



Inside IAQ

EPA's Indoor Air Quality Research Update

We are pleased to be able to resume semiannual publication of *Inside IAQ* after an unavoidable 2-year suspension. This issue is being distributed via first class mail using our most recent mailing list; in addition, copies of this and previous editions of the newsletter are available on the internet at:
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TESTING DEMONSTRATES THAT NOMINALLY IDENTICAL PHOTOCOPIER TONERS CAN HAVE SIGNIFICANTLY DIFFERENT VOC EMISSIONS

A laboratory study has been completed on a series of nominally identical toners, manufactured for use in a specific dry-process photocopier. The objective was to determine the extent to which the emissions of volatile organic compounds (VOCs) from a given toner might be reduced through judicious selection of the process and the polymer feedstock used in the manufacture of that toner.

A cooperating toner manufacturer produced four nominally identical batches of toner for a selected copier, according to a 2x2 matrix: using two different manufacturing processes (vented and unvented extrusion); and using two different lots of polymer feedstock, to be fed to the extruder. The manufacturer also provided samples of the two unprocessed feedstocks. In addition to these manufacturer samples, toner cartridges for this same copier were purchased from two local retailers, representing three different toner lots. The manufacturer, manufacturing process, and feedstock characteristics for these retailer toners were unknown.

These toners were tested using a flow-through thermal desorption test method, developed for this project. In this method, toner samples were ballistically heated to the temperature range of the copier (180 to 200 °C), and the VOCs driven off were captured on Tenax® sorbent. These Tenax® cartridges were then desorbed and analyzed using gas chromatography (GC) with a flame ionization detector (FID), calibrated for up to 21 selected individual VOCs.

Statistical analysis of the results from the manufacturer samples showed that ($p < 0.05$):

- The manufacturing process (vented vs. unvented extrusion) had no effect on toner emissions in this study. That is almost certainly because only a negligible vacuum (2 Pa below atmospheric) was applied in producing the vented toners available for this study; a vacuum perhaps 4 orders of magnitude greater would have been required for effective removal of VOCs.

- The feedstock had little or no effect on the emissions from the toners because there was no difference in the emissions between the two feedstocks used in this study.
- Each unprocessed feedstock generally has 15 to 30% higher emissions of ethylbenzene, p-xylene, and styrene, compared to the toners manufactured using that feedstock. This observation would be consistent with the thesis that some fraction of these compounds – present as impurities in the feedstock – is driven off during the extrusion process.
- Each unprocessed feedstock consistently has about 30 to 60% *lower* emissions of benzaldehyde and acetophenone, compared to the toners manufactured using that feedstock. These observations would be consistent with the thesis that some amount of these oxygenated compounds is created by thermal-oxidative degradation of the polymer during the extrusion process.

Statistical analysis of the results from the retailer toners showed that ($p < 0.05$):

- All of the retailer toners have emissions of ethylbenzene, xylenes, styrene, and acetophenone that are significantly lower (by 15 to 100%) than those from the manufacturer toners (with either feedstock).
- All of the retailer toners have emissions of benzaldehyde that are significantly higher (by 125 to 350%) than those from the manufacturer toners.
- In general, the total VOC (TVOC) emissions from the retailer toners are statistically the same as those from the manufacturer toners, even though the emissions of individual compounds can vary significantly.
- In general, there is no statistical difference in emissions between the retailer toners, within the statistical power of this analysis (two samples per toner).

Overall, the conclusions from this study are:

1. From comparison of the manufacturer and retailer toners tested here, it is clear that nominally identical toners – manufactured to meet the fuser specifications for a single photocopier – can have significantly different emissions of

individual VOCs when heated in the laboratory. Emissions of a given compound can vary by a factor of 2 or more between toners.

2. Even significant differences in emissions of individual VOCs between toners might not indicate one as a clearly preferable low-emitting product. Comparison of the manufacturer and retailer toners indicates that – while the retailer toners had much lower emissions of some compounds (ethylbenzene, xylenes, styrene, acetophenone) – they had higher emissions of other compounds (benzaldehyde, phenol). (All of these compounds, except benzaldehyde, are Hazardous Air Pollutants.) The difference in TVOC emissions between the two toner sets is modest at best, and often not statistically significant.

