

# Quantification of Ozone Levels in Indoor Environments Generated by Ionization and Ozonolysis Air Purifiers

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## ABSTRACT

Indoor air purifiers are advertised as safe household products for health-conscious individuals, especially for those suffering from allergies and asthma. However, certain air purifiers produce ozone ( $O_3$ ) during operation, either intentionally or as a byproduct of air ionization. This is a serious concern, because  $O_3$  is a criteria air pollutant regulated by health-related federal and state standards. Several types of air purifiers were tested for their ability to produce ozone in various indoor environments at 40–50% relative humidity, including office rooms, bathrooms, bedrooms, and cars.  $O_3$  levels generated by personal wearable air purifiers were also tested. In many cases,  $O_3$  concentrations were well in excess of public and/or industrial safety levels established by U.S. Environmental Protection Agency, California Air Resources Board, and Occupational Safety and Health Administration. Simple kinetic equations were obtained that can predict the steady-state level of  $O_3$  in a room from the  $O_3$  emission rate of the air purifier and the first-order decay rate of  $O_3$  in the room. The additivity of  $O_3$  levels generated by independent  $O_3$  generators was experimentally demonstrated.

## INTRODUCTION

### Indoor Air Purifiers and Ozone

Because of growing air pollution problems in urban areas, indoor air purification has gained widespread popularity in recent years, with a large variety of indoor air purifiers being available to the public.<sup>1</sup> The main targets of indoor air purification are odorous volatile organic compounds (VOCs), dust, pollens, and airborne particles, which are suspected exacerbators of respiratory health problems.<sup>2–5</sup> From an operational standpoint, there are three basic

### IMPLICATIONS

Several studies including this one have found that operation of certain  $O_3$ -generating air purifiers in indoor environments can produce  $O_3$  levels exceeding health-related standards established by the U.S. federal and state governments. The steady-state  $O_3$  level produced by an air purifier operated in a closed room is proportional to the  $O_3$  emission rate of the air purifier and inversely proportional to the rate of removal of  $O_3$  from the room. Because of this dependence, even weak  $O_3$  generators, such as certain ionic air purifiers, are capable of maintaining steady-state levels of  $O_3$  in small rooms with unreactive surfaces that are well in excess of the health-protective standards.

types of air purifiers: (1) air filtration, (2) air ionization, and (3) ozonolysis of air impurities. Household use of certain air ionization and ozonolysis air purifiers has raised serious concerns, because they produce ozone ( $O_3$ ), a criteria air pollutant, either as a byproduct of air ionization or intentionally.

Most air ionization (ionic) devices work by charging airborne particles and electrostatically precipitating them on metal electrodes. Ionic air purifiers are available in a broad spectrum of designs, including large units for household use; smaller units for use in bathrooms, refrigerators, and closets; units intended specifically for cars; personal wearable units; ionic brushes; shoe cleaners; toothbrush disinfectors; and so forth. Depending on the design, some ionic air purifiers can emit  $O_3$  with a rate of a few milligrams of  $O_3$  per hour, which is comparable to the amount of  $O_3$  emitted by dry-process photocopiers during continuous operation.<sup>6,7</sup>

Ozonolysis air purifiers typically produce several hundred milligrams per hour of  $O_3$  with a goal of oxidizing VOCs in indoor air. However,  $O_3$  reacts exceedingly slowly with most saturated VOCs.<sup>8</sup> Ozonolysis half-lives of common VOCs found indoors are days or even years at 100 ppb of  $O_3$ .<sup>9</sup>  $O_3$  reacts considerably faster with VOCs containing unsaturated carbon-carbon bonds<sup>8,10</sup> found in cooking oils, air fresheners, cleaning products, and so forth,<sup>9,11</sup> and with certain polycyclic aromatic compounds<sup>12</sup> found in household materials (e.g., pigment dyes in carpets). However, these reactions produce carboxylic acids, epoxides, organic peroxides, aldehydes, and ketones as stable products, some of which may result in adverse health effects.<sup>13–17</sup> Reactions of  $O_3$  with unsaturated VOCs are known to produce hydroxyl radical (OH) as an intermediate,<sup>18–21</sup> which further contributes to the diversity of oxidation products.  $O_3$  treatment may affect the particle size distribution, but it generally does not reduce the overall concentration of particles in the air. In fact, new ultrafine particles are likely to be created if an ozonolysis air purifier is used in a room with a large concentration of gaseous unsaturated VOCs, such as terpenes.<sup>22–24</sup>

The level of  $O_3$  required to efficiently kill bacteria is also harmful to humans. Indeed, U.S. Environmental Protection Agency (EPA) provided a comprehensive assessment of the effectiveness and health consequences of  $O_3$  generation indoors stating that, “at concentrations that do not exceed public health standards,  $O_3$  is generally ineffective in controlling indoor air pollution.”<sup>25</sup> Reviews by Boeniger<sup>26</sup> and Weschler<sup>9</sup> similarly concluded that,

**Table 1.** Health-based standards for O<sub>3</sub> mixing ratio in the air established by the U.S. government.

Agency	Standard	Exposure Time	Mixing Ratio (ppb)
EPA	NAAQS	1-hr average	120
EPA	NAAQS	8-hr average	80
CARB	California AAQS	1-hr average	90
CARB	California AAQS	8-hr average	70
NIOSH	IDLH		5000
NIOSH	PEL	15-min	100
OSHA	PEL	8-hr average	100
OSHA	STEL	15-min	300
CARB	Stage 1 smog alert		200
CARB	Stage 2 smog alert		350
CARB	Stage 3 smog alert		500

“ozone is not a practical and effective means of improving indoor air quality.” The California Air Resources Board (CARB) issued an official statement in early 2005 expressing a serious concern about O<sub>3</sub>-generating air purifiers and recommending the public avoid using these devices.<sup>27</sup> In February 2005, CARB released a draft report to the California legislature on indoor air pollution, which stated that, “Air cleaners that generate ozone intentionally should not be used indoors. Independent studies by the U.S. EPA, the Consumers Union, and others have shown that these devices can emit very high amounts of ozone—several times the state ambient air quality standard. Additionally, ozone generators do not effectively destroy microbes, remove odor sources, or reduce indoor pollutants enough to provide any health benefits.”<sup>28</sup>

