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Gas-Phase Advanced Oxidation for Effective, Efficient in Situ Control of Pollution

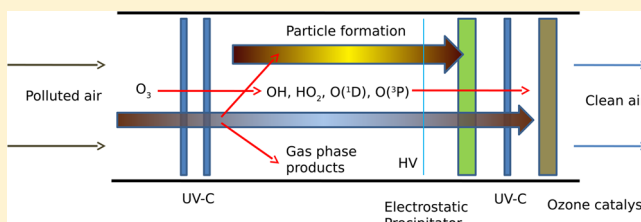
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S Supporting Information

ABSTRACT: In this article, gas-phase advanced oxidation, a new method for pollution control building on the photo-oxidation and particle formation chemistry occurring in the atmosphere, is introduced and characterized. The process uses ozone and UV-C light to produce in situ radicals to oxidize pollution, generating particles that are removed by a filter; ozone is removed using a MnO₂ honeycomb catalyst. This combination of in situ processes removes a wide range of pollutants with a comparatively low specific energy input. Two proof-of-concept devices were built to test and optimize the process. The laboratory prototype was built of standard ventilation duct and could treat up to 850 m³/h. A portable continuous-flow prototype built in an aluminum flight case was able to treat 46 m³/h. Removal efficiencies of >95% were observed for propane, cyclohexane, benzene, isoprene, aerosol particle mass, and ozone for concentrations in the range of 0.4–6 ppm and exposure times up to 0.5 min. The laboratory prototype generated a OH• concentration derived from propane reaction of $(2.5 \pm 0.3) \times 10^{10} \text{ cm}^{-3}$ at a specific energy input of 3 kJ/m³, and the portable device generated $(4.6 \pm 0.4) \times 10^9 \text{ cm}^{-3}$ at 10 kJ/m³. Based on these results, in situ gas-phase advanced oxidation is a viable control strategy for most volatile organic compounds, specifically those with a OH• reaction rate higher than ca. $5 \times 10^{-13} \text{ cm}^3/\text{s}$. Gas-phase advanced oxidation is able to remove compounds that react with OH and to control ozone and total particulate mass. Secondary pollution including formaldehyde and ultrafine particles might be generated, depending on the composition of the primary pollution.



INTRODUCTION

Advanced oxidation processes have found widespread use for removing pollution from wastewater. Hydroxyl radicals generated in situ using a combination of ozone, hydrogen peroxide, and ultraviolet (UV) light can be used to degrade organic (and some inorganic) contaminants.^{1,2} Even though most volatile organic compounds (VOCs) are removed from the atmosphere through sequences of photochemically driven free-radical chain reactions,³ until now, advanced oxidation has not been applied to gas-phase pollution streams for emissions control.

According to the World Health Organization, indoor and outdoor air pollution causes 7 million premature deaths annually; air pollution is the world's largest single environmental health risk.⁴ Pollution in indoor air is linked to heart disease, cancer, asthma, allergy, lost productivity, and irritation.^{5–9} Sources of indoor air pollution include pollution from outside a building and internal sources such as building materials, perfumes and cleaning products, solvents and glues, office machinery, cooking, industrial processes, biological metabolism, and smoking.^{6,7,10} In addition to being the source of indoor air, regional, ambient air pollution is a problem in its own right, with multiple studies showing a positive correlation with increased mortality.^{11,12} A majority of humans now live in urban areas and face daily exposure to the components of urban

air pollution.^{13,14} Industrial emissions impact regional air quality, ground-level ozone, acid rain, particle concentrations, and climate.³ The emissions of volatile organic compounds are regulated because of their adverse impacts on air quality;^{15,16} in addition, some emissions are regulated because of their offensive smells.

Many methods are used to control indoor air pollution; simple ventilation is the most widespread.^{6,17} All methods can be evaluated in terms of energy efficiency; maintenance, installation, and running costs; and control of pollutants. Heat exchangers improve energy efficiency, but because of the latent heat of water vapor, they are less useful in hot, humid climates, and there can be problems with the transfer of odors from the outgoing to the incoming air stream. Filters can remove particles but without removing gas-phase pollution. Particle filters have a significant resistance to air flow. They do not treat VOCs and are themselves sources of odor.^{18,19} Activated charcoal removes VOCs but has a high resistance to air flow and a limited capacity, and can result in a disposal problem. Electrostatic filters and ion air cleaners remove

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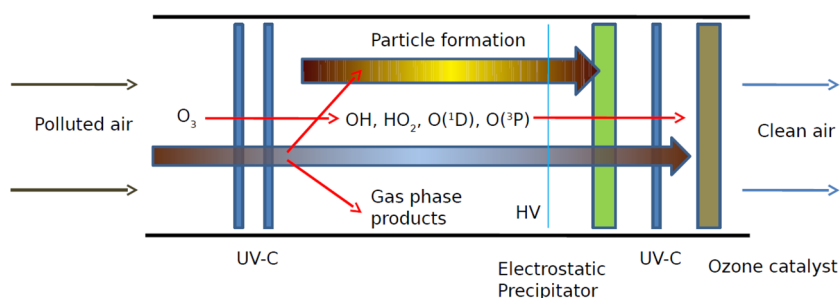


Figure 1. Photochemical air purification process used in the prototypes. Ozone is added to the airstream, and HO_x radicals are generated with UV-C lamps. Particles form and are removed by the electrostatic precipitator. Gas-phase products are removed in a second stage of radical chemistry. Finally, excess ozone is removed using a catalyst.

particles but are a source of ozone that is hazardous, degrades materials, and reacts with unsaturated compounds in a building to give hazardous products.^{8–10,20} Despite years of research, photocatalytic oxidation has not resulted in practical systems used in building heating, ventilation, and air conditioning (HVAC) systems or for emissions control.²¹ There is justified concern that some indoor air purification processes can be unsafe,¹⁰ because of a combination of generation of particles, ozone, and reaction products.

