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# Investigation of Indoor Air Pollution and Volatile Organic Compounds Present in Hospitals and Their Treatment via Photocatalytic Oxidation

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**Investigation of Indoor Air Pollution and Volatile Organic  
Compounds Present in Hospitals and Their Treatment via  
Photocatalytic Oxidation**

By

Michael J. Celente

A Thesis

Presented to the Graduate Research Committee

of Lehigh University

in Candidacy for the Degree of

Master of Science

in

Environmental Engineering

Lehigh University

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This thesis is accepted and approved in partial fulfillment of the requirements for the  
Master of Science

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Date

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# Abstract

While preexisting research regarding cigarette smoke, carbon monoxide poisoning, dust/allergens and other air pollutants exists, studying volatile organic compound (VOC) contamination indoors is a relatively recent endeavor. While certain VOCs are considered carcinogens with known detrimental health effects, new research involves investigating VOC sources, contaminant concentration in ambient indoor air and possible treatment technologies. This paper will not only detail different types of air pollutants, their sources, and health effects, but also delve deeper into VOC contamination in health related facilities (mainly hospitals) and address possible treatment methods such as photocatalytic (PCO) oxidation.

Particulate matter, VOCs, biological contaminants, and heavy metals all represent contaminants of concern in our indoor environments and each of these contaminants have their own health-related impacts. Understanding the sources and effects of these pollutants in health-facilities is crucial to understanding how to prevent exposure and begin treating these contaminants. Health-care facilities in general not only have high levels of many of these contaminants to begin with, but also have high standards of air quality for certain medical procedures and operating rooms. As such, high quality filters, advanced ventilation systems and technical practices help to reduce the risk of contaminant exposure as well as infection. Factors such as temperature, humidity and time of year can additionally affect the indoor environment as indoor air quality is often a product of the outdoor environment and external factors.

Even with specific precautions, patients are still at risk of exposure to multiple air pollutants including microorganisms, particulate matter and VOCs. Even

though published studies have cited VOCs levels below exposure limits, these studies do not include cumulative impacts, chronic effects or short, high-level exposure. Future studies are necessary to determine these cumulative and chronic impacts and also to determine the true threat that these chemical pose to human health.

While treatment technologies such as photocatalytic oxidation are promising and have the potential to remove harmful contaminants, there are still multiple limitations to their feasibility and scaling in environments such as hospitals and other healthcare facilities.

# Chapter 1

## Introduction to Indoor Air Quality

### 1.1 Introduction to Indoor Air Quality

While outdoor pollution has long been recognized as a contributor to adverse health outcomes, indoor air quality (IAQ) has recently been gaining attention and generating research interests as humans are now spending the majority (over 90%) of their time indoors [1]. With a broad spectrum of pollutants present in our indoor environment, including particulate matter (PM) (both viable and unviable), Nitrogen Oxides (NO<sub>x</sub>s), Carbon Monoxide (CO) and volatile organic compounds (VOCs), IAQ represents a quintessential subset of air quality engineering. With an increase in time spent indoors, studying contaminant concentration and health outcomes in different indoor environments represents an important new field. Ensuring that our indoor environments are safe and contaminant-free is crucial in safeguarding a healthy and sustainable future for not just current generations but future ones as well.

### 1.2 Types and Sources of Indoor Air Pollution

When an individual presents symptoms indicating poor health, air pollution may not be the first place that a health care provider may look as a main cause of that poor health; however, the fact of the matter remains that poor air quality can undoubtedly contribute to compromised health. Tobacco smoke, carbon monoxide, animal dander, molds, dust mites, other biological organisms, volatile organic compounds, heavy metals,

asbestos and radon all represent types of indoor air pollution that can seriously affect one's health and wellness [2]. All too often, topics like second-hand smoke or carbon monoxide poisoning appear in the news alongside data showing deaths from each of these. However, volatile organic compounds, heavy metals and other biological contaminants also represent true threats, but are often times ignored, belittled and glazed over.

The locations of highest concern for indoor air pollution are those involving prolonged, continuing exposure, most notably the home, school and workplace [2]. However, this paper will also investigate health-related facilities, mainly hospitals in an effort to determine how an extended stay in a health facility may in fact poorly contribute to an individual's health and wellness.

According to the EPA, contaminant levels of indoor air pollutants may be up to 100 times higher than outdoor levels and are ranked among the top 5 environmental risks to the public [1]. For this reason, understanding the sources of different contaminants and recognizing which contribute the most and in what quantities is important for improving overall air quality in general, which undoubtedly has implications relating to human health. Table 1.3.1 lists several pollutants, their concentrations of concerns and some of their sources [3]. It is important to note that certain sources (e.g. smoking) can lead to the production of multiple contaminants.

<b>Pollutant</b>	<b>WHO concentration of concern</b>	<b>Source</b>
Carbon Monoxide	5	Combustion products, tobacco smoke
Radon and daughters	79Bq/m <sup>3</sup>	Building materials
Formaldehyde	0.12	Furniture, fittings, insulation, paper
Ozone	0.08	Photocopiers, laser printers, ionisers
Carbon dioxide	12000	Occupants, smoking
Sulphur dioxide	1.35	External environment

Table 1.2.1: Gaseous Pollutants in Indoor Air and their Concentrations of Concern (levels in ppm) [3]

The sources of many of these pollutants are varied in nature; some of which cannot be avoided such as the external environment, but others are much more heavily influenced by individual choices such as not smoking or limiting the combustion of fossil fuels. While Table 1.3.1 may seem to present just a few sources and pollutants, the fact of the matter is that many of these sources can contribute more than just one dangerous pollutant. Table 1.1.2, for example, shows just a few of the carcinogens and suspected carcinogens in secondhand cigarette smoke alone: note the large number of compounds present [4]. Each of these contaminants alone have their own health-related risks and concentrations of concern. Combustion products in general don't just include carbon monoxide, they also include carbon dioxide, sulfur dioxide, nitrogen oxide, and in multiple instances heavy metals such as lead (Pb) or mercury (Hg) [4].

