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Published in: AIMS Environmental Science

DOI: 10.3934/environsci.2016.1.141

Publication date: 2016

Document version Publisher's PDF, also known as Version of record

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Citation for published version (APA): Adnew, G. A., Meusinger, C., Bork, N., Gallus, M., Kyte, M., Rodins, V., ... Johnson, M. S. (2016). Gas-phase advanced oxidation as an integrated air pollution control technique. *AIMS Environmental Science*, *3*(1), 141-158. https://doi.org/10.3934/environsci.2016.1.141



AIMS Environmental Science, 3(1): 141-158. DOI: 10.3934/environsci.2016.1.141 Received 4 January 2016, Accepted 21 March 2016, Published 28 March 2016

http://www.aimspress.com/journal/environmental

Research article

Gas-phase advanced oxidation as an integrated air pollution control

technique

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Abstract: Gas-phase advanced oxidation (GPAO) is an emerging air cleaning technology based on the natural self-cleaning processes that occur in the Earth's atmosphere. The technology uses ozone, UV-C lamps and water vapor to generate gas-phase hydroxyl radicals that initiate oxidation of a wide range of pollutants. In this study four types of GPAO systems are presented: a laboratory scale prototype, a shipping container prototype, a modular prototype, and commercial scale GPAO installations. The GPAO systems treat volatile organic compounds, reduced sulfur compounds, amines, ozone, nitrogen oxides, particles and odor. While the method covers a wide range of pollutants, effective treatment becomes difficult when temperature is outside the range of 0 to 80 °C, for anoxic gas streams and for pollution loads exceeding ca. 1000 ppm. Air residence time in the system and the rate of reaction of a given pollutant with hydroxyl radicals determine the removal efficiency of GPAO. For gas phase compounds and odors including VOCs (e.g. C₆H₆ and C₃H₈) and reduced sulfur compounds (e.g. H₂S and CH₃SH), removal efficiencies exceed 80%. The method is energy efficient relative to many established technologies and is applicable to pollutants emitted from diverse sources including food processing, foundries, water treatment, biofuel generation, and petrochemical industries.

Keywords: Gas-phase advanced oxidation; emissions control; VOCs; reduced sulfur compounds; amines

BTEX	Benzene, toluene, ethyl benzene and xylenes
DMEA	N,N-Dimethylethyl amine
ESP	Electrostatic precipitator
FID	Flame ionization detector
GC-FID	Gas chromatography-flame ionization detector
GC-PID	Gas chromatography-photoionization detector
GC-NSD	Gas chromatography-nitrogen sensitive detector
GPAO	Gas-phase advanced oxidation
HEPA	High efficiency particulate filter
HV	High voltage
NO _x	Mono nitrogen oxides (NO and NO ₂)
OU	Odor unit
PID	Photoionization detector
PM	Particulate matter
ppm	Parts per million, µmol/mol
Qair	Volumetric flow rate of air
R	Aryl and/or alkyl group
TD-GC/MS	Thermal desorption-Gas chromatography/Mass spectrometry
UV-C	Ultraviolet radiation (280–185 nm)
VOC	Volatile organic compound

1. Introduction

Abbreviations:

Anthropogenic (and natural) emissions into the atmosphere have a wide range of negative effects including those on air quality, human health, agricultural output and climate [1–4]. Air pollution gives rise to adverse health impacts including cardiorespiratory diseases, cancer, nervous system disorder and death [2–7]. Air pollutants include particulate matter (PM) and heavy metals, and gaseous compounds such as volatile organic compounds (VOCs), SO₂, NO_x (NO and NO₂), ozone and carbon monoxide [4].

A variety of methods are available to improve indoor air quality and reduce industrial emissions. In this section we begin by reviewing the available technologies, and proceed by describing GPAO, an emerging technology. The key properties of the techniques are their initial and operational cost, energy use, sensitivity to conditions such as gas composition, pollution load, temperature, and relative humidity, range of applicable pollutants, long term performance, and the possible formation of unwanted products [8]. Techniques used to maintain indoor air quality include ventilation, particle filters, activated charcoal, electrostatic filters and ion air cleaners [9]. Ventilation, regardless of the costs of installation, operation and maintenance, is limited by outdoor air quality, particularly in heavily polluted areas [10]. With ventilation, pollution is not converted to less hazardous products, but rather, is exchanged and diluted with outdoor air. Particle filters can remove PM, but they are not designed to treat gaseous pollutants and require ongoing maintenance and replacement, and the filters themselves can be a source of odor and VOCs [11,12]. VOCs can be removed using activated charcoal at the expense of energy needed to overcome the pressure drop of

the filter. Charcoal filters give rise to a material disposal problem, and can be a source of odor [9]. Electrostatic filters and ion cleaners remove particles, but may generate ozone, which is hazardous and gives rise to hazardous oxidation products [13–16]. Electrostatic filters charge particles and remove them from the airstream using electrical fields, but are inefficient at removing gaseous pollutants and have a limited effect on nanoparticles [16,17]. Table 1 summarizes technologies used for indoor air purification.