Control of industrial emissions typically involves treatment of large air flows. Although biofiltration is used to treat process emissions from rendering and biogas production, its commercial application is limited by its size and vulnerability to poisoning and changes in VOC concentration.^{22,23} Catalytic and thermal oxidizers can be used effectively for treating high VOC levels ($>1 \text{ g/m}^3$) but require additional fuel when pollution is below the threshold needed to maintain operating temperature; these methods have relatively high costs for installation, operation, and maintenance.²⁴ Regenerative adsorption and cryotrapping remove VOCs but consume energy and are not suitable for wet gas streams. Research has begun on nonthermal plasma air cleaners, a promising technology but with a relatively high energy consumption of hundreds of kilojoules per cubic meter.²⁵

In searching for an ideal pollution control strategy, it can be useful to examine the atmosphere. All pollution is eventually removed from the atmosphere by a variety of mechanisms (oxidation, photolysis, deposition), and the study of atmospheric chemistry shows how different classes of pollution are vulnerable, possibly leading to successful control strategies. VOCs are typically oxidized in chain reactions involving free radicals, and the products are removed by wet or dry deposition.³ In remote low- NO_x conditions, HO_x chemistry is initiated by the photolysis of ozone by UV light, producing electronically excited oxygen atoms, $\text{O}(^1\text{D})$. The reaction of $\text{O}(^1\text{D})$ with water vapor produces OH radicals that react aggressively with VOCs to yield oxidized products including aldehydes and acids. Atmospheric lifetimes of VOCs, largely determined by the OH^\bullet concentration field, range from hours to years. VOC oxidation reactions proceed through addition and fragmentation.^{28–30,42} Oxygen addition to a VOC typically adds a strong carbonyl dipole to the molecule, decreasing vapor pressure and increasing solubility. Fragmentation produces small volatile products such as HCHO , CO , CO_2 , and HCOOH . In the atmosphere, the yield of secondary organic aerosol (SOA) from VOC oxidation varies greatly depending on the mix of VOCs, the relative humidity, the temperature, and the oxidants, with SOA yields typically ranging from 5% to

50%.³¹ Flux estimates suggest SOA (115 Tg of C/year) to be the major type of organic aerosol (150 Tg of C/year).³² Indoor air chemistry is similar and involves reactions of VOCs with ozone and nitrogen oxides that enter a building through ventilation or are produced within the building.^{10,26,27}

The present work presents a new method for air purification that accelerates the photochemical processes that remove pollutants from air. The process is energy-efficient and is effective for a range of pollution levels when catalysis and combustion are not self-sustaining. The principles behind the method are explained, as well as the design and testing of two prototypes. We report the results of experiments for a number of VOCs, ozone, and particles. Although current regulatory efforts focus on total particulate mass (e.g., $\text{PM}_{2.5}$ and PM_{10}), there is growing evidence that ultrafine particles (UFPs), those particles with diameters of less than 100 nm, represent a significant risk to health. UFPs are a persistent air pollutant, and deposition of UFPs in the lung is a direct way to introduce foreign chemicals. In contrast to particles of larger sizes, UFPs are not filtered by the upper respiratory system. This study presents results in terms of both particle mass and particle number, as both are of concern for public health.

EXPERIMENTAL METHODS

Overview of Gas-Phase Advanced Oxidation (GPAO).

An overview of the GPAO process³³ is shown in Figure 1. Polluted air is drawn or blown into the system, and ozone is added. Aerosol surface area might be promoted using water vapor, ammonia, or seed particles to enhance uptake onto particles. Next, radicals are generated from ozone photochemically using UV-C fluorescent lamps. Initial reaction with OH^\bullet is the rate-limiting step for most pollutants, triggering a cascade of oxidation aided by other oxidants in the system: O_2 , O_3 , $\text{O}(^3\text{P})$, and HO_2^\bullet . Species with UV chromophores can be photolyzed, after which the products can be oxidized. The air then flows through a tube whose main purpose is to develop the gas-phase chemistry and allow particles to grow by condensation and coagulation. Secondary organic aerosol (SOA) will form to a variable extent from the larger primary VOC species.^{28–30} A similar approach has been taken in aerosol science with the goal of investigating the heterogeneous processing of aerosols in the atmosphere and quickly measuring SOA yields for a variety of precursors.^{31,48,49} The SOA yield depends on variables including the relative humidity, the mix of VOCs and their degree of oxidation, and the presence of condensation nuclei and bases including amines. The particles are removed by a filter, and in a final step, unreacted ozone is removed before the cleaned air leaves the system.