Carcinogens	Suspected Carcinogens
Arsenic	Acetaldehyde
Benzene	Acetone
Beryllium	Acrolein
1,3-Butadiene	Acrylonitrile
Cadmium	2-Aminonaphthalene
Chromium	Ammonia
Ethylene oxide	Benzo[a]pyrene
Nickel	Butyraldehyde
Polonium-210	Carbon monoxide
Vinyl chloride	Catechol

Table 1.2.2 Carcinogens and Suspected Carcinogens in Secondhand Cigarette Smoke [4]

Just as combustion products and cigarette smoke are complicated, many of the products that we use on a daily basis for one purpose may have a wide variety of chemical constituents [4]. Recent studies suggest an increase in exposure to VOCs over the past two decades such as limonene, linalool, citronellol, eucalyptol, geraniol and alpha-pinene and some new products have over 2600 ingredients [4]. Other household cleaners such as bleach consist of sodium hypochlorite solutions which, when mixed with an acid or ammonia can release toxic chlorine gas. In addition to the materials used to clean our indoor environment, some of our building materials themselves can pose threats to human health. Formaldehyde, for example is a VOC commonly found in wood building materials, more specifically the resins that bind together wood products [4]. It is also often found in plastics, textiles, carpet, furniture, pesticides, paint, glue and cleaning products as well. While the concentrations of the contaminants that individuals come in

contact with on a daily basis may be low, the cumulative impacts and impacts over time can pose more of a threat to human wellbeing.

### **1.3 Potential Health Hazards**

According to the EPA, when an individual sees a healthcare provider, it is vital that the patient's diurnal and other patterns are analyzed because they may provide clues to the patient's link with air pollution. Certain practices in the home or the workplace can place the patient at higher risk of exposure and thus more concentrated health effects [2]. Once signs and symptoms are analyzed in addition to the patient's daily activities, it can be easier to diagnose what type of exposure may exist.

Table 1.3.1, taken from the EPA, shows different types of air pollution and their associated signs and symptoms [2].

It isn't just tobacco smoke and carbon monoxide causing health-related issues; VOCs, biologicals, heavy metals, etc. all lead to respiratory or other signs and symptoms [2]. As mentioned earlier, often times, the sources of these contaminants themselves are quite complex; made up of many constituents, all with serious health implications. This is part of the reason why diagnosing air-pollution related ailments or determining the source of these contaminants can pose such a challenge. While each of the contaminants mentioned above contains its own unique key signs and symptoms, this section will focus in primarily on volatile organic compounds, as they are the primary contaminants of concern for the purposes of this paper.

<b>Diagnostic Quick Reference</b>						
<b>Signs and Symptoms</b>	Environmental Tobacco Smoke	Other Combustion Products	Biological Pollutants	Volatile Organics	Heavy Metals	Sick Bldg. Syndrome
	pg. 5	pg. 7	pg. 10	pg. 13	pg. 15	pg. 17
<b>Respiratory</b>						
Rhinitis, nasal congestion	■	■	■	■		■
Epistaxis				■ <sup>1</sup>		
Pharyngitis, cough	■	■	■	■		■
Wheezing, worsening asthma	■	■		■		■
Dyspnea	■ <sup>2</sup>		■			■
Severe lung disease						■ <sup>3</sup>
<b>Other</b>						
Conjunctival irritation	■	■	■	■		■
Headache or dizziness	■	■	■	■	■	■
Lethargy, fatigue, malaise		■ <sup>4</sup>	■ <sup>5</sup>	■	■	■
Nausea, vomiting, anorexia		■ <sup>4</sup>	■	■	■	
Cognitive impairment, personality change		■ <sup>4</sup>		■	■	■
Rashes			■	■	■	
Fever, chills			■ <sup>6</sup>		■	
Tachycardia		■ <sup>4</sup>			■	
Retinal hemorrhage		■ <sup>4</sup>				
Myalgia				■ <sup>5</sup>		■
Hearing loss				■		

1. Associated especially with formaldehyde. 2. In asthma. 3. Hypersensitivity pneumonitis, Legionnaires' Disease. 4. Particularly associated with high CO levels. 5. Hypersensitivity pneumonitis, humidifier fever. 6. With marked hypersensitivity reactions and Legionnaires' Disease.

Table 1.3.1: Diagnostic Quick Reference – Signs and Symptoms related to Air Pollutants [2]

VOCs are often the cause of the following: conjunctival irritation, nose and throat discomfort, headache, allergic skin reaction, dyspnea, nausea, emesis, epistaxis, fatigue and dizziness [2]. It is important to note that many of these symptoms can also be caused by other conditions or diseases and so understanding a patient's daily routine as well as practices in the home and workplace are crucial in determining possible exposure.

Questions involving the individual's living environment and exposure to pressed wood

products, as well as queries regarding the use of chemical cleaners, pesticides, paints and solvents are all indicators that would suggest exposure to VOCs [2].

While these contaminants may be present in low concentrations in the home and workplace, there are recent concerns that cumulative impacts and repeated, long-term exposure may be posing a more serious threat than one-time exposure. A 2007 European study followed 3503 individuals who had no asthma symptoms when the study began. Over the course of 9 years, 42% of participants who cleaned their houses at least once a week, experienced asthma symptoms or were using asthma medication and wheezing [5].

## **Chapter 2**

### **Air Pollution in Health Facilities**

#### **2.1 An Introduction to Air Quality and Pollution in Hospitals**

Unlike most homes (and a fair amount of work places) health care facilities, especially hospitals, are among the most demanding environments with regards to indoor air quality. These facilities often contain chemicals like waste medical gases (e.g. anesthetic gases), disinfecting and sterilizing substances, microbial contaminants and also other particles such as skin squames, lint, and aerosols [6]. However, in addition to dealing with multiple sources of air pollutants, health facilities must have some of the cleanest air due to the nature of certain treatment processes and operating procedures. Therefore, understanding the nature of contaminants present is crucial for understanding

how best to treat these contaminants and ensure better air quality for patients and healthcare workers alike.

Before investigating contaminant sources in health facilities, it should be noted that other factors such as temperature, humidity, time of year, and ventilation all play an important role in indoor air quality as well [7]. The following graphs show the monthly variation in air temperature, relative humidity and carbon dioxide concentrations in hospital operating rooms. Note the following key: black circles – transplantation rooms, white circles – trauma rooms, black triangle – cardiovascular surgery room, white triangle – colon/rectal surgery room and black rectangle – orthopedic surgery [8].