Air pollution control technology	Target species	Advantages	Disadvantages	Ref
Catalytic Oxidation	Gas-phase pollution	Highly reactive for wide range of pollutants	Price of catalyst Catalyst may contain rare and/or toxic elements Catalyst vulnerable to poisoning Generally not suited to complex or variable mixtures High energy input, high capital cost High pressure drop Potentially high temperature	[8,18–20]
Electrostatic filters and ion cleaners	Particles	Low pressure drop Highly effective	Susceptible to arcing Limited efficiency for nanoparticles (0–50 nm) Source of ozone Require cleaning	[19,21]
Fibrous particle filter (e.g. HEPA)	Particles	Removes particles (0.1–4 µm) Economical and efficient	With time filters generate odor Cannot remove VOCs Release secondary pollutants when in contact with ozone Source of contamination for microorganisms Enable growth of microorganism Pressure drop	[8,18–22]
GPAO	Gas-phase pollutants (organic and inorganic), particles	High reactivity of hydroxyl radical and ozone Low pressure drop Possible removal of biogenic pathogens such as bacteria and viruses due to UV radiation and strong oxidative environment	Removal efficiency depends on residence time of polluted airstream No recovery of pollutants Not equally efficient to all pollutants Source of nanoparticles (0–50 nm) Possible formation of unwanted reaction products such as carbon monoxide and formaldehyde Requires investigation of oxidation products	[9]
Non-Thermal Plasma (NTP)	Gas-phase pollutants (organic and inorganic) and airborne microbes	Removes odor and particles	Produces ozone, NO _x , CO and other by-products.	[8,18]
Ozone	Gas-phase pollutants (organic and inorganic) and airborne microbes	Reactive oxidant Relatively cheap	Reacts slowly with many pollutants Does not react with aliphatic hydrocarbons Incomplete oxidation leads to many byproducts including formaldehyde and carbon monoxide Generation of secondary organic aerosols	[8,19]

Table 1. Comparison of GPAO and other indoor air control techniques.

Photocatalytic Oxidation	Gas-phase pollutants	Can be activated by sunlight or UV light	Limited treatment capacity High energy input to activate surfaces (if using artificial UV-light) Vulnerable to poisoning by particles and foreign species Variable effectiveness Not suited for treatment of very volatile species Generation of partially oxidized products Pressure drop	[8,18–20]
Plasma with catalytic oxidation	Gas-phase pollutants and particles	Removes acetaldehyde and particles with an increased efficiency compared to catalytic oxidation alone	Produces ozone, NO _x and other harmful by-products. The catalyst decreases in efficiency with usage	[23]
Sorption (activated carbon, zeolite, activated alumina, silica gel and molecular sieves)	Gas-phase pollutants (organic and inorganic), particles	Good efficiency for gas phase pollutants Does not generate harmful by-products Allows capture and recycling of vapors, for example fumes to fuel	Needs regeneration Releases airborne microorganisms, enables them to grow Interaction with ozone as pollutant releases harmful secondary products Saturation may cause re-emission	[8,19]
Ultraviolet germicidal irradiation	Airborne microbes	Inactivates airborne microorganisms	May generate ozone and dioxin	[8]

Industrial and agricultural emission control techniques include biofiltration, absorption, adsorption and oxidation [24]. Biofiltration techniques are limited to a certain range of pollutants and are sensitive to environmental conditions such as moisture, temperature, acidity, flow rate and oxygen content, and media characteristics such as porosity [24–27]. Aqueous scrubbers are widespread and a multistage approach is required if both acidic and basic compounds are present in the airstream [27]. Adsorption techniques are dependent on the physicochemical characteristics of the adsorbent and become saturated at higher pollutant concentrations [27]. In addition, the adsorbent filter may be clogged by particles causing a pressure drop, and particles can coat the filter, degrading performance [27]. Combustion (thermal oxidation) techniques require higher temperature and further treatment may be required for nitrogen, sulfur and halogen containing pollutants [24,27–29]. Table 2 summarizes technologies used for treating air pollution in industrial and agricultural settings.

Technology	Pollutant description and removal efficiency	Advantage	Limitation	Ref
Absorption/ scrubbing	$\begin{array}{l} Q_{air} < 1.7 \times \\ 10^5 \ m^3 \ h^{-1} \\ 500 - 15,000 \\ ppm \\ 90 - 98\% \end{array}$	Easy to maintain	Physicochemical characteristics of the VOC affects the removal efficiency Finding proper solvent	[24,30]
Adsorption	Concentration 100–5000 ppm 80–96%	Reduces volumetric flow for downstream pollution control Pollutant recovery possible	The VOC, inlet stream temperature, pressure and flow rate, and the adsorbent, affect the removal efficiency Particles may block they system and increase pressure drop	[24,30]

Table 2. Summary	v of technique	es used for j	pollution (control in	industrial	and ag	ricultural	facilities

