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Presented at the 81st Annual Meeting of the
Air Pollution Control Association, Dallas, TX,
June 20–24, 1988, and to be published in the Proceedings

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April 1988

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Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

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AIR CLEANER EFFICIENCIES FOR REMOVAL OF NITROGEN DIOXIDE AND VOLATILE ORGANIC COMPOUNDS

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ABSTRACT

The objective of this research was to measure the initial effective cleaning rate (ECR) of selected air cleaners for removing NO_2 and six representative volatile organic compounds (VOC) from air. Four portable air cleaners, representing three different principles of particle removal and incorporating activated carbon, were investigated. Experiments were conducted in a closed Environmental Chamber using analyte concentrations similar to those reported in residences. Effects of relative humidity, temperature, filter particle loading and saturation of the adsorbents on the ECRs were not investigated in this preliminary study. However, the effect of extended usage was investigated for one air cleaner.

Two of the air cleaners were found to be reasonably effective initially in removing NO_2 and five of the six VOC. These two devices had relatively high flow rates and the greatest amounts of activated carbon. None of the devices removed dichloromethane, the VOC with the highest vapor pressure. One air cleaner emitted 1,1,1-trichlorethane and formaldehyde. After being used in a residence for 150 hours, the ECRs for the air cleaner which had the highest initial values decreased substantially. This use was only about 15% of the predicted filter lifetime. Conversion of NO_2 to NO was also observed for this device but only after it had been used in the residence.

KEY WORDS: Air cleaners, effective cleaning rate, nitrogen dioxide, volatile organic compounds

INTRODUCTION

An increased public awareness of indoor air pollution has resulted in the development of a substantial market for portable air cleaners for use in residences and offices. Portable air cleaners are designed primarily for removal of suspended particles such as pollen and tobacco smoke. Two earlier studies in this laboratory evaluated a variety of portable air cleaners for removal of respirable particles[1] and radon progeny, both free and particulate - attached.[2] Recently, some manufacturers have claimed that their devices also remove gaseous pollutants such as oxides of nitrogen and sulfur and volatile organic compounds (VOC). There is, however, little information available to consumers on the performance of these devices for gaseous pollutants.

The objective of this research was to investigate the effective cleaning rates (ECR) of selected portable air cleaners for removing NO_2 and VOC from air when first exposed to concentrations typical of those found indoors. This investigation did not examine effects of relative humidity and temperature, the effects of filter loading with particles, saturation of the carbon adsorbents or possible later releases of adsorbed compounds. The effect of usage on VOC removal efficiency was investigated for only one air cleaner.

Nitrogen dioxide and VOC were specifically selected as the indoor pollutants of interest for this research because they are commonly found at elevated concentrations in residential indoor air and because they have documented health effects. High concentrations of NO_2 have been observed in homes with gas stoves and in emissions from gas stoves, kersone heaters, and other unvented comvustion appliances.[3-6] Elevated concentrations of NO_2 have been associated with pulmonary edema, broncho-constriction and increased respiratory infection.[7] The VOC are an ubiquitous mixture of compounds which includes a number of carcinogens and teratogens. Major classes of VOC which have been found in indoor environments include aliphatic and aromatic hydrocarbons, chlorinated hydrocarbons, aldehydes and ketones.[8-11] Irritant and central nervous system effects as well as hypersensitivity reactions have been associated with exposures to these compounds. The VOC may be emitted continuously from

building materials and furnishings and/or intermittently by combustion appliances and the use of a variety of household and personal products.

Four portable air cleaners, representing three different principles of particle removal, were selected for the study. All incorporated some activated carbon. Experiments were conducted in a 20-m^3 Environmental Chamber operated in static mode. For each air cleaner, the chamber was spiked with NO_2 and a mixture of six VOC. The decays in concentrations of these compounds were measured over a period of at least four hours while the air cleaners were in operation. The six VOC were selected to represent the major classes of organic compounds found in indoor air.

As part of this investigation, reactions of NO_2 and VOC on the surface of the activated carbon used in the air cleaners were considered. Several investigators[12,13] have reported evidence for the reduction of NO_2 to NO on materials found in indoor environments. Gundel *et al.*[14] have recently reported that NO_2 is converted to NO on activated carbon in the presence of water vapor. Further reaction led to the formation of nitric and nitrous acids on the carbon surface. If VOC are present, there is a potential for the formation of nitro-organic compounds. The concentration of NO in the chamber was monitored in all experiments as an indicator of possible chemical reactions of NO_2. The concentration of ozone was monitored in the chamber during the experiment with the air cleaner which used an electrostatic precipitator for particle removal.

EXPERIMENTAL METHODS

Description of the Air Cleaners

Table I presents descriptions of each of the four air cleaners used in these experiments. The air cleaners were selected to represent a range of sizes as well as somewhat different principles of particle removal. All are intended primarily for use in residences and are portable, stand-alone devices, not intended for duct installation.

Air flow rates for the four air cleaners, either stated or estimated from product information provided by the manufacturers, range between 68 and 680 m^3h^{-1}. The devices designated PF1 and PF2 have multiple stage filter cartridges employing layers of glass fibers for particle removal. The ES unit has a HEPA filter for particle removal. The fourth device, EP, removes particles by electrostatic precipitation rather than filtration. All of the devices have some activated carbon positioned after the primary particle removal device, although, by visual inspection, the amount of carbon varies considerably among the devices. The ES air cleaner contains the most carbon, which is combined with potassium permanganate. The PF2 air cleaner contains activated carbon in combination with an oxidation catalyst. Only the manufacturer of this device makes specific claims about removal of gaseous pollutants in the product information.