### O<sub>3</sub> Health Effects and Regulations

The detrimental health effects of O<sub>3</sub> are well known and have been extensively reviewed.<sup>29–35</sup> In addition to directly affecting humans breathing O<sub>3</sub>-polluted air, O<sub>3</sub> can react with indoor surfaces,<sup>9,36–39</sup> such as carpets, linoleum, clothing, furniture, and so forth, releasing volatile oxidation products that may have adverse health effects.<sup>15,17</sup> For example, aldehydes are readily produced in reactions between O<sub>3</sub> and C = C double bonds in fatty acid residues, which are found in a number of detergents.<sup>40–43</sup> Carpets were also shown to release a number of volatile aldehydes in the C1-C13 size range upon O<sub>3</sub> treatment, which may change the odor perception.<sup>44–47</sup>

Existing U.S. health-related standards for O<sub>3</sub> are reviewed in Table 1. The National Institute for Occupational Safety and Health (NIOSH) established the immediately dangerous to life or health (IDLH) O<sub>3</sub> level at 5 ppm and permissible exposure limit (PEL) at 100 ppb. The Occupational Safety and Health Administration (OSHA) established a PEL of 100 ppb for an 8-hr exposure and short-term exposure limit (STEL) of 300 ppb for a 15-min exposure. EPA classified O<sub>3</sub> as a criteria pollutant and established National Ambient Air Quality Standards (NAAQS) of 120 ppb for 1-hr exposure and 80 ppb for 8-hr exposure. The California state government has just introduced new 8-hr ambient air quality standards (AAQS) at 70 ppb<sup>48</sup> (the California 1-hr-average O<sub>3</sub> standard is 90 ppb). In California, a stage-1 smog alert is issued whenever the ambient concentration of O<sub>3</sub> is in excess of 200

ppb. O<sub>3</sub> levels of 350 and 500 ppb correspond with stage-2 and stage-3 smog alerts, respectively.

Despite the existing concerns about O<sub>3</sub>-generating air purifiers, no government-imposed restrictions on the use of such devices in occupied spaces currently exist.<sup>28</sup> The U.S. Food and Drug Administration limits the concentration of O<sub>3</sub> produced by medical devices operated in closed spaces to 50 ppb,<sup>49</sup> but this limit does not strictly apply to indoor air purifiers. The EPA Web site states that, “No agency of the federal government has approved these devices for use in occupied spaces.”<sup>25</sup>

### Goals

The main objectives of this work are to: (1) verify whether O<sub>3</sub> generators, such as ionic air purifiers, can produce levels of O<sub>3</sub> in excess of public health standards; (2) quantify the steady-state O<sub>3</sub> levels generated by air purifiers in several representative indoor environments; (3) develop a simple phenomenological model that can be used to predict the steady-state O<sub>3</sub> level generated by an air purifier in a closed space; and (4) test the effect of operating O<sub>3</sub>-generating air purifiers in rooms with preexisting O<sub>3</sub> sources. The following sections describe the experimental procedure, key results, and implications of these measurements.

## EXPERIMENTAL METHODS

### Equipment

O<sub>3</sub> concentration was measured with Ebara Jitsugyo EG-2001 high-accuracy O<sub>3</sub> monitor, which provided O<sub>3</sub> mixing ratio referenced to 1 atm and 295 K conditions with a 1-ppb resolution. The linearity and accuracy of this instrument was verified by cross-referencing it against two homemade absorption cells operating on the 253.65-nm mercury line (base-*e* absorption cross-section of O<sub>3</sub> at 253.65 nm is  $1.136 \times 10^{-17}$  cm<sup>2</sup>).<sup>50</sup> The calibration showed that EG-2001 is accurate to better than 5% for all the O<sub>3</sub> mixing ratios of interest. Before each measurement, the instrument was allowed to warm up for 2–3 hr to achieve better stability. The instrument automatically rezeroed itself every 3 min by passing the sampled airflow through a built-in scrubber. It continuously displayed O<sub>3</sub> mixing ratio averaged over 1-sec intervals between rezeroing cycles. The drift in the output between rezeroing cycles did not exceed 3 ppb. Because all the measurements were done close to atmospheric pressure and room temperature, no explicit temperature or pressure corrections were made.

### Air Purifier O<sub>3</sub> Emission Rates

The O<sub>3</sub> emission rate was measured for each air purifier inspected in this work. For these measurements, the air purifier was placed in a sealed Teflon bag filled with a known volume of dried air (400–700 L; relative humidity [RH] <5%). A fan was placed inside the bag to ensure rapid mixing. The O<sub>3</sub> monitor withdrew air from the bag at a rate of 1.5 standard liters per min (SLM) and returned it to the bag in a closed-loop circuit through all-Teflon gas lines. Although a small amount of O<sub>3</sub> was destroyed by the instrument during rezeroing cycles, the O<sub>3</sub> destruction rate was not fast enough to compete with other O<sub>3</sub> emission and removal processes in the measured volume.

**Table 2.** O<sub>3</sub> emission rates for air purifiers tested in this work.

Air Purifier Name	Model Number	O <sub>3</sub> Emission Rate (mg/hr)
SI Quadra Silent Air-Purifier	SI637	2.2
SI Personal Air Purifier	SI736	0.30
SI IB Pet Brush	SI688	0.71
SI GP Car Air Purifier With Ultraviolet Germicidal Protection	SI710	0.74
SI Dashboard (Plug-In) Ionizer	SI629	0.40
SI Car Air Purifier	SI633	0.48
SI Electrostatic Air Cleaner for Bathrooms and Small Spaces	SI627	0.17/0.24
SI Air Freshener 2.0 for Bathrooms and Small Spaces	SI717	0.16
Ioncare Personal Air Purifier	Ioncare PAP	0.50
EZ-COM Air Purifier (rated at 40 mg/hr)	EZ-COM	68
Air-Zone XT-400 (rated at 400 mg/hr)	XT-400	220
Prozone Air Purifier (rated at 125 mg/hr)	PZ6 Air	42
o3ozone™ PRO 420 Ozone Generator (rated at 420 mg/hr)	PRO 420	132/137

Notes: Ionic and ozonolysis air purifiers are listed on the top and bottom of the table, respectively. The rates were measured in a Teflon bag in dry air with RH <5%. Only a single instrument of each type was tested except for SI627 and PRO 420, where two units were available. All air purifiers were new except for PZ6 Air. All measurements used the highest device settings, where applicable. SI = Sharper Image.

