</sup> Decane not included in standard released at laboratory 2.

<sup>b</sup> Data not reported due to low internal standard area counts in sample.

#### 4.2.2 Emission Rates

The results of the VOC emission rate measurements generated by each round-robin laboratory during copier operation are shown in Table 4-3. Samples collected during copier idle period were only reported by two of the four laboratories. RTI's idle data were similar to those obtained during Phase I testing (see Table 3-12). For all of the tests while the copier was operating, the compounds with the highest emission rates were ethylbenzene, *m*, *p*-xylene, *o*-xylene, and styrene. Results show very good general agreement between laboratories for most compounds. The precision between laboratories 1, 2, and 4 (tests 1 and 3 only since test 2 was incomplete) was excellent with relative standard deviations (RSDs) of 5.0% for ethylbenzene, 4.0% for *m*, *p*-xylene, 14.6% for *o*-xylene, 7.6% for total xylenes, and 3.7% for styrene. (RSD was calculated only for the four chemicals with emissions greater than 1000 µg/h.) These results compare favorably with a previous 20-laboratory round-robin study done with small chambers where RSDs of interlaboratory comparisons ranged from 26 to 42% for a polyvinyl chloride (PVC) flooring material (Colombo et al., 1993).

As discussed below, results of the duplicate analysis suggest that the higher emission rates observed for laboratory 3 are due to a laboratory measurement bias. If the results from laboratory 3 are included in the calculation of precision, RSDs increase to 17.5 % for ethylbenzene, 16.9% for total xylenes, and 20.6% for styrene. However, if the RSDs are calculated instead, using the duplicate samples for laboratory 3 that were analyzed at RTI, the RSDs are considerably better: 6.9% for ethylbenzene, 8.2% for total xylenes, and 4.1% for styrene.

The results for the Phase I testing at RTI are also shown in Table 4-3 for a general comparison between Phases I and II. The results obtained from Phase II are comparable with the Phase I results; however, note that different toner lots were used and some changes were made to the test method for the Phase II testing (e.g., toner depletion and replenishment) so a rigorous comparison between the two Phases is not appropriate.

Results of the duplicate samples collected in the individual laboratories and analyzed by RTI are shown in Table 4-4. When laboratory 3 conducted its own analysis (Table 4-3), the emission rates tended to be at least 30% higher than those reported by the other laboratories. However, when RTI conducted the analysis for duplicate chamber air samples (Table 4-4), emission rate data for laboratory 3 were in agreement with results from the other laboratories (with the exception of toluene which was higher). The results of this duplicate analysis suggest that higher emission rates observed for laboratory 3 in Table 4-3 are due to measurement bias in the analysis at laboratory 3 rather than chamber performance.

Aldehyde/ketone and ozone results for the samples collected and analyzed at each facility are shown in Table 4-5. Laboratory 3 had a high positive bias for formaldehyde as was seen in the VOC analysis. For the data reported, measurements among the four laboratories were generally more variable for the aldehydes/ketones than for the VOCs. For formaldehyde, the precision among laboratories 1, 2, and 4 was fairly good with an RSD of 20.0%. Ozone emission

Table 4-3. Emission Rates Measured During Copier Operation -- Selected VOCs (µg/hour • copier)

Chemical	Phase II					Phase I	
	Lab 1	Lab 2	Lab 3	Lab 4 <sup>a</sup>		RTI	
				Test 1	Test 2 <sup>b</sup>		
Toluene	440	1100	NR <sup>d</sup>	370	BDL <sup>c</sup>	350	760
Ethylbenzene	23000	24000	32000	22000	18000	21000	28000
m,p - Xylene	21000	23000	46000 <sup>c</sup>	21000	17000	21000	29000
Styrene	6100	6600	9600	6200	5200	6000	9900
o - Xylene	11000	14000	NR	10000	8700	10000	17000
Isopropylbenzene	140	220	NR	BDL	BDL	BDL	NR
n - Propylbenzene	340	480	NR	390	350	0.4	790
a-Methylstyrene	500	790	NR	660	610	600	330

<sup>a</sup> Three copier tests performed at Lab 4, values in most cases represent average of two measurements

<sup>b</sup> Test 2, copier paper feed jammed, only 1020 copies produced instead of 1998

<sup>c</sup> Value represents the sum of the ortho, meta, and para-xylene isomers

<sup>d</sup> NR = not reported

<sup>e</sup> BDL = below detection limit

**Table 4-4. Copier Emission Rates During Operation Based on RTI Sample Analysis of Duplicate Samples Collected at Each Laboratory<sup>a</sup> (µg/hour • copier)**

Chemical	Lab 4 <sup>b</sup>			
	Lab 1	Lab 2	Lab 3	Lab 4 <sup>b</sup>
Toluene	590	1000	2000	540 (c)
Ethylbenzene	23000	29000	25000	27000 23000
m,p - Xylene	22000	29000	24000	25000 21000
Styrene	6300	8400	6600	6700 6000
o - Xylene	12000	15000	12000	ND <sup>c</sup> 11000
Isopropylbenzene	160	160	160	ND 160
n - Propylbenzene	360	450	390	ND 330
a-Methylstyrene	500	730	550	25 530
Formaldehyde	1900	2400	3200	2400 2700 2200
Acetaldehyde	1100	1300	1300	510 610 800
Propionaldehyde	- <sup>d</sup>	-	-	- - -
2-Butanone	600	-	570	- - -
Butraldehyde	300	280	410	- - -
Benzaldehyde	1500	1200	980	1000 1200 630
Hexanal	590	690	950	- - 730

<sup>a</sup> Values not corrected for idle concentration - idle samples not collected for analysis by RTI

<sup>b</sup> Three copier tests performed at Lab 4

<sup>c</sup> Test 2, copier paper feed jammed, only 1020 copies produced instead of 1998

<sup>d</sup> ND = not detected

<sup>e</sup> "—" Represents data not listed due to one of the following reasons - not reported by lab, below calibration rate, or not detected.

Table 4-5. Emission Rates Measured During Copier Operation Selected Aldehydes/Ketones and Ozone  
(µg/hour • copier)

Chemical	Phase II					Phase I	
	Lab 1	Lab 2	Lab 3	Lab 4 <sup>a</sup>		RTI	
				Test 1	Test 2 <sup>b</sup>	Test 3	
Formaldehyde	1300	2200	4700	1500	BCR	1700	<500
Acetaldehyde	386	1635	NR <sup>c</sup>	BDL <sup>d</sup>	BDL	BDL	710
Propionaldehyde	192	ND <sup>e</sup>	NR	NR	NR	NR	<100
2-Butanone	307	ND	NR	NR	NR	NR	<100
Butraldehyde	300	ND	NR	NR	NR	NR	160
Benzaldehyde	1139	1834	NR	BCR <sup>f</sup>	BDL	BCR	1800
Hexanal	300	ND	NR	BDL	BDL	BDL	210
Ozone	1700	7500	1700	2000	2900	2400	3000

<sup>a</sup> Three copier tests performed at Lab 4, values in most cases represent average of two measurements

<sup>b</sup> Test 2, copier paper feed jammed, only 1020 copies produced instead of 1998

<sup>c</sup> NR = not reported

<sup>d</sup> BDL = below detection limit

<sup>e</sup> ND = not detected

<sup>f</sup> BCR = below calibration range



rates measured during copier operation were relatively consistent except for the emission rate measured for laboratory 2.

#### ***4.2.3 Headspace Samples***

Results of the headspace samples for Phase II are shown in Table 4-6. All round-robin tests were performed with the same lot of toner although a fresh cartridge was used at each test lab. These results are not comparable with Phase I since this lot was not tested during Phase I, and the analysis temperature was different. These results are reported in ng/mL of headspace and show that for laboratories 1, 3, and 4 no major differences were seen in the concentrations of the various containers of the lot of toner used for the round-robin testing. The toner sample from laboratory 2 was held for approximately 3 months prior to being analyzed. Volatile losses may have occurred during this time as indicated by the lower headspace results.

#### ***4.2.4 Particle Samples***

As stated previously (Section 3.2), accurately measuring chamber recovery for particulates is complex. While an attempt was made to measure particle emissions, results are not reported since the tests were not conducted at all facilities, and the results obtained from those that did are inconclusive. In general, no weight gain was measured on the filters by gravimetric analysis.

**Table 4-6. Toner Headspace Results from Round-Robin Study <sup>a</sup> (ng/mL headspace)**

Chemical	Lab 1	Lab2 <sup>b</sup>	Lab 3	Lab 4
Toluene	4	0.8	2.1	3
Ethylbenzene	620	260	460	580
m,p - Xylene	620	270	440	570
Styrene	200	100	140	180
o - Xylene	410	210	300	380
Isopropylbenzene	7	4	5	6
n - Propylbenzene	14	9	21	14
a-Methylstyrene	28	23	22	33

<sup>a</sup> All headspace analyses were performed at RTI.

<sup>b</sup> Sample held for ~ 3 months; volatile losses may have occurred during this time.

## **5.0 ADDITIONAL ISSUES RELATED TO OFFICE EQUIPMENT EMISSIONS**

Throughout this project, several issues were raised as either having potential pollution prevention implications or areas requiring additional research:

- paper type and its effect on emissions from photocopy machines;
- recycled toner cartridges and the effect of their use on photocopier emissions; and
- emissions from color versus monochromatic copiers.

While each of these issues could constitute a significant research effort on their own, they were investigated to a varying degree throughout this cooperative agreement and are summarized in the following sections.

### **5.1 Paper Type**

The technical advisors for this research effort indicated that emissions from copy machines and printers would be different depending on the paper type being used. Specifically they were referring to paper such as preprinted forms, labels, coated paper, transparencies, and both recycled and virgin office paper. The literature review that was conducted as the first step in this cooperative agreement identified several references discussing the effect of carbonless copy paper on worker health complaints (Morgan and Camp, 1986; Marks et al., 1984; Marks, 1981; and LaMarte et al., 1988). Carbonless copy paper was considered an "office product" and therefore outside the scope of this research. In addition, it was decided that evaluation of the other types of paper with respect to their emissions and their effect on overall copier emissions, while it may have an impact, was not the highest priority. The primary goals were to develop a method that could be used for evaluating emissions from office equipment and to use that method to identify pollution prevention opportunities. Because of the complexity of developing the method and the number of variables that are introduced by using several different types of copy machines, it was decided that the paper supply should be kept constant throughout the research effort. This allowed the number of experimental variables to be reduced and the data analysis to be simplified.

Paper from the same manufacturer and lot (with a recycled content of 25 %) was used throughout all Phase II testing. In the beginning stages of Phase I, a different type of paper was used (recycled content of 20 %) but experienced some paper jamming. The 25 %-recycled paper performed well in all subsequent testing. Questions have been raised concerning the use of recycled paper and its effect on copy quality, runnability, and emissions. The issue of varying emissions from both recycled and virgin copy paper, even from the same manufacturer, is very complex. Emissions not only are dependent on the specific manufacturing and recycling technologies but also can be affected by variables such as the tree species and recycled material that was used to derive the pulp.

Buyers Laboratory, Inc. (BLI) conducted a survey of its subscribers to obtain information on use and problems associated with recycled copy paper (BLI, 1995). They received 210 responses, of which 91 % indicated overall satisfaction with recycled paper. One of the greatest concerns that was expressed by recycled paper users was runnability. Of the respondents, 82% rated the runnability of the recycled paper that they use as good or excellent. In general, "it is the physical characteristics of the paper, such as surface smoothness, thickness and porosity--not recycled paper content--that determines whether the paper will run well (BLI, 1995)." It should be noted that these important physical characteristics are easier to control when the source of fiber used to manufacture the paper is consistent. A consistent source of fiber cannot always be obtained from recycling operations because of the nature of the supply of waste paper. For the photocopier testing that was done as part of the RTI/EPA cooperative agreement, better machine runnability was obtained when using a paper with 25 % post-consumer recycled content as opposed to a paper with 20 % recycled content. Researchers also found that some machines were better able to run various types of paper without experiencing paper jams. In general, the BLI report suggests that buyers purchase paper that falls within their machine's specifications and stay with the type(s) that work well.

Runnability can also be affected by humidity and/or the moisture content of the paper used. The BLI report states that moisture has a greater effect (and hence greater potential for paper jams) on recycled paper than on virgin paper because it is more attracted to the recycled fiber. Some high-speed copy machines are equipped with dehumidifiers to maintain the optimum conditions for paper. Storage of paper in a climate-controlled environment can help to reduce the impact of humidity on recycled paper runnability.

Another significant concern that is often expressed regarding the use of recycled paper is its effect on equipment service (requiring a technician) and/or user maintenance. Of the respondents to BLI's survey, 84% indicated that they saw no change in the need for equipment servicing by a technician after switching to recycled paper. Also, 70% said that the need for user maintenance, such as cleaning, was the same with both virgin and recycled paper. The most significant factors that contribute to the need for service/maintenance include contaminants, such as glue, that may be contained in the recycled pulp and paper dust. Contaminants in the recycled paper fiber, resulting from inconsistent raw materials or glue remaining after the de-inking process, may leave a residue on the internal components of copy machines. This residue may build up over time and increase the need for equipment servicing.

BLI's survey results indicated that "in general, users of recycled paper with the higher post-consumer materials complained more about paper dust than users whose recycled paper contained lesser amounts." Excess paper dust in copy machines was linked to spots on copies and resulted in the need for more frequent cleaning of the machine parts. BLI's report noted that a survey respondent using recycled paper with 25 % post-consumer waste had no more dust than when using virgin paper. It is interesting to note that this paper was the same brand that was used during the round-robin evaluation that was part of this research. Dust generation was reported as being less of a concern for printer and fax operation--likely due to less throughput, slower operating speeds, and shorter paper paths.

## 5.2 Recycled Toner Cartridges

Several manufacturers have initiated recycling consumable materials, including toner cartridges and photoconductive drums. It has been reported that 30 million laser toner cartridges were sold and discarded in 1993 and that, industry-wide, refilling would reach 22 % in the year 1998 (Global Recycling Network--Recycle Talk Answers from Fred Friedman 11-27-96; Internet source). Another source estimated that in 1996, over 40,000 tons of unrecycled cartridges, which are generally made from non biodegradable plastic, went into landfills in the United States (Internet source: <http://www.laserlux.com>). This same source reports that one pint of oil is required to produce each new cartridge and therefore remanufacturing would save over 2.5 million gallons of oil in 1997.

Laser printer toner cartridges are the most frequently recycled element, both by the original manufacturer and by small businesses dedicated to that purpose, although cartridges from photocopiers, fax machines, and inkjets are also remanufactured. A 1994 survey in *Recharger Magazine* (Vernon, 1994) showed that approximately 5,000 companies remanufactured cartridges. Nearly one-third of all remanufacturers represented by the survey had been in business for less than 2 years, and only 5 % of the industry had been in business for more than 7 years.