Table 1. Reaction Rates and Estimated Lifetimes for Test Compounds and Selected Other Species

| compound | formula | reaction rate $k(298\text{ K})$ ($\text{cm}^3\text{ s}^{-1}$) | | natural lifetime τ (s) | |
|------------------|--------------------------------|---|-------------------------|-----------------------------|-----------------------------|
| | | OH ^a | O ₃ | OH ^a | O ₃ ^b |
| benzene | C ₆ H ₆ | 1.28×10^{-12c} | 1.72×10^{-22d} | 31 | 2.3×10^8 |
| carbon monoxide | CO | 2.30×10^{-13e} | <i>f</i> | 170 | <i>f</i> |
| cyclohexane | C ₆ H ₁₂ | 6.97×10^{-12g} | <i>f</i> | 5.7 | <i>f</i> |
| formaldehyde | CH ₂ O | 8.50×10^{-12e} | <i>f</i> | 4.7 | <i>f</i> |
| isoprene | C ₅ H ₈ | 1.00×10^{-10e} | 1.29×10^{-17h} | 0.4 | 3.1×10^3 |
| propane | C ₃ H ₈ | 1.10×10^{-12e} | <i>f</i> | 36 | <i>f</i> |
| hydrogen sulfide | H ₂ S | 4.7×10^{-12i} | 2×10^{-20j} | 8.5 | 2×10^6 |
| methane | CH ₄ | 6.4×10^{-15e} | <i>f</i> | 6.2×10^3 | <i>f</i> |
| nitrogen dioxide | NO ₂ | 4.1×10^{-11i} | <i>f,k</i> | 1.0 | <i>f</i> |
| styrene | C ₈ H ₈ | 4.3×10^{-11l} | 1.4×10^{-17m} | 0.9 | 2.8×10^3 |

^aThe decrease in propane was used to estimate $[\text{OH}^\bullet] = 2.5 \times 10^{10}\text{ cm}^{-3}$, as explained in the Supporting Information. ^bAssuming 1 ppm of ozone. ^cAtkinson. ⁴² ^dToby et al. ⁴³ ^eAtkinson et al. ³⁴ ^fNo reaction. ^gAtkinson. ⁴¹ ^hGrosjean and Grosjean. ⁴⁴ ⁱAtkinson et al. ⁴⁰ ^jDeMore et al. ⁴⁶ ^kNO₂ and O₃ react, but the NO₃ product is quickly photolyzed. ^lBaulch et al. ⁴⁵ ^mLe Person et al. ⁴⁷

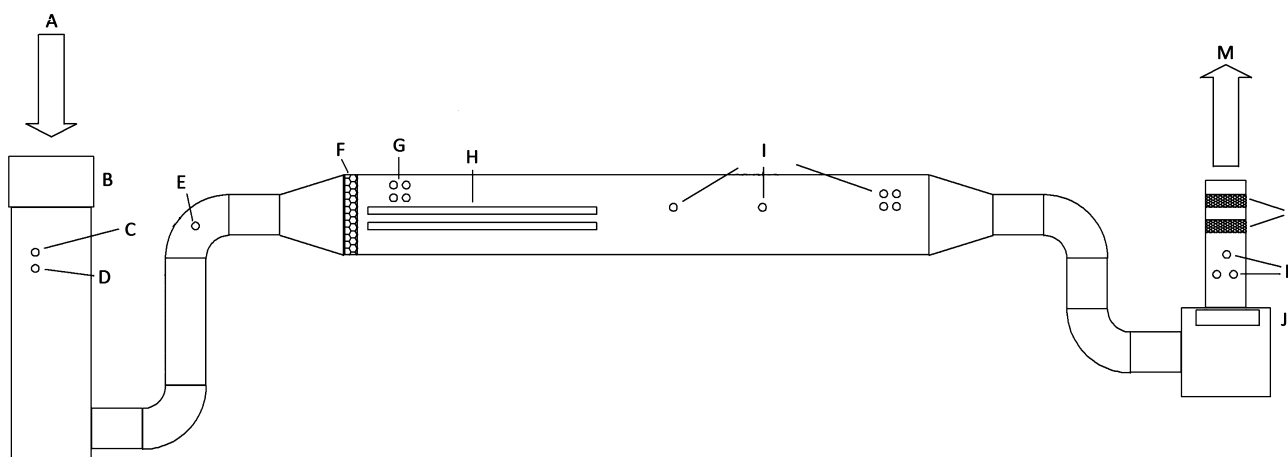
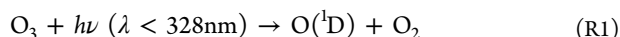


Figure 2. Drawing of the laboratory prototype: (A) Air intake, (B) variable-speed fan, (C) sample port, (D) water vapor inlet, (E) ozone inlet, (F) aluminum honeycomb, (G) electronics feedthrough and sampling ports, (H) UV-C lamps, (I) sampling ports, (J) electrostatic precipitator, (K) sample ports, (L) ozone filter, (M) clean air outlet.