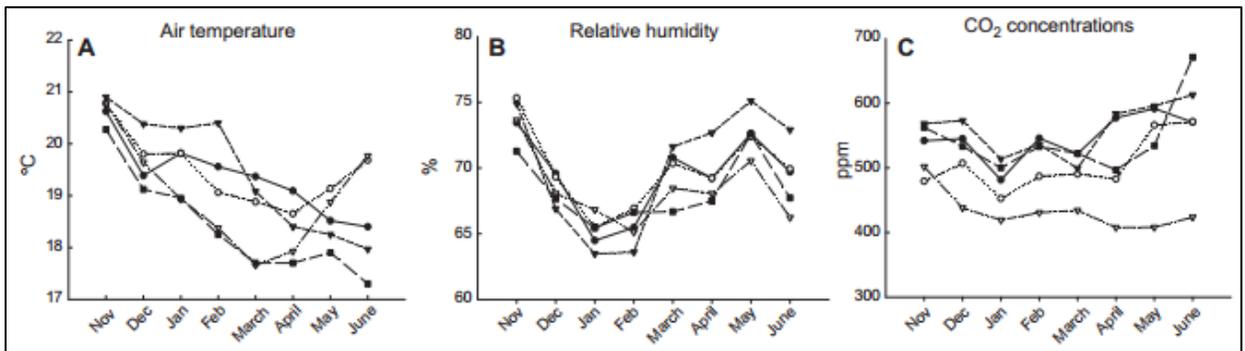


Figure 2.1.1 Monthly Variations of Indoor Air Quality in Operating Rooms

It is important to note the variation in each of these parameters based on the month and how some trends may seem counterintuitive. For example, even though months such as April, May and June have higher average temperatures than winter months, the indoor temperature of these different operating suites was actually lower. This inversely proportional temperature relationship would suggest that the air conditioning system was frequently operated during the summer months. This is important to note, because an increased stress on the HVAC system could pose a greater

threat to human health by leading to an increase in contaminant levels as well as favoring the growth of certain microbial organisms [8].

The American Society of Heating, Refrigerating and Air-Conditioning Engineers recommends controlling air requirements (air flow rate of 15cfm/person) and limiting the number of occupants to 20 persons/1,000ft<sup>2</sup> in operating rooms where pollutant concentration is strongly correlated to number of individuals [8]. This would suggest that high-traffic operating rooms are at greater risk of poor indoor air quality. The American Conference of Governmental Industrial Hygienists recommends maintaining relative humidity under 60% in indoor environments to help prevent microorganism growth and it should be noted that relative humidity level was not attained in any of the operating rooms in this study [8].

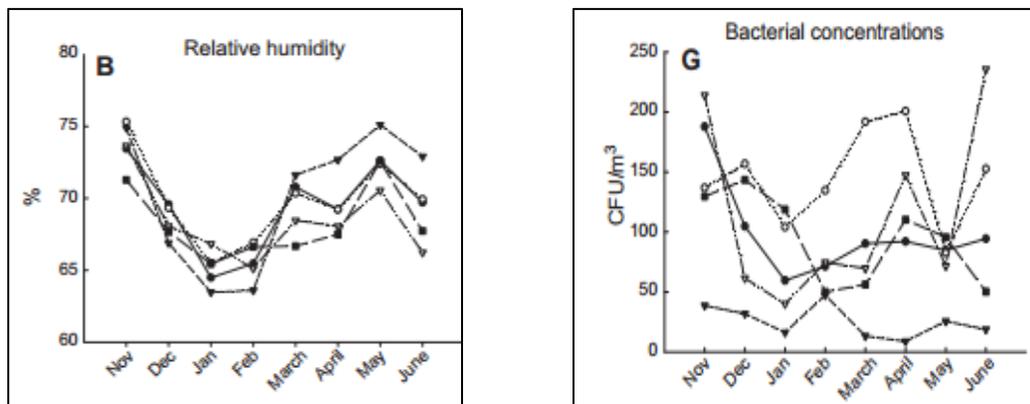


Figure 2.1.2 Comparison of Relative Humidity and Bacterial Concentration

The graphs above show the relationship between relative humidity and bacterial concentration and would seem to agree with the recommendation from the industrial hygienists. Months where the relative humidity levels were higher tended to see higher concentrations of bacteria [8]. A large turnover of patients not only requires the use of disinfectants and other sanitizing agents, thus increasing VOC concentration, but this turnover also can lead to microorganism growth and the possibility of bacterial infection.

Particulate matter (including biologicals) represents a pollutant of concern in many hospitals, necessitating the use of high efficiency particulate air (HEPA) filters, while advanced ventilation systems and technologies like anesthetic gas scavenging systems (AGSS) to recover waste anesthetic gases (WAG) are crucial for VOC removal [6]. Ventilation systems can either have positive or negative effects on indoor air quality depending on their current state of contamination. For example, HVAC systems can affect contamination of operating rooms by carrying unfiltered aerobic bacteria both in and out of the room of concern. Once a system is compromised, it can continue to pollute an indoor air environment even though it is assumed that it is actually improving air quality. Technologies such as laminar air flow (LAF) ventilation have been shown to effectively reduce both content of particles in the air and bacteria on the floor when compared to conventional ventilation systems [9]. High turbulence air flow corresponds to higher mixing rates than laminar flow, thus increasing the risk for contaminant travel and cross contamination of systems.

Research has shown; however, that greater potential for transmission of infection exists in surfaces such as tables, and operating instruments themselves rather than surfaces such as the walls or floor [10]. This would suggest that operating room air doesn't have as large an effect on bacterial contamination as long as air exchanges are performed regularly and ventilation methods are up to date and not compromised [10]. In fact, unlike the required sterilization of tools and operating surfaces, weekly decontamination of walls with specific chemicals seems to have little role to play in minimizing postoperative infection [11]. Although these disinfectants may be used to

decrease the risk of infection, they may be having little impact and could possibly be increasing VOC concentration posing even more of an air quality threat.

## **2.2 Volatile Organic Compounds in Hospitals**

Anesthetic gases and disinfectants/sterilants represent specific categories of VOCs that are undoubtedly required in hospitals for patient comfort and operational procedures, but also to maintain a clean environment. As such, ensuring proper air quality in consideration of these chemicals is of critical importance. Most general anesthesia involves the use of gases or volatile liquids that are vaporized and then inhaled with medical air, nitrous oxide or a combination, as well as drugs that are delivered intravenously [12]. Halothane, enflurane, isoflurane, sevoflurane and nitrous oxide are all examples of anesthetic gases which all have the potential to escape delivery. When these gases escape, they are considered WAG and are usually treated by AGSS [6]. It is important to note; however, that even operating rooms with AGSS still have the potential for poor air quality as issues such as inadequate ventilation, poor work practices or inadequate maintenance can all effect the treatment of these volatile gases. Figure 2.2.1 shows the concentration of anesthetic compounds (isoflurane, sevoflurane) in a sample of operating rooms [6].