In a typical measurement, the air purifier was turned on, and the build-up of O<sub>3</sub> with time was recorded. The concentration was logged every 0.5–5 min depending on the rate of O<sub>3</sub> concentration increase. A slightly modified procedure was used for highly efficient O<sub>3</sub> generators. These were turned on for a preset period of time (20–30 sec) and turned off. The resulting O<sub>3</sub> concentration increment was then recorded after the air in the Teflon bag was well mixed. The procedure was reiterated several times for repeatability.

When the concentration of O<sub>3</sub> in the bag reached a certain level, typically 500–1000 ppb, the air purifier was turned off, and the decay of O<sub>3</sub> concentration was recorded. O<sub>3</sub> concentration typically dropped with exponential lifetime of 3–5 hr, because Teflon is relatively unreactive toward O<sub>3</sub>. The resulting data were analyzed, as described in the kinetics section below, to extract the O<sub>3</sub> emission rate. The results of the measurements are summarized in Table 2.

### Measurements in Rooms

Several types of indoor environments were examined (Table 3) including: (1) two medium-size office rooms in the Rowland Hall building on campus of the University of California, Irvine, (2) medium-size bathroom, (3) small bathroom, and (4) small furnished bedroom. The last three rooms were located in a 3-year-old house in Irvine, CA. All of the measurements were done in rooms with doors and windows closed. In some measurements, forced air circulation from the building ventilation system was present. The amount of admitted air was varied from measurement to measurement to control the decay rate of O<sub>3</sub> from the room. In rooms with forced ventilation, the air-exchange rate was estimated from the time it took to fill a plastic bag of known volume through the air intake vent. No measurements of air exchange rates were performed in rooms without forced ventilation. The O<sub>3</sub> monitor, which was installed in an adjacent room, was withdrawing and returning air at 1.5 SLM through Teflon

tubes. The rate of O<sub>3</sub> removal by the instrument (during its rezeroing cycles) was always negligible compared with other O<sub>3</sub> emission and removal processes in the room. A large fan was placed in the room for better circulation of air to avoid significant O<sub>3</sub> concentration gradients across the room volume.

During the measurements, the air purifier was turned on, and the O<sub>3</sub> concentration buildup was traced until either a steady-state concentration level was reached or the concentration exceeded the levels deemed to be safe for occupants of neighboring rooms and offices. After that, the air purifier was turned off, and the decay rate of O<sub>3</sub> in the room was measured.

### Measurements in Cars

A few measurements were performed in a stationary unoccupied car (Lexus ES 250, 1991) outfitted with leather seats and carpeted floors. The car was positioned in a driveway with its doors and windows closed. The O<sub>3</sub> monitor was installed in a nearby garage, and it withdrew air from the car at 1.5 SLM through a Teflon line. The measurements were done at dusk hours at a temperature of ~15 °C to avoid possible artifacts from inhomogeneous heating of the vehicle by the sun and to minimize the effect of variations in the ambient O<sub>3</sub> level. No measurements of air-exchange rate were performed.

### Personal Air Purifiers

Personal air purifiers (PAPs) were tested in a way that is similar to a previous study of PAPs by CARB researchers.<sup>51</sup> The PAP was suspended from a ring stand, and O<sub>3</sub> concentration was sampled a certain distance away from the PAP (typically 10 cm) through a Teflon tube withdrawing air at 1.5 LPM. In initial experiments, the ring stand was positioned on a bench in a laboratory with a lot of air currents (because of two fume hoods withdrawing air from the room and forced ventilation admitting air to the room). In subsequent tests, the ring stand was surrounded by a large Plexiglas cylinder to minimize the effect from

**Table 3.** Measurements of steady-state O<sub>3</sub> concentrations during operation of selected air-purifiers in various environments.

Environment	Floor Area, ft <sup>2</sup> (m <sup>2</sup> )	Volume, ft <sup>3</sup> (m <sup>3</sup> )	Air Exchange Rate (k <sub>air</sub> ) <sup>-1</sup> (min)	Air Purifier	Rate (mg/hr)	Measured [O <sub>3</sub> ] <sub>ss</sub> Increase (ppb)	Measured (k <sub>loss</sub> ) <sup>-1</sup> (min)
Bathroom A	23 (2.1)	207 (5.9)	-	SI637	2.2	135	20
			-	SI637	2.2	165	29
			-	SI627 + SI717 <sup>a</sup>	0.40	40	53
Bathroom B	46 (4.3)	370 (10.4)	-	EZ-COM	68	Stopped at 450 <sup>b</sup>	18
			-	SI637	2.2	22	11
Bedroom	125 (11.6)	1110 (31.4)	-	EZ-COM	68	260	30
Office A	138 (12.9)	1245 (35.2)	12	EZ-COM	68	240	12
			12	PRO 420	132	320	10
			12	SI637	2.2	9	13
			12	PZ6 Air	42	120	11
Office B	120 (11.1)	957 (27.1)	11	PZ6 Air	42	140	9.3
			11	PRO 420	137	340	9.2
			11	EZ-COM	68	180	9.5
			-	PRO 420	137	650	12
			-	PRO 420	137	290	6.3
			-	PRO 420	137	310	8.4
			-	SI637	2.2	12	12
			-	PRO 420	137	307	7.7
			-	PRO 420 + XT-400 <sup>a</sup>	357	582	7.7
			-	XT-400	220	276	7.7
Lexus ES250	-	~50 (1.4) <sup>c</sup>	-	SI633	0.48	6	~2
	-	-	-	SI710	0.74	9	~2

Notes: The O<sub>3</sub> emission rates refer to dry air; they are listed for reference only. Different [O<sub>3</sub>]<sub>ss</sub> and k<sub>loss</sub> values are reported for the same room/air purifier combinations, because the air exchange rate in the room was varied from test to test by partially blocking the air intake. Uncertainties in k<sub>loss</sub> are ~10% (σ). The air exchange rates were quantified only for selected measurements in offices; <sup>a</sup>Operated simultaneously; <sup>b</sup>The steady state was not reached for safety reasons (See Figure 2b); <sup>c</sup>Estimated.

the strong lateral air currents in the laboratory. A few additional measurements were done using a human-sized stuffed doll wearing a PAP around its neck, with O<sub>3</sub> level being sampled next to the doll's "mouth" (10 cm away from PAP).