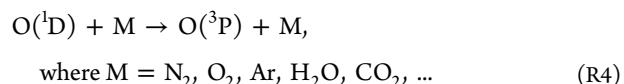
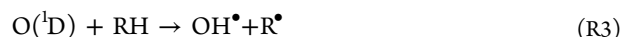
Photochemical Oxidation of VOCs to Form SOA.

Ozone is a cheap reagent, and modern discharge generators can generate >1 mol of ozone using 1 kWh of electricity. However, ozone itself reacts slowly or not at all with many important VOCs (Table 1). Ozone is a starting point for the gas-phase radical chemistry

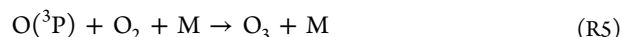


The photolysis rate depends on the lamp emission spectrum and power, the transmission of the air, and the geometry and reflectivity of the reactor; UV lamps use ~90% of the energy in GPAO. Mercury discharge lamps, similar to common fluorescent lamps, are a reliable and efficient UV source, and the emission of mercury atoms at 254 nm matches the maximum in the ozone absorption cross section. Depending on the model of lamp, Hg emission at 185 nm can produce additional ozone through the photolysis of molecular oxygen, as well as OH[•] from H₂O photolysis. Lamp efficiency varies with temperature and wind speed; reactor materials should be UV-compatible.

O(¹D) is highly reactive and will undergo any of several reactions



In reaction R2, the oxygen atom reacts with water vapor to produce hydroxyl radicals (OH[•]), which are powerful oxidants. Although typically $[\text{H}_2\text{O}] \gg [\text{VOC}]$, reaction R3 also produces hydroxyl radicals, while at the same time degrading VOCs. In reaction R4, O(¹D) is quenched through collision with O(³P). The ground-state oxygen atom then reacts with molecular oxygen to regenerate ozone



O(³P) can also add into unsaturated compounds. The yield of OH[•] for a given amount of ozone and UV light depends on a competition between reactions R2 and R3 versus reaction R4. OH[•] reacts with VOCs in the air; for example, it can add into an unsaturated VOC or abstract hydrogen



The organic radical R[•] will be oxidized to one of a variety of stable products including aldehydes and organic acids, depending on its identity and the concentrations of reagents in the

system.³ There are three mechanisms: addition (functionalization), fragmentation, and oligomerization. The first is the addition of oxygen resulting in a drop in vapor pressure and increase in hygroscopicity, leading the products to partition to condensed-phase particles.^{28–30} In the second mechanism, the molecule breaks apart into small volatile fragments such as CO₂, CO, HCHO, and HCOOH.³⁴ Oligomerization reactions build low-vapor-pressure oligomers from the oxidized precursors.

The chemical lifetime of a pollutant is determined by the concentrations of the oxidants in the system. The OH• and O₃ reaction rates of the studied compounds and other selected pollutants are summarized in Table 1. We analyzed the data by assuming constant O₃ and OH• concentrations in the reaction zone. The chemical lifetime τ of compound X toward oxidant Q, where X and Q react at the rate $r = k[Q][X]$, is given by

$$\tau = [X]/r = 1/(k[Q])$$

where the concentration as a function of time is given by $[X]_t = [X]_0 \exp(-t/\tau)$. Estimated lifetimes are reported in Table 1. The OH• reactions dominate removal, with O₃ either not reacting or reacting over a million times slower than OH•. The nominal OH• concentration in the table is $2.5 \times 10^{10} \text{ cm}^{-3}$, estimated using the propane results as described in the Supporting Information. OH• is responsible for the high degree of treatment for relatively short air residence times in the photochemical system. Because $[\text{H}_2\text{O}] \gg [X]$ for ambient relative humidities, OH• reactions are also more important than O(¹D) reactions. At higher O₃ concentrations and/or lamp powers, second-order O_x–HO_x reactions limit the rate of photooxidation, for example, $\text{O}(\text{}^3\text{P}) + \text{O}_3$, $\text{OH}^\bullet + \text{O}_3$, $\text{HO}_2^\bullet + \text{O}_3$, $\text{OH}^\bullet + \text{OH}^\bullet$, and $\text{OH}^\bullet + \text{HO}_2^\bullet$. To summarize, the exposure to OH• in the GPAO system depends on the pollution load, ozone concentration, relative humidity, lamp intensity, and air flow rate/residence time in the reaction chamber.

Laboratory Prototype. The laboratory “proof-of-concept” prototype is shown in Figure 2. This system allows tests of the effects of treatment variables, including air flow, lamp power, relative humidity, ozone dose, and pollutant concentration. Technical data for the device are summarized in Table 2.

Table 2. Key Parameters for the Portable and Laboratory Prototypes

| property | units | portable prototype | laboratory prototype |
|--------------------------------|--------------------------------|--------------------|----------------------|
| reaction volume | L | 70 | 180 |
| ingoing air linear velocity | m s ^{−1} | 3.0 | 0.05–3.0 |
| volumetric flow through device | m ³ h ^{−1} | 46 | 15–850 |
| residence time for air | s | 5.5 | 1.0–45 |
| power at maximum | W | 135 | 267 |
| specific energy input | kJ m ^{−3} | 10 | 3 ^a |

^a1 m/s flow.