Even operating rooms that had AGSS still saw elevated concentrations of anesthetic gases compared to rooms that did not have the technology in place. This would suggest that there are multiple factors involved that are able to affect the treatment of these operating room volatile liquids and gases.

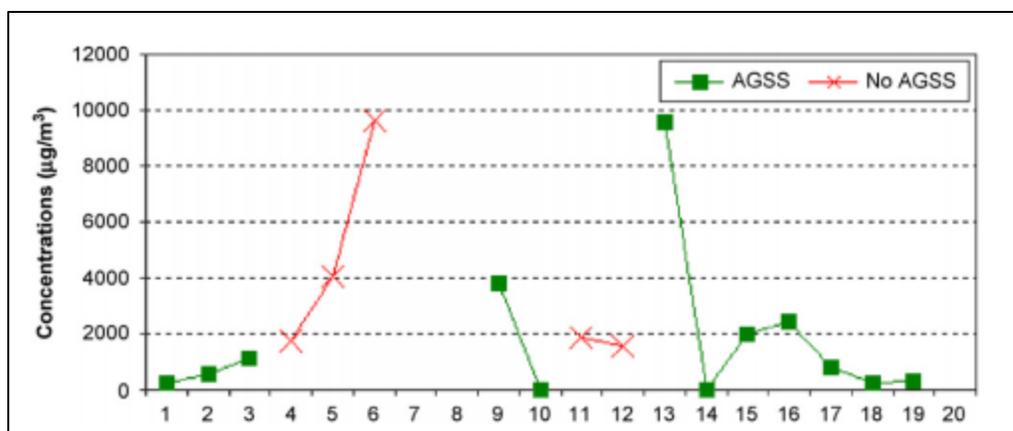


Figure 2.2.1 Measured Concentration of Anesthetic Gases in 17 out of 20 Audited Operating Rooms (missing data corresponds to hospitals that did not grant permission to make measurements) [6]

In addition to anesthetic gases, hospitals also have large concentrations of aldehydic compounds such as formaldehyde and glutaraldehyde as well as other sterilants and general disinfectants (e.g. ethylene oxide) [6]. These compounds are unavoidable in many cases as they ensure minimal transfer of biological contaminants and the overall cleanliness of health-related facilities in general. However, as mentioned earlier, many of these VOCs also have health impacts if individuals are exposed chronically or in conjunction with other chemicals. Table 2.2.1 shows the occupational exposure limits of many of these compounds encountered in operating rooms (OR) including anesthetic gases [6]. TLV refers to the threshold limit value for an 8 hour exposure, TWA refers to the time weighted average and STEL refers to short-term exposure limit.

Compounds	Exposure limits
Halogenated anaesthetic agents	TLV (NIOSH): 8-h TWA: 2 ppm without concomitant N <sub>2</sub> O exposure 0.5 ppm with concomitant N <sub>2</sub> O exposure
Nitrous oxide	TLV for hospital environments (NIOSH): 8-h TWA: 25 ppm (40 mg/m <sup>3</sup> )
Formaldehyde	8-h TWA: 0.75 ppm (0.94 mg/m <sup>3</sup> ) 15-min STEL: 2 ppm (2.5 mg/m <sup>3</sup> )
Glutaraldehyde	TLV: 0.2 ppm (0.82 mg/m <sup>3</sup> ) (ceiling level)
Ethylene oxide	8-h TWA: 1 ppm 15-min STEL: 5 ppm Action level 8-h TWA: 0.5 ppm

Table 2.2.1 Occupational Exposure Limits for Compounds Encountered in ORs [6]

In addition to general health effects like headaches, nausea, dermal irritations and difficulty in breathing, formaldehyde is considered carcinogenic and ethylene oxide is considered both carcinogenic and mutagenic with other symptoms including anemia, secondary respiratory infections, skin sensitization, miscarriages and reproductive problems [6]. STEL limits can be higher than TLA and TWA values as short concentrations are more tolerable for 15 minutes as opposed to inhaling a compound for 8 hours or longer.

A 2008 study investigating 20 different operating rooms (OR) in Hellenic hospitals was designed to quantify the total concentration of volatile organic compounds present (TVOC) [6]. Samples of the organic compounds were collected in tenax-TA tubes using low flow sampling pumps (about 1m from the floor). The sampling volume was 3000mL and the analysis was performed using thermal desorption (Tekmar 2000), gas chromatograph (Varian Star 3400 CX) equipped with a capillary column and mass spectrometry [6]. Table 2.2.2 present the VOC data for different groups of compounds [6].

Group of compounds	Concentrations ( $\mu\text{g}/\text{m}^3$ )		
	Average	Min	Max
Anaesthetic compounds (isoflurane and sevoflurane)	2362	– <sup>a</sup>	9652
Aromatic compounds	239	21	564
Formaldehyde and glutaraldehyde	495	– <sup>a</sup>	1425
Other aldehydes, oxides, alcohols	1920	107	5268
Other	3846	31	41,255
Total volatile organic compounds (TVOC)	8862	279	46,904

<sup>a</sup>Non-detectable values.

Table 2.2.2 Average Concentrations of Volatile Organic Compound in the Indoor Air of Audited Operating Rooms [6]

Overall, the concentrations of anesthetic gases were quite high and exceeded the exposure limit in 18% of the audited operating rooms, while the values were usually significantly lower in operating rooms with AGSS [6]. Formaldehyde concentrations were found to be quite high in some instance while concentrations of glutaraldehyde were always below the exposure limit in each of the operating rooms. It should be noted that the contaminants measures (i.e. anesthetic compounds, formaldehyde, and glutaraldehyde) did not make up the entirety of the TVOC concentration. In fact, in addition to the expected compounds, various other compounds existed in the indoor air environment accounting for 54% or more than half of the TVOC concentration of  $8862\mu\text{g}/\text{m}^3$  [6]. This suggests that a fair amount of other VOCs are present in hospital operating rooms than those that were studied and a more comprehensive study is required to analyze the other compounds present.

Another, more recent study in 2013 investigated six sampling sites throughout a French teaching hospital and detailed the concentrations of more than 40 VOCs. The six sampling sites included the reception hall, patient room, nursing care, post-anesthesia care unit, parasitology-mycology laboratory and flexible endoscope disinfection unit [13]. Unlike the previous study, which just investigated operating rooms, this more recent study not only extended to different labs, patient rooms and reception areas, but also represents a more comprehensive sampling of VOCs. For the study, air samples were dynamically collected using low flow pumps (LFS 113 DC) and air flow was set with a Gilian Gilibratir 2 calibrator.