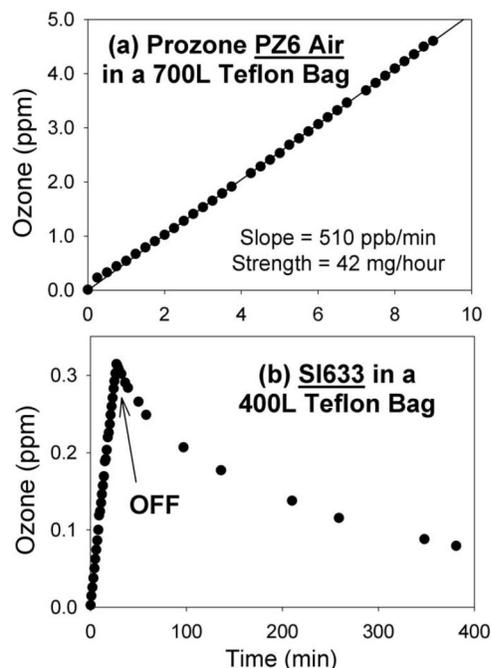
**RESULTS AND DISCUSSION**

**Air Purifier O<sub>3</sub> Emission Rates**

Figure 1 provides an example of measurements of O<sub>3</sub> emission rates by air purifiers under dry-air conditions. For PZ6 Air, a fairly powerful O<sub>3</sub> generator, the observed O<sub>3</sub> concentration in a 700-L Teflon bag reaches 5 ppm in just 10 min. The concentration increase is linear in time with no visible signs of saturation. For SI633, which is a much less efficient O<sub>3</sub> producer, the rate of increase is also linear but considerably slower. The observed concentration profiles can be fitted to the kinetics model described below ([O<sub>3</sub>](t) ≈ k<sub>source</sub> × t for small t) to obtain the air purifier O<sub>3</sub> emission rates in milligrams per hour.

An example of O<sub>3</sub> concentration decay taking place after the air purifier is turned off is given in Figure 1b. The observed decay profile deviates slightly from the single exponential dependence. It is somewhat better described as a second-order loss at concentrations >200 ppb, suggesting that the loss of O<sub>3</sub> on Teflon surfaces is not a first-order process. Indeed, O<sub>3</sub> reactions on hydrophobic soot<sup>52</sup> and self-assembled organic monolayers<sup>43</sup> are known to be governed by a Langmuir-Hinshelwood mechanism. It is possible, that decomposition of O<sub>3</sub> in a Teflon bag follows a similar mechanism, wherein O<sub>3</sub> molecules participate in a rapid adsorption-desorption equilibrium with the surface, with a very slow O<sub>3</sub> + O<sub>3</sub> surface

reaction removing the O<sub>3</sub>. There was no evidence of the second-order O<sub>3</sub> loss in normal environments (rooms); all



**Figure 1.** Sample measurements of O<sub>3</sub> emission rates for PZ6 Air and SI633. O<sub>3</sub> concentration buildup is measured in a Teflon bag of a known volume after turning the air purifier on. The initial concentration rise is linear, O<sub>3</sub> ≈ k<sub>source</sub> × t. The lifetime of O<sub>3</sub> in the Teflon bag after the air purifier is turned off is very long (~5 hr).

of the decays could be fit to a single exponential decay within the measurement uncertainties.

Table 2 reports the O<sub>3</sub> emission rates measured in a Teflon chamber in dry air with RH <5%. All of the measurements use the highest air purifier settings. Although the measurements are quite repeatable for one and the same air purifier, it is not appropriate to place well-defined error bars on these values without testing multiple copies of the same model. Two identical units were available for SI627, with one producing 0.17 mg/hr and the other 0.24 mg/hr of O<sub>3</sub> (30% difference in the O<sub>3</sub> emission rates). The measured O<sub>3</sub> emission rates should be treated as approximately representative values for a given class of air purifiers.

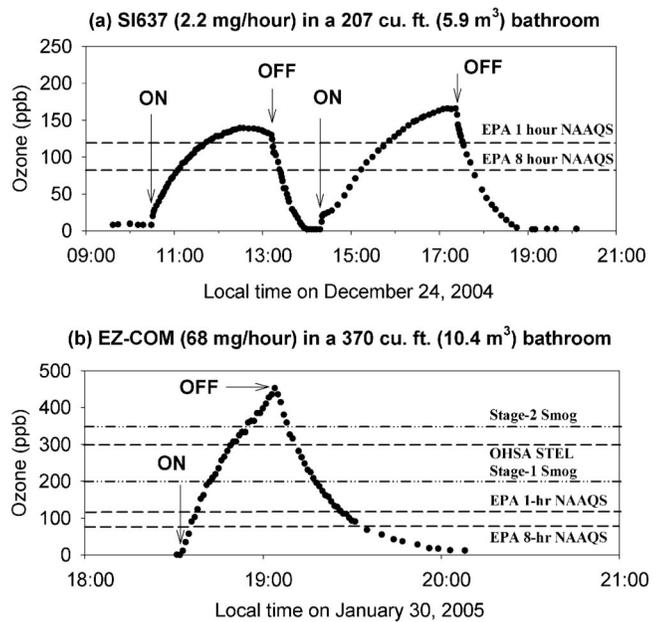
Because the O<sub>3</sub> emission rate by air purifiers can be affected by RH, the effect of RH was tested on two ionic air purifiers, SI637 and SI627. The O<sub>3</sub> emission rates for both models decrease at higher RH; the effect is stronger for SI637. Specifically, SI637 produces 2.2, 1.9, and 1.4 mg/hr of O<sub>3</sub> at RH of 5%, 30%, and 60%, respectively. The output of SI627 drops from 0.24 mg/hr at RH of 5% to 0.18 mg/hr at RH of 60%. The RH dependence of the O<sub>3</sub> emission rates for other air purifiers was not explicitly measured. It is expected that air purifiers generating O<sub>3</sub> by an electrical discharge (every model in Table 3 except PZ6 Air) should reduce their O<sub>3</sub> emission rates somewhat at elevated RH.

The effect of particulate matter on SI637 O<sub>3</sub> emission rate was investigated by purposely injecting NaCl aerosol particles into the Teflon bag (~10<sup>5</sup> particles per cm<sup>3</sup> with a mean particle diameter of 0.2 μm). The presence of particles caused no significant change in the O<sub>3</sub> emission rate, suggesting that O<sub>3</sub> production and particle ionization processes are fairly independent of each other in ionic air purifiers. The effect of particles on the performance of ozonolysis air purifiers was not explicitly investigated in this work.