The performance of a recycled toner cartridge can vary based on the condition of the cartridge and the process used to remanufacture it (U.S. EPA, 1994). When the industry began remanufacturing cartridges, "drill and fill" cartridges gave remanufactured toner cartridges a poor reputation. A hole was drilled in the bottom of a cartridge and sealed with tape, and the cartridge was sold to consumers along with two bottles of toner and two tape seals. When the cartridge ran out of toner, the customer removed the tape and poured the toner from one of the bottles into the cartridge and resealed the hole. This process was repeated when the toner ran out again. The drill-and-fill cartridges caused quality problems because the toner debris cavity was not emptied each time; if this cavity overfills, excess toner leaks into the machine.

There is currently no standard remanufacturing process in the cartridge recharging industry. Each company remanufactures its product to its own standard; however, BLI performs certification of remanufactured cartridges. The certification procedure includes on-site inspection and analysis of a remanufacturer's procedure and facilities and testing of the remanufactured cartridges. BLI certifies that a company uses sound remanufacturing procedures and that the remanufactured cartridges perform as well as or better than new cartridges.

Although no standard process exists, the remanufacturing process is similar for each type of cartridge: the cartridge is tested for any deficiencies that would prohibit it from being remanufactured and is taken apart, cleaned and inspected for worn parts that need to be replaced, and refilled. If there is no replacement part available for a cartridge, the cartridge may only be used for one cycle or may not be used at all.

The waste toner cannot be reused for its original purpose and is generally disposed of in a landfill. In some circumstances, waste toner can be mixed with asphalt for highway construction. Most toner cartridges, including wet- and dry-toner cartridges, generate approximately 20-30

grams of waste per cartridge. There is generally 150 to 700 grams of toner in a newly manufactured cartridge.)

In addition to environmental benefits, using remanufactured toner cartridges has financial benefits as well. It was reported in 1994 that the average price of a new laser printer cartridge was \$100, while a remanufactured cartridge for the same machine cost \$45 (Clayton, July 1994). One cartridge remanufacturer advertises that its remanufactured cartridges cost 30 to 75 % less than new ones (Internet source: <http://www.laserlux.com>). These cost differences can be significant because the toner accounts for approximately 75 % of the total cost over the life of a printer (Table 5-1).

**Table 5-1. Approximate Cost Percentages over the Lifetime of Laser Printers**

<b>Parts</b>	<b>% of Total Costs</b>
Laser printer--original equipment cost	10%
Paper	15%
Toner cartridges (original equipment manuf.)	75%

Source: Clayton, 1994.

### **5.3 Color Photoimaging Machines**

One of the recommendations from the March 1994 technical advisors planning meeting for this project was to evaluate the emissions from color dry-process photocopiers and/or printers. The technical advisors as well as the scientific literature indicated that the emissions from both dry- and wet-process color photoimaging are not well characterized and therefore should be evaluated further. They suggested that an evaluation should include an investigation to determine the relative toxicity of color toners with respect to the traditional black toners and the potential need for reformulation. Color image processing requires the use of lower fuser temperatures, requires multiple passes within the machine, and uses characteristically different toners. Each of these requirements may affect IAQ and subsequent pollution prevention strategies. The lower the fuser temperature, the lower the anticipated rate of emissions of VOCs; however, the need for multiple passes increases the time that the image may be subjected to heat and therefore may also affect emissions. Therefore, an investigation of the balance between the fuser temperature and time in contact with the fuser rollers is needed.

The initial research plans for this project included color copiers. Due to the high demand and low supply of these copiers at the time of the early testing, a color copier was unavailable. Color copying has increased substantially in the past 3 years, and that trend is likely to continue as the technology matures and prices become lower. Therefore, emissions from color dry- and wet-

process photoimaging machines is still an important issue that should be considered for future research efforts.

## **6.0 POLLUTION PREVENTION OPPORTUNITIES**

An initial objective of this research was to identify and evaluate potential pollution prevention technologies that could be used to reduce indoor air emissions from office equipment. As stated in Section 2, the initial literature search revealed a lack of data on emissions as well as the lack of a standard method that could be used to evaluate thoroughly both VOC and ozone emissions from office equipment. Without a standard test method, the impact of pollution prevention in the form of design, technology, or raw material changes could not be measured. Therefore, research priorities were broadened to include the development of an emissions testing guidance document that could be used both by manufacturers and by other researchers to evaluate emissions in order to identify and evaluate pollution prevention opportunities.

Throughout the literature review, test method development, and emission measurement activities, pollution prevention options have been identified that may result in reduced emissions from office equipment. In some cases, testing has confirmed literature data and/or identified areas where more research is needed. The following sections are organized according to pollution prevention options identified through the published literature and through laboratory testing conducted as part of this project.

### **6.1 Literature**

#### ***6.1.1 Pollution Prevention for Reducing Ozone Emissions***

Ozone is one of the most significant pollutants generated in dry-process photoimaging. As described in Section 2.2.2.1, some equipment manufacturers have modified their printers and photocopiers to reduce ozone emissions. In previous and some current designs, electrically charged corona wires are used to add a uniform primary charge across the surface of the photosensitive drum and the paper surface. The corona wires are separated from the drum by a small distance and, therefore, high voltages are applied to the corona wires to attain the needed charge. Electrical arcing results from the corona wire, which produces ozone. In newer designs, the two corona wires are replaced with “charging” rollers. Unlike the corona wires, the charging rollers are in direct contact with the photosensitive drum, which eliminates the need for high voltage and prevents the formation of electrical arcs and ozone. A recent NIOSH study (Gressel, 1996) of printer emissions indicates that ozone emissions from printers with corona wires were high enough (0.005-0.06 mg/min) to cause concern in an indoor environment. While the ozone emissions from a printer with the newer charged roller design produced very little ozone (0.0008 mg/min). During Phase I evaluation of different dry-process photocopiers in this project, a wide range of ozone emission rates were observed (1,300 to 7,900 µg/hr · copier). The copier with the lowest emission rate was advertised as a low-ozone-emitter. The charged roller system presently has copy rate limitations, so future research investigating the application of this system to higher throughput machines could yield pollution prevention benefits.



### ***6.1.2 Pollution Prevention Opportunities for Toner***

One manufacturer has developed a technology for improving toner transfer efficiency through the use of a replaceable cartridge system. The cartridge system houses the toner as well as the photosensitive drum and other consumables. As the photoconductive surface of the drum deteriorates, the toner transfer efficiency decreases, increasing the potential for indoor air emissions. The photosensitive drum is automatically replaced at regular intervals (whenever the toner is changed), thereby restoring the transfer efficiency to its original state and preventing increasing particulate pollution. Printers in which the photoconductive drum are not replaced as part of regular maintenance will suffer a gradual decrease in toner transfer efficiency as the drum ages, leaving more toner particles within the printer chassis or in the indoor air. Therefore, expanding the use of this technology to other manufacturers or other types of equipment could result in pollution prevention by minimizing particulate emissions.

For dry-process systems, reducing the temperature of the fusing operation to reduce the volatilization of VOCs from the toner may be a pollution prevention option for consideration. Elevated temperatures used in the fusing process can increase the volatilization of VOCs present in the toner as confirmed by the toner headspace tests conducted as part of this cooperative agreement (see Section 3.4.6.1). Reducing the fusing temperature (by changes in pressure or in toner formulation) may result in lower VOC emissions. Therefore, an investigation of the balance between the fusing temperature and time in contact with the fuser rollers may result in pollution prevention benefits. Indoor air emissions may be reduced through a greater reliance on pressure fusing than on heat fusing.

Changes in toner particle size may have an impact on toner transfer efficiency, the fusing process, print quality, and overall emissions. The size of the particles emitted also influences the degree to which they are inhaled and the potential for adverse health effects. Therefore, research focused on toner chemistry and reformulation could also consider the potential pollution prevention benefits of various toner particle sizes. It should be emphasized that the different aspects of the fusing process--temperature, pressure, and toner formulation--are interrelated; therefore, any changes in one aspect may require changes in the others for proper equipment operation.

In wet-process systems, toners (and developers, where applicable) are the major source of indoor air emissions. These emissions occur from the volatilization and/or aerosolization of toner and toner solvents. Reformulation of toners using lower-volatility solvents can result in lower emissions. However, changing solvents may impact the quality of the printed images and may lead to mechanical problems such as clogging of the ink or bubble jets. Pollution prevention research taking place within the printing and publication industry could also be considered for other toner options. For example, water-based toners and ultraviolet (UV)-cured solid toners used in the printing industry may prove useful for some printers and photocopiers.

The toner cartridge is the most common element being recycled, or remanufactured, both by the original manufacturer and by small businesses dedicated to that purpose. In 1993, approximately 30 million toner cartridges were sold in the U.S. and after use, most discarded in

landfills (Global Recycling Network--Recycle Talk Answers from Fred Friedman 11-27-96; Internet source). Toner cartridge recycling is projected to reach 22 percent in 1998 and not only diverts plastic from landfills, but it also saves oil. It is reported that one pint of oil is required to produce each new cartridge and therefore remanufacturing will save over 2.5 million gallons of oil in 1997 (Internet source: <http://www.laserlux.com>). This topic is discussed in Section 5.2.

### ***6.1.3 Pollution Prevention Related to Equipment Maintenance***

Pollution prevention may also be achieved through modified equipment maintenance procedures or by redesigning machines so that less maintenance is needed. Organic solvent-based products are typically used to clean glass, mirrors, and rollers; the use of water-based products should be investigated. Reformulation of solvents for cleaning glass and mirrors may be easily accomplished but may be more difficult for other cleaning products that not only clean but also replenish the rubber parts (rollers) within the machine. In addition, because emissions have been shown to increase with time since the previous maintenance cycle (Claridge, 1983), reduced indoor air emissions can be expected from proper and timely equipment maintenance. In one study of five different photocopy machines, ozone emissions before maintenance ranged from 16 to 131  $\mu\text{g}/\text{copy}$ . Emissions after maintenance were 4  $\mu\text{g}/\text{copy}$  or lower in all five machines (Selway et al., 1980).

## **6.2 Pollution Prevention Opportunities Resulting from Laboratory Testing**

Laboratory testing efforts were focused in these areas: (1) measurement of emissions from dry-process photocopiers, (2) evaluation of ozone emissions, and (3) evaluation of emissions circuit board laminates used in electronic equipment such as computer monitors.

### ***6.2.1 Reduced Emissions from Toners Used in Dry-process Photocopiers***

Initial research conducted as part of this cooperative agreement identified toners as a primary contributor to indoor air emissions from dry-process photocopiers. Toners supply the image to the page and generally consist of a polymeric resin carrier (e.g., styrene-based copolymers) between 5 and 10  $\mu\text{m}$  in diameter. There are two types of toner used in dry-process photocopiers depending on the machine: monocomponent toners and dual-component toners. Machines that use monocomponent toners use toner only; the toner may also include a magnetic material to aid in toner transfer. Machines that use dual-component toners include a carrier (sometimes referred to as developer) in the toner. These particles generally consist of iron particles between 50 and 200  $\mu\text{m}$  in size and serve to deliver the toner particles to the photoconductive drum during the photocopy process.

Toners are commonly manufactured by melt-mixing pigment and polymers together, followed by high-impact fracture. Toner processing is most commonly carried out in an extruder, Banbury® mixer, or continuous mixer. As a general rule, extruded toners are “cleaner” than toners produced in a Banbury® mixer. The extrusion process is more modern and, in addition, the toner can be manufactured under a vacuum, which may decrease the amount of volatile compounds in the toner (Bever, 1986).

To better understand the relative contribution of toner emissions, two methods were used to collect the data presented in this section: (1) the large chamber test method developed specifically for this project and (2) headspace analysis. The data collected from the large chamber test are from the Phase I testing of four different dry-process photocopy machines (see Section 3 for details). Three of the machines use dual-component toners, and the fourth machine uses monocomponent toners. The data presented from the headspace analysis were obtained using the procedure described in Section 3.4.6.1 (although the testing described in this section was conducted at 150 °C) and are from three dual-component toners. The toner evaluated in the headspace analysis is manufactured by the same manufacturer as one of the machines tested in the large chamber.

Calculated VOC emission rates resulting from the Phase I large chamber tests are summarized in Section 3. These results show that the lowest VOC emission rates were measured for copier 3 (the only copier with monocomponent toner). It is hypothesized that differences in emission rates for VOCs from different copiers may be due to differences in the chemical composition of the toners. Such variations in emissions indicate a potential opportunity for pollution prevention through copier redesign, toner reformulation, and/or specification of “cleaner” raw materials for the toner to reduce emissions of concern (e.g., sensory irritants and/or HAPs).

As presented in Section 3, in most cases, emission rates from the four copiers tested during Phase I were low in the idle mode ( $<500 \mu\text{g/h}$ ) when compared with emissions in the print mode. Where this was the case, the impact on indoor air quality should also be low. Two exceptions were relatively high measured emission rates for formaldehyde and acetone from copier 3. It is possible that differences in toner type could be responsible for elevated emission rates for these two chemicals in the idle mode. This result suggests that the most important impacts on IAQ will occur during printing; as a corollary, pollution prevention strategies should focus on the print operation.

To determine the effect of toner age on emission rates, two large chamber tests were conducted during Phase I using an existing toner cartridge and compared with results from three tests conducted immediately after a new toner cartridge had been installed. A comparison of results for the tests conducted with new vs. old toner cartridges showed substantially elevated emission rates for the tests with the new toner. For the aromatic hydrocarbons, such as ethylbenzene, the xylenes, and styrene, the emission rates with new toner were approximately 50 percent higher than the emission rates with old toner. These results show the substantial impact that toner age may have on emission rates and support the conclusion that pollution prevention research specifically focused on toner manufacturing and formulation be pursued.

The results from the toner headspace analysis are shown in Table 6-1 and compare three different toners that are manufactured for use with copier 1. Please note that these results are not comparable to those shown in Table 3-26 although the same lots were analyzed. These results are from headspace samples heated to 150 °C, not 35, 100, or 200 °C. According to the Material Safety Data Sheets, all three toners are comprised of: 80-90 weight percent styrene/acrylate copolymer; 5-10 weight % carbon black; 5-10 % polypropylene wax; 1-3 % titanium dioxide; and less than 1 % quarternary ammonium salt. The three toners are each manufactured at different plants using the same raw materials, but the manufacturing process for toner C is different than the process for toners A and B. Toner C is manufactured using the extrusion process, while toners A and B are manufactured using the Banbury® process. The data shown in Table 6-1 indicate that headspace concentrations resulting from toners A and B are typically 2 to 5 times higher than concentrations from toner C. As previously stated, the extrusion process (toner C) is more modern; additionally, the toner can be manufactured under vacuum, which may decrease the amount of VOCs in the toner (Bever, 1986). Based on these limited results, it is recommended that the extrusion process be further explored as a potential option for producing lower-emitting toners.