Very low concentrations were expected, so VOC samples were pre-concentrated on solid samples and then enriched with tubes containing three different carbon-based sorbents. Two different sorbent systems were used as analyses were split between two laboratories. Aromatic and halogenated hydrocarbon, alcohol, and ketone sampling was carried out with a multisorbent tube packed with Carbopack C, Carbopack B and Carboxen 1000 (with a pumping flow rate of 30mL/min). Whereas aliphatic hydrocarbons, ethers and terpenes were sampled with a multisorbent tube packed with Tenax TA, Carbograph 1 TD and Carboxen 1000 (with a pumping flow rate of 50mL/min) [13].

For VOC analysis, a combination of automatic thermal desorption, capillary gas chromatograph and mass spectrometer were used to analyze the different concentrations. In terms of validation, the limit of detection (LOD) was defined as the concentration at which the signal-to-noise ratio (S/N) was equal to 3, and the limit of quantification

(LOQ) was defined as the lowest concentration at the signal-to-noise ratio of greater than or equal to 10 with a precision less than 25%.

Table 2.2.3 shows the products used at the hospital in general and where each of those types of products are predominantly utilized [13].

<b>Class of Products</b>	<b>PR</b>	<b>NC</b>	<b>PACU</b>	<b>DU</b>	<b>PL</b>	<b>RH</b>
Laboratory products	0	0	0	0	24	0
Cleaning/disinfectant products	6	6	4	9	8	4
Alcohol-based products	4	4	4	1	0	0
Pharmaceutical product/antiseptics	11	4	1	0	1	0
Anesthetic gases	0	0	3	0	0	0
<b>Total</b>	<b>21</b>	<b>14</b>	<b>12</b>	<b>10</b>	<b>33</b>	<b>4</b>

PR: patient room; NC: nursing care; PACU: post-anesthesia care unit; DU: endoscope disinfection unit; PL: parasitology laboratory; RH: reception hall.

Table 2.2.3 List and Number of Different Class of Products Used in the Six Sampling Sites [13]

Of the 58 different products used, laboratory products made up 41% while anesthetic gases only comprised 5%, suggesting a large number of laboratory products in general and a very limited use of the anesthetic gases. It is also important to note that certain classes of products, (e.g. cleaning/disinfecting) were prevalent in nearly each of the six sampling sites. Overall, the parasitology laboratory was the site with the highest number of products used (33) while 73% of those were strictly laboratory products (chemicals and reagents) [13].

Table 2.2.4 details the distribution of indoor air concentrations of the target compound measured in all sites.

Compounds	Concentration ( $\mu\text{g}/\text{m}^3$ )						
	<LOQ (%)	Mean (SD)	Min	25 <sup>th</sup> p.	50 <sup>th</sup> p.	75 <sup>th</sup> p.	Max
<b>Aromatic hydrocarbons</b>							
Benzene	71	1.6 (1.5)	0.5	0.6	0.8	2.3	5.1
Ethylbenzene	54	1.8 (1.8)	0.1	0.7	0.8	2.9	6.6
m,p-Xylene	51	3.6 (3.1)	1.0	1.4	1.7	6.0	10.6
o-Xylene	63	1.6 (1.6)	0.5	0.7	0.8	1.1	6.2
Styrene	6	0.6 (0.6)	0.1	0.1	0.4	0.8	2.3
Toluene	17	4.7 (3.8)	0.5	1.3	4.3	6.0	16.5
1,2,4-Trimethylbenzene	3	0.5 (0.3)	0.1	0.3	0.5	0.6	1.1
Naphthalene	88	0.3 (0.1)	0.2	0.2	0.2	0.3	0.6
Phenol	3	2.3 (1.4)	0.2	1.2	2.1	3.1	5.9
<b>Aliphatic hydrocarbons</b>							
n-Hexane	88	1.9 (6.4)	0.6	0.7	0.8	0.9	39.0
Cyclohexane	85	0.9 (0.5)	0.6	0.6	0.8	0.9	2.6
n-Heptane	91	0.9 (0.9)	0.6	0.6	0.7	0.8	6.1
n-Decane	100	-	-	-	-	-	-
n-Undecane	97	3.8 (0.6)	2.9	3.3	3.8	4.1	5.5
<b>Halogenated hydrocarbons</b>							
1,1,1-Trichloroethane	34	0.6 (1.2)	0.1	0.2	0.3	0.6	6.7
Trichloroethylene	71	0.3 (0.3)	0.1	0.2	0.2	0.3	1.7
Chloroform	6	6.3 (5.3)	0.2	1.9	5.6	10.4	23.8
1,4-Dichlorobenzene	40	0.2 (0.2)	0.1	0.1	0.1	0.3	1.1
1-Bromopropane	100	-	-	-	-	-	-
<b>Alcohols</b>							
Ethanol	6	928 (958)	0.3	327	495	1297	3956
Isopropanol	14	47.9 (52.2)	0.7	4.5	20.3	87.8	174
Propan-1-ol	3	5.9 (5.6)	0.5	2.9	4.1	5.5	24.9
2-Ethyl-1-hexanol	11	3.1 (2.3)	0.1	1.6	2.2	4.9	8.8
<b>Aldehydes</b>							
Acrolein	14	4.7 (4.4)	0.1	1.3	3.9	7.0	18.1
Formaldehyde	17	5.8 (4.0)	1.5	2.2	5.1	8.7	14.8
Acetaldehyde	20	5.7 (4.3)	1.0	2.6	4.1	9.1	16.2
Propionaldehyde	100	-	-	-	-	-	-
Butyraldehyde	100	-	-	-	-	-	-
Isovaleraldehyde	74	2.2 (1.6)	1.0	1.3	1.5	1.8	5.9
Valeraldehyde	100	-	-	-	-	-	-
Hexaldehyde	68	1.9 (0.9)	1.0	1.3	1.5	2.6	4.2
o-Tolualdehyde	100	-	-	-	-	-	-
m-Tolualdehyde	100	-	-	-	-	-	-
p-Tolualdehyde	100	-	-	-	-	-	-
<b>Ketones</b>							
Acetone	11	22.6 (20.6)	0.1	5.9	18.5	32.6	82.3
2-butanone	37	8.7 (32.6)	0.1	0.5	0.7	1.6	174
Cyclohexanone	48	3.3 (5.4)	0.1	0.1	0.9	4.1	20.1
<b>Ethers</b>							
Ether	43	75.6 (157)	0.6	0.8	2.5	50.0	678
2-Ethoxyethanol	94	0.8 (0.2)	0.6	0.6	0.8	0.8	1.6
2-Butoxyethanol	100	-	-	-	-	-	-

Table 2.2.4 Distribution (mean, standard deviation (SD), minimum, 25<sup>th</sup> percentile, median, 75<sup>th</sup> percentile and maximum) of Indoor Air Concentrations of Target Compounds Measured in all Sites (n=36) [13].