3. The differences in emissions between the manufacturer and retailer toners are almost certainly due to differences between the manufacturing processes and/or the feedstock polymers used in the two cases. But without information on the retailer process(es) and feedstocks, the specific factors creating the differences could not be identified in this study.

4. Because the specific factors creating the emission differences between the manufacturer and retailer toners cannot be identified, it is not possible from this study to make specific recommendations regarding how process or feedstock might be modified in order to produce lower-emitting toners for a given copier.

5. The tests on the manufacturer toners showed that vented extrusion did not produce toners having lower emissions than did unvented extrusion; but this result was almost certainly obtained because only a negligible vacuum (2 Pa) was applied during vented extrusion. These tests also showed that the feedstock had only modest, if any, impact on toner emissions; but the feedstocks were almost identical, creating this result.

6. The tests on the manufacturer toners and feedstocks demonstrated that essentially all of the compounds observed in the toner emissions result, at least in part, from impurities that are present in the feedstocks to begin with. The tests also demonstrated that the concentrations of some species can be increased during the extrusion process, presumably by oxidative degradation of the polymer. These observations can be used to postulate explanations for the differences in emissions between the manufacturer and retailer toners. (EPA Contact: Bruce Henschel, 919-541-4112, henschel.bruce@epa.gov)

IDENTIFICATION OF HAZARDOUS AIR POLLUTANTS EMITTED FROM A SHOWER CURTAIN

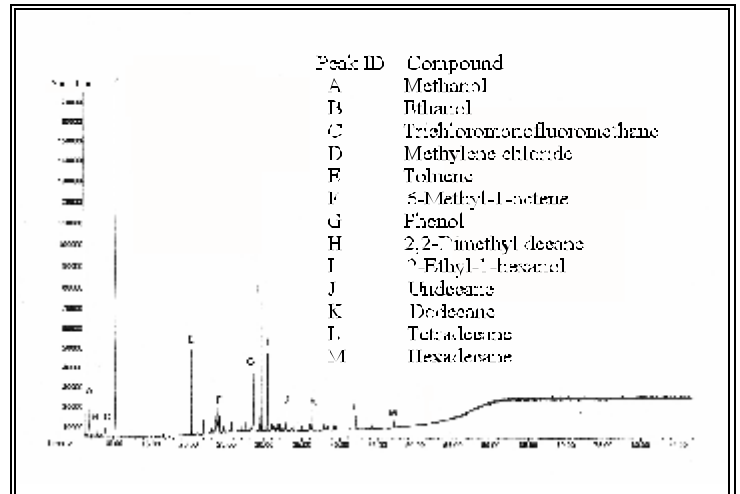
A single soft vinyl shower curtain was tested. The 70 by 72-inch shower curtain was 100% vinyl, manufactured in China for a large U.S. retailer. The product was purchased at a local retail outlet. The shower curtain was colored, primarily blue. It had a strong "plastic" odor when removed from the package.

Equilibrium headspace was analyzed using a newly developed static chamber test method. The test was performed by placing samples of the shower curtain in a 53-L stainless steel chamber. After loading the shower curtain samples, the chamber was sealed and placed in an incubator set at 23°C. The tests were static with no air flow to the chamber. Special racks were constructed to suspend the shower curtain in the chamber to maximize the exposed surface area and accelerate the experiments. The racks consist of a frame with stainless steel bars on the top and bottom spaced approximately 2 cm apart. The shower curtain was cut into strips with nominal width of 34.3 cm and the strips were woven through the bars.

Headspace chamber air samples were collected on Tenax sorbent tubes using a sampling pump. The samples were analyzed by thermal desorption interfaced to a gas chromatograph equipped with a flame ionization detector.