**Table 6-1. Headspace Analysis of Toner Samples (ng/mL) <sup>a</sup>**

<i>Chemical Emitted</i>	<i>Toner A (Lot 1-3)</i>	<i>Toner B (Lot 1-4)</i>	<i>Toner C (Lot 1-5A)</i>
<b>Ethyl benzene</b>	1100	950	220
<b><i>m,p</i>-Xylene</b>	1100	930	470
<b>Styrene</b>	290	260	130
<b><i>o</i>-Xylene</b>	740	660	290

<sup>a</sup> Tests at 150 °C.

### **6.2.2 Reduced Ozone Emissions from Copiers**

As presented in Section 3 (Table 3-20), substantial differences in ozone emission rates were seen between the four copiers tested during Phase I, ranging from 1,300 µg/h · copier for copier 4 to 7,900 µg/h · copier for copier 3. Copier 4 was advertised as a low ozone emitting copier. Results show that the techniques applied to this copier for reducing ozone emissions have been successful and should be further explored.

## **7.0 CONCLUSIONS AND RECOMMENDATIONS**

The research that was conducted as part of this cooperative agreement is separated into four major activities:

- literature review;
- Phase I method development and testing;
- Phase II round-robin evaluation; and
- identification of pollution prevention opportunities.

The conclusions and recommendations resulting from each of these four activities follow.

### **7.1 Literature Review**

At the beginning of this cooperative agreement, a literature review was conducted to obtain information on office equipment technologies, emissions, and measurement methods. A separate report (Hetes et al., 1995) resulted from this review. General conclusions that can be made from the report are:

1. Sources of emissions from office equipment include materials of construction (e.g., plastic casings, printed circuit board laminates), supplies used (e.g., toner), and generation of emissions during operation (e.g., ozone).
2. No standard method for measuring emissions from office equipment was available. Therefore, development and validation of an emissions testing guidance document was a top priority for this research.
3. Office Equipment technologies (see Table 2-1) showing rapid growth in market share (e.g., color coping, printing) should be considered a priority for any future research.

### **7.2 Phase I Testing**

Results of Phase I testing provided valuable information on the performance of the test method and the emissions characteristics of dry-process photocopiers. Conclusions and recommendations resulting from the Phase I testing are:

1. The large chamber test method developed as part of this project provided acceptable performance for characterizing emissions from dry-process photocopy machines. Percent recovery for calculated emission rates for standard materials emitted into the chamber at known rates was generally greater than 85%. Ozone was the exception with only 72% recovery. Precision of replicate tests using both standard emitters and photocopiers was good (% RSD<20 in most cases). In general, precision was much better for the emission rate measurements in the print mode than in the idle mode where measured emission rates had much lower values.

2. Measuring emissions from office equipment can present numerous challenges and complications. Specific considerations identified and addressed during this study follow.
  - Heat Generation: Depending on the machine, heat generation in the chamber may be a problem. As a result, the test method developed as part of this project specifies a temperature range of  $28.5 \pm 2.5$  °C and 2 ACH.
  - Limited Paper Supply: A finite paper supply for copy machines limits the duration of the test. For this study, a paper supply of 2,000 sheets was used for each test. This supply was exhausted after 20 to 40 minutes for the mid-range dry-process machines evaluated. Collection of integrated chamber air samples continued for an additional 4 air changes (i.e., 2 hours for this study).
  - Power Requirements: The type of outlet required varies among copiers. Therefore, installation of new outlets, changing outlets, or multiple outlet formats may be required.
  - Remote Starting: Remote starting of the machines is necessary to maintain the integrity of the chamber. Complications from remote starting can result from either the software (automatic reset) and/or hardware (lack of electronic overdrive capability). These problems can be minimized if an experienced service technician installs, sets up, and checks out the equipment.
  - Toner Depletion and Replenishment: Testing indicated that toner age can have a significant impact on photocopier emissions, as can a variation between different lots of toner. To control for this variable it was determined that residual toner in the toner delivery system needed to be depleted and replenished with fresh toner when changing cartridges or when a period of more than two weeks elapsed between tests using the same toner lot. A procedure for this was developed and included in the standard test guidance.
3. During Phase I testing, chamber air concentrations of styrene in the range of 40-60  $\mu\text{g}/\text{m}^3$  (7,000-10,000  $\mu\text{g}/\text{hour} \cdot \text{copier}$ ) were observed (Tables 3-12, 3-15). Emissions testing was conducted using chamber conditions that approximate conditions found in office buildings; therefore, it is possible that indoor air concentrations of this magnitude could also be found in offices. For comparison, median indoor air concentrations for styrene measured in the Total Exposure Assessment Methodology (U.S. EPA, 1987b) study were about 1.0  $\mu\text{g}/\text{m}^3$ .
4. Although many of the same compounds tended to be detected in emissions from each of the four photocopiers, the relative contribution of individual compounds varied considerably between machines, with differences greater than an order of magnitude for some compounds. The variation in compounds is most likely due to different toner formulations used for the different machines.

5. Many of the compounds detected in this study--benzaldehyde, ethylbenzene, nonanal, ozone, styrene, and xylenes--were consistent with compounds identified in the literature from photoimaging equipment. Again, any variation in compounds is most likely due to the different toner formulations used for different machines.
6. The integrated sampling approach for generating emission rate data was determined to be acceptable. Although the use of time-point samples provides some additional information, it is more labor-intensive and costly.
7. Toner headspace testing indicated that increased temperatures resulted in increased organic concentrations in the headspace gas. Results from the toner headspace analysis also indicated that there may be some correlation between toner headspace analysis and copier emissions; however, more testing of this relationship is required before any conclusions can be drawn.
8. Toner lot, manufacturing process, and age (as measured by the amount of time that a cartridge has been opened) has a significant impact on organic emissions during both headspace tests and copier operation. Therefore, any organization planning to conduct photocopier emission tests or analyze emissions data needs to consider and control for this variable. In addition, it is recommended that further investigation be conducted to evaluate the effect of toner manufacturing process and purity of raw materials on photocopier emissions.
9. Because the large chamber emissions measurement method developed during this cooperative agreement requires specialized facilities and is relatively expensive to perform, preliminary investigations were conducted of an option for rapid-screening of copier organic emissions: copier vent gas analysis. Results from the very preliminary vent gas sampling and analysis appeared to indicate that a correlation exists between the vent gas concentrations and the chamber data for the one copier that was evaluated. However, because each copier is designed differently, with a different number of vents and different vent flow rates, a single screening method that could be used for all copiers is highly unlikely.

### **7.3 Phase II Testing**

In general, the results show fairly good accuracy and precision for the round-robin chamber test results. The results demonstrate that the emissions testing guidance document can be used successfully by other laboratories to measure VOCs and aldehydes/ketones from dry-process photocopiers. Conclusions and recommendations from the results are:

1. Results obtained from different chamber facilities are comparable. The VOCs reported to have the highest emission rates by all of the participating laboratories were ethylbenzene, *o*-, *m*-, *p*-xylenes, and styrene. These were also the compounds with the highest emission rates reported from the Phase I testing.

2. Excluding problems with analytical bias as seen from one laboratory, the precision between laboratories for VOC measurements was excellent (RSD of less than 10% in many cases). This can be compared to other round-robin studies for small chamber tests where agreement between laboratories was not as good (RSD 25-46 %). Aldehyde/Ketone and ozone emission rates were more variable.
3. Differences in chamber design and construction at the different laboratories seemed to have little effect on the test results. Perhaps more important than the chamber construction is the analytical methodology used to analyze the sample cartridges.
4. The methods of introducing standard emission sources to the chambers seemed to work well with the exception of formaldehyde at laboratory 2.
5. Sufficient test parameters seem to have been addressed to provide consistent results with this photocopier during this phase of testing. However, some photocopiers or other types of office equipment may not allow depletion/ replenishment of toners as easily as the copier that was used during the round-robin testing. This is an issue that should be addressed with further investigation.
6. Based on the results from Phase I and Phase II, the emissions testing guidance document can be used as written for generating emission rate data from dry-process photocopiers. Laboratories that are planning to conduct these tests must first demonstrate proficiency in the method using the same evaluation procedures that were used for the round-robin study.
7. Throughout the method development and testing, a single paper supply and lot of toner supplied by the copier manufacturers was used. The reason for this was to limit the number of copier-related variables. It is recommended that future testing evaluate the effect of different paper types (including pre-printed forms, labels, transparencies, etc.), remanufactured toner, and color technologies on emissions.

#### **7.4 Potential Pollution Prevention Opportunities**

Potential opportunities for reduced emissions from photocopiers were identified from the literature, discussions with manufacturers, and from the tests conducted as part of this research. They are:

1. The use of charged roller systems decreases ozone emissions; however, the charged roller system presently has copy rate limitations. Therefore, it is recommended that future research focus on investigating the application of this design change to higher throughput machines.
2. Both the literature and laboratory testing indicate that the greatest level of organic emissions from dry-process photocopiers results from the toner during the operating mode. Additionally, higher temperatures were shown to result in higher organic emissions



during toner headspace tests. Therefore, pollution prevention research should focus on the relationship between toner formulation and the fusing process. Specifically this could include:

- investigating the relationship between fusing temperature and time in contact with the fusing rollers;
- testing of designs that use only pressure fusing;
- evaluating specific differences between mono- versus dual-component toners and the resulting differences in emissions;
- evaluating the effect of toner particle size on toner transfer efficiency and particulate emissions;
- investigating methods for increasing the life of the photosensitive drum that would result in better transfer efficiency;
- identifying options for toner reformulation and the use of high purity raw materials; and
- evaluating other toner/fuser combinations, such as ultraviolet (UV)-curing technologies, that are being used by other sectors of the printing industry.

3. The research indicated that emissions can vary depending on the specific toner manufacturing process. The extrusion process for manufacturing toner should be investigated further. It should be noted that while this process may result in lower-emitting toner to an indoor air environment, the multimedia pollution prevention implications of the extrusion process should also be investigated. As one measure for ensuring that multimedia pollution prevention is being achieved, specifications should be refined to ensure consistent and “clean” raw materials for the toner manufacturing process.
4. Photocopier emissions have been shown to increase between routine maintenance cycles. Therefore, development of new equipment designs that require less (or even no) maintenance but are still able to operate with the lowest possible emission rates could result in pollution prevention benefits over the life of a copier.

## **8.0 DATA QUALITY**

Quality assurance (QA) activities were an integral part of this research program. QA activities that were conducted in support of this study included:

- Preparing quality assurance project plans (QAPPs),
- Developing data quality indicator goals for data collected,
- Monitoring quality control procedures and results, and
- Conducting inspections, audits, and data reviews.

### **8.1 Quality Assurance Project Plans**

RTI prepared two, Category III QAPPs addressing all of the aspects of each phase of the research. Each QAPP was approved by EPA prior to testing.

### **8.2 Data Quality Indicator Goals**

Chamber air concentrations and emission rates were the critical measurements in this study. The data quality indicator goals proposed in the QAPP are shown in Table 8-1. This table was prepared to insure that each participating laboratory was aware of the level of accuracy, precision, and completeness desired for the round-robin testing. Each laboratory was responsible internally for assuring compliance of the details such as relative humidity, temperature, sample collection, air flow measurements, and chamber air concentrations. Since this was a performance based evaluation (results evaluated based on each laboratories' recovery of the standard emitters), not all of this information was provided to RTI by each participating laboratory. Only the final calculated emission rates of the standard emitters and copier tests were required to be reported. From these reported data, Tables 8-2 and 8-3 have been constructed to show the within (intra) and between (inter) laboratory summaries of the precision and accuracy. These tables are based on reported emission rates provided by each laboratory.

In general the data quality goals were met. There were some specific cases in which the goals were not met; however, these cases usually indicated a specific problem associated with a laboratory or variation in the analytical methods and/or chambers at the different laboratories. Refer to Section 4 for technical evaluations of the observed differences. (Example: aldehyde/ketone interlaboratory precision goal for emission rates during copying,  $\leq 35\%$  RSD goal vs. 62 %RSD measured for all labs and 21%RSD measured for samples collected at other labs but analyzed at RTI. This indicates an analytical problem at a lab, not a problem with the test method.)

**Table 8-1. Summary of Data Quality Indicator Goals**

Parameter	Precision (% RSD)		Accuracy (% Recovery)	Completeness (%)
	Intralaboratory	Interlaboratory		
VOCs				
Air Flow Measurements	≤ 10	NA <sup>c</sup>	≥ 90	95
Chamber Air Concentrations	≤ 20	≤ 30	≥ 75	80
Emission Rates	≤ 25	≤ 35	≥ 70	80
Headspace Equilibrium Concentrations	≤ 25	≤ 25	≥ 75	100
Aldehydes/ketones				
Sample Collection Air Flow	≤ 10	NA	≥ 90	95
Chamber Air Concentrations	≤ 15	≤ 30	≥ 80	80
Emission Rates	≤ 20	≤ 35	≥ 70	80
Ozone				
Air Flow Measurements	≤ 10	NA	≥ 90	95
Chamber Air Concentrations	NT <sup>a</sup>	NT <sup>b</sup>	≥ 80	80
Emission Rates	≤ 15	≤ 25	≥ 70	80

<sup>a</sup> Not tested - duplicate ozone monitors not available.

<sup>b</sup> Not tested - materials for assessing accuracy not available.

<sup>c</sup> NA-Not applicable

**Table 8-2. Summary of Emission Rate Accuracy and Precision for Standard Emission Sources**

Parameter	Accuracy (% Recovery)			Precision (%RSD)		
	Intralab (RTI)	Interlab Analysis at RTI <sup>a</sup>	Interlab Analysis at each lab <sup>b</sup>	Intralab (RTI)	Interlab Analysis at RTI <sup>a</sup>	Interlab Analysis at each lab <sup>b</sup>
<u>Chamber Evaluation</u> (Standard Emitters)						
Toluene	115 <sup>c</sup>	119	112	2.9	8.2	22
Chloroform	94 <sup>d</sup>	NT <sup>f</sup>	NT	7.6	NT	NT
Decane	NT	104	112	NT	4.8	24
Formaldehyde	93 <sup>e</sup>	82	155	2.2	36	89
Ozone	72 <sup>e</sup>	NT	57	9.3	NT	44

<sup>a</sup> Releases made at each participating lab; duplicate samples collected at each lab and analyzed at RTI.

<sup>b</sup> Releases, collection, and analysis performed at each participating lab.

<sup>c</sup> Calculations based on five standard emitter releases.

<sup>d</sup> Calculations based on four standard emitter releases; five releases actually made; however, internal standard in one sample was low indicating desorption problem during analysis.