Ozone is produced from air using a plasma discharge ozone generator (ACP 3000, O₃ Technology). The discharge also produces trace levels of nitrogen oxides that are converted to nitrate in the oxidation process. Ozone concentrations in the reaction zone are a few parts per million, depending on the air flow rate. UV-C light is generated by 60 W fluorescent lamps (TUV PL-L, Phillips). Following photooxidation and particle

formation, the air stream passes a high-voltage corona discharge wire that gives an electrical charge to the particles, which are then removed by an electrostatic precipitator (ESP). Residual ozone is removed from the air stream using a manganese dioxide catalyst (Tombo no. 8803-CZH2 from Nichias Corp., Tokushima, Japan). The filter consists of MnO₂ powder on a honeycomb support designed to minimize pressure drop, which is <20 Pa at 1 m/s flow velocity. Clean laboratory air was used as the bath gas for tests of the laboratory prototype. Total nonmethane VOC levels were less than 100 ppb, and particle concentrations were up to 3000 cm^{−3}. Air exiting the prototype contained less ozone than the ambient levels found in the laboratory air, regardless of whether the ozone generator was turned on or not, demonstrating the efficiency of the filter. Ozone levels in the exiting air were measured to be 20 ppb or less at an air velocity of 1.3 m/s.

Portable Prototype. The second prototype, shown in Figure 3 with specifications summarized in Table 2, was built in

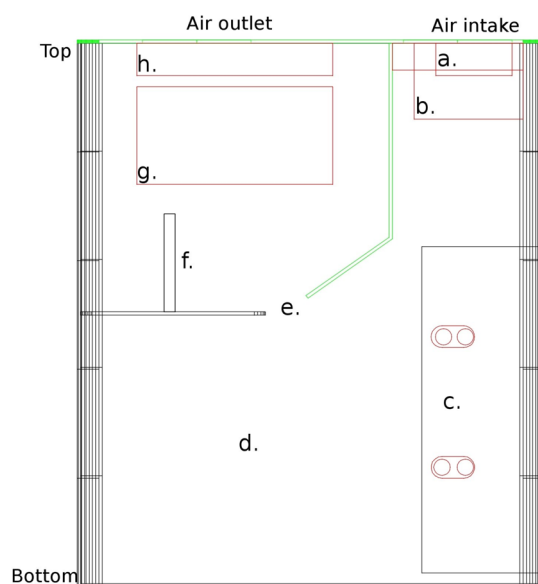


Figure 3. Drawing of the portable prototype: (a) Fan, air intake; (b) ozone generator; (c) UV-C lamps; (d) reaction volume; (e) passage for air leaving the reaction volume; (f) charging electrode; (g) particle filter; (h) ozone filter and outlet.

an aluminum flight case. It was sized to clean the air in a small room (flow rate = 46 m³ h^{−1}). The portable prototype was designed to operate as a well-mixed continuous-flow reactor. The performance of the prototype was determined by comparing the rate of decay in the concentration of the pollutant compared to the background rate of decay through ventilation alone. The portable prototype was characterized using a 23 m³ test chamber at the Technical Research Institute of Sweden.³⁵ Conditions were the same for all of the experiments, with a temperature of 23 °C and 50% relative humidity. About 5.5 m³ of (filtered) chamber air was replaced each hour, giving an air exchange rate of 0.24 h^{−1} that resulted in a ventilation lifetime of 4.2 h. For comparison, the 46 m³ h^{−1} flow rate of the prototype gives a treatment lifetime of 0.5 h. A few milligrams of a given substance was added to the chamber, and the development of the concentration with time was recorded. The goal of the experiments was to determine the pollution removal efficiency of the portable air purifier.

Air Analysis. Isoprene and cyclohexane were analyzed by drawing air through Tenax TA tubes (Markes International), and benzene was analyzed using Chromosorb tubes, after which they were analyzed by gas chromatography/mass spectrometry (GC/MS). A Markes Unity 2 autosampler was used for sample desorption and injection into an Agilent 6850 GC instrument with an Agilent 19091S-105E HP-5MS (5% phenyl methyl siloxane) capillary column (50.0 m \times 200 μ m \times 0.33 μ m) coupled to an Agilent 5975C VL triple-axis mass spectrometric detector. Propane was quantified by sampling ca. 40 L of air into an infrared multipass cell;³⁶ infrared spectra were recorded using a Bruker IFS 66 v/S vacuum interferometer and analyzed using nonlinear least-squares fitting algorithm³⁷ with reference line parameters from the HITRAN database.³⁸ Aerosol size distributions were monitored using a scanning mobility particle sizer (SMPS, TSI model 3080) comprising a model DMA 3081 differential mobility analyzer and a CPC 3772 condensation particle counter. Ozone concentrations were determined using a dual-beam UV photometer ozone monitor (BMT Messtechnik model 930).