Figure 1 is a chromatogram of the headspace sample taken at the 168th h. Among the 14 compounds identified, methyl alcohol (methanol), methylene chloride, toluene, and phenol were classified as hazardous air pollutants by the 1990 Clean Air Act Amendments. (EPA Contact: John Chang, 919-541-3747, chang.john@epa.gov)

Figure 1. Chromatogram identifying hazardous compounds.



A PILOT HOME ASTHMA INTERVENTION STUDY IN BOSTON PUBLIC HOUSING

A small study was recently completed to investigate the feasibility of implementing asthmagen reduction measures in Boston Public Housing. The study is a community/university/government collaboration between the Tufts University School of Medicine, the Harvard University School of Public Health, the Committee for Boston Public Housing, the Tenant Task Force of the Franklin Hill Housing Development (Figure 2), Boston Medical Center, and the U.S. Environmental Protection Agency's Office of Research and Development and Region 1. The goal of the program was to reduce household environmental factors, such as allergens, airborne particles, and irritant gases, that contribute to the exacerbation of asthma symptoms. The program was designed to carry out interventions in a manner that maximized participation from both community organizations and individual tenants involved in the study. This was a pilot-scale study, intended primarily to gain experience working in the public housing arena in order to develop hypotheses and methods for future research projects.

Nine families with asthmatic children living in Franklin Hill Housing Development in Boston were enrolled in the asthma intervention program. At the beginning of the study, the asthmatic children were evaluated by a pediatric pulmonologist. The evaluation included administration of a symptom frequency questionnaire, review of medication use, and physical examination. A computerized pneumotachometer (MultiSpiro) was used to perform pulmonary function testing on all children over 4 years of age. Allergy skin testing was performed for cat, mouse, dog, cockroach, and dust mite antigens. Over the course of the study, the participants kept a diary of asthma symptoms and medication use.

Asthmagen-reduction Interventions

Interventions started with thorough cleaning of the apartments and furniture, using a machine that applied an atomized water-based solution at 200 psi, which was extracted to leave little moisture in fabric, upholstery, and

carpeting. In addition, cracks and crevices that might allow pest entry were sealed, and pest repellent devices were installed in some apartments. In many cases, exposed steam piping was present, resulting in high indoor temperatures and burn hazards. This was insulated. Mattresses and pillows on the children's beds, and any other beds the children slept on, were encased in dust-mite-proof covers. Some tenants were provided with high-efficiency particulate air (HEPA)-filtered vacuum cleaners for their own use. Some apartments were equipped with air filtration systems: electrostatic filters, HEPA filters, or a modified clean-room system containing a HEPA filter and an ozone lamp, followed by an activated charcoal filter. The filter systems were maintained by project staff. The specific intervention used for each apartment was tailored to the conditions in that apartment.

Data Collection

In-depth qualitative and quantitative information was collected from these nine apartments and their residents. The qualitative information included asthma symptom diaries and resident responses in focus group discussions both before and after the interventions were implemented. This provided valuable insight into the institutional, social, economic, and personal factors that affect the use of asthma prevention interventions in public housing. Quantitative data, from intensive environmental monitoring, was collected to thoroughly characterize the state of the nine public housing apartments, and to cull hypotheses about the effectiveness of the interventions.

Monthly monitoring visits were made to each apartment. During these visits, the study team made a visual inspection for mold, wetness, cockroaches, rodent droppings, etc. Temperature and relative humidity were measured. Inhalable and respirable particulate matter—with aerodynamic diameters of $< 10 \mu\text{m}$ (PM_{10}) and $< 2.5 \mu\text{m}$ ($\text{PM}_{2.5}$), respectively—were collected on 37 mm Teflon 2 μm -pore

filters. Twenty-four hour, time-integrated passive nitrogen dioxide (NO_2) samples were taken using Yanagisawa Badges and analyzed by light spectrometry. Twenty-four hour VOC samples were collected passively on thermal desorption tubes packed with Carbotrap B, and analyzed by gas chromatography/mass spectroscopy (GC/MS).