Air flow rate measurements were made at each speed setting of each air cleaner. The flow rate measurement was made using either a pitot tube or an orifice plate flowmeter.[15] These devices were installed in a 4-m length of 15-cm ID pipe. A blower was installed at one end of the pipe to exhaust air through the pipe. The intake of the air cleaner was coupled to the other end of the pipe with a flexible polyethylene bag. Flows through the system were matched by adjusting the speed of the blower motor with a Variac so that the static pressure in the polyethylene bag was zero when the air cleaner was operating at the desired speed. Thus, the air flow through the air cleaner was not affected by the attachment of the measurement system. Differential pressure measurements were made with either a micromanometer or a Magnahelic gauge. Air flow rates were also measured using a calibrated hot-wire anemometer. Each air cleaner was set at its maximum speed and a minimum of nine

measurements of air velocity were made across the face of the air inlet. Flow rates for each device were calculated as the average of the measurements times the inlet area and were compared to those determined using the orifice plate or pitot tube.

Table I presents the maximum air flow rates measured for each of the four air cleaners. The EP air cleaner had the highest flow rate while the PF1 air cleaner, the smallest device, operated at the lowest flow rate. For three of the air cleaners, the agreement in the air flow rates measured by the pitot tube or orifice plate and by the hot-wire anemometer were within ten percent. However, for the PF2 unit, the flow rate determined with the anemometer was 21 % higher than that determined by the other method. Because of the design of this device, the flow rate is very sensitive to the pressure drop across the fan and the polyethylene-bag interface probably introduced a small additional pressure resulting in an erroneously low flow rate. For this device, the flow rate measured with the anemometer was judged to be the more accurate measure and was used in calculations. For the other air cleaners, the pitot tube or orifice plate measurement was used. With the exception of the PF1 air cleaner, the measured flow rates were all much lower than those indicated by the manufacturers. Olander *et al.*[16] have reported similar discrepancies between the flow rates reported by manufacturers and those measured in the laboratory.

Protocols for Chamber Experiments

Experiments were conducted in the LBL Environmental Chamber. The chamber encloses a volume of 20 m^3 with interior dimensions of 3.66 m (length) x 2.46 m (width) x 2.23 m (height). The walls, floor and ceiling are insulated with a 10-cm layer of high-density polyurethane foam. All interior surfaces are clad with stainless steel. The door and interior seams are sealed with silicone gasket material. Electrical and plumbing feedthroughs are also sealed. The synthetic materials used in construction of the chamber were selected, in part, for their low emissions of VOC. Background concentrations of ten common low-boiling organic compounds were measured in chamber air and were found to be less than 2 ppbv for each compound. The chamber is equipped with a single-pass ventilation system. Inlet air is drawn from outside the laboratory building by a variable-speed blower and passes through a coarse filter, a HEPA filter, and a charcoal filter in series. The chamber was ventilated prior to each experiment and then was operated in static mode (without mechanical ventilation), during the experiments with the air inlet and exhaust sealed at the chamber wall.

Atmospheric pressure inside the chamber was 742 ± 5 torr during the experiments. Air temperature in the chamber was maintained at 23 ± 2 °C. Relative humidity in the chamber was not controlled but averaged 47 ± 9%.

The air cleaners were used as received without modification. Each air cleaner was operated at its maximum speed setting. The air cleaner was positioned in the center of the chamber on a table at a base height of 70 cm. New filter cartridges or charcoal filters were used in all experiments, except for the duplicate experiments conducted with the PF2 device in which the same filter cartridge was used in both experiments. The only prior usages of the devices were for checkout and for air flow rate measurements.

During the ventilation period, the air cleaner and an oscillating fan used for mixing were positioned in the chamber. The ventilation system was then turned off and the air inlet, air outlet, and the door were closed. These remained closed until the conclusion of the experiment. At this point, the laboratory and chamber background of NO_2 and NO were measured and a sample for the determination of the chamber background of VOC was collected. Next, the chamber was spiked with the analytes to the desired concentrations. For NO_2, a gaseous standard was injected into a port connected to an air stream flowing to the mixing fan. For the first six experiments, VOC were introduced into the chamber by injecting

a measured volume of a liquid mixture of the VOC into the same port, which was heated. For the last two experiments, a measured volume of a liquid mixture of VOC was placed in a Petri dish on a hot plate near the mixing fan and evaporated over a 10-minute period. Chamber air was mixed for approximately thirty minutes after injecting the analytes. At the end of this period, the mixing fan was turned off and the air cleaner was turned on remotely from the outside of the chamber. Monitoring for NO_2 and NO commenced with the injection of the analytes. Sample collection for VOC commenced approximately ten minutes after the injection of the VOC. Nitrogen dioxide and NO were monitored continuously throughout the remainder of the experiment. Duplicate samples of VOC were collected at regular intervals throughout the experiment. The sampling interval was varied depending upon the decay rate of the VOC, determined from semi-quantitative measurements made with an on-line gas chromatograph. If these measurements indicated that the decay rate was relatively high, the initial sampling intervals were ten minutes and were then extended as the experiment progressed. Sample volumes increased proportionately.