<sup>e</sup> Calculations based on three standard emitter releases

<sup>f</sup> NT = not tested

**Table 8-3. Summary of Emission Rate Accuracy and Precision**

Parameter	Accuracy (% Recovery)			Precision (%RSD)		
	Intralab (RTI)	Interlab Analysis at RTI <sup>a</sup>	Interlab Analysis at each lab <sup>b</sup>	Intralab (RTI)	Interlab Analysis at RTI <sup>a</sup>	Interlab Analysis at each lab <sup>b</sup>
<u>Analytical Methods</u> (Spikes, Replicate Samples)						
VOC	NT <sup>c</sup>	NT	NT	NT	NT	NT
Formaldehyde	93	NT	NT	2.7	NT	NT
Ozone	NT	NT	NT	NT	NT	NT
<u>Emission Rate Determination</u> (Same Copier)						
VOC <sup>d</sup>	NT	NT	NT	5.5	12	20
VOC <sup>e</sup>	NT	NT	NT	5.7	21	60
Aldehydes/ketones <sup>f</sup>	NT	NT	NT	11	19	62
Aldehydes/ketones <sup>g</sup>	NT	NT	NT	15	21	62
Ozone	NT	NT	NT	7.1	NT	88

<sup>a</sup> Releases made at each participating lab; duplicate samples collected at each lab and analyzed at RTI.

<sup>b</sup> Releases, collection, and analysis performed at each participating lab.

<sup>c</sup> NT = not tested

<sup>d</sup> Average %RSD of target VOC compounds with emission rates >1000 µg/hr•copier.

<sup>e</sup> Average %RSD of all target VOC compounds.

<sup>f</sup> Average %RSD of target aldehydes/ketones with emission rates >1000 µg/hr•copier.

<sup>g</sup> Average %RSD of all target aldehyde/ketone compounds.

### 8.2.1 Precision

Precision is expressed as the percent relative standard deviation (%RSD) between replicate samples or tests. The %RSD is calculated as

$$\%RSD = \frac{S}{Y} \times 100$$

where:      %RSD =      relative standard deviation  
              S        =      standard deviation  
              Y        =      mean of replicate samples

Intralaboratory precision of the quantitative analytical methods for measuring chamber air concentration was evaluated by collecting and analyzing duplicate chamber air samples. Intralaboratory precision of the emission rates in Phase I was evaluated by conducting triplicate emission tests on a single dry-process photocopier (see Tables 3-12 and 3-13).

In Phase II, interlaboratory precision for the measurements were based on chamber air measurements for the standard emitter. In addition, replicate samples were collected by each laboratory and shipped to RTI for analysis. Interlaboratory precision of emission rate measurements was evaluated by comparing emission rates for known emission standards and for the same copier tested at the four laboratories. A summary of the precision and accuracy for the standard emission sources is shown in Table 8-2. A summary for the emission rate precision and accuracy is in Table 8-3.

Toner headspace results were evaluated for precision only. These analyses were performed to verify that the toner cartridges from the “same lot” of cartridges used for the round-robin testing were uniform in initial composition. These analyses were used for comparison purposes only with no intent to directly link the concentrations found from the toner headspace to the resulting emission rates during operation. No recovery experiments were performed to demonstrate the accuracy of the headspace analyses. All toner headspace samples were prepared and analyzed in duplicate with the exception of the toner collected at Lab 4 in which case four samples were analyzed. Results of these analyses are shown in Table 8-4.

### 8.2.2 Accuracy

Accuracy of chamber air concentrations was evaluated by determining the percent recovery of VOCs, aldehydes, and ketones from spiked sample cartridges:

$$\%REC = (A_m/A_s) \times 100\%$$

where  $A_m$  is the amount of VOC measured during chemical analysis and  $A_s$  is the amount of VOC spiked onto a sampling cartridge. For ozone, measurement accuracy for chamber air concentrations was evaluated by determining the ozone concentration at the generator source using Dräger tubes.

**Table 8-4. Summary of Round-Robin Toner Headspace Analysis Precision <sup>a,b</sup>**

Compound	Precision (%RSD)				Average
	Lab 1	Lab 2	Lab 3	Lab 4	
Toluene	1.8	18	20	26	17
Ethylbenzene	1.4	15	4	7.8	6.9
m,p-Xylene	1.5	14	8	8.3	8.0
Styrene	2.1	16	18	5.3	10
o-Xylene	1.0	13	10	7.2	8.1
Isopropylbenzene	1.1	13	16	6.8	9.1
n-Propylbenzene	0.5	14	18	6.0	9.8
a-Methylstyrene	12	37	42	22	28

<sup>a</sup>Based on duplicate samples collected at labs 1, 2, 3 and four samples at lab 4. All samples analyzed at RTI

<sup>b</sup> Toner samples collected from toner cartridge immediately after copier chamber test.

Accuracy of emissions factors was evaluated by determining the percent recovery of VOCs, aldehydes/ketones, and ozone spiked into chamber air at measured concentrations:

$$\%REC = (C_{in}/C_s) \times 100\%$$

where  $C_{in}$  and  $C_s$  are the chamber air concentrations measured at the inlet and the sampling port of the test chamber, respectively. Summaries of the accuracies for the standard emission sources and for emission rates are presented in Tables 8-2 and 8-3, respectively.

### **8.2.3 *Completeness***

General goals for completeness were met for this project. All laboratories reported emission rate measurements for the copier and standard emitters tested.

## **8.3 Quality Control**

Chamber air samples collected from empty test chambers and blank cartridges were analyzed to monitor background and accidental contamination. Calibration curves were prepared prior to analysis of chamber air samples, and check standards were analyzed at regular intervals to assure that the calibration remained valid. All data were generated when the analytical systems were operating within the control criteria.

## **8.4 Inspections, Audits, and Data Reviews**

Throughout the research, several inspections, audits, and data reviews were conducted by QA officers at RTI to ascertain that standard operating procedures (SOPs) for instrumentation were being implemented; procedures in the QAPPs were being followed; data were being recorded properly; and that records and controls conformed to good laboratory practice. In addition, QA audits of both the RTI large chamber and the EPA large chamber were conducted by the EPA QA Officer. Copies of the reports resulting from these audits are in Appendix D.



## 9.0 REFERENCES

- Allen, R.J., R.A. Wadden, and E.D. Ross. 1978. Characterization of potential indoor sources of ozone. *American Industrial Hygiene Association Journal*, 39. University of Illinois School of Public Health, Chicago, IL.
- American Society of Heating, Refrigerating and Air-conditioning Engineers (ASHRAE) Standard 62-1989, "Ventilation for Acceptable Indoor Air Quality," Atlanta, GA, 1989, page 10.
- Bever, Michael B. 1986. *Encyclopedia of Material Science and Engineering*, Vol. II. MIT Press, Cambridge, MA.
- Brooks, B.O., G.M. Utter, J.A. DeBroy, W.F. Davis, and R.D. Schimke. 1993. Chemical Emissions from Electronic Products, Proceedings of the International Symposium on Electronics and the Environment, Sponsored by the Institute of Electrical and Electronics Engineers, Inc., Arlington, VA, May 10-12, 1993.
- Buyers Laboratory, Inc. 1995. Special Report--Recycled Paper: The Good, The Bad and The Ugly. Buyers Laboratory, Inc., Hackensack, NJ.
- Canon, Inc. 1990. *Fundamentals of Copier Technology*. Japan.
- Claridge, M. 1983. Photocopiers: An Office Hazard. *Environmental Health*. Vol. 91, pp.246-247.
- Clayton, Bill. 1994. Laser Plus. Personnel Communication. June 16, June 22, July 20, and August 30, 1994.
- Colombo, A., M. De Bortoli, and B.A. Tichenor. 1993. *International Comparison Experiment on the Determination of VOCs Emitted from Indoor Materials Using Small Test Chambers*, Proceedings of Indoor Air '93, Vol. 2, pp. 573-578.
- Cornstubble, D.R. and D.A. Whitaker. 1998. Personal Computer Monitors: A Screening Evaluation of Volatile Organic Emissions from Existing Printed Circuit Board Laminates and Potential Pollution Prevention Opportunities, EPA-600/R-98-034 (NTIS PB98-137102), U.S. EPA, National Risk Management Research Laboratory, Research Triangle Park, NC.
- De Nucci, P.P. 1992. Printing/Plotting Pros and Cons, *CADENCE*, p. 30-36.
- Etkin, D.S. 1992. Office furnishings/equipment & IAQ: health impacts, prevention & mitigation. *Indoor Air Quality Update*. Cutter Information Corp., Arlington, MA.

- Gallardo, M., P. Romero, M.C. Sanchez-Quevedo, and J.J. Lopez-Caballero. 1994. Siderosilicosis due to Photocopier Dust. *The Lancet*, Vol. 344, 412-413.
- Greenfield, E.J. 1987. *House Dangerous: Indoor Pollutants in Your Home and Office*. Vintage Books, New York. pp. 234 (as cited in Etkin, 1992).
- Gressel, Michael G. 1996. Final Report: Methods for Characterizing Emissions from Laser Printers. Report No: 211-04. National Institute for Occupational Safety and Health, U.S. Department of Health and Human Services, Cincinnati, OH.
- Hannsen, T.B., and B. Anderson. 1986. Ozone and other pollutants for photocopying machines. *American Industrial Hygiene Association Journal*, pp. 659-665.
- Hetes, R., M. Moore, and C. Norheim. 1995. Office Equipment: Design, Indoor Air Emissions, and Pollution Prevention Opportunities. EPA-600/R-95-045 (NTIS PB95-191375), U.S. EPA, Air and Energy Engineering Research Laboratory, Research Triangle Park, NC.
- Hodgson, A.T., and J.M. Daisey. 1989. *Source Strengths and Sources of Volatile Organic Compounds in a New Office Building*. Presented at the 82<sup>nd</sup> Annual Meeting of the Air and Waste Management Association, 89-80.7.
- Kreiss, K. 1989. The Epidemiology of Building-related Complaints and Illness, In *Problem Buildings: Building-Associated Illness and the Sick Building Syndrome*, Cone, J.E. and M.J. Hodgson (eds) Occupational Medicine: State of the Art Reviews, Volume 4, No. 4, October-December. Hanely & Belfus, Inc., Philadelphia, PA.
- LaMarte, F.P., J. A. Merchant, and T.B. Casale. 1988. Acute Systemic Reactions to Carbonless Copy Paper Associated with Histamine Release. *Journal of American Medical Association (JAMA)*, Vol. 260, No. 2, pp. 242-243.
- Maren, T. 1991. *Dry Toner Fundamentals*. Presented at the 8th Annual Toner and Developer Conference and Tutorial, Diamond Research Center.
- Marks, J.G., J.J. Trautlein, C.W. Swillich, and L.M. Demers. 1984. Contact urticaria and airway obstruction from carbonless copy paper. *JAMA* 252:1038-1040 (as cited in Kreiss, 1989).
- Marks, J.G. 1981. Allergic contact dermatitis from carbonless copy paper. *JAMA* 245:23331-2332 (as cited in Kreiss, 1989).
- Morgan, M.S., and J.E. Camp. 1986. Upper respiratory irritation from controlled exposure to vapor from carbonless copy forms. *J Occup. Med.* 28:415-419 (as cited in Kreiss, 1989).

- National Institute of Occupational Safety and Health (NIOSH). 1991. *Indoor Air Quality and Work Environment Study, Library of Congress, Madison Building, Health Hazard Evaluation Report*. HETA 88-364-2104.
- Sarsony, Chris. 1993. Proceedings: EPA/AEERL's Indoor Air Quality/Pollution Prevention Workshop. EPA-600/R-93-198 (NTIS PB94-114782). U.S. EPA, Air and Energy Engineering Research Laboratory, RTP, NC.
- Schnell, R.C., G.A. Allen, and A.D.A. Hansen. 1992. *Black Carbon Aerosol Output from a Photocopier*. Presentation at the 85<sup>th</sup> Annual Meeting & Exhibition Air & Waste Management Association, Kansas City, MO, June 21-26, 1992.
- Selway, M.D., R.J. Allen, and R.A. Wadden. 1980. Ozone production from photocopier machines. *Am. Ind. Hyg. Assoc. J.*, (41)455-459.
- Tsuchiya Y., M.J. Clermont, and D.S. Walkinshaw. 1988. Wet process copying machines: a source of volatile organic compound emission in buildings. *Environmental Toxicology and Chemistry*, 7:15-18.
- Tuskes, P.M., M.A. Tilton, and R.M. Greff. 1988. Ammonia exposures of blueline printers in Houston, Texas. *Applied Industrial Hygiene*, 3(5).
- U.S. Environmental Protection Agency. 1987a. *Unfinished Business: A Comparative Assessment of Environmental Problems*. EPA-230/2-87-025a-e (NTIS PB88-127030), Office of Policy, Planning and Evaluation, Washington, DC.
- U.S. Environmental Protection Agency. 1990. Pollution Prevention Act of 1990, Washington, DC.
- U.S. Environmental Protection Agency. 1994. Comprehensive guidelines for procurement of products containing recovered materials. *Federal Register*, 59(76):18852-18891. Washington, DC.
- U.S. Environmental Protection Agency. 1987b. *Total Exposure Assessment Methodology (TEAM) Study*. EPA-600/8-87-002a-d (NTIS PB88-100052), Office of Acid Deposition, Washington, DC.
- Vernon, Will. 1994. *Recharger magazine*. Personnel Communication. September 20, 1994.
- Wolkoff, P., C.R. Johnsen, C. Franck, P. Wilhardt, and O. Albrechtsen. 1992. A study of human reactions to office machines in a climatic chamber. *Journal of Exposure Analysis and Environmental Epidemiology*, Supp. 1:71-96.

Wolkoff, P., C. K. Wilkins, P.A. Clausen, and K. Larsen. 1993. Comparison of volatile organic compounds from office copiers and printers: methods, emission rates, and modeled concentrations. *Indoor Air*, 3:113-123.

**APPENDIX A. Participants and Recommendations from Technical Advisors Meeting on  
Application of Pollution Prevention Techniques to Reduce  
Indoor Air Emissions from Office Equipment  
March 9, 1994**

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Association of Reproduction Materials

## RECOMMENDATIONS

1. Paper phenol circuit board card. It was suggested that a low emitting substitute for paper phenol circuit board cards could reduce emissions and would have a broad-based application in numerous technologies. However, the replacement will need to be economically feasible or industry will not accept it.
2. Supplies and paper types. In some cases, equipment can be poisoned by the operating environment (e.g., filters) which should be considered when setting up the models and testing protocol for this research. The issue of different paper types needs further investigation (e.g., preprinted paper, carbonless paper, recycled paper). Competitive supplies should also be considered in the design of any research program. The type of supplies used can also have a dramatic effect on emissions. One approach for applying pollution prevention to reduce indoor air emissions from office equipment could be through modifications of the supplies (e.g., toner, paper).
3. Standard testing methodology. It was strongly recommended that a subcommittee be formed to develop a representative test/screening method for evaluating emission from office equipment.
4. Effect on the indoor environment with proper maintenance. In general, emissions tend to increase with equipment age and the time between maintenance. It was recommended to look at the issue of maintaining equipment properly and how the lack of maintenance and proper procedures effect the overall emission rate. A pollution prevention strategy may be to focus on overall maintenance, changing the ease of maintenance, or changes in technology which reduce maintenance needs.