				-
Biofilter	$\begin{array}{l} Q_{air} < 1.7 \times \\ 10^5 m^3 h^{-1} \\ \text{Concentration} \\ < 1000 \text{ppm} \\ 6095\% \end{array}$	Low operation cost Long media life	Less effective at higher concentrations and for halogenated/aromatic compounds Sensitive to environmental conditions including variations in concentration, temperature and humidity Large ground area May produce secondary pollutants which are more toxic Dependent on degradability of the compound Pollutants may be toxic to the microbe	[24,28,29, 31–34]
Catalytic oxidation	$\begin{array}{l} Q_{air} < 1.3 \times \\ 10^5 \ m^3 \ h^{-1} \\ 100 - 2000 \\ ppm \\ 90 - 98\% \end{array}$	Requires less heat and fuel than thermal oxidation Higher removal efficiency at lower temperature due to the presence of catalyst	Overloading of catalyst with particles decreases efficiency Catalyst is sensitive to inlet stream concentrations and flow conditions Catalyst can be poisoned by sulfur, chlorinated compounds or heavy particle loadings Catalyst needs regular replacement, Halogenated and sulfur compounds converted to acids need further treatment Expensive rare elements used	[24,28,29]
Condensation	$\begin{array}{l} Q_{air} < 5.1 \times \\ 10^3 \ m^3 \ h^{-1} \\ 5000 - 10,000 \\ ppm \\ 70 - 85\% \end{array}$	Solvent able to be re-used Efficient for compounds with boiling point above 311 K Suitable for compounds which have high boiling point and high vapor phase concentration	High capital and operation cost Less effective at low concentration Higher cooling power required to recover volatile species	[24,29,30]
Gas- phase advanced oxidation (GPAO)	85–99% 1300–40,000 m ³ h ⁻¹	High reactivity of hydroxyl radical and ozone Low pressure drop Possible removal of biogenic pathogens such as bacteria and viruses due to UV radiation and strong oxidative environment	Removal efficiency depends on the flow rate and residence time of polluted airstream Requires investigation of oxidation products No recovery of pollutants Not equally efficient for all pollutants Source of nanoparticles (0–50 nm) Possible formation of unwanted reaction products such as carbon monoxide and formaldehyde	[9]
Non-thermal Plasma	$\begin{array}{c} Q_{air}\!<\!200,\!000 \\ m^3 \ h^{\!-\!1} \end{array}$	Smaller volume relative to adsorption and absorption techniques	Undesirable side products (CO, NO _x and O ₃)	[35–37]
Thermal oxidation	$\begin{array}{c} Q_{air} \! < \! 8.5 \times \\ 10^5 m^3 h^{\!-\!1} \\ Concentration \\ 100\!-\!2000 \\ ppm \\ Residence \\ time \\ 0.5\!-\!1.0 s \\ 95\!-\!99\% \end{array}$	Treats a majority of pollutants	Affected by turbulence (for mixing) and the amount of oxygen Generates NO_x , CO, CO ₂ Halogenated compounds require additional treatment due to release of acids May require additional fuel to maintain combustion	[24,28,29]

The term *gas-phase advanced oxidation* (GPAO) is an extension of the traditional method of *advanced oxidation* which includes different techniques for generating the hydroxyl radical for water purification [30]. GPAO is an air pollution control technique based on the photochemical reaction mechanisms occurring in the atmosphere [6]. An overview of the technique is presented below, while

the principles were detailed by Johnson et al. [9,38]. As shown in Figure 1, polluted air is blown or drawn into the system. Ozone is added and photolyzed by UV-C lamps, producing highly reactive singlet oxygen atoms (O^1D), reaction R1. Singlet oxygen abstracts hydrogen from water, reaction R2, or VOCs, reaction R3, to generate reactive hydroxyl radicals (OH·), reaction R2 [39].



Figure 1. Schematic of pollution removal using GPAO.

$$O_3 + hv (\lambda < 328 \text{ nm}) \rightarrow O(^1\text{D}) + O_2$$
(R1)

$$O(^{1}D) + H_{2}O \rightarrow 2OH$$
 (R2)

$$O(^{1}D) + R-CH_{3} \rightarrow OH + R-CH_{2}$$
(R3)

 $O(^{1}D)$, due to its high reactivity, collides with molecules present in the air stream yielding ground state oxygen ($O(^{3}P)$) (R4). The ground state oxygen reacts with molecular oxygen to generate ozone (R5) which can be photolysed again in (R1), restarting the production of OH; $O(^{3}P)$ could also react directly with unsaturated VOCs [6,9].

$$O(^{1}D) + M \rightarrow O(^{3}P) + M$$

Where M = N₂, O₂, Ar, H₂O, CO₂, ... (R4)
$$O(^{3}P) + O_{2} + M \rightarrow O_{3} + M$$
 (R5)

The hydroxyl radical abstracts hydrogen from VOCs (R6) or it can add to unsaturated VOCs.

$$OH^{\cdot} + R - CH_3 \rightarrow H_2O + R - CH_2^{\cdot}$$
(R6)

The radical R-CH₂· will react further via one of three different mechanisms (addition, fragmentation and oligomerization) depending on the details of the chemistry in the GPAO system [9].