RESULTS AND DISCUSSION

Laboratory Prototype. Figure 4 summarizes the results and experimental parameters for tests of propane, cyclohexane,

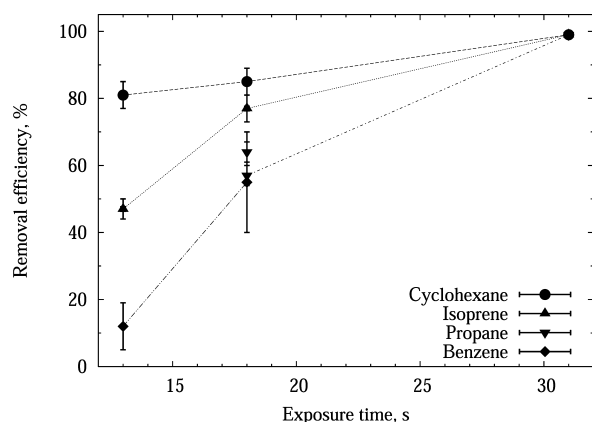


Figure 4. Removal efficiencies for propane, cyclohexane, isoprene, and benzene as functions of exposure time in the laboratory prototype. The experimental conditions are given in Table S1 (Supporting Information).

benzene, and isoprene; experimental conditions are summarized in Table S1 (Supporting Information). There is a strong correlation between residence time (exposure to radicals) and removal efficiency. In all cases where the maximum residence time in this study (31 s) was used, contaminant concentrations were reduced to below the detection limit, <1%. We thus conclude that all investigated compounds can be efficiently removed. Blank experiments were performed using room air without the addition of further pollutants and using the same air with toluene vapor added at different concentrations. Toluene is a common indoor air pollutant and was chosen as a test substance because its particle forming capacity has been described.³⁹

Aerosol particle size and mass distributions were recorded; propane and cyclohexane, for example, did not result in appreciable SOA formation. The air in the laboratory was somewhat polluted due to vacuum pumps, solvents, electronic equipment, and other sources; typical concentrations of

particles in the detectable range of 7–289 nm were 2500–3000 cm^{-3} with a total particle mass of 3–4 $\mu\text{g}/\text{m}^3$ at an assumed density of 1.2 g/mL . The abundance of the smallest particles (<50 nm) was very low, and the number of particles increased with particle size in the measurement range, indicating that the laboratory air was aged (see Figure 5).

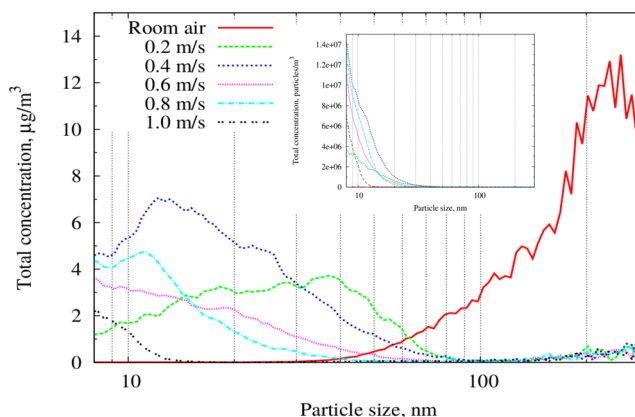


Figure 5. Mass and number (inset) distributions of particles exiting the laboratory gas-phase advanced oxidation prototype as functions of linear flow velocity from an airstream containing 25 ppm of toluene and the electrostatic particle filter turned on. Results for untreated ambient room air is shown for comparison.

Particle removal was achieved using an ESP with a high-voltage power supply of 10 kV. The filter had an open geometry to minimize the pressure drop in the system. Figure 6

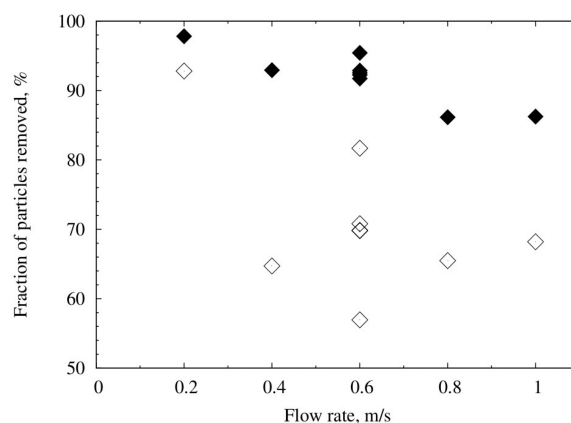


Figure 6. Particle removal efficiencies by mass (solid diamonds) and number (open diamonds) as functions of linear flow velocity, demonstrating the performance of the electrostatic filter.

shows the removal of particles in the 7–289 nm range as a function of flow rate. The removal efficiency of the ESP was very high, >85% at the highest flow rate, and the harvesting of pollution by the particles became increasingly efficient as the residence time increased.