## **APPENDIX B. Emissions Testing Guidance Document for Dry-Process Photocopiers**

### **1.0 Scope/Objective**

The overall objectives of this cooperative agreement between the Research Triangle Institute (RTI) and the U.S. Environmental Protection Agency (EPA) are to identify pollution prevention opportunities for manufacturers and/or users of office equipment and to measure the effectiveness of proposed pollution prevention actions. This guidance document was developed to measure emissions from dry-process photocopiers.

Based on triplicate measurements at RTI and on a four-laboratory comparison study with one copier, it was found that the test method is analytically sensitive and generally applicable to all types of dry-process photocopiers. This method is intended to characterize emissions and to support identification of potential pollution prevention strategies. It is intended to promote uniform testing and research into pollution prevention opportunities rather than to determine regulatory compliance (i.e., if occupational exposure standards are met).

### **2.0 Facilities and Equipment**

Flow-thorough dynamic test chambers are recommended because they are generally applicable to all types of equipment, and they provide data that can be compared with other emission sources and used as inputs for indoor air quality models. The major components of a dynamic environmental test chamber include the chamber, the clean air supply, operational and control systems, sample collection and analysis equipment, and standards generation and calibration systems. A schematic of a test chamber is shown in Figure 1 as an example. Attachment A provides a specific description of the chamber facilities used for this study, performance characteristics, and guidance on how to demonstrate chamber performance. Minimum chamber performance requirements are presented in the guidance.

**2.1 Chamber Construction** - Chambers should be constructed so that the interior surfaces are smooth, nonadsorbent, and chemically inert to minimize the potential for interior walls to act as either sinks or sources. Inert surfaces such as electro or Summa polished stainless steel or aluminum are recommended for this purpose. Other materials (e.g., Tedlar) may be used provided inertness is demonstrated. Inertness can be demonstrated by conducting recovery efficiency tests for target analytes. All joints should be permanently sealed (except required openings) to minimize the potential for leakage. Seals and sealant must be nonadsorbent with minimal use of caulks and adhesives that may emit or adsorb VOCs. An airtight access door, inlet and outlet ports for air flow, and temperature and humidity probes are also required. The chamber's linear dimensions should be a minimum of 1.4 times the dimensions of the product tested to be consistent with typical industry practice. If multiple machines are used in the test chamber, the minimum dimensions of the chamber should be 1.4 times the total dimensions of the equipment tested. The chamber should be designed to operate under positive pressure to

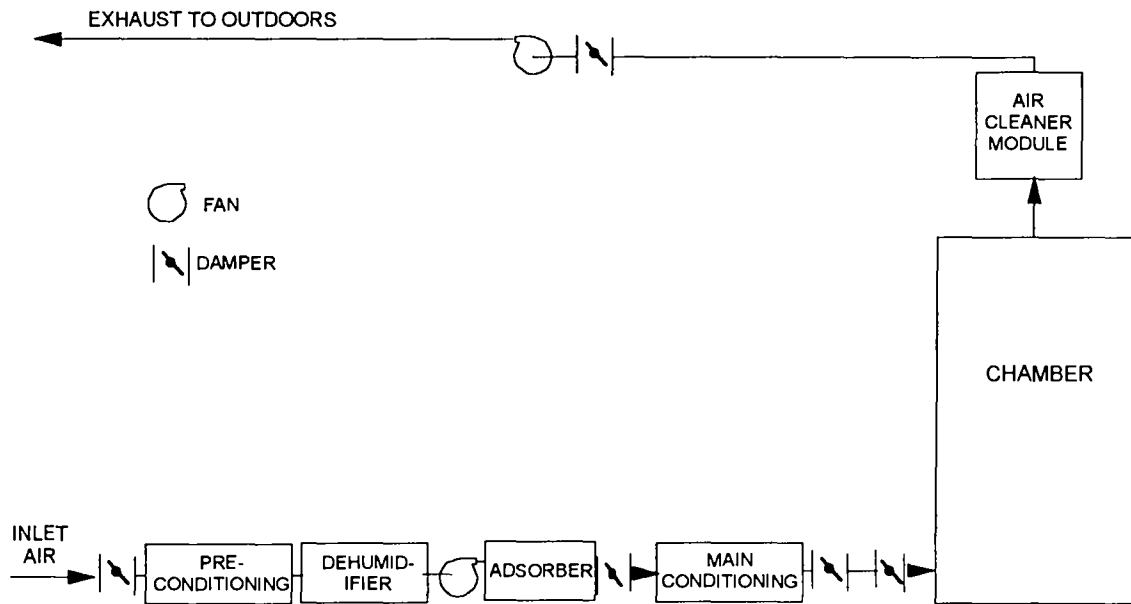


Figure 1. Schematic of a large test chamber.



eliminate the infiltration of contaminants from the exterior of the chamber. The air-intake port and exhaust port should be on different walls of the chamber and at different elevations; alternative designs are allowed if it can be shown that the chamber is well-mixed (see Section 2.2).

**2.2 Mixing** - Mixing is important to ensure that emissions resulting from equipment operation are accurately measured. Low-speed mixing fans or multiport inlet and outlet diffusers should be used. The completeness of mixing must be characterized within the chamber. There is currently no definitive quantitative guidance on completeness of mixing. However, mixing should be assessed according to the guidelines established in ASTM D5116-90, "Standard Guide for Small-Scale Environmental Chamber Determinations of Organic Emissions from Indoor Materials/Products." Mixing should be measured by introducing a tracer gas (e.g., SF<sub>6</sub> or CO) with the inlet air at known concentration, quantity, or flow, and measuring the concentration in the chamber outlet over time. Examples of two methods for determining mixing both based on the same equation are described as follows.

The first method is to introduce a constant source of tracer gas into the chamber and then compare chamber air concentration to a theoretical curve for a completely mixed chamber based on the equation:

$$C = C_o(1 - e^{-Nt}) \quad (1)$$

where

C = chamber concentration

C<sub>o</sub> = inlet concentration

t = time

N = air exchange rate, calculated as  $N=Q/V$

Q = flow rate through the chamber

and

V = chamber volume

The second approach is to inject or introduce a "slug" of a known quantity of tracer gas (e.g., CO) into the chamber and measure the decay in concentration. The measured concentrations must then be compared to the following equation:

$$\ln(C_o/C) = Nt \quad (2)$$

where the variables are the same as those defined above.

If the measured data closely approximate the curve (e.g., within 5 %), the chamber may be considered well mixed. If the measured data lie above the theoretical concentration versus time curve, the flow is being short circuited, perhaps because of poor placement of the air inlet and/or outlet ports. If measured data fall below the curve, some of the tracer gas may be adsorbing or

absorbing onto the chamber surfaces, the chamber may be leaking, or incomplete mixing may be occurring. Tests should be conducted, not only on the empty chamber but also with equipment of the types to be tested, to ensure that the placement of the samples in the chamber will not result in inadequate mixing.

**2.3 Environmental Control Systems** - Controls required for air flow, temperature, and humidity, can be either automated or manual. Specific systems that are required are described in the following sub sections.

**2.3.1 Temperature Control** - Temperature within the chamber should be maintained at 26 – 31°C by conditioning the inlet air. This range is a practical compromise between typical chamber conditions, (i.e. 23°C) and what is achievable when equipment with a high thermal load is tested. Temperature should be measured via thermocouples or thermistors and should characterize the immediate operating environment of the device being tested. Temperature maintenance may be improved by using a larger chamber (with respect to the equipment tested), if available, to better dissipate the heat load. The temperature of both the inlet and chamber air should be continuously monitored and recorded.

**2.3.2 Clean Air Generation** - The background chamber air concentration must be maintained at or below detection limits for the target analytes (described in Section 2.5) by using clean inlet air. The purity of the supply air should guarantee that inlet air is below the minimum detection limits established for the samples and described in Section 2.5. In general, background air should be maintained at or below 2.5 µg/m<sup>3</sup> for individual volatile organics, 5 ppb for ozone, and 5 µg/m<sup>3</sup> (gravimetric) for particulates. Organics and ozone can be removed using charcoal filters, oxidizing filters, and catalytic oxidizers; high-efficiency particulate air (HEPA) filters can effectively remove suspended aerosols.

**2.3.3 Flow Control** – Based on a single-pass system, the air flow rate through the chamber should be maintained at 45±5.0 m<sup>3</sup>/h. For a 22m<sup>3</sup> chamber that air flow rate is equivalent to approximately 2 ACH. For some photocopiers, large amounts of heat (up to 24,000 BTU/h) can be produced during testing. To offset this heat load, air flow rate through the chamber can be increased from 22 m<sup>3</sup>/h (equal to 1 ACH for a 22 m<sup>3</sup>/h chamber) to 45 m<sup>3</sup>/h (equal to 2 ACH for a 22 m<sup>3</sup> chamber).

**2.3.4 Humidity Control** – Test conditions have been set so that a constant water concentration, not a constant relative humidity (RH) is maintained in the chamber. Given the target temperature range of 26° to 31°C, a RH maintained between 30 and 35 percent corresponds to typical test conditions of 50% RH at 23°C. Adjustments in water concentration can be achieved by adding deionized water or HPLC-grade distilled water to the air stream as steam, injected directly into the air stream (controlled by the pump setting), or saturated air can be mixed with dry air (controlling the temperature of the water and flow of saturated air) to achieve the desired concentration. Water concentration can be measured using several types of sensors, including dewpoint detectors and thin-film capacitors.

**2.4 Sample Collection System** - The chamber design and operation should allow for continuous equipment operation and sampling of chamber air without violating chamber integrity. The exhaust flow from the chamber (outlet air stream) may be used as the sampling point or, alternatively, separate sampling ports in the chamber may be used. Particle collectors and counters should be located as close as possible to the exhaust port of the copier. External particle counters must be connected through sample lines designed to minimize losses of particles up to 10  $\mu\text{m}$ . Multiport sampling manifolds can be used for duplicate sampling. All sampling systems that come in contact with the chamber air prior to collection or measurement should be constructed of inert materials. For example, ozone must contact only Teflon and glass surfaces. Chamber air concentrations may be low for many contaminants, requiring larger sample volumes and the use of integrating sample collection media (e.g., adsorbent).

There are a number of sorbent materials available for the collection of volatile organic compounds (VOCs). Sorbents are available either singly or in combination (e.g., activated carbon, glass beads, Ambersorb, Tenax, and XAD-2). Multisorbent sampling tubes are recommended and the air sample volumes collected for analysis should be based on detection limits and breakthrough volumes. Sampling flow rates will be determined by total sampled volume over the desired test period.

Given the reactive nature of aldehydes/ketones, alternative sampling methods to those used for VOCs are recommended. Aldehydes/ketones should be collected by passing chamber air through cartridges containing silica gel impregnated with 2,4-dinitrophenylhydrazine (DNPH). Formaldehyde, as well as other aldehydes and ketones, reacts with the DNPH and is collected on the cartridge material. To account for the potential interference of ozone with the DNPH method, it is recommended that a potassium iodide-coated tubular denuder or scrubber be placed upstream of the DNPH cartridge to remove ozone.

The recovery efficiency must be determined for collection and analysis of each chemical constituent. Background concentration recoveries must meet designated performance standards or the analytical data are not acceptable.

**2.5 Sample Analysis** - The analytical systems used to analyze chamber air concentrations should be selected based on the physical and chemical properties of the pollutants being analyzed and must meet the minimum detection limits established in this guidance.

**2.5.1 Volatile Organic Compounds** - Collected chamber air samples should be analyzed for organic chemicals to identify and quantitate individual volatile organic compounds (IVOC) and total volatile organic compounds (TVOC). Gas chromatography/ mass spectrometry (GC/MS) analysis is required for the identification of unknown IVOCs in chamber air samples. Due to its selectivity, GC/MS analysis is strongly recommended for quantitative analysis. Detection limits for both chamber air concentrations and emission rates should be as low as possible to effectively measure the efficiency of pollution prevention efforts. Target detection limits for chamber air concentrations are set at 2.5  $\mu\text{g}/\text{m}^3$  (general background for IVOCs in indoor air), levels of

concern for specific health effects, odor thresholds, or 1% of the threshold limit value (TLV), whichever is smaller. For TVOC, a target detection limit of 10 µg/m<sup>3</sup> has been set. The relatively low detection limits are necessary to identify the range of individual compounds emitted from operating dry-process photocopiers.

When sorbent tubes are used for sample collection, the analysis usually is performed by thermal desorption, focusing, and subsequent injection into a GC/MS system. For qualitative analysis, components in the GC/MS chromatogram are identified by comparing the mass spectrum of the sample component to a library reference spectrum (NIH/EPA/MSDC Mass Spectral Data Base and the Registry of Mass Spectral Data). This is most effectively accomplished using an electronic database search with manual verification of results. Qualitative results are then used to select a list of target IVOCs for quantitative analysis. Relative abundance, adverse health effects, or adverse sensory effects are criteria that are commonly used to select target VOCs.

For quantitative analysis, the GC/MS instrument must be calibrated prior to analysis. This is done by analyzing sorbent cartridges spiked with known levels of target IVOCs at four to six different concentrations. During analysis, identification of target IVOCs is based on chromatographic retention times relative to the standard cartridges and on the relative abundances for the extracted ion fragment selected for quantitation. Quantitation of IVOCs is performed using chromatographic peak areas derived from extracted ion profiles. Relative response factors (RRFs) for each target compound are generated from the calibration standards as:

$$RRF = \frac{(A_T)(Amt_{QS})}{(A_{QS})(Amt_T)}$$

where

- $A_T$  = peak area of the quantitation ion for the target IVOC
- $A_{QS}$  = peak area of the external standard
- $Amt_T$  = mass of the target compound on the calibration cartridge
- $Amt_{QS}$  = mass of the external standard in the calibration cartridge

These RRF values are then used to calculate the mass of the target IVOC on each cartridge. TVOC is quantitated using the GC/MS reconstructed ion chromatogram (RIC). The total area of the RIC is in the retention window from n-hexane to n-tetradecane. The RRF generated for toluene is often used for quantitating TVOC. Performance requirements for this method are given in Table 1. This method is the same as EPA Method TO1, except that multisorbent rather than Tenax cartridges are used. Alternative methods may be used if performance similar to Method TO1 can be demonstrated.