The first mechanism is addition of oxygen to the organic radical ($R-CH_2$ ·) producing oxidized products including aldehydes and acids [40–43]. The peroxy radical (·OOCH₂-R) yields aldehydes reacting with hydrogen peroxide and hydroxyl radical (R8 and R9) or with other peroxy radicals (R10 and R11). Further oxygen addition and reaction with hydroxide with the aldehyde generates acids (R11–R16).

$$R-CH_2 + O_2 + M \rightarrow OOCH_2 - R + M$$
(R7)

$$OOCH_2 - R + OOH \rightarrow HOOCH_2 - R + O_2 (R8)$$

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$HOOCH_2\text{-}R + OH \rightarrow HC(O)\text{-}R + OH + H_2O$	(R9)
$\cdot OOCH_2\text{-}R + \cdot OOCH_2\text{-}R \rightarrow \cdot OCH_2\text{-}R + \cdot OCH_2\text{-}R + O_2$	(R10)
$\cdot OCH_2\text{-}R + O_2 \rightarrow OCH\text{-}R + \cdot OOH$	(R11)
$OCH-R + OH \cdot \rightarrow \cdot C(O)-R + H_2O$	(R12)
$\cdot C(O)\text{-}R + O_2\text{+} M \rightarrow \cdot OOC(O)\text{-}R + M$	(R13)
$\cdot OOC(O)\text{-}R + \cdot OOH \rightarrow HOOC(O)\text{-}R + O_2$	(R14)
$\cdot OOC(O)$ -R + $\cdot OOH \rightarrow HOC(O)$ -R + O ₃	(R15)
$HOOC(O)-R + H_2O \rightarrow HOC(O)-R + H_2O_2$	(R16)

The GPAO method is able to treat compounds with an OH· reaction rate faster than ca. 5×10^{-13} cm³ s⁻¹ in a matter of seconds provided that the oxidation capacity of the system is not saturated [9]. The oxidized products of the reactions initiated by OH· radicals are typically less volatile and more hygroscopic than their reduced counterparts [41] and the products will partition onto pre-existing particles (or form new particles) that will continue to grow by taking up additional pollution. The particles are charged using high voltage (HV) and removed, e.g. by an electrostatic precipitator (ESP) while excess ozone is removed from the airstream by a manganese dioxide catalyst.

In the second mechanism, the organic radical may fragment in to smaller volatile fragments such as carbon dioxide, carbon monoxide, formaldehyde and formic acid which may pass through the system with the air stream, if they are not first oxidized by $OH \cdot [6,44-46]$. The alkoxy radical ($\cdot OCH_2$ -R) will decompose to give formaldehyde and an organic radical (R17). The formaldehyde formed is either released with the air stream or may be converted to carbon monoxide or carbon dioxide (R17-R21) [6,45].

$$OCH_2 - R \to CH_2O + R \cdot$$
 (R17)

$$CH_2O + hv + O_2 \rightarrow CHO + HO_2$$
 (R18)

$$CH_2O + OH \rightarrow CHO + H_2O$$
 (R19)

 $CH_2O + hv \rightarrow CO + H_2$ (R20)

$$\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$$
 (R21)

Finally, the third mechanism is oligomerization in which oxidation products join together to form low volatile products within particles.

This study describes applications of gas phase advanced oxidation, a new and emerging pollution control technique, to indoor air pollution and to industrial and agricultural emissions control. The technology is presented in the context of earlier work (cf. Tables 1 and 2) in the field of waste air management. An earlier paper presented laboratory results [9], and in this study we present the results of a series of real-world tests, in addition to a laboratory test applying the technology to indoor air. The goal is to characterize the performance of GPAO towards a wide range of pollutants in the laboratory and to investigate the performance in commercial scale applications.

2. Indoor air purification

2.1. Laboratory testing

The laboratory system is designed to characterize the effect of treatment variables such as air flow, ozone dose, lamp power, relative humidity and pollution concentration on GPAO removal efficiency. The laboratory testing is described in a previous publication [9] and is summarized here for comparison to the new applications detailed in the subsequent sections. Performance was quantified using propane, cyclohexane, benzene and isoprene as test compounds [9]. These compounds were selected as being representative of a wider range of VOCs. The first three, propane, cyclohexene and benzene, are often found in industrial exhaust streams; isoprene is a common biogenic VOC [6,47].

In the experiment, ozone is generated using a plasma discharge ozone generator (ACP 3000, O₃ Technology) and UV-C light is emitted by four 55 W fluorescent discharge lamps (Philips TUV 55W HO, G55 T8). Laboratory air is used as the bath gas and individual pollutants are supplied to the GPAO prototype via a saturated airstream using an impinger as a bubbler. The airstream went through the stages of GPAO treatment shown in Figure 1: ozonolysis, photolysis, particle growth and filtration. Finally the airstream passes a MnO₂ catalyst (Tombo no. 8803-CZH2 from Nichias Corp., Tokushima, Japan) to remove residual ozone. Isoprene and cyclohexane are sampled by drawing air to Tenax TA adsorbent tubes (Markes International) and benzene is sampled using Chromosorb tubes. Outlet measurements are performed after the MnO₂ catalyst in each of the experiments. Samples are analyzed using thermal desorption gas chromatography mass spectrometry (TD-GC/MS). Propane is analyzed using multipass infrared absorption cell [9,48]. Ozone concentrations are determined using a dual-beam UV photometer ozone monitor (model 930, BMT Messtechnik). The volumetric flow rate is quantified by measuring the airflow in and out of the prototype using a wind speed anemometer (Testo 405, Testo AG, Germany).