Air cleaner removal efficiencies for NO_2 were determined at a chamber concentration of ~500 $\mu g\ m^{-3}$. This concentration is about five times the mean NO_2 level reported for kitchens equipped with gas stoves[17] but is within the range of peak (<30 minutes) indoor concentrations recently reported by Harlos and Spengler[18]. The average initial concentration for five experiments was 484 $\pm$ 53 $\mu g\ m^{-3}$. Six VOC, representative of five major classes of VOC typically found in indoor environments were selected for the experiments: 1) n-heptane for aliphatic hydrocarbons, 2) toluene for aromatic hydrocarbons, 3) dichloromethane (methylene chloride) and tetrachloroethylene for chlorinated hydrocarbons, 4) hexanal for aldehydes, and 5) 2-butanone (methylethylketone) for ketones. The average initial chamber concentrations for these compounds for the first five experiments were: 1) n-heptane - 683 $\pm$ 150 $\mu g\ m^{-3}$, 2) toluene - 651 $\pm$ 131 $\mu g\ m^{-3}$, 3) dichloromethane - 258 $\pm$ 100 $\mu g\ m^{-3}$, 4) tetrachloroethylene - 353 $\pm$ 102 $\mu g\ m^{-3}$, 5) hexanal - 185 $\pm$ 17 $\mu g\ m^{-3}$, and 6) 2-butanone - 131 $\pm$ 27 $\mu g\ m^{-3}$. These concentrations and the relative proportions of the six VOC were selected to reflect those reported for their respective classes in indoor air[8,9,11].

Experiments were generally conducted over four hours. If the decay rates of NO_2 and VOC were relatively low, all of the valid data for this period, starting with the time the air cleaner was turned on, were included in the linear regression analyses. In experiments in which the decay rates were rapid, concentrations decreased to very low values before the end of the experiment. For NO_2, decay rates were calculated from the time the air cleaner was turned on until concentrations decreased to 15 to 40 $\mu g\ m^{-3}$ and the decay rate began to decline. This leveling off of concentrations was due in part to the increased significance of infiltration at low concentration. In addition, the equilibrium between adsorption and desorption from the activated carbon may have been reached at this level[19]. For VOC, decay rates were calculated using the data from the start of air cleaner operation until concentrations declined to less than 5 $\mu g\ m^{-3}$ (approximately 1 ppbv for the compounds in this study). This cut-off was selected since the sample volumes were not optimized for these lower concentrations.

Background decay rates of NO_2 and VOC in the chamber were determined in two initial experiments in which an air cleaner was operated without its filter to provide mixing which would be similar to that which would occur during subsequent experiments. These background decay experiments also provided information on the reproducibility of the decay rates. To further evaluate the reproducibility of the decay rates, duplicate experiments were conducted with one air cleaner which was expected to have relatively high removal rates. At the conclusion of the study, an additional experiment was conducted with the same air cleaner, after it had been used in a residence, to obtain an indication of the effects of extended use on removal rates.

Air Sampling and Analysis

Air for measurement of NO_2 and NO was drawn from multiple locations in the chamber to a common mixing manifold. Fifteen sample locations were used. The sample locations were near the four corners and near the center of the chamber at three heights - near the floor, mid-height and near the ceiling. With the exception of the central sampling location, sample locations were 25-30 cm from adjacent chamber surfaces. Total flowrate was 2 L min^{-1}. Although not regulated, flow rates at the individual locations were approximately equal. Components of the sample line were Teflon and stainless steel.

A chemiluminescent NO_x analyzer (Model 14 D/E, Thermo Electron Corp.), was used for the analysis of NO_2 and NO. The instrument has a noise level of 10 $\mu g\ m^{-3}$ and a lower limit of detection of 20 $\mu g\ m^{-3}$ for NO_2. Standards of NO_2 for calibration of the analyzer were generated by gas dilution of the output of a NO_2 permeation cylinder held at 50±0.1°C in a permeation oven (Model 8500 Permacal, Monitor Labs, Inc.). Electronic mass-flow controllers were used to regulate flow through the oven and the flow of dilution gas. Standards of NO were generated by dilution of the output of a 5.4 ppmv gas standard cylinder. Multipoint calibration curves for NO_2 were generated immediately before and after each experiment.

During the experiment with the EP air cleaner, ozone concentrations in the chamber were monitored with a Model 1003AH Ozone Monitor (Dasibi Environmental Corp.). The instrument zero and span were checked at the beginning and end of the experiment as recommended by the manufacturer. Air was drawn from mid-chamber to the Ozone Monitor through Teflon tubing.

Samples for VOC were collected from air drawn from a location near the center of the chamber through Teflon tubing. Duplicate samples were collected on multisorbent samplers containing Tenax-TA, Ambersorb XE-340 and activated charcoal (Part No. ST-032, Envirochem, Inc.). Sampling flow rates were 113 $cm^3\ min^{-1}$ (20°C, 760 torr). Flow rates were regulated with electronic mass-flow controllers placed between the samplers and the vacuum source. Sample volumes were varied according to expected analyte concentrations, and typically ranged between 0.5 and 2 L. Samplers were capped and stored at -10°C in glass tubes until analysis.

The analytical procedure for samples collected on multisorbent samplers has previously been described[11,20]. In brief, the VOC are thermally desorbed from a sampler and introduced into a capillary gas chromatograph (GC) with a UNACON® Model 810A (Envirochem, Inc.) sample concentrating and inletting system. Sample components are resolved with a GC (5790A series, Hewlett Packard Co.) equipped with liquid-nitrogen subambient cooling and a fused-silica capillary column (DB-1701, J and W Scientific, Inc.). The GC is connected via a direct capillary interface to a 5970B series Mass Selective (MS) Detector (Hewlett-Packard Co.). The detector is operated to monitor multiple, individually-selected mass ions. For each compound of interest, a mass ion with high relative intensity is chosen as the quantitative ion, and a characteristic ion is chosen as a qualifying ion for confirmation of compound identity. A standard gas mixture was prepared by injecting an aliquot of a liquid mixture of the six VOC into a helium-filled 2-L flask with septum cap which was then heated and maintained at 65°C. A sample was withdrawn from the flask with a gas-tight syringe and was injected onto a multisorbent sampler for analysis. Multiple-point calibration curves were prepared for the six VOC for each experiment. At the beginning and end of each experiment, a large air-volume sample was collected for GC-MS scan analysis to determine if compounds other than the six VOC added to the chamber were present.