Table 1. QA/QC Requirements for VOC and Aldehyde Analysis

Pollutant Measurement	Requirement
VOCs (Tenax and multisorbent method)	<p>Initial demonstration of laboratory capability</p> <ul style="list-style-type: none"> <li>• Analysis of 3 laboratory blanks. Acceptance criteria = &lt;5ng of any target VOC and 100 ng of TVOC on cartridges.</li> <li>• Analysis of 3 laboratory controls spiked at 100 ng for selected VOCs. Acceptance criteria = recovery of 100 ± 25%.</li> </ul> <p>Sample Analysis</p> <ul style="list-style-type: none"> <li>• Multipoint calibration (25-500 ng). Acceptance criteria = %RSD of mean relative response factor &lt;25%.</li> <li>• Lowest calibration standard within the linear range, signal-to-noise ratio for lowest standard of 10 to 1.</li> <li>• Calibration check sample - measured value - 75 to 125% of known value.</li> </ul> <p>Analysis of QC samples per test</p> <ul style="list-style-type: none"> <li>• One chamber blank - acceptance criteria = &lt;2.5 µg/m<sup>3</sup> for each specific VOC; &lt;10 µg/m<sup>3</sup> for TVOC.</li> <li>• One field control - acceptance criteria = recovery of 75 to 125%.</li> <li>• One duplicate sample collected and analyzed - acceptance criteria = RSD of duplicate measurement &lt;25%.</li> </ul>
Formaldehyde and other aldehydes	<p>Blank analysis of 10% of all cartridges before use, acceptance criteria = &lt;50 ng aldehyde/cartridge.</p> <p>Initial demonstration of laboratory capability</p> <ul style="list-style-type: none"> <li>• Analysis of 3 laboratory blanks. Acceptance criteria = &lt;30 ng aldehyde/cartridge.</li> <li>• Analysis of 3 laboratory controls spiked at 3 concentrations. Acceptance criteria = recovery of 100 ± 20%.</li> </ul> <p>Sample Analysis</p> <ul style="list-style-type: none"> <li>• Multipoint calibration (0.05-20 ng/µl, DNPH-aldehyde derivative). Acceptance criteria = correlation coefficient &gt;0.995.</li> <li>• Lowest calibration standard within the linear range, signal-to-noise ratio for lowest standard of 10 to 1.</li> <li>• Calibration check sample - measured value - 80 to 120% of known value.</li> <li>• Every 8 hours of analysis, midpoint check standard, acceptance criteria = measured concentration within 15% of prepared value.</li> </ul> <p>Analysis of QC samples per test</p> <ul style="list-style-type: none"> <li>• One chamber blank - acceptance criteria = &lt;2.5 µg/m<sup>3</sup> for each target aldehyde.</li> <li>• One field control - acceptance criteria = recovery of 80 to 120%.</li> <li>• One duplicate sample collected and analyzed - acceptance criteria = &lt;25% RSD.</li> </ul>

Aldehyde analysis must be conducted independently of the IVOC analysis. When aldehydes are collected on DNPH cartridges, the aldehyde/DNPH derivatives are eluted from the cartridge with 5 mL of acetonitrile. The extract is then analyzed by high performance liquid chromatography (HPLC) with ultraviolet (UV) detection at 347 nm. Quantitation of target aldehydes is accomplished by the external standard method using calibration standards prepared in the range of 0.05 to 15 ng/ $\mu$ L ( $\mu$ g/mL) of the DNPH/aldehyde derivatives. Target aldehydes will be identified based on chromatographic retention time of the sample components relative to calibration standards. Performance requirements for this method are also given in Table 1. This method is essentially the same as EPA Method TO11 (Winberry, 1988). Alternative methods may be used if similar performance can be demonstrated for the aldehydes of interest.

**2.5.2 Ozone** – Continuous monitoring of ozone should be conducted with an EPA-designated equivalent monitor so that a minimum detection limit of 10 ppb is achieved. A monochromic, UV spectrophotometer specific to ozone can be used for this purpose. Continuous measurements can be made and the output connected to a data logger for data recording and storage. Particulates have been shown to interfere with ozone measurement when these continuous monitors are used. Where particulate levels are high, or where sampling occurs for long periods of time, a (Teflon) particulate filter can be placed upstream of the ozone monitor. However, using a particulate filter will typically slow the response of the instrument. Past testing on equipment in chambers has shown that particulate levels are not expected to interfere with ozone measurements and are, therefore, not recommended for initial testing. However, a particulate filter may be required if initial results indicate levels sufficiently high to warrant it.

**2.5.3 Particulate/Aerosol** – Continuous sampling of aerosols should be conducted at the exhaust outlet of the copier. Gravimetrically based sampling for PM<sub>10</sub> is recommended with the desired supplement of an optical particle counter to report the emission rate in particles/time for specified particle size ranges. Particles less than 10  $\mu$ m (aerodynamic mass median diameter) are considered to be those of most concern.

### **3.0 Test Procedure**

**3.1 Chamber Preparation** – The chamber should be thoroughly cleaned prior to testing. Background levels of target pollutants in the chamber air should be measured before each test and should be below the detection limits established for the individual pollutants analyzed. The chamber should also be purged between runs until the air concentrations of targeted contaminants are below analytical limits of detection.

**3.2 Recovery Tests** – A recovery efficiency test for gas-phase contaminants should be conducted in the empty chamber to determine the potential for wall effects (where a chemical may adhere to chamber walls, gaskets, or other chamber materials). This test should be conducted by spiking the chamber with a known amount (e.g., minimum of 10 times the detection limit) of particular pollutants in the inlet air and measuring the amount of contaminant recovered by the sample analysis.

Chamber dosing and recoveries can be determined by introducing known amounts ( $E_{as}$ ) of toluene, *n*-decane, formaldehyde, and ozone into the chambers at known rates. Chamber air samples should be collected and analyzed using procedures identical to those used during the photocopier emission tests (Section 3.3). The measured amount of pollutant emitted during each test is calculated as,

$$E_m = C_c \times V_c \times A_c \times T_s \quad (4)$$

where

$E_m$	=	the measured amount of target pollutant emitted during each test in $\mu\text{g}$ .
$C_c$	=	the measured chamber air concentration in $\mu\text{g}/\text{m}^3$ .
$V_c$	=	the chamber volume in $\text{m}^3$ .
$A_c$	=	the air exchange rate in $\text{h}^{-1}$ .
$T_s$	=	the sample collection time in h.

Percent recovery of the emitted pollutant is used to evaluate the accuracy of the emission test method. Percent recovery, %R, is calculated as:

$$\%R = E_{am}/E_{as} \times 100 \quad (5)$$

where  $E_{am}$  is the amount measured during the recovery test in  $\mu\text{g}$ , and  $E_{as}$  is the amount that is introduced into the chamber during the test in  $\mu\text{g}$ .

**3.3 Overview of Test Procedures**-The following steps should be performed for each test once the chamber has been prepared and recovery tests performed. Detailed information on test duration (Section 3.3.1) and photocopier preparation, handling, and operation follow (Section 3.3.2):

- Step 1. Checkout of copier by service representative;
- Step 2. Perform toner depletion/replenishment (Section 3.4);
- Step 3. Collect background air samples from empty chamber;
- Step 4. Place copier in chamber;
- Step 5. Power up copier, load paper and standard test image, and test remote start;
- Step 6. Equilibrate copier in chamber overnight in idle mode, i.e., powered but not copying;
- Step 7. Collect integrated chamber air samples for the copier in the idle mode for a total of anticipated copying time plus a time period equal to 4 air changes;
- Step 8. Collect integrated chamber air samples during full copier operation (i.e., until paper supply is gone) and continue air sample collection for a post-copying time period equal to 4 air changes; and
- Step 9. Determine air exchange rate during test using pulse injection of a tracer gas (e.g., carbon monoxide,  $\text{SF}_6$ ).

3.3.1 Test Duration – Steps 7 and 8 above describe the test duration used for this study. The paragraphs below discuss other alternative approaches that could be used.

The chamber should operate for a sufficiently long initial period to ensure that chamber equilibrium is reached prior to beginning sampling. In general, 4 air changes are required to replace 99% of the air in the chamber. For example, based on an ACH of 2.0, about 2 hours is required. Three alternative approaches can be used.

1. Operate the equipment for 2 hours continuously, at which time sampling could occur and, with the absence of wall effects, the chamber air concentration is assumed to be in equilibrium.
2. Operate the equipment for a defined period of time, collecting an integrated sample from the start of operation until 2 hours (i.e., 4 air changes) after the equipment is turned off. In the absence of wall effects, this sample should represent about 99% of total emissions during operation for the chamber used in this study.
3. Take short-term periodic samples throughout the period of operation. This approach should be used when information on the time course of emissions is required. This option is useful to determine how emissions change with time of operation.<sup>1</sup>

Dry-process photocopiers are limited as to the length of time they can operate continuously (due to paper supply limitations). If the equipment cannot operate continuously for the 2 hours required for the chamber to reach equilibrium plus the 2 hours required to collect a VOC sample, then one of the following approaches must be used:

- Multiple machines must operate sequentially so that operation is continuous for the time period required (2 hours); or
- An integrated sample must be taken from the start of operation until 2 hours after the cessation of operation.

The latter approach was followed for the testing and evaluation in this study.

3.3.1 Photocopier Preparation, Handling, and Operation – Before testing of the photocopier can begin, several preparative steps must be addressed. Due to the various designs of photocopiers, specific instructions for each cannot be described in this text; however, the following provides general information regarding what issues to address.

The photocopier must be configured for remote start and operation from outside the test chamber. This will vary depending on the specific model and must be customized for each. This is best done through discussions with the manufacturer's engineers and field technicians. Examples of possible approaches include the addition of contact switches that simply start the

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<sup>1</sup>It should be noted that using multisorbent collection media requires a 2-hour sampling period that may not be appropriate for this alternative. A grab sample using canisters may be more appropriate.



copier when pressed or removal and extension of the keypads to allow more complete operations. Also, any timed features such as automatic resets for number of copies must be disabled to allow remote operation.

To control for toner offgassing and toner carryover, a process of depletion and replenishment of the toner is required to insure consistent, representative results. This is especially necessary if the toner cartridge has been changed or if the toner has been in the machine for a prolonged period of time (greater than 1 month) prior to the test. The specific method for toner depletion and replenishment is dependent on the particular copier model being tested. Each copier model must be evaluated individually to determine the appropriate steps for toner depletion and replenishment based on its toner delivery system. Methods should be developed through discussions with the manufacturer's engineers and field technicians to prevent damage to the copier. Toner depletion and replenishment probably is not necessary between tests if only a short (several days) time passes between tests.

As an example, the following procedure for toner depletion/replenishment was developed specifically for one of the photocopiers used in this study. To deplete the toner, the toner cartridge was removed from the copier, and 3500 copies of the standard image were made. As the toner in the delivery system was depleted, the image became very faint on the paper. To replenish the toner in the delivery system, a new toner cartridge was inserted into the copier, and 500 copies of the standard image were made. At this point, the copy images appeared uniformly dark. To verify that the toner had been properly restored, a copy of the manufacturer's test pattern/image was made and compared against the original. This procedure appeared to be effective in "flushing" the older toner from the machine, replacing it with toner from the "fresh" cartridge.

Ideally, a study should yield emission factor estimates for all phases of product operation, i.e., continuous monitoring of emissions. However, designing a study to accomplish that could be resource intensive given the number of factors to be considered. Therefore, this method recommends that the copier be tested while idling (powered up but not operating) and at full maximum operation to define the maximum emissions. The standard operating conditions described previously will allow for comparison among various manufacturers. For example, for image processing machines (i.e., copiers and printers), a standard image (percent coverage) will be processed that represents a typical maximum image to define worst-case emissions and exposure. For monochromatic machines, a standard image of about 15% coverage is used. The standard image to be printed or copied on monochromatic machines is described in Attachment B. Manufacturer-recommended supplies should be used including toner and paper. Recycled paper and toner cartridges can also be used to compare their effect on overall emission rates.

## **4.0 Data Analysis**

**4.1 Environmental Data** – Environmental data (i.e., temperature and RH) should be recorded continuously. This can be done by a PC-based system. Summary statistics that describe the

environmental condition "setpoints" and the actual values achieved (including variability) should be computed and a data summary sheet prepared.

**4.2 Chemical Analysis Data** – The environmental information and the chemical analysis results are combined to give chamber air concentrations for individual compounds. In calculating concentrations the following factors are considered:

- Chemical analysis system background (including sorbent blanks for sampling cartridge)
- Chamber background
- Sampling time
- Sampling volume
- Mass observed for individual selected organic compounds, ozone, and particulates.

**4.3 Chamber Air Concentration** – Chamber air concentration for individual pollutants for each sample are calculated by dividing the mass by the sample volume.

**4.4 Emission Factor Calculation** – The emission rate ( $ER_i$ ) in the idle mode is calculated assuming steady-state conditions after the copier has been idling in the chamber overnight.

$$ER_i = [(C_i - C_b) \times V_c \times A_c] / n \quad (6)$$

where,

$ER_i$	=	emission rate in the idle mode in $\mu\text{g/h} \cdot \text{copier}$
$C_i$	=	chamber air concentration in the idle mode in $\mu\text{g/m}^3$
$C_b$	=	background chamber air concentration in $\mu\text{g/m}^3$
$V_c$	=	chamber volume in $\text{m}^3$
$A_c$	=	chamber air exchange rate in $\text{h}^{-1}$
$n$	=	number of copiers in chamber.

The emission rate of VOCs attributed to printing ( $ER_c$ ) is calculated using a simple mass balance equation and applying the following assumptions:

1. There is no reversible or irreversible adsorption of the target organics in the chamber during the testing period. This is demonstrated to be true through chamber recovery tests.
2. The chamber air is well-mixed. This is demonstrated for each test through the release and measurement of CO in the chamber air during testing.
3. The chemicals in the chamber are in the vapor phase and uniformly distributed in the chamber air. This is a property of VOCs.
4. The steady state emissions measured in the idle mode remain constant during the copying mode. Any changes are considered to result from copying, therefore by definition, a change will be attributed to printing.