The study results show that the contamination of indoor air was dominated by alcohols and the concentration of ether and acetone were relatively high compared to other compounds. The overall concentration of aromatic hydrocarbons was less than  $10\mu\text{g}/\text{m}^3$ , while the concentrations of formaldehyde and glutaraldehyde were equally distributed between the sites. Overall, the nature of the contamination was not significantly different between the sampling sites ( $p>0.05$ ). Interestingly, the reception hall (initially chosen as the references because no health related activities occur there) had similar VOCs concentrations as the other sites [13]. This would suggest that even areas where there are no health-related activities performed could still pose a threat to human health as VOC levels were not that different from laborites and operating rooms.

It should be noted that for all of the target compounds, the concentrations measured in the indoor air were below the occupation exposure limit values set in France, the European Union and the United States [13]. In fact, in certain instances concentrations of aromatic hydrocarbons measured are similar or lower than those found in residential and non-residential indoor environments [14-16].

### **2.3 Health Related Effects of Volatile Organic Compounds**

Even though these VOC concentrations were found to be below the exposure limits, the study does not take into account long-term, chronic exposure, or intense short-term exposure effects. In fact, chronic exposure to benzene may induce genotoxic, immunological and hematological effects [17]. Exposure to naphthalene can lead to respiratory issues such as lesions and infections [17] and acute exposure to certain aliphatic hydrocarbons which are commonplace in paints, adhesives and building

materials can affect the central nervous system and induce drowsiness and dizziness [18]. Although many of the chemicals were technically below what would be considered dangerous concentrations, coming into contact with VOCs, especially carcinogens in any capacity can have poor health effects especially over an individual's lifetime.

## **2.4 Limitations of Previous and Current Studies**

While the studies discussed in the previous section detail VOC exposure and concentrations, and provide crucial information for understanding VOC and contaminant exposure in general, they have multiple limitation that should be addressed in further studies. The first study of Hellenic hospital operating rooms only focused on a few target VOCs (mainly anesthetic gases, formaldehyde and glutaraldehyde) and did not indicate the compounds which composed the majority of TVOC concentration. While it assessed 20 different operating rooms, there is variability in each of the hospitals and health-facilities that may have affected the baseline VOC level [6].

The second study; while providing a more detailed profile of VOC contamination was limited to only one French teaching hospital. However, cleaning/disinfecting products and chemicals in general are most likely commonplace across hospitals which would suggest a similar VOC profile in other hospitals. However, it should be noted that VOCs and other contaminants in general are released from multiple sources not just related to health facilities. Building materials, the outdoor environment and other outside sources are all possible contributors [13].

Overall, both studies reflected stationary sampling of ambient air and do not truly reflect the real exposure of patients and workers. The duration of exposure is also unaccounted for with stationary sampling as is cumulative impact (e.g. a worker traveling

from room to room during peak exposure levels). While ambient VOC concentrations are a quintessential starting point for understanding both healthcare worker and patient exposure, they are not comprehensive in describing true cumulative or chronic impacts.

## **Chapter 3**

### **Treatment of VOCs via Photocatalytic**

### **Oxidation (PCO)**

#### **3.1 Introduction to Photocatalytic Oxidation**

Due to the undisputed health effects and carcinogenic properties of many VOCs, new and improved treatment technologies represent a growing area of interest for many scientists and engineers. While different treatment techniques exist to help treat VOCs such as activated carbon adsorption or afterburners, these techniques usually involve transfer of contaminants from one phase to another and require further disposal or treatment or high energy inputs. Photocatalytic Oxidation (PCO) represents an alternative: a semiconductor catalyst (often times  $\text{TiO}_2$ ) is used in the presence of a light source to degrade pollutants into primarily anodyne products (usually  $\text{CO}_2$  and  $\text{H}_2\text{O}$ ) [20]. PCO also operates at room temperature and exhibits activity towards a large variety of contaminants [19].

In PCO, energy, in the form of light (photons) is able to excite an electron from the valence band (VB) to the conduction band (CB), consequently leaving a positive hole in the VB. This photoreaction leads to the formation of electron-hole pairs, which in turn, drive oxidation and reduction reactions at the surface of the photocatalyst [21]. This process is described more specifically by Hay *et. al.* first, pollutant species are adsorbed onto the semiconductor surface. Then, the semiconductor surface is activated by light (usually UV) and electron-hole pairs are formed which lead to the formation of hydroxyl ( $\text{OH}^\bullet$ ) and superoxide ( $\text{O}_2^{\bullet-}$ ) radicals. Third, these free radicals then attack the pollutant to be oxidized (e.g. VOCs). Lastly, these sequential free radical attacks degrade the pollutant to form  $\text{CO}_2$  and  $\text{H}_2\text{O}$  (as well as other possible by-products) [22]. PCO leads to the formation of water and carbon dioxide (usually in very small amounts) and represents a more viable option than some other techniques, as the products formed are primarily benign. Filtration requires cleaning of the filtrate and activated carbon adsorption requires removal via desorption. In both of these techniques, the target contaminants are not degraded, but only transferred.

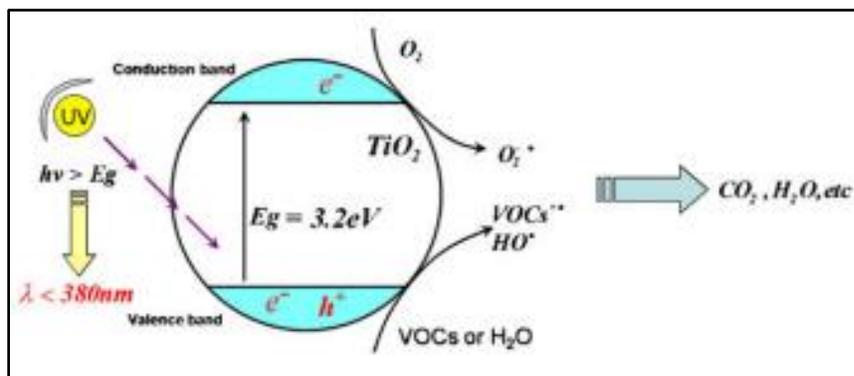
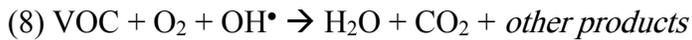
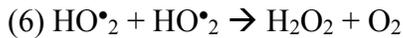
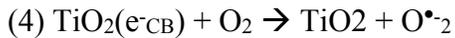


Figure 3.1.1  $\text{TiO}_2$  UV Figure 3.1 Photocatalytic oxidation of VOCs [21]

Figure 3.1 [21] shows an electron in the VB of  $\text{TiO}_2$  excited to the CB and the subsequent formation of radicals. Note, the energy required is  $3.2\text{eV}$  and that this value

varies depending on the semiconductor catalyst used. If the energy from the light source is not at least 3.2eV in this case, the electron will not be excited into the CB and photocatalytic oxidation will not occur (i.e. no pollutant degradation).