Table 3 shows the experimental conditions and removal efficiency ($RE = \frac{[X]_{inlet} - [X]_{outlet}}{[X]_{inlet}} \times 100$,

where [X] is pollutant concentration) for the laboratory scale experiments. GPAO enables removal with an efficiency of more than 98% with the exception of benzene, and a residence time of 12 to 31 s, a volumetric energy input of ca. 3 kJ m⁻³ and volumetric flow rate of ca. 170 to 400 m³ h⁻¹. Given the reactor volume of 180 L, this implies a space velocity of 940 to 2200 reactor volumes treated per hour.

	Compound	Inlet concentration	Speed of air	Residence time	<i>RE</i> /%
		/ppm	$/{\rm m}~{\rm s}^{-1}$	/s	
Laboratory	Benzene	0.38–0.54	1.4 to1	13–18	$12\pm7-55\pm15$
scale	Cyclohexane	0.4–1.1	1.4–0.6	13–30	$81 \pm 4 - 99 \pm 1$
prototype [9]	Isoprene	2.4–5.9	1.4–0.6	13–31	47±3–99±1
	Propane	3.8–0.64	1–0.6	18–31	57±3–99±1
Indoor	α-pinene	1.94	1.9	12	80±0.6
prototype					

Table 3. Summary of experimental conditions and resulting removal efficiencies (RE).

Table 3 lists ranges of inlet concentration, speed of air, residence time and removal efficiency. The range of inlet concentrations of propane for example spans from 3.8 to 0.64 ppm. Experiments at

high concentrations were performed at 1 m s⁻¹ corresponding to 18 s residence time, and a recorded removal efficiency of 57.3%.

The removal efficiency of pollutants depends on their reaction rate constants with hydroxyl radicals e.g. the lower removal efficiency for benzene compared to other pollutants is due to its slower reaction rate constant with OH· [46,49–54]. The other factor affecting the removal efficiency of pollutants is residence time. As shown in Table 3, the higher the residence time, the higher the removal efficiency. A decrease in air speed from 1.4 to 0.6 m s⁻¹ corresponds to an increase in residence time from 13 to 30 seconds which increases the removal efficiency of isoprene from 47 to 99%. Residence time has a higher impact on removal efficiency than changes in inlet concentration as shown in Table 3 for isoprene, cyclohexane and benzene. This means that the oxidation capacity of the laboratory scale prototype is not saturated under these conditions. The optimal residence time for a specific operating condition depends on several factors including pollutant type and concentration, initial air flow rate, and dimensions of GPAO. In addition to OH· radical reactions, UV-C radiation may accelerate the removal of pollutants that have significant absorption cross sections. Some odorous pollutants including reduced sulfur compounds and oxygenates like aldehydes and esters have UV-active chromophores.

2.2. Indoor applications

An indoor prototype was built to study the efficiency of GPAO for indoor air pollution treatment. Figure 2 shows a schematic of this setup. The indoor laboratory scale prototype is smaller in size and has a rectangular cross section (with dimension of 1.52 m \times 0.26 m \times 0.24 m (length \times width \times height)) compared to the cylindrical laboratory scale prototype discussed above. The total volume is 95 L with a reaction chamber volume of 62.6 L. Monoterpenes are one of the most common VOC indoor air pollutants [55]. In this study α -pinene was chosen as a representative to study the efficiency of GPAO in controlling pollution due to monoterpenes since their atmospheric reactions are well investigated [56–60]. α -pinene was supplied to the GPAO prototype via a saturated airstream at a flow rate of 100 mL min⁻¹ using an impinger as a bubbler. The volumetric flow rate was established by measuring the airflow in and out of the prototype using a wind speed anemometer (Testo 405, Testo AG, Germany). The total volumetric flow rate was maintained at 18.7 m³ h⁻¹ corresponding to a residence time of 12 seconds and a space velocity of 300 h^{-1} . The volumetric energy input of this prototype was ca. 4.6 kJ m⁻³. Ozone is generated using a plasma discharge ozone generator (ACP 500, O₃ Technology) and 60 W flouorescent lamps (TUV PL-L 60W HO/4P UV) were used to generate UV-C light. Ozone concentrations were determined using an ozone monitor (Eco Sensor model UV-100). Laboratory air was used as the bath gas.

Analysis of α -pinene was performed using a photoionization detector (PID) (Procheck Tiger V1.9, Ion Science, USA) and the same TD-GC/MS system described by Johnson et al. [9]. Tests were performed in three scenarios: using only ozone with the UV-C light turned off, using only UV-C light without ozone supply, and using ozone in the presence of UV-C light. A removal efficiency of 60±1.6% was observed using only ozone while UV-C lamps are turned off. UV-C light alone did not have an observable removal efficiency towards α -pinene. As shown in Table 3, a removal efficiency of 80% was observed at a residence time of 12 seconds using GPAO when both UV light and ozone were present.