For certain air purifiers, the O<sub>3</sub> emission rate was specified by the manufacturers. With the exception of Ioncare PAP, which was advertised to produce 44 mg/hr as opposed to the measured rate of 0.5 mg/hr, the measurements were within a factor of 3 of the specifications. For EZ-COM air purifier, the measured rate of 68 mg/hr is a factor of 1.7 larger than its 40-mg/hr manufacturer's rating. The PZ6 Air purifier had been used for an unknown number of hours before this study, which may account for its lower output of 42 mg/hr compared with its 125-mg/hr rating. The Pro-420 model produced 132 mg/hr instead of the quoted 420 mg/hr. After the manufacturer replaced the unit (initially believed to be defective), the replacement performed at a similarly low 137-mg/hr level. XT-400 model generated O<sub>3</sub> at a measured rate of 220 mg/hr compared with its 400-mg/hr rating.

### O<sub>3</sub> Measurements in Rooms

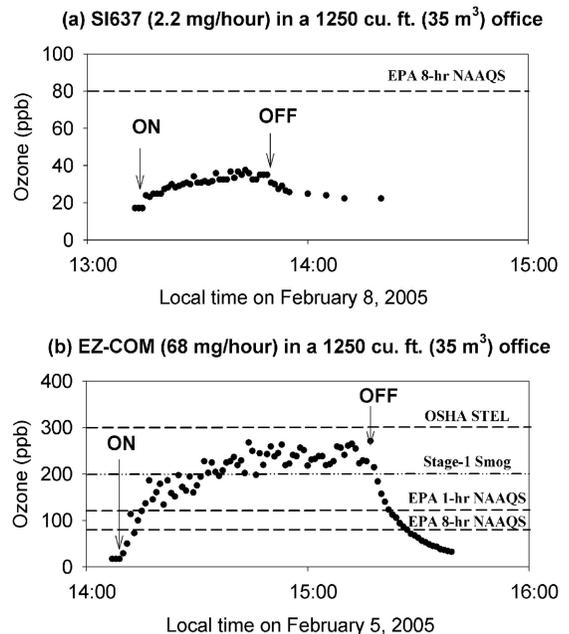
Sample measurements of emission of O<sub>3</sub> by air purifiers operated in rooms and offices are shown in Figures 2-4. In all of the examined cases, the O<sub>3</sub> concentration in the room increases to some steady-state level after the air purifier is turned on. It decreases exponentially to the background level after the air purifier is turned off. The steady-state O<sub>3</sub> concentration and the rate with which O<sub>3</sub>



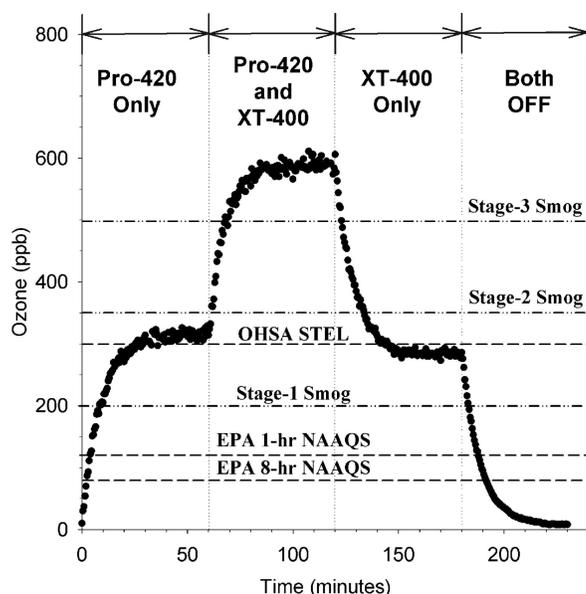
**Figure 2.** Sample measurements in bathrooms: (a) SI637 operated in a small bathroom; (b) EZ-COM operated in a larger bathroom. No forced ventilation is used in both cases. Dashed lines correspond to EPA 1-hr (80 ppb), EPA 8-hr (120 ppb), and OSHA STEL (300 ppb) standards. Dash-dotted lines are stage-1 (200 ppb) and stage-2 (350 ppb) smog alerts.

is removed from the room depend on the specific environment. Table 3 provides a comprehensive listing of all air purifier/environment combinations examined in this work.

Figure 2 shows sample results for unventilated bathrooms. Bathrooms are uniquely different from other



**Figure 3.** Sample measurements in ventilated office rooms: (a) SI637 operated in an office room; (b) EZ-COM operated in the same room. The air-exchange rate is one room volume every 12 min. Dashed lines correspond to EPA 1-hr (80 ppb), EPA 8-hr (120 ppb), and OSHA STEL (300 ppb) standards. Dash-dotted line is stage-1 smog alert level (200 ppb).



**Figure 4.** Back-to-back operation of two different air purifiers in the same office. First, Pro-420 is turned on for 60 min, followed by Pro-420 and XT-400 both on for the next 60 min, followed by XT-400 on for the next 60 min, followed by the decay of  $O_3$  after everything is turned off. Dashed lines correspond to EPA 1-hr, EPA 8-hr, and OSHA STEL standards. Dash-dotted lines are California stage-1, -2, and -3 smog alerts.

kinds of indoor environments in that they have a relatively small volume, little or no furniture, and fairly unreactive surfaces (ceramic tile, glass, enamel painted walls, etc.). As a result, even weak  $O_3$  generating appliances can be rather effective in building up large  $O_3$  concentrations in bathrooms. For example, Figure 2a shows that SI637, which has an  $O_3$  emission rate of 2.2 mg/hr in dry air, can easily maintain levels of  $O_3$  in excess of 150 ppb in a small bathroom. EZ-COM, a 30-times more powerful  $O_3$  generator, only needs ~15 min to reach the OSHA STEL  $O_3$  level of 300 ppb in a larger bathroom (Figure 2b). For this specific measurement, the steady-state level was not reached because of safety issues (a strong smell of  $O_3$  was detected in the adjacent rooms). The extrapolated steady-state value in Figure 2b is in excess of 1 ppm.

Figure 2 also illustrates the effects of environmental variables on measurements in rooms. The SI637 measurement in Figure 2a took ~10 hr from 9:30 a.m. in the morning until 8:00 p.m. in the evening on a Christmas day. The temperature in the bathroom was ~5 °C higher in the afternoon (between ~12:30 p.m. and 3:00 p.m.) compared with that in the morning and evening hours. This small temperature variation had a visible effect on the rate of  $O_3$  decomposition on the room surfaces. Indeed, the observed exponential lifetime for the first decay in Figure 2a is ~20 min as opposed to 29 min for the second decay measured later in the evening. As a direct result of this temperature variation, the steady-state level achieved in the afternoon is somewhat lower than that in the evening. The temperature variation is also responsible for the observed decline in the steady-state  $O_3$  level between 12:30 p.m. and 1:00 p.m.