Dust samples were collected on cellulose extraction thimbles (Whatman Inc., Hillsboro, OR) using a small, portable vacuum cleaner (Eureka Mighty Mite). Composite samples were taken from asthmatic children's bedrooms by vacuuming the children's bedding and the carpeting around the beds. These were analyzed for dust mite antigens, Der p 1 and Der f 1; cat antigen, Fel d 1; dog antigen, Can f 1; fungi; and endotoxin. Other samples were collected from the seats and carpeting of the apartments' main living areas, and analyzed for dust mite antigens, Der p 1 and Der f 1; cat antigen, Fel d 1; fungi; and dog antigen, Can f 1. A third set of samples was collected from kitchen cabinets and analyzed for rodent antigen, Mus m 1; and cockroach antigen, Bla g 1. Dust was also analyzed for viable fungus by plating onto

malt extract agar. Endotoxin, and dust mite, cat, dog, roach, and mouse antigens were measured using a spectrophotometric Enzyme-Linked-ImmunoSorbent-Assay (ELISA) method.

Current Progress

Initial results and recommendations from this study were presented at the Engineering Solutions to Indoor air Quality Symposium held July 17-19, 2000, in Raleigh, North Carolina. The conference was sponsored jointly by the Air & Waste Management Association and the U.S. EPA. The research was completed in the autumn of 2000, and final articles are being prepared for submission to peer reviewed journals (EPA Contact: Betsy Howard, 919-541-7915, howard.betsy@epa.gov)

Figure 2. Franklin Hill Apartments



CANDLE BURNING AS A POTENTIAL SOURCE OF INDOOR AIR POLLUTION

Candle burning has been associated with human living conditions for at least 1,000 years. Although no longer primarily a means of lighting, candles are still popular in households and certain public places, mainly for creating a unique atmosphere. Candle sales in the United States keep growing – about 10 to 15% per year in the last 10 years. Industry estimates put 1999 sales at \$1.3 billion for scented candles and up to \$2.3 billion for all candles.

A special issue that has drawn some attention recently is the lead emissions from lead-wick candles. According to the National Candle Association, most U.S. manufacturers have ceased lead-wick production, but some imported candles on the market still contain lead in their wicks. EPA bought 100 sets of candles that appeared to contain metal-cored wicks. Eight sets had lead wicks with lead contents ranging from 51 to 74%. While burning, they emitted lead at a rate from 100 to 1400 Og/hour. Under certain indoor conditions, burning these candles may result in lead concentrations above EPA recommended thresholds. Furthermore, inhalation exposure is not the only pathway for lead intake. Unlike gaseous air pollutants, particle-bound lead tends to settle on interior surfaces, where young children can be exposed to lead dust through skin contact. The U.S. Consumer Product Safety Commission is currently in the process banning the sales of lead-wick candles in the United States.

Another issue associated with candle burning is the emissions of fine particulate matter (PM). Although all candles generate carbon particles during the burning process, a well-designed and well-maintained candle emits negligible

fine PM because almost all the particles are consumed by the flame. In fact, it is the combustion of the carbon particles that gives the flame its bright golden color. This process was artfully described by Michael Faraday in 1861 in his famous book *The Chemical History of a Candle*. On the other hand, several factors (e.g., candle composition and design, wick length, and drafty air) may result in imperfect combustion. A smoldering candle could cause an indoor fine PM concentration higher than permitted by the ambient air quality standards. Heavy and frequent candle burning in homes may be a contributing factor to soot deposition on interior surfaces, causing blackened walls, ceilings, and carpets. The exact mechanism of this phenomenon is not well understood, however.