Figure 2. Indoor prototype. 1) inlet fan, 2) O₃ generator, 3) UV-C lamp, 4) reaction chamber, 5) HEPA (high-efficiency particulate) filter, 6) MnO₂-catalyst, 7) clean air, 8) outlet fan.

3. Industrial and agricultural pollution control

The goal of this section is to describe several examples of GPAO systems used in commercial environments where there is significant variation in temperature, relative humidity and concentration of pollutants. The photochemical mechanism is the same as for the laboratory scale prototype but the dimensions of the system, air flow, dose of ozone, UV-C lamp power, and the possible addition of an aqueous scrubber are determined based on the specific case. Installations are designed based on the concentrations of pollutants determined using standard methods including TD-GC/MS, PID and flame ionization detectors (FID).

Sector	Location	GPAO system	Target pollution	Concentration	${{Q_{air}}/}{{(m^3 h^{-1})}}$	Residence time /s	RE /%
Fiberglass	Jutland, Denmark	Shipping container prototype	Styrene	11 ppm	1500 ¹	120	99
Ferrous	Saarbrücken,	Modular	BTEX ² ,	80 ppm	Variable	Variable	>89
Foundry	Germany	prototype	amines				
Waste water	Jutland,	CLIMATIC ⁴	Odor, VOC, oil	200 to 1400	14,000	10–20	92
treatment ³	Denmark		mist	ppm			
Animal fodder ⁵	Jutland	CLIMATIC ⁴	Odor,	10,000 OU ⁶	10,000	30	95
	Denmark		Acetic acid	N/A	10,000	30	99
Food processing ⁷	Sk åne, Sweden	CLIMATIC ⁴	Odor, oil mist	>100 ppm	6000	10	90

Table 4.	Test	details	of	selected	industrial	GPAO	systems.

 $^1\mbox{Tests}$ were run at 1500, 6200 and 10,400 \mbox{m}^3/\mbox{h}

²Carbon monoxide concentrations were variable. For some foundries there is enough CO to interfere with BTEX treatment.

³Treatment of technical water from ships containing a mixture of heavy marine diesel oil (3% elemental sulfur by weight), fresh and salt water, engine waste, etc.

⁴Commercial scale GPAO installation (Infuser ApS)

⁵Production and dehydration of fermented plant material for pigs, a type of silage or sauerkraut.

⁶OU means Odor Units.

⁷Potato chip factory

Three types of industrial GPAO systems are presented: a "portable chimney" unit built into a standard 40-foot shipping container, a portable modular prototype, and commercial scale installations, called CLIMATIC (produced by Infuser ApS). Table 4 lists some of the installations and industries where GPAO has been tested. During tests, samples taken before the system are compared to those taken at the air exit after the electrostatic precipitator to determine the removal efficiency of the system. In all of the cases examined here GPAO achieved a removal efficiency greater than 89%.

3.1. Shipping container prototype to remove styrene emission from fiberglass

Styrene vapor is produced during the production of fiberglass-reinforced plastics, used for example in fiberglass boats, airplanes, water containers and windmill blades. Styrene is regulated as an air pollutant; it is a suspected carcinogen [61]. A GPAO prototype was installed in a shipping container of dimensions 12.4 m \times 2.4 m \times 2.6 m (length \times width \times height). The container had two sets of 2.4 kW UV-C lamps and a total reaction volume of 50 m³. The shipping container was connected to the exhaust of a fiberglass factory. Ozone was generated using a plasma discharge ozone generator (ACP 3000, O₃ Technology) and 60 W lamps (TUV PL-L, Phillips) were used to generate UV-C light. Measurements were performed at different ozone production rates (160, 80, 40 and 20 g O₃ h^{-1}) and with a total UV lamp power of 4.8, 2.4 and 1.2 kW). Ozone concentrations were determined using an ozone monitor (BMT Messtechnik model 930). Measurements were performed at a series of flow rates: 10,400, 6200, and 1500 m³ h⁻¹ with residence times of 17, 29, and 120 seconds respectively. The volumetric flow rate was established by measuring the airflow in and out of the prototype using a wind speed anemometer (Testo 405, Testo AG, Germany). Styrene was analyzed using a photoionization detector (PID) and by sampling on Tenax A tubes for analysis with TD-GC/MS. Acetone was observed in small concentrations at the inlet. The optimum removal efficiency (99%) of 11 ppm of styrene was achieved with an ozone production rate of 160 g O_3 h⁻¹ and UV-C lamp power of 4.8 kW with 120 s residence time [62].