After 4 air changes, 99% of the chamber air is exhausted from the chamber. Under these

conditions:

$$ER_c = M_t / (T_p \times n) \quad (7)$$

where,

$$\begin{aligned} ER_c &= \text{emission rate attributed to printing in } \mu\text{g/h} \cdot \text{copier} \\ M_t &= \text{total net mass of VOC measured in the chamber air in } \mu\text{g} \\ T_p &= \text{time the copier was printing in h} \end{aligned}$$

$$M_t = (C_p - C_i) \times T_{av} \quad (8)$$

where

$$\begin{aligned} C_p &= \text{measures time-integrated chamber air concentration measured during the chamber test in } \mu\text{g/m}^3 \\ C_i &= \text{chamber air concentration measured during idle mode in } \mu\text{g/m}^3 \\ T_{av} &= \text{total volume of air that passed through the chamber during testing in m}^3. \end{aligned}$$

This assumes that the concentration of VOCs in the chamber air attributed to printing can be estimated by correcting the total concentration measured during the chamber copying experiment by the concentration measured during the chamber idle experiment.

$$T_{av} = V_c \times A_c \times T_c \quad (9)$$

where

$$\begin{aligned} V_c &= \text{chamber volume in m}^3 \\ A_c &= \text{chamber air exchange rate in h}^{-1} \\ T_c &= \text{time the sample was collected for in h.} \end{aligned}$$

Equations 4, 5, and 6 are then combined, resulting in the following equation:

$$ER_c = [(C_p - C_i) \times V_c \times A_c \times T_c] / (T_p \times n) \quad (10)$$

If time-course data are collected, average emission rates for each time interval are calculated using the chamber air concentration at that time interval as

$$ER_t = (\Delta C_i / \Delta T_i + A_c C_i) \times V_c / n \quad (11)$$

where,

$$\begin{aligned} ER_t &= \text{emission rate for time interval T in } \mu\text{g/h} \cdot \text{copier} \\ \Delta C_i &= \text{change in chamber air concentration for time interval T in } \mu\text{g/m}^3 \\ \Delta T_i &= \text{length of time interval T in hours} \\ C_c &= \text{average measured chamber air concentration for time interval T in } \mu\text{g/m}^3 \end{aligned}$$

For ozone, emission rates are calculated as

$$ER_o = [(C_e * A_c * V_c)/(1 - e^{-A_c T_p})]/n \quad (12)$$

where

$ER_o$  = emission rate for ozone in  $\mu\text{g}/\text{h} \cdot \text{copier}$   
 $C_e$  = equilibrium chamber air concentration in  $\mu\text{g}/\text{m}^3$

## 5.0 Quality Assurance/Quality Control

Standard analysis methods, such as EPA and the National Institute for Occupational Safety and Health (NIOSH) methods, should be used when available and practical. In all cases, testing should include meeting existing standards addressing analytical techniques and chamber operation and calibration, including:

- ASTM D3195 Recommended Practice for Rotameter Calibration
- ASTM D1356 Definitions of Terms Related to Atmospheric Sampling and Analysis
- ASTM E355 Recommended Practice for Gas Chromatography Terms and Relationships
- ASTM D3609 Practices for Calibration Techniques using Permeation Tubes.

The QA/QC procedures described in the methods should be followed. Specific QA/QC activities for consideration include sample logbook, standard operating procedures, standards preparation log, calibration logs, instrument maintenance logs, materials testing logs, sorbent cartridge cleanup/desorption logs, log of electronically stored data, routine maintenance, daily recording of calibration, timely monitoring and percent recovery of internal and spiked standards, chamber background determination, duplicate chamber runs and duplicate samples, blanks, methods detection limit checks, and audit gas analysis.

## 6.0 Reporting Test Results

The report of the test results should contain the following sections:

- Facilities and Equipment: description of test chambers, clean air system, environmental measurement and control, sample collection, analytical instrumentation, and standards generation and calibration;
- Experimental Design: test conditions including temperature, RH, and air exchange rate;
- Sample Descriptions: complete description of product tested;
- Experimental Procedures: procedures used in testing including sampling and analysis;
- Data Analysis: show methods including appropriate models and equations (sample test data sheet provided in Attachment C);
- Results: chamber air concentrations and emission factor for each type of sample and test condition (including the detection limits for testing);
- Discussion and Conclusions: discuss relevance and conclusions (e.g., the effect of equipment cycle or percent coverage on emission rate); and
- Quality Assurance/Quality Control: compare the test data to the data quality objectives.

## 7.0 References

- American Society for Testing and Materials. *Small-Scale Environmental Chamber Determinations of Organic Emissions from Indoor Materials and Products*, ASTM Standard Guide D5116-90, Philadelphia, PA, 1990.
- American Society for Testing and Materials. *Recommended Practice for Rotameter Calibration*, ASTM D3195-94, Philadelphia, PA, 1994.
- American Society for Testing and Materials. *Practices for Calibration Techniques using Permeation Tubes*, ASTM D3609-96, Philadelphia, PA, 1996.
- American Society for Testing and Materials. *Recommended Practice for Gas Chromatography Terms and Relationships*, ASTM E355-96, Philadelphia, PA, 1996.
- American Society for Testing and Materials. *Definitions of Terms Related to Atmospheric Sampling and Analysis*, ASTM D1356-97, Philadelphia, PA, 1997.
- Gressel, Michael G. Final Report: Methods for Characterizing Emissions from Laser Printers. Report No: 211-04. National Institute for Occupational Safety and Health, U.S. Department of Health and Human Services, Cincinnati, OH, 1996.
- Winberry, W.T.; Murphy, N.T., Riggan, R.M. "Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air," EPA/600-4-89/017 (NTIS PB90-127374); U.S. Environmental Protection Agency, Research Triangle Park, NC, 1988.

**Attachment A:**  
**Description of Environmental Test Chamber**

Size	800 ft <sup>3</sup> (22.7 m <sup>3</sup> ), 10 x 10 x 8 ft (3.05 x 3.05 x 2.44 m)
Construction Materials	Ducts: Aluminum Ceiling/Walls: Aluminum Floor: Stainless steel gaskets: Viton®
Air Supply Systems	Outside air passed through particulate filters then through Carasorb 200 filters for organics removal, followed by HEPA filtration
Temperature Control	65 to 94 ± 2 °F (18 to 35 ± 1 °C)
Humidity Control	35 to 70% RH, ±5%
Air Exchange Rate	0 air changes to 120 air changes/hour
Sampling Ports	1/4-inch stainless steel Swagelok, adaptable to meet other requirements
Measurement Systems	Temperature/Humidity - General Eastman Model 850 Air Flow - Carrier Comfort Network Distributed Controller Data Acquisition - 386 PC

**Experimental Work to Demonstrate Chamber Capabilities**

Purpose	Approach	Acceptance Criteria
Demonstrate acceptable chamber operation	Air exchange rate validation - air exchange rate measured in chambers at 0.2 and 0.5 ACH using SF <sub>6</sub> or CO  Air mixing - SF <sub>6</sub> measurements compared to curve  Temperature and RH - measured constantly over 8-hour period	Air exchange rate must be within ±10% of specified  SF <sub>6</sub> curve must be within 5% of predicted values  Temperature must be within ±2 °C Relative humidity must be within ±5%
Chamber background	Measurements taken from chamber air using the proposed sampling and analytical methods	Background must be less than 1 µg/m <sup>3</sup> . Method quantitation limit estimated as 3xS.D of replicate measurements.
Recovery of constituents	Standards (VOC, formaldehyde) are introduced into chamber air at 10 to 20 µg/m <sup>3</sup> (≈ 10 times estimated method quantitation limit) over a 4-hour period	Recovery of constituents should be 80 to 120%

## Attachment B

### Description of Test Page

To allow for comparison between machines, a standard test image is recommended. This image was also used by the National Institute for Occupational Safety and Health\* (NIOSH) as part of their testing program. The page is described below and a sample test page follows.

Font:	Prestige Elite
Size:	10 point
Lines/page:	54
Character/line:	78
Top Margin:	1 inch
Bottom Margin:	1 inch
Left Margin:	1 inch
Right Margin:	1 inch
Program:	WordPerfect 5.1

See sample on next page.

\* Gressel, ----- 1996.

B-18



## Attachment C

### TESTING DATA FOR EMISSIONS FROM PHOTOCOPIERS

Test Run:	Determination of Zero Value	1. Measurement	2. Measurement
Time of Measurement	Date: _____ From: _____ To: _____	Date: _____ From: _____ To: _____	Date: _____ From: _____ To: _____
Temperature (°C)	Average: _____ Max: _____ Min: _____	Average: _____ Max: _____ Min: _____	Average: _____ Max: _____ Min: _____
Humidity (%)	Beginning: _____ Max: _____	Beginning: _____ Max: _____	Beginning: _____ Max: _____
Copier Output/ Measurement Period		_____ Copies = _____ % Max. Output	_____ Copies = _____ % Max. Output
<b>OZONE</b>			
Meter reading	_____ µg/m <sup>3</sup>	1. 1/2 h avg: _____ 2. 1/2 h avg: _____ 3. 1/2 h avg: _____ 4. 1/2 h avg: _____ Avg (2,3,4): _____	1. 1/2 h avg: _____ 2. 1/2 h avg: _____ 3. 1/2 h avg: _____ 4. 1/2 h avg: _____ Avg (2,3,4): _____
Calculation under consideration of zero value		1. 1/2 h avg: _____ 2. 1/2 h avg: _____ 3. 1/2 h avg: _____ 4. 1/2 h avg: _____ Avg (2,3,4): _____	1. 1/2 h avg: _____ 2. 1/2 h avg: _____ 3. 1/2 h avg: _____ 4. 1/2 h avg: _____ Avg (2,3,4): _____
<b>PARTICULATE</b>			
Optical particle counter	_____ particles /min	1. 1/2 h avg: _____ 2. 1/2 h avg: _____ 3. 1/2 h avg: _____ 4. 1/2 h avg: _____ Avg (2,3,4): _____	1. 1/2 h avg: _____ 2. 1/2 h avg: _____ 3. 1/2 h avg: _____ 4. 1/2 h avg: _____ Avg (2,3,4): _____
Gravimetric method		Wt of filter + dust = _____ Wt of filter = _____ Dust collected= _____ Vol of air sample = _____ Dust concentration = _____	Wt of filter + dust = _____ Wt of filter = _____ Dust collected= _____ Vol of air sample = _____ Dust concentration = _____
<b>TOTAL VOLATILE ORGANICS (TVOC)</b>			

Test Run:	Determination of Zero Value	1. Measurement	2. Measurement
INDIVIDUAL VOLATILE ORGANIC COMPOUNDS			
Compound:			
Compound:			
Compound:			
Compound:			
Compound:			
Compound:			
Compound:			
Compound:			
Compound:			

## **APPENDIX C. Other Sources of Information on Indoor Air Emissions from Office Equipment**

The following is a list of sources or groups that may be contacted to obtain additional information related to office equipment, indoor air emissions, and general environmental, health, and safety issues in the work and home environment.

### ***Blue Angel***

(German Eco-labeling program started in 1977. Other countries have similar programs.)

<http://www.ecomarkt.nt/europe/label/bengel.html>

### ***Consumer Product Safety Commission (CPSC)***

Washington, DC 20207

Hotline: 800-638-2772

Health Sciences Directorate

301-504-0477

301-504-0051 (fax)

<http://www.cpsc.gov>

### ***EnviroCenter***

(Internet source of information on IAQ information, products and services)

<http://www.envirocenter.com/>

### ***EPA's Energy Star Program***

(Specifically related to energy efficient office equipment)

U.S. EPA

Mail Code 6202J

401 M Street, SW

Washington, DC 20460

202-233-9114

<http://www.epa.gov/docs/appdstar/esoe/index.html>

### ***EPA's Indoor Air Quality Home Page***

<http://www.epa.gov/docs/iedweb00/index.html>

### ***EPA Indoor Air Quality Information Clearinghouse***

P.O. Box 37133

Washington, DC 20013-7133

800-438-4318

301-585-9020

<http://www.epa.gov/iaq/iaqinfo.html>

***Green Seal***

(Independent non profit org dedicated to protecting the environment by promoting the manufacture and sale of environmentally responsible consumer products.)

1730 Rhode Island Avenue

Suite 1050

Washington, DC 20036-3101

202-331-7337

<http://www.greenseal.org/index.htm>

***National Institute of Occupational Safety and Health (NIOSH)***

(Work environment only)

Technical Information Branch

Mail Stop C19

4676 Columbia Parkway

Cincinnati, OH 45226

800-356-4674

<http://ftp.cdc.gov/niosh/homepage.html>

***Occupational Safety and Health Administration (OSHA)***

Directorate of Technical Support

200 Constitution Ave. N.W.

Rm. N3653

Washington, DC 20210

202-219-7031

<http://www.osha-slc.gov/>

***Technical Association of the Pulp and Paper Industry***

(Paper manufacturing industry trade association)

<http://www.tappi.org>

***The IAQ Insider: Home Page***

[envirovillage.com/newsletters/PureAir/Tdefault.htm](http://envirovillage.com/newsletters/PureAir/Tdefault.htm)

**APPENDIX D. EPA Quality Assurance Audit of the  
RTI and EPA Large Chamber Laboratories**

**RTI AUDIT**

Performed by

Air Pollution Prevention and Control Division  
National Risk Management Research Laboratory  
Office of Research and Development  
U.S. Environmental Protection Agency  
Research Triangle Park, NC 27711

Quality Assurance No.	93029/III
Audit Type	Performance Evaluation
Audit Date	January 23, 1997
Research Project	Application of Pollution Prevention to Reduce Indoor Air Emissions from Office Equipment
Project Officer	Kelly Leovic Indoor Environment Management Branch (MD-54)
Auditors	Shirley J. Wasson, Jeff Ryan QA Staff, Technical Services Branch (MD-91)  Paul Groff Acurex Environmental
Audit Site	RTI Large Chamber Herbert Building Research Triangle Institute Research Triangle Park, NC 27711
Auditees	Colleen Northeim, Project Leader Linda Sheldon, Supervisor Don Whitaker, Test Coordinator Jeffrey Keever, Analyst
Date Issued	May 1997

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## **1.0 Introduction**

### **1.1 Purpose of Audit**

The U.S. EPA is participating in a research project to identify office equipment which performs well in the prevention of polluting emissions. Research Triangle Institute (RTI) has performed the preliminary work of measuring emissions from dry-process office photocopiers using RTI's large chamber, and writing a generic protocol. The project has progressed to phase II in which copier QC2 is being round-robin tested in several large chambers using the protocol. RTI participated in the round-robin by testing copier QC2 in their large chamber in January, 1997. The independent performance evaluation audit (PEA) tested the ability of project personnel to measure some of the volatile organic compounds (VOCs) which were emission targets of the study, using the protocol. A further audit objective was to compare the results of the independent audits from dissimilar large chambers.

### **1.2 Audit Preparation**

The auditors studied project materials including the phase II QA plan for the round robin testing entitled *Application of Pollution Prevention to Reduce Indoor Air Emissions from Office Equipment, Phase II: Round-Robin Testing*. Arrangements for the audit were made through pre-audit contact with the project leader and test coordinator. The performance audit was partially funded through QA WA 3/02 with EPA's on-site contractor, Acurex Environmental, who identified a certified cylinder containing the specified target VOCs, arranged for recertification by the commercial vendor, and participated in the audit. Funding for RTI to perform the analysis of the multisorbent cartridges which were used to trap the audit target compounds was provided by the QA contract with RTI. Plans for this audit closely followed the plans for the audit of the EPA large chamber (LC). The equipment used for measurement and delivery of the audit gas included a mass flow controller, a proper regulator for the cylinder, an electronic flowmeter, a 3-way stainless steel valve, Teflon tubing, a thermometer, and a stopwatch.