A Photovac 10S50 portable gas chromatograph (Photovac, Inc.), equipped with a CSP 20M column and a photoionization detector, was used for near real-time monitoring of the VOC. This information was used to determine the collection intervals and sample volumes for the

VOC samples obtained with the multisorbent sampler.

Data Analysis

Data analysis was similar to that used for previous studies of particle removal by air cleaners[1,2]. The rate of decay of NO_2 or VOC concentration, C, within a chamber of volume, V, with the air cleaner in operation, can be described by the differential mass balance equation:

$$\frac{dC}{dt} = -\frac{Q_v C_{ex}}{V} - KC - \frac{Q_d (C_{in} - C_{out})}{V} , \qquad (1)$$

where

Q_v = The flow rate of ventilation air (infiltration),

C_{ex} = the concentration of analyte in outgoing ventilation air,

K = a constant that accounts for analyte removal by mechanisms other than ventilation, such as losses to walls,

Q_d = the flow rate of air through the air cleaner,

C_{in} = the analyte concentration in the air entering the air cleaner, and

C_{out} = the analyte concentration in the air leaving the air cleaner.

The chamber was used in static mode, i.e., without constant mechanical ventilation. Past experiments indicate that infilitration is 0.03 ± 0.01 h^{-1}. Therefore, Q_v is approximately zero and equation (1) may be written

$$\frac{dC}{dt} = -KC - \frac{Q_d (C_{in} - C_{out})}{V} . \qquad (2)$$

The efficiency of the air cleaner in removing gaseous pollutants is defined as:

$$\eta = \frac{(C_{in} - C_{out})}{C_{in}} . \qquad (3)$$

Because of the close proximity of the inlet and outlet of the air cleaner, there may be a short-circuiting effect, i.e., some of the "cleaned" air is re-entrained into the inlet of the device rather than mixing completely with the air in the chamber. Thus, a short-circuiting factor, E_d, is defined as:

$$E_d = \frac{C_{in}}{C} . \qquad (4)$$

Substituting Equations (3) and (4) into Equation (2) yields

$$\frac{dC}{dt} = - \left[K + \frac{\eta E_d Q_d}{V} \right] C \quad . \tag{5}$$

This describes the experimental decay rate of the analyte in the chamber with the air cleaner in operation, and the term in brackets is the experimental decay constant, λ_{ex}. Integration of Equation (5) between t = o and t = t_1 yields

$$\ln C = - \lambda_{ex} t_1 + \ln C_o \quad , \tag{6}$$

where C_o is the initial concentration in the chamber and C is the concentration at time, t_1.

The slope of a plot of ln C versus time is then equal to λ_{ex}. This slope was determined by a least squares analysis of the data. The standard error of the slope was used to estimate the 95% confidence interval of λ_{ex}. Assuming that the decay in analyte concentration due to chamber losses, K, is the same with mixing only and with the air cleaner in operation, then the rate of removal by the air cleaner, $\lambda_{ac} = \eta E_d Q_d / V$, can be determined as the difference between the slopes determined with mixing only and with the air cleaner in operation.

Two additional parameters were calculated from the experimental data, the effective cleaning rate (ECR) and the system efficiency. The ECR is the product of λ_{ac} and the chamber volume. This is an air flow rate that represents the effective amount of analyte-free air produced by the air cleaner per unit time and is useful in estimating the effects of the air cleaner in rooms of various sizes and in comparing air cleaning to ventilation as a mitigation technique. The system efficiency is the ECR divided by the actual air flow through the air cleaner, Q_d. The uncertainties in these calculated quantities were estimated by the propagation of errors.

RESULTS

The PF2 air cleaner was operated, without its filter cartridge, in the two experiments which were conducted to measure the background decay rates of NO_2 and VOC. Background removal rates for NO_2 and the VOC ranged from 0.08 to 0.12 h^{-1} and were not significantly different for the different compounds. The differences in the background decay rates between the first and second experiments ranged from about three to ten percent for the individual VOC compounds, and were not statistically significant ($p<0.05$). The average background decays for the individual compounds were subtracted from the total removal rates measured in the experiments with the air cleaners to obtain the removal rates due only to the operation of the air cleaners.

The four air cleaners were evaluated on the basis of their effective cleaning rates (ECRs) for NO_2 and the six VOC. These ECRs are summarized in Table II which shows that there were substantial variations among the air cleaners with respect to ECRs. The PF2 device had the highest ECR for NO_2, which averaged 74 m^3 h^{-1}. The ES air cleaner had the next highest ECR for NO_2 of 41 m^3 h^{-1}, while the remaining devices were quite ineffective for NO_2 removal. None of the air cleaners removed dichlormethane. Both the PF2 and ES devices had nearly equivalent ECRs of 30 to 50 m^3 h^{-1} for the other five VOC. The EP air cleaner was less effective for these compounds with ECRs of 8 to 18 m^3 h^{-1} while the PF1 device was relatively ineffective for VOC removal.

Figure 1 presents the decay curves for NO_2 and the VOC which were obtained during the second experiment with the PF2 air cleaner, which had relatively high rates of removal. The

concentrations range over several orders of magnitude and are plotted on a logarithmic scale. The decay of NO_2 is very linear. Instrumental noise increased as the NO_2 concentration approached the 20 $\mu g\ m^{-3}$ detection limit (ln = 3). The slopes of the decay curves for 2-butanone, n-heptane, toluene and tetrachloroethylene are also very linear and are nearly equivalent to each other. Hexanal initially decayed at about the same rate, but the rate decreased at concentrations below 20 $\mu g\ m^{-3}$ yielding a lower overall decay rate.