Protecting the public from these potential indoor pollution problems requires a joint effort by the industry, the public, and governments. Some manufacturers are developing low-emission candles. Product labeling may help consumers identify cleaner products and learn how to use them. To some extent, burning candles is an art, and proper use of this product can reduce emissions. Thus, public education is a cost-effective way to deal with this kind of product. We observed that blowing out candles could instantly produce a large amount of particles. Some simple measures -- using a wet cloth, candle scissors, or snuffer – could greatly reduce such emissions. Emissions from candles vary from product to product and from time to time. To obtain representative emissions data, there is a need to develop standard methods for testing. (EPA Contact: Zhishi Guo, 919-541-0185, guo.zhishi@epa.gov)

THE IMPACT OF OZONE ON INDOOR AIR QUALITY

EPA's Indoor Environment Management Branch (IEMB) is conducting experiments to characterize the impact of ozone on indoor air quality (IAQ). The goal of this research is to improve our understanding of the relationship between ozone and risk in indoor environments. Ozone is transported indoors from ambient air and may be generated indoors by a variety of sources including office equipment and consumer appliances. Consumer appliances marketed as air cleaners that intentionally produce ozone are of particular interest because of their potential to create high ozone concentrations and because they are advertised to improve IAQ by reacting objectionable or odor causing volatile organic compounds

(VOCs) with ozone. The immediate focus of our work is to characterize sources of ozone in indoor environments and determine how ozone affects VOC and particle concentrations in indoor air.

Little data are available that may be used to model and predict the impact of ozone on IAQ. To fill this gap, we have characterized ozone and oxides of nitrogen (NO_x) emission rates from selected consumer appliances under controlled conditions in a room-sized environmental chamber and evaluated their performance in our research test house. These tests include limited evaluation of a feedback control

system designed to maintain in-room ozone concentrations at or below 50 parts per billion (ppb).

We are currently investigating the impact of operating an ozone generator air cleaner on VOC concentrations in the controlled environment of the test chamber. The objectives of these tests are to identify reaction products and determine if reactions proceed at rates that are consistent with reaction rate constants that have been determined for the troposphere. The reason for this objective is obvious: ozone reacts too slowly with most VOCs to have much impact on indoor air concentrations – emission rates from the source(s) and air exchange rates generally govern concentrations. However, if an ozone generator produces other radicals such as hydroxyls ($\cdot\text{OH}$) that react with VOCs much more quickly than ozone, then operation of the device may actually alter indoor air concentrations of some VOCs. Whether or not this improves indoor air quality is another matter. Some of our current research findings are presented below.

Characterization of Ozone Generator Air Cleaner Appliances

Emissions characterization tests were conducted in the room sized environmental chamber (see Figure 3) to determine how much ozone and NO_x these devices generate and what factors influence generation rate.

Ozone emission rates for a widely marketed appliance were determined at various dial set points (in ft^2 of floor treatment area) at 50% RH in the room-sized environmental chamber and are shown in Figure 4. We found that ozone generation rates (<1 to >150 mg/h) were generally consistent with the rates stated by the manufacturers, although the relationship between dial setting of the ozone generator and ozone emission rate was not linear across the range of the dial.

The chamber tests also revealed that ozone generation rates decreased as relative humidity increased for all appliances tested. As may be seen in Figure 5, the rate of decrease was greatest for the appliance with the highest ozone generation rate.

Figure 3. Characterizing ozone emission rates in EPA's room-sized test chamber.