### **1.3 Audit Activity**

The audit was performed on January 23, 1997. To prepare for the audit, RTI provided multisorbent cartridges containing Tenax and Carboxen 1000 sorbents. The test coordinator operated the chamber in the same range of temperature, relative humidity, and air exchange rate as was used for the copier test. Meanwhile the auditors conditioned the regulator and delivery system with the audit gas (venting it outside the room) and determined the delivery flow rate using the electronic bubble flow meter. The audit gas, from cylinder ALM057570, containing the target VOCs, was then released into the chamber for 38 minutes by stopwatch to simulate the amount of time that the copier operated. The gas was delivered through unheated Teflon tubing by connection with a Swagelok fitting through a wall port which extended into the chamber 12 inches. During the release, RTI large chamber personnel collected duplicate multisorbent cartridge samples from the chamber port. Sampling continued for 4 air changes after the release for a total

of 158 minutes. After the sampling the cartridges were taken by the RTI test coordinator for analysis by the RTI project analyst.

A letter report from RTI project personnel was delivered on March 13, 1997. It contained chamber conditions (see Table 1) and a table containing concentrations and emission rates of the duplicate samples taken during the chamber release.

Table 1. Process Conditions During the VOC Release as Reported by the Auditees

Condition	Permissible Range	Actual Range
Chamber Temperature	$26^{\circ}\text{C} \leq T \leq 31^{\circ}\text{C}$	26 - 27°C
Relative Humidity	30 to 35%	27 to 30%
Air Exchange Rate	NA	1.90/h
Chamber volume	NA	22.7 m <sup>3</sup>
Sample flow rate	25 to 30 mL/min	26 mL/min, (nominal)
Collection time	150 to 160 min	158 minutes
Analysis	Thermal Desorption, GC/MS	Thermal desorption, GC/MS

Recertified values for the audit cylinder were available to the auditors on March 10, 1997.

## 2.0 Audit Summary

All of the target compounds contained in the certified cylinder of audit gas except toluene were identified and quantified within the accuracy and precision goals of the project.

The auditors were not aided by RTI's audit report in their objective to compare the two different independently-audited large chambers. Most of the information requested in the memorandum of January 22, 1997, to the Project Leader, was not provided.

## 3.0 Audit Findings

### 1. LC project personnel recovered all of the target compounds within the data quality accuracy goals of 75 to 125% except toluene.

The auditors compared the total mass injected as calculated by project personnel with the total mass injected as calculated by audit personnel using the recertified audit cylinder concentrations. The results are given in Table 2.



Table 2. Total Mass VOCs Released into the Chamber

Compound	Reported by Auditees-- Sample 1 (µg)	Reported by Auditees-- Sample 2 (µg)	Calculated by Auditors (µg)	Recovery-- Sample 1 (%)	Recovery-- Sample 2 (%)
Toluene	5200	5000	3770	138	133
Ethyl Benzene	5400	5300	4370	124	121
m,p-Xylene	10000	10000	8700	115	115
Styrene	3200	3200	4100	78	78

2. **The reported values for chamber air concentrations (Table 3) met the interlaboratory goal for precision, ≤25%.**

Table 3. Reported Values for Chamber Air Concentrations

Compound	Reported by Auditees--Sample 1 (µg)	Reported by Auditees--Sample 2 (µg)	Relative % Difference
Toluene	5200	5000	2
Ethyl Benzene	5400	5300	2
m,p-Xylene	10000	10000	0
Styrene	3200	3200	0

3. **Due to the lack of information in the report, nothing can be said about actual conditions during the audit other than the information given in Table 1.**

Although planning information was available in the QA plan, not enough was available for the auditors to achieve on of their audit objectives. They wanted to be able to compare several specific parameters for each of the chambers during the audit to show that chamber or audit conditions dissimilarity is not a barrier to achieving comparable results. Nothing is known about chamber background, blanks, chain-of-custody procedures, calibration procedures, holding time or storage conditions until analysis, what instrument was used for the analysis, minimum detection limits, quantitation limits for project samples, any QC samples run with the audit samples, or actual conditions of sampling (actual rate of sampling and actual sample volume).

#### **4.0 Conclusions and Recommendations**

The audit showed that RTI's large chamber is adequate to measure the volatile target analytes of the project. Without calibration, blank, background, or surrogate recovery information, the auditors cannot determine why toluene was recovered outside of accuracy goal limits. We recommend that reports of results of performance evaluation audits contain at a minimum the following information: results of blanks, baseline samples, calibration checks, surrogate or QC check samples analyzed at the same time as the project samples, holding time and storage conditions of samples, date of analysis, analysis instrument and conditions, name of analyst, chain-of-custody information, and actual sampling conditions.

#### **5.0 References**

1. Quality Assurance Project Plan, *Application of Pollution Prevention to Reduce Indoor Air Emissions from Office Equipment, Phase II: Round-Robin Testing*, Research Triangle Institute, October 10, 1996.

## EPA AUDIT

Performed by

Air Pollution Prevention and Control Division  
National Risk Management Research Laboratory  
Office of Research and Development  
U.S. Environmental Protection Agency  
Research Triangle Park, NC 27711

Quality Assurance No.	IA03/III
Audit Type	Performance Evaluation
Audit Date	December 26, 1996
Research Project	Application of Pollution Prevention to Reduce Indoor Air Emissions from Office Equipment
Project Officer	Kelly Leovic Indoor Environment Management Branch (MD-54)
Auditors	Shirley J. Wasson Jeff Ryan QA Staff, Technical Services Branch (MD-91)
Audit Site	EPA Large Chamber Indoor Emissions Management Branch U.S. EPA Environmental Research Center 86 T.W. Alexander Drive Research Triangle Park, NC 27711
Auditees	Betsy Howard, Project Leader, U.S. EPA Andy Kegl, SEE Employee Ivan Dolgov, SEE Employee U.S. EPA Environmental Research Center 86 T.W. Alexander Drive Research Triangle Park, NC 27711
Date Issued	May 1997

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## **1.0 Introduction**

### **1.1 Purpose of Audit**

The U.S. EPA is participating in a research project to identify office equipment which performs well in the prevention of polluting emissions. Research Triangle Institute has performed the preliminary work measuring emissions of dry-process office photocopiers and writing a generic protocol. The project has progressed to phase II where copier QC2 is being round-robin tested in several large chambers using the protocol. The EPA large chamber (LC) laboratory operated by the Indoor Emissions Measurement Branch (IEMB) of APPCD is participating. Copier testing was performed in December, 1996. The performance evaluation audit (PEA) independently tested the ability of project personnel to measure some of the volatile organic compounds (VOCs) which were emission targets of the study using the protocol.

### **1.2 Audit Preparation**

The auditors studied project materials including the phase II QA plan for the round robin testing entitled *Application of Pollution Prevention to Reduce Indoor Air Emissions from Office Equipment, Phase II: Round-Robin Testing*, and the draft and final *Dry-Process Photocopier Test Plan*. The auditors were also familiar with the approved manual which details every operation of the LC facility. One of the auditors met with IEMB and contractor personnel to determine appropriate audit target compounds and expected concentration ranges. The performance audit was funded through QA WA 3/02 with the on-site contractor, who identified a certified cylinder containing the specified target VOCs, and arranged recertification by the commercial vendor. The contractor also performed the analysis of the multisorbent cartridges which were used to trap the audit target compounds. The other auditor designed and produced the setup for the performance audit. The equipment included a mass flow controller, a proper regulator for the cylinder, an electronic flowmeter, a 3-way stainless steel valve, Teflon tubing, a thermometer, and a stopwatch. An audit plan was prepared.

### **1.3 Audit Activity**

The first attempt to perform the audit occurred on 12/23/96. Due to a miscalculation by one of the auditors, not enough VOC audit gas was released into the chamber to provide a measurable concentration. The collected samples were scrapped, and the audit was rescheduled for 12/26/96.

To prepare for the audit, LC personnel obtained properly quality-controlled multisorbent cartridges from the contractor analytical personnel. They operated the chamber in the same range of temperature, relative humidity, and air exchange rate as was used for the copier test. These conditions are given in Table 1. Having flushed the chamber during the previous two days, they performed background testing by taking duplicate background VOC samples from the chamber

port and chamber exhaust for analysis. They also sampled the background with the Xontech analyzer. They determined air exchange rate by injecting a known amount of sulfur hexafluoride (SF6) into the chamber and analyzing it using a B & K analyzer. Meanwhile the auditor conditioned the regulator and delivery system with the audit gas (venting it outside the building) and determined the delivery flow rate using the electronic bubble flow meter. The audit gas from cylinder ALM057570 containing the target VOCs was then released into the chamber for 38 minutes by stopwatch to simulate the amount of time that the copier operated. The gas was delivered through unheated Teflon tubing by connection with a Swagelok fitting through a wall port which extended into the chamber 15 inches. During the release, LC personnel collected duplicate multisorbent cartridge samples from the chamber port, duplicate samples from the exhaust, and continued the Xontech measurements. Sampling continued for 4 air changes after the release for a total of 197 minutes. After the sampling the cartridges were stored in an IEMB freezer until analysis. Process and sampling data were collected in bound laboratory notebooks and on data sheets.

Table 1. Process Conditions During the VOC Release as Recorded by Auditor

Condition	Permissible Range	Actual
Chamber Temperature	$25.5^{\circ}\text{C} \leq T \leq 31^{\circ}\text{C}$	$25.51^{\circ}\text{C}$ to $25.84^{\circ}\text{C}$
Relative Humidity	~30%	26.8%
Return Relative Humidity	~30%	28.3%
Return flow rate	~26.5 cfm	26.0 cfm
Ambient Temperature	NA	$21.9^{\circ}\text{C}$ to $22.0^{\circ}\text{C}$
Barometric Pressure	NA	766.1 mm Hg

A report entitled *Large Chamber Audit Test Results* was delivered on 2/20/97. According to the report, the samples were analyzed on 12/27/97. Recertified values for the audit cylinder became available on 3/10/97.

## 2.0 Audit Summary

Three of the four target compounds contained in the certified cylinder of audit gas were identified and quantified within the accuracy goals of the project. Styrene was recovered at slightly below the 75% recovery goal.

There was a VOC sample cartridge misidentification by the analytical laboratory. The sample they reported as background exhaust was in fact a blank sample.

### 3.0 Audit Findings

1. **LC project personnel recovered all of the target compounds except styrene within the data quality goals of 75 to 125%.**

The auditors compared the total mass injected as calculated by project personnel with the total mass injected as calculated by audit personnel using the recertified audit cylinder concentrations. The results are given in Table 2.

Table 2. Total Mass VOCs Released into the Chamber

Compound	Reported by Auditees-- Exhaust (mg)	Reported by Auditees-- Chamber (mg)	Calculated by Auditors (mg)	Recovery-- Exhaust (%)	Recovery-- Chamber (%)
Toluene	3.845	3.972	3.74	104	106
Ethyl Benzene	4.657	4.765	4.33	108	110
m,p-Xylene	9.190	9.368	8.62	107	109
Styrene	2.91	2.97	4.06	72	73

2. **The exhaust background sample was not analyzed. The blank sample was analyzed and reported as the exhaust background.**

Lack of chain-of-custody (COC) documentation may have contributed to the miscommunication between LC personnel and contractor personnel regarding the identity of the samples which were required to be analyzed. Chamber personnel usually provided COC documentation, but COC sheets were temporarily not available on audit day. ID 2560 was reported as chamber exhaust by analytical laboratory personnel, but in fact was the blank sample. The exhaust background is not known for the audit.

### 4.0 Discussion

The results for styrene were slightly below QA goals. This loss may be the result of sticking to delivery vehicles or LC surfaces, or failure to desorb from the multisorbent tubes.

There are some discrepancies among the data and summary sheets. For instance, the sample volume of the chamber release sample is reported as 4035 mL on page 3 and 4038.5 mL in the first Analytical Results table. Sample ID 2560 is listed as exhaust background in the first Analytical Results table, as a blank in the sample identification table on page 3, as a blank in the reproduced laboratory notebook page on page 4, and as exhaust background in "Table 1. Analytical Results", on page 8. Fortunately the sample confusion did not materially alter the result

of the audit, but it may have been prevented by the LC's usual COC documentation procedures.

## **5.0 Conclusions and Recommendations**

The audit shows that LC personnel are providing excellent measurement capability for VOC emissions measurement. We recommend validating styrene measurement if it is considered an important target compound for this project.

We recommend keeping a good supply of COC documents on hand to ensure clear communication between project and analytical laboratory personnel.

## **6.0 References**

1. Quality Assurance Project Plan, *Application of Pollution Prevention to Reduce Indoor Air Emissions from Office Equipment, Phase II: Round-Robin Testing*, Research Triangle Institute, October 10, 1996.
2. E.M. Howard, *Dry-Process Photocopier Final Test Plan*, December 6, 1996.
3. Facility Manual, *Large Indoor Air Quality Environmental Test Chamber*, Revision IV, approved November 18, 1996.



<b>TECHNICAL REPORT DATA</b> <i>(Please read Instructions on the reverse before complete)</i>		
1. REPORT NO. EPA-600/R-98-080	2.	3.
4. TITLE AND SUBTITLE Indoor Air Emissions from Office Equipment: Test Method Development and Pollution Prevention Opportunities		5. REPORT DATE July 1998
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) C. Northeim, L. Sheldon, D. Whitaker, B. Hetes, and J. Calcagni		8. PERFORMING ORGANIZATION REPORT NO.
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16. ABSTRACT The report describes the development and evaluation of a large chamber test method for measuring emissions from dry-process photocopiers. The test method was evaluated in two phases. Phase 1 was a single-laboratory evaluation at Research Triangle Institute (RTI), using four mid-range dry-process photocopiers. Phase 1 results indicate that the test method provides acceptable performance for characterizing emissions, adequately identifies differences in emissions between machines both in compounds emitted and their emission rates, and is capable of measuring both intra- and inter-machine variability in emissions. Toners appear to be the primary source of organic emissions from the photocopiers. To investigate whether all chambers produce similar results, a four-laboratory round-robin evaluation of the test method was performed in Phase 2. A single dry-process photocopier was shipped in turn to each of four laboratories along with supplies (i.e., toner and paper). Phase 2 results demonstrate that the test method was used successfully in the different chambers to measure emissions and that differences in chamber design and construction appear to have minimal effect.		
17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
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