The PF2 device was found to emit 1,1,1-trichloroethane at a rate of about 19.2 mg h^{-1}. This compound reached a maximum concentration in the chamber of 740 $\mu g\ m^{-3}$ after about an hour of operation. The concentration then decayed at a rate of 0.09 h^{-1} (chamber background decay rate) over the remainder of the experiment. This organic solvent is presumably used in the manufacture of one of the components of the air cleaner.

In the second experiment which was conducted with the PF2 air cleaner, the ECR for NO_2 decreased from 79 to 71 $m^3\ h^{-1}$ and the difference was statistically significant ($p=0.01$). The ECRs for 2-butanone, n-heptane and hexanal in the second experiment were also significantly lower ($p \leq 0.05$) than in the first. Differences in the ECRs of the remaining compounds were less than 10 % and were not significant. The statistically significant differences which were observed for four of the compounds may reflect changes in the capacity of the filter element due to use (the same filter was used in both experiments), e.g., saturation of adsorption sites with VOC, NO_2 and water vapor, or other variables in the experiments which are not reflected in the estimated uncertainties.

The efficiencies of removal, obtained by dividing the ECRs by the measured flow rates, are summarized in Table III. Efficiencies of removal ranged from a few percent to as high as 42 %. The PF2 air cleaner had the highest efficiency for removal of NO_2 while the PF2 and ES devices had similar efficiencies of about 20 % for the removal of VOC, exclusive of dichloromethane. The PF1 and EP air cleaners had the lowest efficiencies for removal of both NO_2 and VOC, ranging from 0 to 6.3 %.

Concentrations of NO were monitored in the chamber in all of the experiments to investigate possible chemical reactions that might occur on the surface of the activated carbon. There was no evidence of NO formation in any of the experiments using new filter elements. In the experiment with the EP device, no ozone generation was observed. The GC-MS scan analyses for additional VOC that might have been formed by reactions on the activated carbon showed no evidence of such compounds.

After the experiments to determine the initial effectiveness of the air cleaners with new filters were completed, the PF2 air cleaner was operated for two and a half months in the residence of non-smokers. The same filter cartridge that was used in the duplicate experiments in the chamber was used. The device was operated in this residence at the medium speed setting (111 $m^3\ h^{-1}$) for several hours a day, for a total time of about 150 hours. Thus, total operating time was about 160 hours and total air volume was approximately 18,500 m^3. Table IV compares the ECRs measured in the first experiment in the chamber to those measured in an identical experiment conducted after the device (and filter cartridge) had been operated in the residence. For NO_2, the ECR was reduced to about one-third of the initial value. For the five VOC which were removed by the air cleaner, the ECRs after field operation were about half of the initially measured values. The product literature for this device states the estimated filter life is about 1000 hours or about 3 months.

Emissions of 1,1,1-trichloroethane from the PF2 air cleaner were considerably reduced compared to the initially measured rate. The occupants of the residence had complained of an odor emitted by the air cleaner. Since the housing of this device is particleboard with an exposed surface area of one square meter, formaldehyde was also measured in the chamber during this last experiment. The measured formaldehyde emission rate of 0.5 mg h^{-1} is

consistent with values reported in the literature for particleboard with this surface area.[21] The presence of acetone and propanol were also noted in the chamber during this experiment. These compounds were presumably adsorbed in the house and subsequently desorbed in the chamber.

Figure 2 shows the concentrations of NO, NO_2 and NO_x in the chamber over the course of the last experiment. In contrast with previous experiments, conversion of NO_2 to NO, a less toxic compound, was observed. Nitrous and nitric acids were not measured but, within the experimental uncertainties, all of the NO_2 can be accounted for by conversion to NO. The GC-MS analysis of a large volume air sample collected at the end of this experiment gave no evidence of the formation of nitro-organic compounds.

DISCUSSION

Whitby *et al.*[22] have suggested as a criterion for evaluating air cleaners that the ECR should be equivalent to one air change per hour for a given room. This is based on the assumption that this is about the minimum ventilation rate needed to control a moderate contamination problem. For any individual air cleaner, the air flow through the device as well as the amount of adsorbent material and the configuration of the adsorbent filter will affect the ECRs.

The PF2 and ES air cleaners have high air flow rates and, from visual inspection, have the highest amounts of activated carbon of the four air cleaners investigated. Correspondingly, these two devices had the highest ECRs for both NO_2 and VOC, exclusive of dichloromethane which was not removed by any device. The ECRs for these two air cleaners generally meet the criterion suggested by Whitby *et al.* for a room volume of about 40 m^3 (approximately 13 ft x 13 ft x 8 ft). With the PF2, device which had a catalyst mixed with the activated carbon, the ECR for NO_2 was almost twice those for the five VOC. More effective removal of NO_2 than of VOC was not observed for any of the other devices. This suggests that the catalyst enhances the removal of NO_2 over that obtainable with activated carbon alone.

The other two air cleaners, the small PF1 device and the EP device had lower ECRs for the removal of NO_2 and VOC. The PF1 device has the lowest air flow rate and also, from inspection, only a small amount of activated carbon. The EP device has the highest flow rate and more carbon than the PF1 device but was much less effective than either the PF2 or the ES air cleaners in removing NO_2 and the VOC. The filter in this device has granulated activated carbon (1-2 mm in diameter) loosely dispersed throughout a cardboard grid of open triangles. There was considerably less carbon and more void space between the carbon pellets in the EP device than in the ES device which has an activated carbon filter of similar design. Thus, in order to be adsorbed by the carbon, the gases have to diffuse across greater distances. The high volumetric flow rate also reduces the residence time of the gases in the vicinity of the carbon.