3.2. Modular prototype for treatment of VOCs emitted from foundry

Waste air from a ferrous metal foundry was treated using a modular prototype. Ferrous metal foundries are sources of multiple VOCs including the group of compounds benzene, toluene, ethyl benzene and the xylenes, denoted BTEX [63,64]. In this prototype, polluted air enters an ozone-infused scrubber followed by two sets of modules with UV-C light and a module for particle growth. Finally, the air passes through an electrostatic precipitator and an MnO₂ catalyst. The modular prototype was tested over the course of 3 months at a foundry in Saarbrücken, Germany. Table 5 shows experimental conditions and performance of the modular prototype used at the foundry. Ozone is generated using a plasma discharge ozone generator (ACP 3000, O3 Technology) and UV-C light by up to twelve 220 W fluorescent lamps. Ozone concentrations were determined using an ozone monitor (Eco Sensor model UV-100). The volumetric flow rate was measured by measuring the airflow out of the prototype using a wind speed anemometer (Testo 405, Testo AG, Germany). Analysis of BTEX was performed using GC-PID (Delta, Synspec, Groningen, The Netherlands) while total hydrocarbon concentrations (THC) and non-methane total hydrocarbon (NMTHC) concentrations were determined using GC-FID (Alpha, Synspec, Groningen, The Netherlands). In

general, the modular prototype allowed removal of BTEX with an efficiency of 90–97% and other VOCs with an efficiency in the range of 85–90%.

Pollutant	Compound	Inlet concentration	Outlet concentration /ppm	RE /%
category		/ppm		
VOCs	Benzene	9.26	2.00	78
	Ethyl benzene	6.23	0.19	97
	Phenol	8.23	0.05	99
	Toluene	7.57	0.16	98
	m and p-Xylene	6.52	0.22	96
	o-Xylene	6.06	0.12	98

Table 5. Summary of experimental conditions and results for pollution control at foundry.

3.3. Modular prototype for treatment of amines from foundry emissions

In addition to the VOCs including BTEX presented in the previous section, depending on the process, waste air from foundries may contain amines. In the cold box process, amines are used as a catalytic hardener in producing the sand cores. Amines are used to improve results and increase production capacity. Which amine or amines are present depends on the catalyst that the foundry uses. A modular GPAO prototype with three consecutive UV sections, one ozonized scrubber, an ESP and an MnO₂ section with dimensions of 1 m × 1 m × 1 m for each section was installed. Polluted air was sampled using Dräger ADS sample tubes for amines (Drägerwerk AG, Germany) and analysis was performed by gas chromatography with a nitrogen selective detector (GC/NSD) (Agilent 5977A). The major amine emitted from the foundry was N,N-Dimethylethylamine (DMEA). Two ozone generators which produce 20 g h⁻¹ ozone (ONY-20, Infuser, Denmark) and one ozone generator generating 80 g h⁻¹ ozone (ONY-80, Infuser, Denmark). Ozone concentrations were determined using an ozone monitor (Eco Sensor model UV-100). A removal efficiency of >96% was achieved for DMEA and total amines with 13.5 kW lamp power and 120 g h⁻¹ ozone supply at air flow rate of 4530 m³ h⁻¹.

3.4. Modular prototype for treatment of agricultural emissions

Pig farms and other agricultural facilities are well known sources of malodorous compounds. In particular, the emission of reduced sulfur compounds, including H₂S, gives rise to complaints due to the very low odor detection limits of such compounds [65,66]. Recently, the same modular prototype used in the foundry in Saarbrücken was used to test the removal of reduced sulfur compounds at concentrations typical for pig farm exhaust streams. Removal efficiencies of >90% were achieved for hydrogen sulfide (H₂S), methane thiol (CH₃SH) and dimethyl sulfide ((CH₃)₂S), with a volumetric energy input of \leq 13.2 kJ m⁻³ [Meusinger et al., unpublished data].

3.5. Commercial scale GPAO for odor removal

Commercial scale GPAO units (CLIMATIC) have been installed at three factories: a waste water treatment plant, a food processing plant and a fermentation plant producing animal fodder. The first commercial scale GPAO was installed at a water treatment plant in Aarhus, Denmark which

treats waste water and oil produced by container ships and industry. The factory generates a waste air stream of 15,000 m³ h⁻¹. Chemical analysis of the untreated water shows that it is polluted with hydrocarbons (143–424 g kg⁻¹) that contain 0.94–1.40% sulfur by weight. Such high sulfur levels are typical for heavy marine diesel oil. Due to the presence of sulfur and organic compounds, the emitted polluted air had a heavy unpleasant smell, giving rise to persistent complaints from residents in other areas of the city. Ventilation air analysis was performed using GC/MS and volatile organic compounds were observed including C_4 - C_{14} aliphatic alkanes, C_7 - C_{11} alkenes, and aromatic compounds (toluene, xylene, and other alkyl benzenes). While trace sulfur compounds were not observed in the chromatogram, likely due to the range and sensitivity of the system, traces of 1propyl mercaptan and other sulfur compounds were observed from the chromatogram when using ion extraction. A scrubber was added to the shipping container described above and connected to the factory ventilation system. After successful tests with the shipping container a commercial scale GPAO was installed. The dimensions of the CLIMATIC are 10 m \times 2.4 m \times 2.4 m (length \times width \times height). Ozone is generated using a plasma discharge ozone generator (ACP 3000, O₃ Technology) and mercury vapor discharge fluorescent lamps were used to generate UV-C light. An ozone-infused aqueous scrubber and two UV-C sections are used. Ozone concentrations were determined using ozone monitor (Eco Sensor model UV-100). The commercial scale GPAO installation reduced the smell by 92% with a residence time of 30 seconds at 160 g h^{-1} ozone supply, as assessed by a professional smell panel. The volumetric energy input of the installation is ca. 4 kJ m⁻³.