Figure 3 shows the result of using the same air purifiers, EZ-COM and SI637, in a ventilated furnished office

room. Because of the increased room volume, larger available area for  $O_3$  surface decomposition reactions, and presence of forced air ventilation with an air-exchange rate of ~5 room volumes per hour, the observed increase in the steady-state  $O_3$  level is not as dramatic as in bathrooms. SI637 increases the  $O_3$  level by ~9 ppb. EZ-COM is capable of driving the  $O_3$  concentration up by ~240 ppb, which is higher than both 1-hr and 8-hr EPA NAAQS standards. The loss of  $O_3$  from the air after the generator is turned off is considerably faster: the exponential lifetimes measured from data in Figures 3a and 3b are  $13 \pm 3$  and  $12 \pm 2$  min, respectively. This is essentially identical to the time needed for the ventilation to displace one room volume (measured to be  $12 \pm 1$  min from the rate of filling a plastic bag of calibrated volume through the air inlet), suggesting that the removal of  $O_3$  from the office in this particular case is dominated by physical rather than chemical loss. More measurements in offices will be discussed after introducing the kinetic model.

### Car Air Purifiers

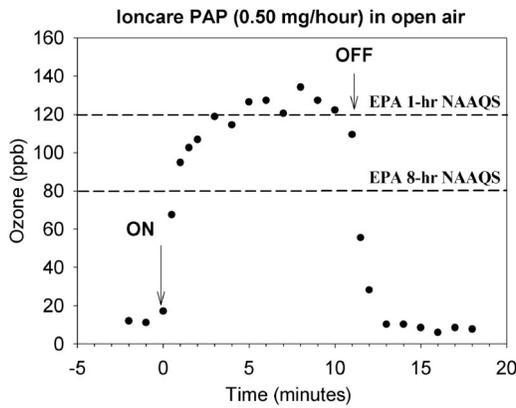
Two car air purifiers were tested as described in the experimental section. The observed  $O_3$  concentration behaved similarly to the results obtained in rooms: an increase in the steady-state concentration during the air purifier operation and an exponential decline after the air purifier is turned off. The observed  $O_3$  decay rate was very rapid (lifetime ~2 min) presumably because of the presence of a number of reactive surfaces inside the car (e.g., leather upholstery, carpet floors, rubber, insulation) and also because of a relatively facile exchange of air between the car interior and the outside (not quantified in this work). As a result, the incremental  $O_3$  concentration increase caused by the air purifier was relatively small: <10 ppb (Table 3).

### PAPs

In addition to experiments with air purifiers designed for rooms and cars, several tests were done with PAPs. The previous findings of CARB researchers<sup>51</sup> that PAPs can expose the wearer to  $O_3$  levels in excess of public health standards were fully confirmed by the present work. For example, in tests with Ioncare PAP worn by a human-sized doll, peak  $O_3$  concentrations near its "mouth" were as high as 700 ppb, and average concentrations were in excess of the EPA 1-hr NAAQS standard of 120 ppb. The concentrations were highly variable and depended strongly on the pattern of air drafts in the room. Figure 5 shows the result of using Ioncare PAP in a quiet air environment, wherein the air currents are controlled solely by diffusion. One can see that the  $O_3$  level was quickly brought up to 120 ppb above the PAP. The results of Figure 5 were obtained with a 10-cm separation between the PAP and the  $O_3$  meter sampling inlet; the measured concentration increased rapidly as this distance was reduced, in agreement with the results of Phillips et al.<sup>51</sup>

### Kinetic Treatment

The  $O_3$  concentration time dependence and steady-state level observed in experiments in closed volumes, such as rooms, cars, and Teflon bags, can be described by a simple model. The linearity of the initial  $O_3$  concentration rise in



**Figure 5.** Sample measurement for Ioncare PAP. Sampling takes place 10 cm above the PAP. Dashed lines correspond to EPA 1-hr (80 ppb) and EPA 8-hr (120 ppb) standards.

Teflon bag measurements (Figure 1) suggests that the production of O<sub>3</sub> by an air purifier is a zero-order process with respect to O<sub>3</sub>:

$$\begin{aligned} \text{Air} \rightarrow \text{O}_3 \quad \frac{d[\text{O}_3]}{dt} &= k_{\text{source}}(\text{cm}^{-3}\text{s}^{-1}) \\ &= 1.23 \times 10^{11} \times \frac{\text{Rate}(\text{mg}/\text{hr})}{V(\text{cu.ft.})} \end{aligned} \quad (1)$$

The measured O<sub>3</sub> emission rates for several air purifiers are reported in Table 2. The zero-order assumption was observed to be valid for all of the air purifiers listed in Table 2 for O<sub>3</sub> mixing ratios in the ppb–low ppm range. The conversion factor in eq 1 is valid for 1 atm, 25 °C, and for volume measured in the units of cubic feet (1 ft = 30.48 cm). Equation 1 implicitly assumes that the rate of mixing of air within the room volume, *V*, is considerably faster than the rate of O<sub>3</sub> removal from the room. This condition was satisfied for all of the measurements reported here (except for measurements with PAPs).

The loss of O<sub>3</sub> from the room is, in principle, a complicated process because of the presence of multiple surfaces with varying degree of reactivity toward O<sub>3</sub> (including the body of the air purifier itself), complicated pattern of air mixing in the room, and coupling between air-transport and surface kinetics.<sup>53</sup> However, in the present measurements in closed, well-mixed indoor environments, the observed O<sub>3</sub> decay could be described as a first-order process to an excellent degree of approximation (i.e., there were no apparent deviations from the first-order kinetics within the measurement uncertainties):

$$\text{O}_3 \rightarrow \text{products} \quad \frac{d[\text{O}_3]}{dt} = -k_{\text{loss}}(\text{s}^{-1})[\text{O}_3] \quad (2)$$

The decay rate constant, *k*<sub>loss</sub>, is a combination of physical removal because of the air exchange, chemical removal because of heterogeneous reactions on surfaces, and chemical removal because of reactions with air impurities.<sup>9</sup> In cases when the wall loss dominates, the decay rate-constant can be related to the deposition velocities

customarily reported in the research literature on surface decay rates:

$$k_{\text{loss}} = \frac{1}{V} \sum A \times v_d \quad (3)$$

where *A* is the surface area, *v*<sub>*d*</sub> is the deposition velocity of O<sub>3</sub> on that particular type of surface, and the summation extends over all of the available surfaces in the room.