The results reported here for NO_2 can be compared to those reported by Humphreys[23] and by Canine[24]. Humphreys evaluated two air cleaners with activated carbon, one of which incorporated a catalyst. He reported ECRs of 13 and 68 $m^3\ h^{-1}$ for NO_2 removal, with the higher value found for the device with the catalyst. The high value is in very good agreement with the average of 74 $m^3\ h^{-1}$ measured for the PF2 device which also incorporates a catalyst. Canine reported removal rates for NO_2 and formaldehyde for 15 air cleaners, most of which had activated carbon. The ECRs which can be calculated from the data ranged from 0 to 10.2 $m^3\ h^{-1}$ for NO_2 and from 0 to 5.1 $m^3\ h^{-1}$ for formaldehyde. Although air cleaners of comparable size and type to those in this study were included, the values for NO_2 removal are low relative to those for the PF2 and ES devices. The reason for this discrepancy cannot be determined since the Canine report contained little experimental detail.

None of the air cleaners investigated here removed dichloromethane, an organic solvent commonly used in paint removers and other consumer products. The vapor pressure of this compound at 25°C of 427 mm[25] is four times higher than that of the compound with the next highest vapor pressure, 2-butanone (95.5 mm).

The effects of extended operation of the air cleaners on the ECRs and removal efficiencies were investigated for only one air cleaner in this study, the PF2 unit. The manufacturer of this device recommends changing the filter after about 1000 hours of operation. The second experiment with the PF2 unit, in which the same filter cartridge was used and small reductions in the ECRs for NO_2, n-heptane, toluene and hexanal were observed, suggests that removal efficiencies may be reduced after only four hours of operation. When the PF2 air cleaner was reexamined after 160 hours of operation (approximately 15% of the filter lifetime), the ECRs were half or less than half of the initially measured values. Further investigation of changes in the ECRs with use over extended periods would be of value for air cleaners which have high initial ECRs and removal efficiencies.

For all of the experiments conducted with new filters, no products resulting from chemical reactions occurring on the surface of the activated carbon were observed in the chamber air. One air cleaner, the PF2 device, did, however, emit 1,1,1-trichloroethane and formaldehyde. The 1,1,1-trichloroethane was presumably from the materials used in the manufacture of some component, while the formaldehyde was probably from the exposed particleboard. After this air cleaner had been operated in a residence for 150 hours, it converted NO_2 almost entirely to NO in a subsequent experiment (Figure 2). There was no evidence of the formation of nitrous or nitric acids or of nitro-organic compounds in this experiment. However, the work of Gundel *et al.*[14] suggests that, for more extended operation at high concentrations of NO_2, both nitrous and nitric acid might be formed. In view of this, further investigations of possible chemical reactions would be prudent.

In summary, both the PF2 and ES air cleaners were reasonably effective <u>initially</u> in removing NO_2 and five of the six VOC from a room-sized chamber. The PF1 device, however, was not effective for these compounds, and the EP device was only slightly better. None of the four air cleaners removed dichloromethane. The PF2 air cleaner emitted both 1,1,1-trichloroethane and formaldehyde, presumably from materials used for its construction. The ECRs and efficiencies of the PF2 air cleaner decreased substantially after 150 hours of operation in a residence. Similar decreases in ECRs and efficiencies with use can reasonably be expected for the other air cleaners, as well. There was also evidence of chemical reactions occurring after extended operation which was not observed in the initial experiments. Within the experimental uncertainties and conditions of the experiment, the PF2 air cleaner converted all of the NO_2 to NO, a less toxic compound. Further investigation is needed to determine ECRs and efficiencies over periods of extended use for air cleaners which have relatively high ECRs. Investigation of possible chemical reactions occurring with extended use is also warranted.

ACKNOWLEDGEMENTS

This work was supported by the U. S. Consumer Product Safety Commission under Contract No. CPSC-IAG-86-1259 and by the Assisstant Secretary for Conservation and Renewable Energy, Office of Building and Community Systems, Buildings Systems Division of the U. S. Department of Energy under Contract No. DE-AC03-76SF00098. The authors gratefully acknowledge the assistance and comments of Bharat Bhooshan, Pauline Johnston, Warren Porter, Dave Grimsrud and Rich Sextro. We thank John Girman for special contributions in both the experimental stages and the final review of this research.

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TABLE I. Descriptions of air cleaners

AIR CLEANER TYPE	AIR CLEANER ID	DIMENSIONS W x H x D (IN)	DIMENSIONS $(FT)^2$ AND LOCATION OF AIR INTAKE	MAXIMUM AIRFLOW RATE[a] $m^3 h^{-1}$	BLOWER AND FILTRATION SYSTEM
Panel Filter	PF1	10 x 7 x 8	0.24 left	78	2-speed; foam prefilter; 3-stage filter cartridge with pleated and smooth layers of Filtrete material and activated charcoal pad; filter life ~3 months.
Panel Filter	PF2	17 x 20 x 12	1.30 back	226	3-speed; foam prefilter; 2-stage filter cartridge with pleated layer of borosilcate glass fibers and bonded filter of activated charcoal and a catalyst which removes or adsorbs CO, O3, NO_x, SO_x; filter life 1000 hr or ~3 months.
Extended-surface Filter	ES	14 x 11 x 19	0.69 front	228	Variable speed; foam prefilter; H.E.P.A.[b] filter; activated charcoal/Purasorb after-filter; H.E.P.A. filter life 2-4 years; charcoal filter life 4-6 months with average use (3-6 hr/day).
Electrostatic Precipitator	EP	23 x 14 x 8	0.55 bottom	274	Variable speed; expanded metal prefilter; electrostatic precipitator cell; activated charcoal after-filter; charcoal filter life 3-6 months.