The following represent the reactions involved in this process as outlined by Mamaghani *et al.* [19]:



These reactions show light energy ( $h\nu$ ) leading to the formation of electron-hole pairs ( $\text{TiO}_2(e^-_{\text{CB}} + h^+_{\text{VB}})$ ) in the  $\text{TiO}_2$ . These then react with hydroxide, water and oxygen to form the free radicals that are able to degrade the VOCs. Note that there is the possibility to form other products, which can include ozone ( $\text{O}_3$ ) as well as hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and other intermediate radicals.

While  $\text{TiO}_2$  is currently the most promising photocatalyst (primarily due to its stability and suitable positions of VBs and CBs), other options (including  $\text{ZnO}$ ,  $\text{ZrO}_2$ ,  $\text{SnO}_2$ ,  $\text{WO}_3$ ,  $\text{CeO}_2$ ,  $\text{ZnS}$  and  $\text{Fe}_2\text{O}_3$ ) all exhibit semiconductor photocatalytic properties and can also potentially degrade VOCs and other gaseous pollutants [21].

## 3.2 Air Purification Design, Light Sources and Pollutants

### Degraded

Design of different air purification systems using photocatalytic oxidation is dependent on multiple factors including pretreatment of contaminated air, capital costs, light sources and catalyst choice. While these factors can all vary, the generic design for the reactor is presented in Figure 3.2.1 [22].

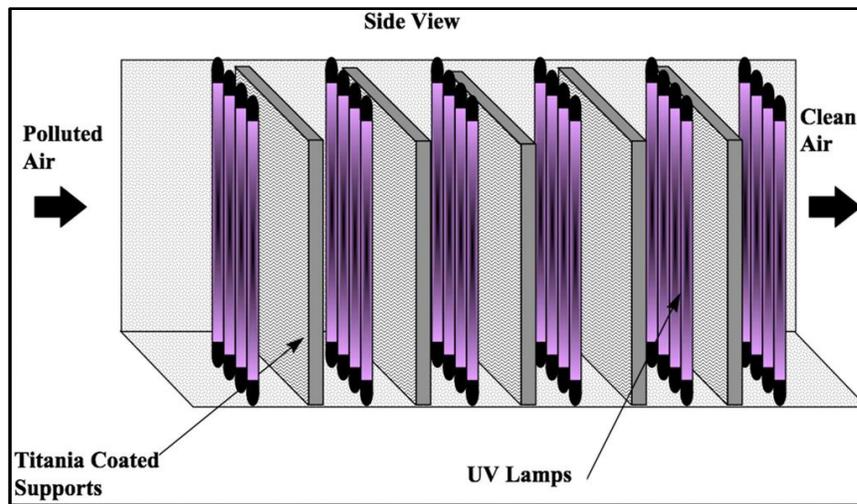


Figure 3.2.1: Generic Multi-Stage, Honeycomb-Monolith Photocatalytic Reactor [22]

In this design, there are multiple stages where UV light is able to excite electrons on the Titania coated supports. 100% removal efficiency is not a viable option so 10-20% removal per pass is desired. Oxidation occurs at each of the stages and the light sources depend on the desired contaminant degradation. For example, there are differences between germicidal lamps, UV fluorescent lamps, black light fluorescent lamps and LED light sources. The sun can technically also be used, but its penetration into indoor environments (especially inside the reactor) is quite limited. Each of these different light

sources operates at different wavelengths, which correspond to different energy levels [22].

It is important to consider the implications of the light source used in PCO, in regards to cost, contaminant activity and resilience. Table 3.2.1 [22] presents information regarding different light sources:

Photon Emitter	UV Wavelength Range	Approximate Lifetime
Sun	UVA and UVB; most UVC absorbed in atmosphere	Exists with daylight
Black Light Fluorescent	UVA (20nm ± 50nm FWHM)	5,000-12,000 hr (usually limited by phosphor degradation)
Germicidal Fluorescent	UVC (254nm)	10,000-20,000 hr
LEDs	Various, 190nm to 1100nm	Wavelength dependent, a few thousand hours at short wavelengths

Table 3.2.1 Common UV Light sources for an Ultraviolet Photocatalytic Oxidation (UVPCO) Air Purifier [22]

Different light sources are chosen based on target contaminants. For example, if the goal is to inactivate viable bioaerosols (such as bacteria, mold spores and airborne viruses), a germicidal lamp is required, although filters (such as HEPA) can also be used as pretreatment to prevent catalyst deactivation [22]. Unfortunately, PCO is not capable of degrading all biological contaminants, and normally can only break down the smaller spectrum of bioaerosols before deactivation takes place. Previous research shows photokilling of bacteria and viruses using TiO<sub>2</sub> in aqueous media and evidence suggests this capacity can be exhibited in air as well. Both *Escherichia coli* and *Legionella pneumophila* (similar in size: 1-1.5 microns) have the possibility to be removed via

photocatalysis and Keller *et al.* report concentrations less than 1 CFU (colony-forming unit) in the purified outlet air stream after the photocatalytic reactor [23]. Table 3.2.2 shows *E. coli* inactivation as a function of total flow rate and bacteria concentration.