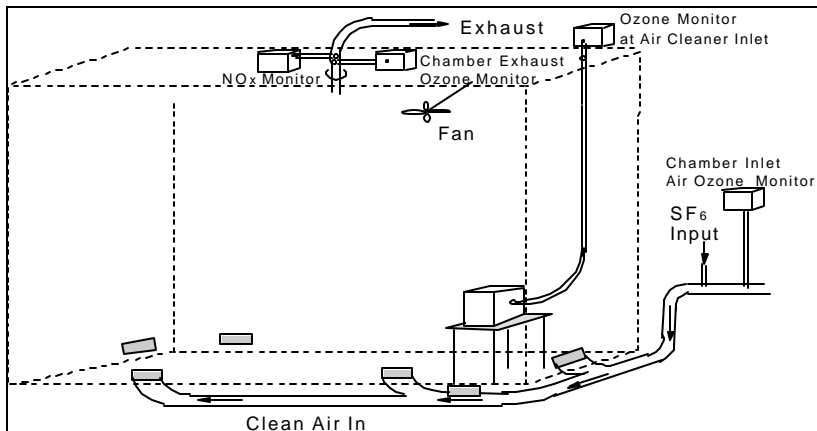
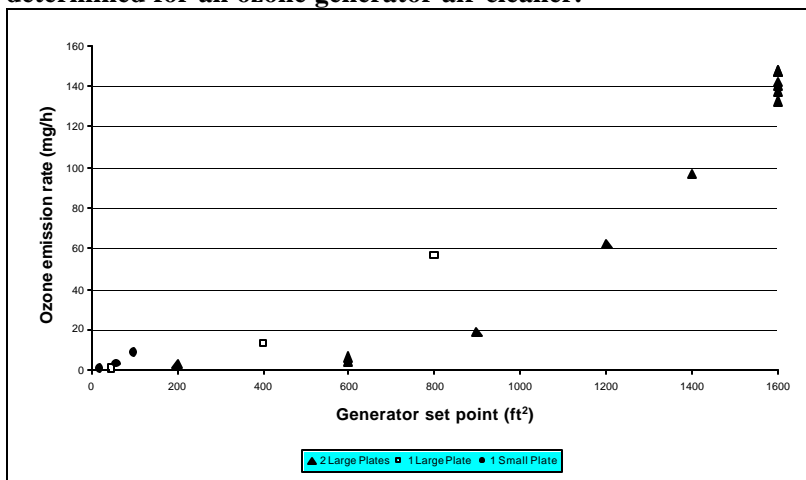


Figure 4. Ozone emission rates at generator set points determined for an ozone generator air cleaner.



NO_x [as nitrogen dioxide (NO_2)] is generated by silent discharge ozone generators. As shown in Figure 6, NO_x emission rates, determined at 50% RH, varied between appliances from different manufacturers and ranged from 6 to 16 % mg/h of the ozone emission rate.

Performance of the Ozone Generator Appliance in the Research Test House

A series of tests in the research test house investigated our ability to predict indoor ozone concentrations from chamber derived emission rates, and investigated the performance of a sensor-feedback control system designed to maintain ozone concentrations at or below 50 ppb.

We determined the ozone deposition velocity in the house, determined the penetration factor for ambient ozone, and used the IAQ model RISK to predict the time history of ozone in the house during operation of an ozone generator air cleaner. We found that steady state predictions were generally good (e.g., within $\pm 15\%$ of observed) though the model did not always represent the concentration/time history as well. We also observed that in-room ozone concentrations stayed at or below 50 ppb when the generators were operated with the controller activated (see Figure 7). The tests of the ozone generator air cleaner with the sensor-controller activated were of 14 to 24 hr duration. Thus, these tests do not characterize long-term performance or effects of environmental variables on sensor-controller performance.

We are in the process of evaluating data from tests conducted to investigate the impact of the ozone generator on concentrations of VOCs in the environmental test chamber. Preliminary tests with styrene and limonene, common indoor air contaminants, suggest that the effect that the ozone generator has on IAQ can be predicted from ozone/VOC reaction rate constants published by atmospheric researchers over the past 30 years. Reaction products for the styrene/ozone tests are primarily benzaldehyde and formaldehyde.

To summarize what we have learned to date: Ozone generators may produce sufficient ozone to create hazardous ozone concentrations in indoor environments. The ozone emission rates vary as a function of RH. NO_x is produced as a byproduct of ozone generation. The model RISK appears to be useful for prediction of indoor concentrations of ozone. Limited tests in the research test house indicate that the feedback control system provided by one manufacturer maintains ozone concentrations at or below 50 ppb. On the other hand, though tests to date indicate that operation of an ozone generator air cleaner may result in somewhat lower concentrations of some compounds, greater exposure to formaldehyde and other aldehydes and organic acids is likely to result. (EPA Contact: Mark A. Mason, 919-541-4835. mason.mark@epa.gov)

Figure 5. The relationship between ozone generation rate and RH for three ozone generator air cleaners.