a. Measured at highest speed setting with pitot tube or orifice plate for the PF1, ES and EP devices and with anemometer for the PF2 device
b. High Efficiency Particulate Arrestance

TABLE II. Effective cleaning rates for NO_2 and VOC

COMPOUND	EFFECTIVE CLEANING RATE ± 95% C.I.[a], $m^3\ h^{-1}$				
	PF1	PF2		ES	EP
		EXP 1	EXP 2		
NO_2	5.14 ± 0.08	79 ± 1	71 ± 2	42 ± 1	6.2 ± 0.2
Dichloro-methane	0	0	0	2 ± 1	0
2-Butanone	0	49 ± 13	37 ± 4	31 ± 4	8 ± 2
n-Heptane	3.1 ± 0.6	51 ± 2	41 ± 3	47 ± 1	18 ± 1
Toluene	3.2 ± 0.6	45 ± 2	41 ± 2	43 ± 4	17 ± 1
Tetrachloro-ethylene	2.5 ± 0.6	44 ± 2	41 ± 2	41 ± 2	14 ± 1
Hexanal	4.6 ± 0.9	39 ± 6	18 ± 4	37 ± 6	10 ± 2

a. C.I. = confidence interval

TABLE III. Efficiencies of removal for NO_2 and VOC

COMPOUND	EFFICIENCY OF REMOVAL ± 95% C.I.[a], Percent				
	PF1	PF2		ES	EP
		EXP 1	EXP 2		
NO_2	6.6 ± 0.4	42 ± 5	37 ± 4	18 ± 1	2.3 ± 0.1
Dichloro-methane	0	0	0	1.0 ± 0.5	0
2-Butanone	0	22 ± 8	16 ± 3	14 ± 2	3.0 ± 0.5
n-Heptane	4.0 ± 0.9	22 ± 3	18 ± 2	21 ± 2	6.4 ± 0.3
Toluene	4.2 ± 0.9	20 ± 3	18 ± 2	19 ± 3	6.3 ± 0.4
Tetrachloro-ethylene	3.2 ± 0.9	19 ± 3	18 ± 3	18 ± 2	5.2 ± 0.3
Hexanal	6.0 ± 1.4	17 ± 5	8 ± 2	16 ± 4	3.7 ± 0.6

a. C.I. = confidence interval

TABLE IV. Effective cleaning rates of the PF2 air cleaner before and after operation in a residence for approximately 150 hours

COMPOUND	EFFECTIVE CLEANING RATE ± 95% C.I.[a.], $m^3\ h^{-1}$	
	BEFORE (EXP 1)	AFTER
NO_2	79 ± 1	24 ± 1
Dichloromethane	0	0
2-Butanone	49 ± 13	14 ± 3
n-Heptane	51 ± 2	23 ± 4
Toluene	45 ± 2	19 ± 4
Tetrachloroethylene	44 ± 2	19 ± 4
Hexanal	39 ± 6	18 ± 4