The inverse of the decay rate constant, *k*<sub>loss</sub><sup>-1</sup>, can be viewed as the characteristic lifetime of O<sub>3</sub> in a given environment. It can range from several hours in a highly unreactive Teflon bag (e.g., 5 hr in Figure 1) to just a few minutes in a well-ventilated office (Table 3). The decay rate constants measured here (Table 3) are consistent with previous measurements of similar parameters in houses and offices.<sup>9,54</sup> In well-ventilated, sparsely furnished rooms, the O<sub>3</sub> decay rate is observed to be very close to the air-exchange rate, which suggests that the decay is dominated by physical removal of O<sub>3</sub> from the room. However, when the air-exchange rate is slow or the room contains reactive surfaces, the observed decay rate should be faster than the air-exchange rate. In this case, the removal is mostly because of the chemical reactions with the surfaces and/or with gas-phase organics. The effect of air exchange and transport limitations on concentrations of indoor air pollutants is discussed in more detail in refs. 11,53.

Equations 1 and 2 can be integrated to give the O<sub>3</sub> concentration buildup after the air purifier is turned on (assuming very low background O<sub>3</sub> concentration):

$$[\text{O}_3](t) = \frac{k_{\text{source}}}{k_{\text{loss}}} (1 - e^{-k_{\text{loss}}t}) \quad (4)$$

The O<sub>3</sub> concentration builds up from zero to a steady-state value in which the emission rate is exactly balanced by the decomposition rate:

$$[\text{O}_3]_{\text{ss}} = \frac{k_{\text{source}}}{k_{\text{loss}}} \text{ or } [\text{O}_3]_{\text{ss}}(\text{ppb}) = \frac{300 \times \text{Rate}(\text{mg}/\text{hr})}{k_{\text{loss}}(\text{min}^{-1}) \times V(\text{cu.ft.})} \quad (5)$$

Once again, eq 5 is valid only when the rate of mixing of air within the room volume is considerably faster than the rate of O<sub>3</sub> removal from the room. The conversion factor in eq 5 is equal to 300 purely by accident; it is valid for the conditions of 1 atm, 25 °C, and the specified set of units. In cases where the O<sub>3</sub> loss is dominated by the wall decomposition, the product *k*<sub>loss</sub> × *V* in the denominator can be equivalently replaced by the product of the deposition velocity and the room surface area, *A* × *v*<sub>*d*</sub>.

After the air purifier is turned off, the O<sub>3</sub> concentration decays exponentially:

$$[\text{O}_3](t) = [\text{O}_3]_{\text{ss}} e^{-k_{\text{loss}}t} \quad (6)$$

with the decay rate constant, *k*<sub>loss</sub>. Figures 2–4 provide clear examples of this behavior. Except for measurements

inside Teflon bags, no significant deviations from the single exponential decay were observed in this work.

### Verification of the Kinetic Model

Equation 5 has several interesting ramifications. For example, it confirms the suggestion of ref. <sup>51</sup> that the effect of putting several O<sub>3</sub> generators in the same room is additive, with contributions of each generator to the total steady-state O<sub>3</sub> concentration being proportional to its O<sub>3</sub> emission rate. Indeed, if there is an additional source of O<sub>3</sub> present, for example, from a steady intake of polluted air from the outside or from another O<sub>3</sub>-generating device inside, it will create a background concentration of O<sub>3</sub>,

$$[\text{O}_3]_{\text{bg}} = \frac{k_{\text{ext}}}{k_{\text{loss}}}, \quad (7)$$

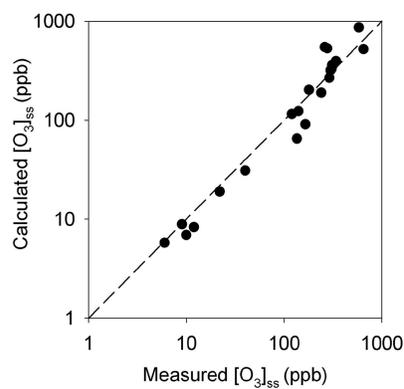
where  $k_{\text{ext}}$  is the effective zero-order rate constant for the background source, and  $k_{\text{loss}}$  is the first-order O<sub>3</sub> decay rate constant for the room (or any other closed space in question). A simple exercise in kinetics shows that turning on an air purifier with O<sub>3</sub> emission rate constant  $k_{\text{source}}$  will further increase the steady-state O<sub>3</sub> concentration to

$$[\text{O}_3]_{\text{ss}} = \frac{k_{\text{ext}} + k_{\text{source}}}{k_{\text{loss}}} = [\text{O}_3]_{\text{bg}} + \frac{k_{\text{source}}}{k_{\text{loss}}}. \quad (8)$$

The last term in this equation is exactly equal to the steady-state level of O<sub>3</sub> that the air purifier would have produced in the absence of the background O<sub>3</sub> source.

This additivity of contributions from different O<sub>3</sub> sources was explicitly tested by running two air purifiers in the same room at the same time. Figure 4 shows the result for operating Pro-420 in a ventilated office for an hour, followed by simultaneously operating Pro-420 and XT-400 for another hour, followed by operating XT-400 for another hour. The measured steady-state levels of O<sub>3</sub> for individual air purifiers (corrected for the small background level of 8 ppb) are 307 ppb (Pro-420 only) and 276 ppb (XT-400). The uncertainties in the measured steady-state values are ~5 ppb. The sum of these values, 584 ppb, is essentially identical to the steady-state level of 582 ppb measured during the Pro-420 and XT-400 concurrent operation.

To further test the predictive power of eq 5, Figure 6 compares incremental [O<sub>3</sub>]<sub>ss</sub> measured in experiments (Table 3) with [O<sub>3</sub>]<sub>ss</sub> calculated from the room volume, measured decay rate constant for the room, and the air purifier O<sub>3</sub> emission rate measured in separate experiments in a Teflon bag. The data in Figure 6 reflect the results obtained for several ionic and ozonolysis air purifiers operated in cars, offices, bathrooms, and bedrooms. The O<sub>3</sub> emission rates of air purifiers in Figure 6 span 3 orders of magnitude (from 0.4 mg/hr to 357 mg/hr in dry air). Nevertheless, the agreement between the measured values and those predicted from the simple kinetic model can be regarded as excellent over the entire range of environmentally relevant O<sub>3</sub> concentrations (10–1000 ppb).