The second commercial scale GPAO was installed at a potato chip factory in southern Sweden. The factory releases a mixture of saturated and unsaturated fatty acids and aldehydes that cause an unpleasant smell [67]. Ozone is generated using a plasma discharge ozone generator (ACP 3000, O3 Technology) and mercury vapor fluorescent discharge lamps were used to generate UV-C light. Ozone concentrations were determined using an ozone monitor (Eco Sensor model UV-100). The installation of a commercial scale GPAO solution of similar characteristics as described above yielded removal of 90% unpleasant odor. Odor was measured by a professional smell panel.

The third commercial scale GPAO system was installed at a factory that produces fermented plant material as animal feed that is known to be a significant source of odor. During fermentation many compounds, in particular short chain fatty acids and esters, are produced that have strong odor. Ozone and UV light are generated as before. Ozone concentrations were determined using an ozone monitor (Eco Sensor model UV-100). GPAO removes 99% of acetic acid and 95% of odor.

4. Discussion

Table 1 shows the techniques that are most commonly used to control indoor air pollution, along with GPAO. Most of the techniques are specific to certain pollutant groups and some of them also emit toxic compounds. GPAO is advantageous compared to the techniques which are traditionally used to control indoor air pollution, since it covers a wide range of pollutants, has a low energy input, and is easy to maintain.

VOC control techniques can either destroy or recover the pollutants. Destructive techniques include oxidation and bio-filtration, while recovery techniques include absorption, adsorption and condensation. Thermal oxidation and adsorption techniques are widely used to control VOC emissions [24]. In thermal oxidation pollutants are combusted at high temperature. The technique often requires natural gas to burn the pollutant when the concentration of emitted pollutants (i.e. the

fuel concentration) is too small. This approach is associated with increased costs due to the added fuel and CO₂ emissions. Thermal oxidation generates NO_x and acids which can necessitate additional treatment systems if for example sulfur and halogen containing compounds are present in the airstream [24]. Adsorption is a technique where the pollutant is concentrated on the surface of the adsorbent material. Adsorption techniques are associated with relatively high capital and running costs [24]. The temperature of the desorption stage is commonly much higher than that of the adsorption stage, drawing power. If ozone is present in the airstream it will react with adsorbed molecules generating secondary pollution. If pollutants are emitted at low concentrations, adsorption techniques are less effective at higher pollutant concentrations due to saturation of adsorption sites. Adsorption is the most important method used when recovery of the organic pollutant is a major concern, while thermal oxidation is commonly used when only removal is required [24,68].

In the systems we have tested, a number of limitations have been noted. For example there is a limit to the oxidation capacity of the systems. In certain situations the system may become saturated by high concentrations of NH₃ or CO limiting the ability to treat other compounds. Gas phase advanced oxidation is not suitable for use at elevated temperatures when ozone is no longer stable. Nor is it suited to environments, due to excessive cold or heat, that are outside the operating range of the fluorescent lamps. Further, the method relies on oxygen in the atmosphere as an oxidant. Some waste gas streams, e.g. from combustion and agricultural sources, may not have enough oxygen. It is necessary to be aware of the possible formation of unwanted reaction products such as formaldehyde and ultrafine particles. Further studies should be performed to characterize the toxicity of the products. Additionally, the oxidation products in the treated air should be examined on a case by case basis to assure that unwanted products are not formed.

Gas-phase advanced oxidation (GPAO) is an emerging technology for air pollution control. It enables removal of organic and inorganic pollutants which can be gaseous or particulate. The technology works well in controlling a range of air pollutants emitted from different sources. It shows efficient removal of indoor pollutants and industrial emissions. The removal efficiency of the technology depends on the residence time and the physicochemical properties of the pollutant. The technology was implemented in the market as an in situ pollution control technology to prevent undesired emission of pollutants and/or malodorous compounds. The technology is easy to maintain, applicable to a wide range of pollutants, energy efficient and suitable for a wide variety of pollution control situations including odor control for livestock and biogas production, wastewater treatment, and indoor air purification.

Acknowledgments

We thank Infuser ApS for their help with building and installing test prototypes and support during measurements. We also thank Jes Andersen, Andrew Butcher, Kristoffer Nannerup, Anders Brostrøm Bluhme and Jonas Ingemar for their collaboration during industrial scale testing. The authors thank Verena Rauchenwald, Nanna Sander and Kjertan Lyster for their help with indoor pollution control measurements. Finally we thank Denis Wistensen and Jørgen Jørgensen of the Niels Bohr Institute Workshop for designing and construction of laboratory scale and indoor prototypes. We thank the Copenhagen Cleantech Cluster, Innovation Fund Denmark, the Department of Chemistry and Infuser ApS for funding.

Conflict of interest

All authors declare no conflict of interest in this paper other than the association of the technology with Infuser ApS, Airlabs, and the University of Copenhagen, as described in the text.

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