Toluene (25 ppm) was added to the air stream to generate SOA. Figures 5 and 7 show the particle mass distributions with and without the ESP, respectively, at a series of flow velocities. These results demonstrate that gas-phase advanced oxidation generates particles from VOC pollution and removes the particles. Larger particles formed when the residence time was longer, and the size distribution shifted toward larger particles. When comparing the scales, it can be seen that, at all flow rates,

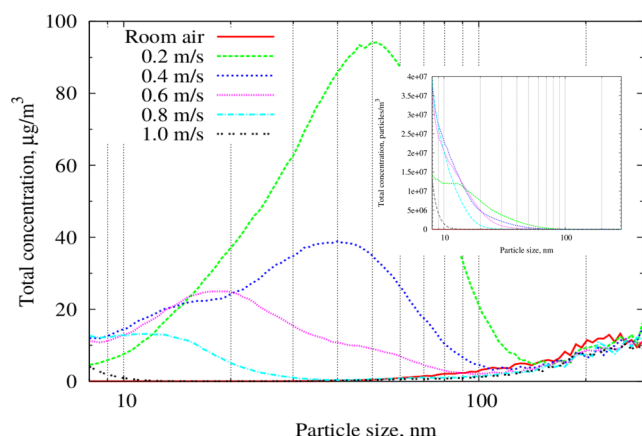


Figure 7. Mass and number (inset) distributions of particles formed in the air purification system in an air stream dosed with 25 ppm of toluene. This test was similar to that shown in Figure 5, but with the electrostatic precipitator turned off. This figure shows the generation of ultrafine particles by the system.

the removal of particles by the filter was significant. At the lowest flow, the removal was about 98%.

Portable Prototype. The particle size distributions were fairly uniform during all experiments, being approximately log-normal with median diameters around 10–60 nm. The amplitude of the distributions showed large quasiperiodic variations due to wall interactions. When the device was on, the particle concentration decreased substantially. The change in the shape of the distribution shows that particle removal efficiency changed with size and that the device removed particles over the whole size range. The rates of removal of cyclohexane, due to ventilation alone and due to ventilation together with the portable prototype, were measured in the test chamber. The results are shown in Figure 8 and were used to

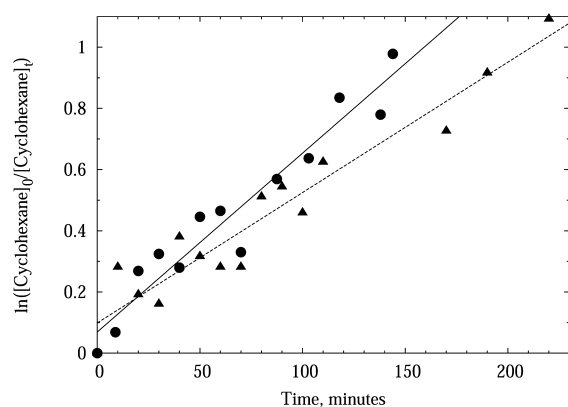


Figure 8. Time evolution of cyclohexane concentration in the chamber test of the portable prototype: prototype on (circles) vs off (triangles).

determine an average OH radical concentration of $(4.6 \pm 0.4) \times 10^9 \text{ cm}^{-3}$ in the reaction volume of the portable device. The ability of the prototype to remove particles is shown in Figure S1 (Supporting Information).

Comparison and Outlook. For the laboratory prototype, a specific energy input (SEI) of 3 kJ m^{-3} produced an average OH \cdot concentration of $(2.5 \pm 0.3) \times 10^{10} \text{ cm}^{-3}$, and for the portable unit, 10 kJ m^{-3} produced a OH \cdot concentration of $(4.6 \pm 0.4) \times 10^9 \text{ cm}^{-3}$. In comparison, the average tropospheric OH \cdot number concentration, $1.2 \times 10^6 \text{ cm}^{-3}$, is many orders of

magnitude smaller.³ The physically larger laboratory system was able to use the UV light more efficiently because of its longer absorption path length and the higher reflectivity of smooth shiny stainless steel as opposed to somewhat oxidized and rough aluminum. These hydroxyl radical concentrations were found to be sufficient to oxidize a wide range of VOCs that are interesting from the standpoint of emissions control and indoor air quality. A commercially interesting maximum residence time of 60 s in the treatment region with $[\text{OH}\cdot] = 2.5 \times 10^{10} \text{ cm}^{-3}$ means that >50% removal can be achieved for compounds with a OH \cdot reaction rate higher than $5 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$. Hundreds of industrially important VOCs including unsaturated compounds and those with secondary and tertiary hydrogen atoms fall into the accessible range; however, in each case, the potential formation of unwanted reaction products should also be considered. Examples of molecules that cannot be treated with the current OH \cdot exposure include some important small molecules: CH_4 ,³⁴ $k(298) = 6.4 \times 10^{-15}$; CO ,³⁴ $k(298) = 1.5 \times 10^{-13}$; NH_3 ,⁴⁰ $k(298) = 1.6 \times 10^{-13}$.