**Figure 6.** Comparison of the measured steady-state O<sub>3</sub> concentrations with those calculated using eq 5 from the decay rate constants, air purifier O<sub>3</sub> emission rates, and room volumes. Plot includes all data from Table 3. Sources of the scatter are discussed in the text.

Possible sources of scatter in Figure 6 include: (1) use of O<sub>3</sub> emission rates for dry air (Table 2) instead of those for the actual RH in the room (in this work, RH was 40% ± 5% in offices and 50 ± 10% in the house); (2) uncertainties in measuring  $k_{\text{loss}}$  (10–20%); and (3) air-transport limitations. The last source refers to either inhomogeneous or insufficiently rapid mixing of air across the room volume by the fan. These two conditions required for the validity of eqs 1 and 5 are not always trivial to meet in actual environments because of the presence of furniture, sharp room corners, temperature and pressure gradients across the room, and nonuniform distribution of O<sub>3</sub> deposition velocities on the room surfaces. In spite of all these limitations, the model performs quite well; the largest deviation between measured and observed steady-state concentrations in Figure 6 is by a factor of 2.

### Implications of the Model

In the absence of indoor O<sub>3</sub>-generating sources, indoor O<sub>3</sub> concentration is known to track the outdoor O<sub>3</sub> concentration.<sup>9</sup> The observed ratios of indoor-to-outdoor O<sub>3</sub> levels (I/O) are generally in the range of 0.1–0.7,<sup>9</sup> with larger values correlating with higher air exchange rates between the inside and outside. Operation of an O<sub>3</sub>-generating air purifier can make the I/O ratio considerably larger than 1, with the incremental increase in indoor O<sub>3</sub> level being directly proportional to the air purifier O<sub>3</sub> emission rate. Therefore, people occupying rooms with an operating O<sub>3</sub>-generating air purifier are more likely to be exposed to levels of O<sub>3</sub> in excess of the public health standards. Depending on the way the air purifier is used, the exposure level can be as high as the equivalent of stage-1 or even stage-2 smog alert (Figures 2–4). For reference, the last smog-2 alert in the South Coast Basin, which includes Los Angeles, occurred in 1988, and there was only one smog-1 alert in this area between 1999 and 2003.<sup>55</sup>

Equations 3 and 5 suggest that the increase in O<sub>3</sub> concentration driven by an air purifier should be inversely proportional to the total room surface area in the limit when the O<sub>3</sub> removal from the room is dominated by the wall loss and the surfaces in the room have similar reactivity toward O<sub>3</sub> (i.e., similar O<sub>3</sub> deposition velocities). Everything else being equal, operation of an O<sub>3</sub>-

generating air purifier in rooms with smaller floor areas (i.e., bathrooms) should produce higher steady-state levels of O<sub>3</sub>. In the limit when the O<sub>3</sub> removal is dominated by air exchange, the steady-state increase in O<sub>3</sub> level is inversely proportional to the room volume instead of the total surface area. Again, the prediction is that operation of an air purifier in smaller rooms should result in larger O<sub>3</sub> level rises. Data in Table 3 fully confirm these predictions.

As a final note, eq 5 can be of some potential value for future regulatory decisions affecting O<sub>3</sub>-generating appliances and for checking compliance with already existing regulations. Consider an example of a calculation of the maximal O<sub>3</sub> emission rate for a medical device subject to the *Code of Federal Regulations* 21 CFR 801.415 set forth by the U.S. Food and Drug Administration in 1976. According to the code, such a device should not generate O<sub>3</sub> at a level in excess of 50 ppb in an "enclosed space intended to be occupied by people for extended periods of time."<sup>49</sup> Assuming that the device is to be operated in a 2000-ft<sup>3</sup> enclosed space characterized by an O<sub>3</sub> lifetime of 30 min, one calculates 11 mg/hr for the maximal O<sub>3</sub> emission rate under such conditions. The chief advantage of eq 5 is that one does not need to conduct actual measurements of O<sub>3</sub> concentrations to obtain the steady-state level of O<sub>3</sub> resulting from the device. Indeed, the room volume and surface area can be easily measured, O<sub>3</sub> emission rate is an intrinsic property of the device, and the O<sub>3</sub> decay rate can be estimated from deposition velocities for surfaces used in construction. Tables of O<sub>3</sub> deposition velocities are available from multiple sources.<sup>9,37,38</sup>

### Educational Considerations

O<sub>3</sub> generators are useful for demonstrating simple kinetic and indoor air pollution phenomena in classes designed for high school, undergraduate, and continuing education students. Based on the results of this work, we designed a 4-hr teaching laboratory for a summer training program for high school science teachers. The laboratory was offered for the first time in July 2005 to a class of 20 teachers. The teachers (in groups of two to three people) were able to measure the O<sub>3</sub> emission rates from two randomly selected indoor air purifiers. They used their data to calculate the expected O<sub>3</sub> concentration resulting from placing such air purifiers in a typical room and compared the results with the health standards (Table 1). In addition, they measured O<sub>3</sub> concentrations produced by a PAP under realistic conditions. They used their data to estimate O<sub>3</sub> exposure for several scenarios of using such air purifiers. Such projects are highly effective in educating the public about the issues associated with indoor air pollution.

### CONCLUSIONS

Operation of an O<sub>3</sub>-generating air purifier in a closed indoor environment results in an increase in the steady-state O<sub>3</sub> concentration that is directly proportional to the O<sub>3</sub> emission rate of the air purifier. Depending on the mechanism of O<sub>3</sub> removal from the room, the magnitude of the increase is inversely proportional to either the surface area of the room (the loss is dominated by heterogeneous removal on surfaces) or the total volume of the

room (the loss is dominated by air exchange). In either case, the largest increase in the steady-state O<sub>3</sub> level is anticipated for small, poorly ventilated rooms, especially if they are constructed from materials with low reactivity toward O<sub>3</sub>. In such rooms, even a device with an O<sub>3</sub> emission rate of a few milligrams per hour can maintain an O<sub>3</sub> level in excess of public health standards. The O<sub>3</sub> level generated by an air purifier is in addition to the normal indoor O<sub>3</sub> level resulting from the air exchange between inside and outside. Therefore, persons operating O<sub>3</sub>-generating air purifiers in their houses and/or offices may be more frequently exposed to O<sub>3</sub> levels in excess of the health standards compared with an average person living in the same area.

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