a. C.I. = confidence interval

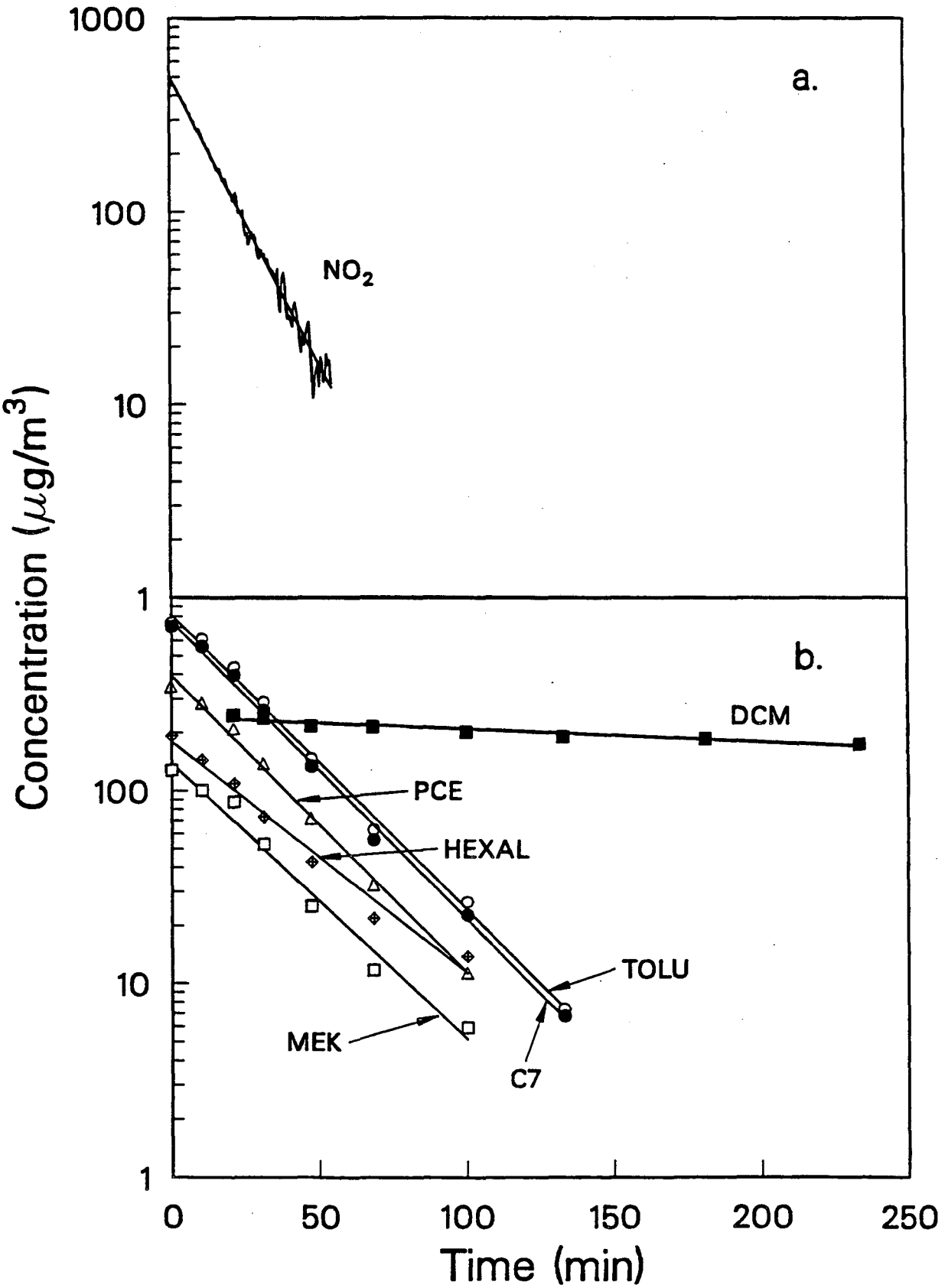

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Figure 1. Decay curves for NO_2 (a) and the six VOC (b) in the second experiment with the PF2 air cleaner. DCM = dichloromethane; MEK = 2-butanone (methyl ethyl ketone); C7 = n-heptane; TOLU = toluene; PCE = tetrachloroethylene (perchloroethylene); and HEXAL = hexanal.

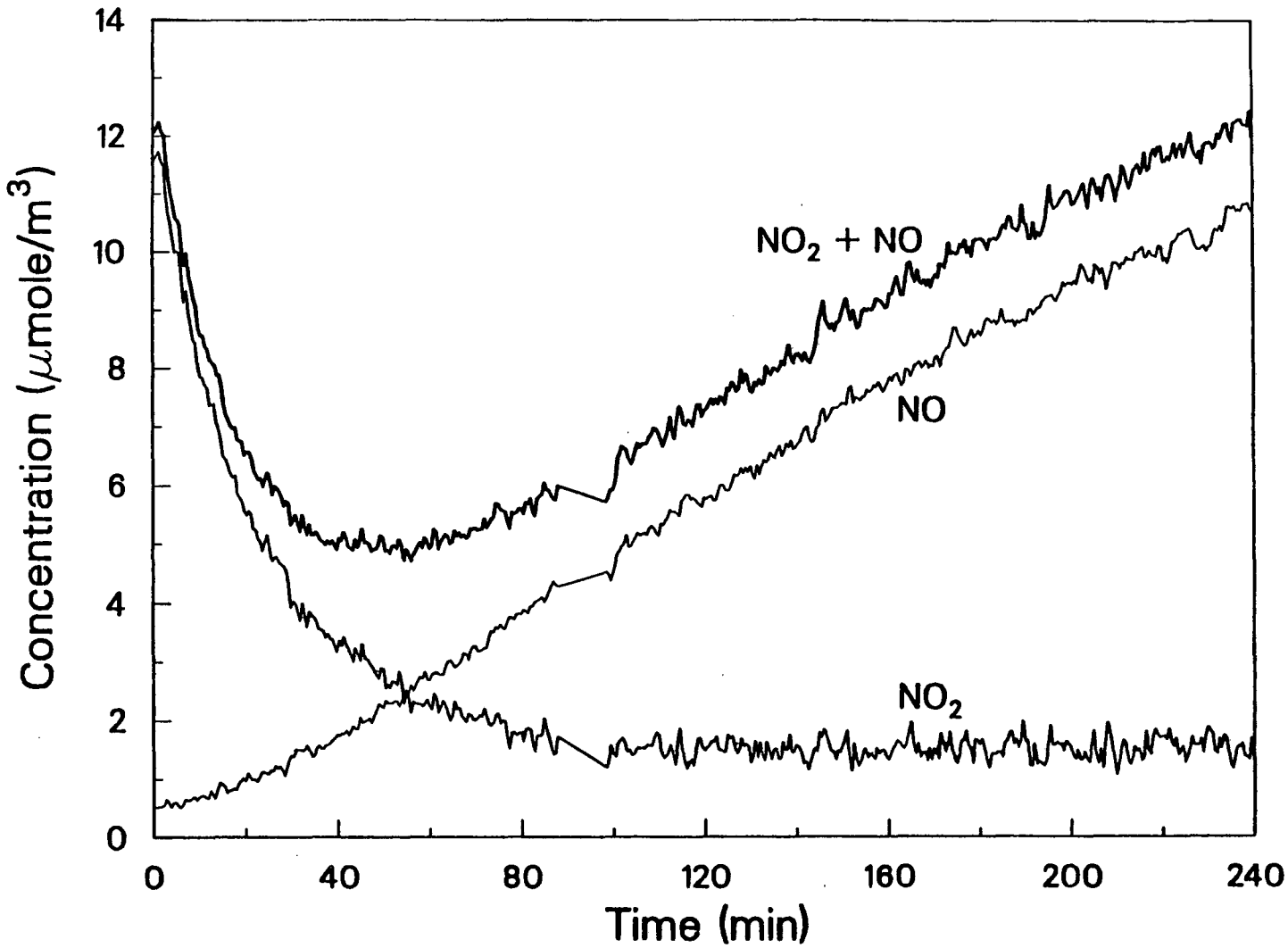

Figure 2. Concentrations of NO_2, NO and NO_x during the experiment with the PF2 air cleaner which was previously operated in a residence for 150 hours.

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