The formation of secondary pollution needs to be considered carefully, especially given the large number of pollutants that could be processed in GPAO systems. The formation of air pollution in the atmosphere is a useful first approximation. For example, in situ photochemistry produces ca. 16 Tmol a^{-1} of CO from nonmethane VOC.³ Because the emission of isoprene, terpenes, and other organic species is around 12 Tmol a^{-1} , this shows the potential for the formation of CO with the same order of magnitude as the VOC pollution itself. Depending on the application, this might not be a serious concern, as odors occur in the part-per-billion range, well below the U.S. Occupational Safety and Health Administration (OSHA) workplace exposure limit of 50 ppm. However, CO in the atmosphere and in the GPAO system is primarily formed from formaldehyde, and formaldehyde is already a concern at concentrations of tens of parts per billion. As shown in Table 1, the OH chemical lifetime of formaldehyde is a few seconds, demonstrating that formaldehyde concentrations, although lower than those of CO, can be significant. Our experiments using infrared detection did not show any evidence of formaldehyde formation, but an unknown amount might have been lost in the transfer between the GPAO system and the multipass cell. In addition, as shown in Figures 5 and 7, the GPAO system generated a significant concentration of ultrafine particles. Because their small size, UFPs are not removed effectively by an electrostatic precipitator, especially at particle diameters below ca. 30 nm. These particles can be effectively removed using high-efficiency particulate air (HEPA) filters, however, with the disadvantage of increased expense and pressure drop. Peroxides formed in GPAO will likely be decomposed by the catalyst. Other minor but more complex secondary pollutants including epoxides, aldehydes, and oxidized and/or nitrated aromatics are of concern and should be quantified in specific applications. In general, vapor pressure will drop with oxidation,^{28–30} and this will lead many but not all of these species to be trapped in the particle filter. In summary, we strongly recommend that the formation of secondary pollutants be considered on a case-by-case basis, and it will be the subject of future studies by our group.

In addition to a broad scope, gas-phase advanced oxidation has a low SEI relative to those of many existing control methods. In situ radicals are generated using ozone generated from air and electricity. Modern ozone generators yield over 1 mol of ozone per kilowatt-hour of electricity. UV lamps are

efficient at turning power into high-energy photons. Once generated, the hydroxyl radicals are robust and survive multiple collisions with atmospheric components such as N_2 , O_2 , and H_2O until they find a reaction partner. Current technologies energize the entire air stream (low-temperature plasma, pyrolysis, cryocondensation) or come into physical contact with the airstream (biofilters, activated carbon filters, high temperature catalysis, photocatalytic oxidation), generating an energy-intensive pressure drop, and therefore have uneconomic SEIs.²⁴ In contrast, GPAO works through the in situ diffusive mixing of OH^\bullet followed by reactive collision, so the oxidative capacity can be adjusted to match the load. A survey of the literature on photocatalytic oxidation shows SEIs around 50 times higher than is used by gas-phase advanced oxidation.²¹ In addition, many industrial production cycles produce bursts of pollution when a mold is opened, a batch is finished, a car is painted, and so on. Many pollution control systems are either on or off (low-temperature plasma, combustion, catalysis). In contrast, the flow rate, lamp intensity, and ozone concentration in GPAO can easily be controlled to optimize energy use. There might be applications in which 185 nm radiation would be an advantage, justifying the increased cost of these bulbs, for example, for pollutants with a high absorption cross section at this wavelength and a low OH reaction rate.

GPAO shows significant potential for efficiently removing a wide range of pollutants including saturated and unsaturated VOCs, particles, and ozone. The method has been tested for hydrocarbons with different functionalities and for particles. The nature of the method is such that it will be advantageous to design air purifiers for different pollutant scenarios. Parameters that can be varied to optimize the performance are residence time, irradiation, ozone concentration, and relative humidity. These tests were performed using relatively high pollution loads. Given the chemical lifetimes arising from the demonstrated OH radical concentrations, GPAO will also be applicable to lower pollutant concentrations.

Long-term testing is needed to investigate the lifetimes of different components of the system and to determine the need for maintenance of the components. It is also necessary to thoroughly examine the outgoing air, for example, to check for elevated levels of carbon monoxide or peroxides and hydroperoxides that could potentially cause irritation.

Applications of in situ gas-phase advanced oxidation include odor control for livestock and biogas production and wastewater treatment, indoor air purification, and emissions control from processes emitting VOCs, such as use of solvents, plastics manufacturing, foundry operations, and food processing.

■ ASSOCIATED CONTENT

● Supporting Information

Table detailing experimental conditions used to determine removal efficiencies, and figure showing particle concentrations in the test chamber. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare the following competing financial interest(s): M.S.J. is coauthor of a patent that describes gas-phase advanced oxidation. The patent rights are controlled by the University of Copenhagen Technology Transfer Office according to Danish Law for University Employees. M.S.J. is a member of the board of directors of Infuser ApS, which has a license for the patent. The research was funded in part by O3 Technology, which is currently owned by Infuser ApS.

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■ ABBREVIATIONS

| | |
|---------------|--|
| CPC | condensation particle counter |
| DMA | differential mobility analyzer |
| ESP | electrostatic precipitator |
| GC/MS | gas chromatography/mass spectrometry |
| GPAO | gas-phase advanced oxidation |
| HO_x | family of atmospheric oxygen radicals |
| HV | high voltage |
| HVAC | heating, ventilation, and air conditioning |
| NO_x | family of atmospheric nitrogen oxide radicals |
| SEI | specific energy input |
| SMPS | scanning mobility particle sizer |
| SOA | secondary organic aerosol |
| UV-C | ultraviolet radiation with a wavelength between 280 and 100 nm |
| VOC | volatile organic compounds |

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