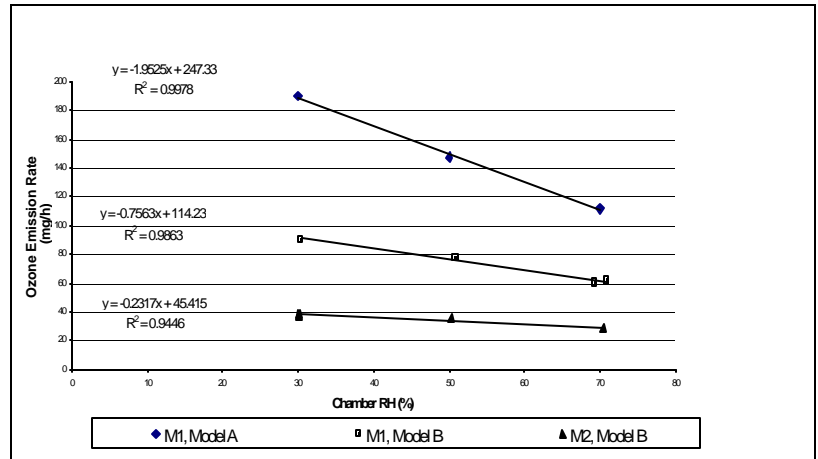


Figure 6. NO_x emission rates for selected ozone generator air cleaners determined at 50% RH.

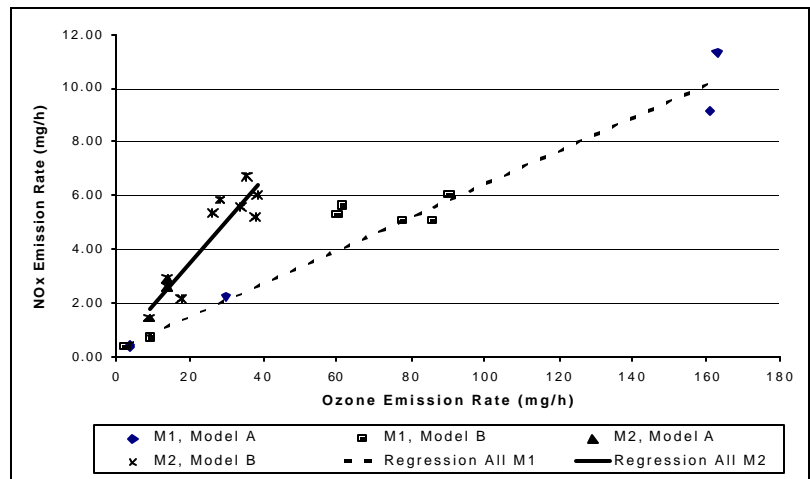
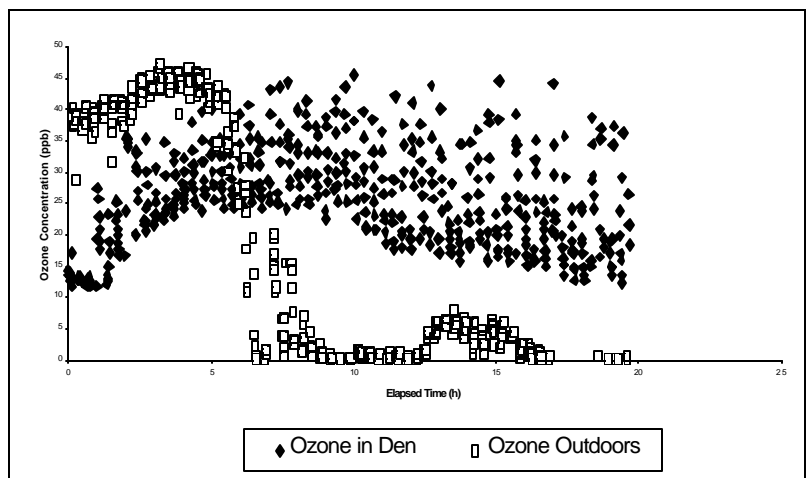


Figure 7. Ozone concentration out of doors and in a room of the research test house with ozone sensor-controller system of the ozone generator air cleaner activated.



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