Aerosol Flow Rate		90L/hr (1.5L/min)	240L/hr (4L/min)	350L/hr (6L/min)
Bacteria Concentration (CFU/m <sup>3</sup> of flowing air)		15,000	12,000	7,500
Bacteria content (CFU) collected on sampling membranes	Contaminated-inlet air stream (before reactor)	110	160	220
	Purified-outlet air stream (after reactor)	0	0	0
Bacteria removal efficiency (%)		>99.1	>99.4	>99.5

Table 3.2.2 *E. coli* Inactivation via Photocatalysis [23]

In addition to biological contaminants, TiO<sub>2</sub> also acts as a substrate for VOC removal, with the most common VOCs in the built environment found by the EPA BASE (Building Assessment Survey and Evaluation) study being benzene, toluene, ethylbenzene, and o-xylene (referred to as BTEX), as well as formaldehyde, naphthalene, and acetaldehyde [24]. These different VOCs have different PCO reaction rates based on their chemical and physical properties. Certain species saturate the surface, others can form additional layers and still others chemisorb as intermediates; each contaminant behaves differently competing against water as well as the other pollutants present in the air. These different contaminants of interest are graphed in Figure 3.2.2 [22].

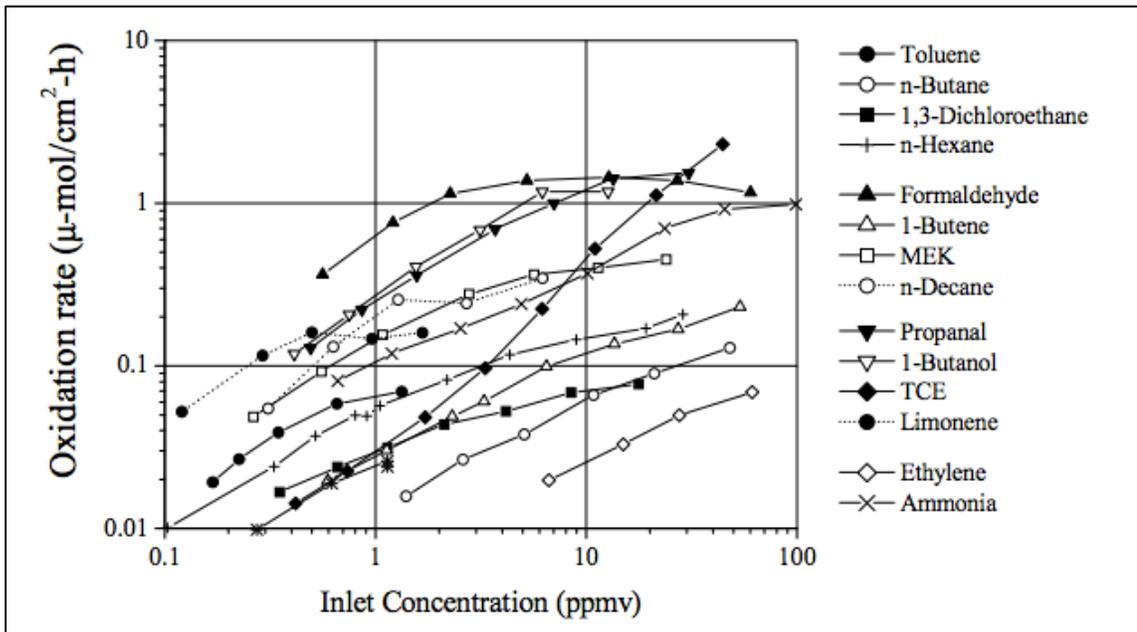


Figure 3.2.2: Measured PCO Reaction Rates for VOCs of Interest in Indoor Air.

UV 1mW/cm<sup>2</sup>, 6000ppm water level [22]

The oxidation rate vs. gas phase concentration is primarily linear at lower concentrations, seems to plateau at higher concentration rates and either decreases or increases (depending on the pollutant) at the highest concentrations, thus graphically representing the disparities between pollutants. In addition to bioaerosols and VOCs, studies have shown that photocatalysts can also remove NO; this will be discussed in more detail in the case studies portion of this paper.

### 3.3 Case Study 1: Enhanced Photocatalytic Degradation of VOCs using Ln<sup>3+</sup> - TiO<sub>2</sub> Catalysts for Indoor Air Purification [25]

Multiple research efforts have sought to either improve removal efficiency of contaminants, use other materials in conjunction with photocatalysts (e.g. doping) or

study the removal efficiency of chemicals that may have not previously exhibited degradation via photocatalysis. The following case studies were investigated in detail to determine disparities and long term viability.

Research has shown that multiple additions/improvements can be made to preexisting photocatalysts to improve their surface area and contaminant intake. Li *et al.* have prepared two new lanthanide ion doped photocatalysts via the sol-gel method: (1)  $\text{La}^{3+}$  -  $\text{TiO}_2$  and (2)  $\text{Nd}^{3+}$  -  $\text{TiO}_2$ . These catalysts have an increased specific surface area, micropore volume and an increased adsorption capacity for both nitrogen and VOCs. [25] Previous research indicates that incorporating certain lanthanides into catalyst substrates could improve the overall adsorption capacity for photocatalysis [26] while simultaneously improving the photochemical properties (mainly the conversion efficiency in certain light wavelengths) [27].

In this study,  $\text{La}^{3+}$  and  $\text{Nd}^{3+}$  were used to dope  $\text{TiO}_2$  in varying lanthanide concentrations (0.7%, 1.2%, 1.6% and 2.0%) via a sol-gel process. This involved formation of a colloidal suspension, which was subsequently stirred and aged to form a gel. The gel was later dried, ground and then calcined in preparation for loading onto the substrate [25].

A continuous gas flow reactor system with a photoreactor and 365nm wavelength UV lamp were used in this study in addition to two different gas cylinders containing the pollutants. The first cylinder contained benzene, toluene, ethyl-benzene and *o*-xylene (BTEX) (1:1:1:1 ratio, 1ppmv concentration) and the second contained NO (50ppmv concentration). The removal efficiency of these pollutants was determined to be greater with lanthanide-doped photocatalysts. Table 3.3.1 shows the improvements that

lanthanide doped catalysts exhibit in terms of surface area, micropore volume and total pore volume.

Crystal parameters and BET data of TiO <sub>2</sub> and Ln <sup>3+</sup> -TiO <sub>2</sub> catalysts							
Photocatalysts	Pure TiO <sub>2</sub>	La <sup>3+</sup> -TiO <sub>2</sub>			Nd <sup>3+</sup> -TiO <sub>2</sub>		
		0.7%	1.2%	2.0%	0.7%	1.2%	2.0%
Crystal pattern	A <sup>a</sup>	A <sup>a</sup>	A <sup>a</sup>	A <sup>a</sup>	A <sup>a</sup>	A <sup>a</sup>	A <sup>a</sup>
Crystal size (nm)	32.9	22.9	17.7	17.6	19.2	19.80	17.8
The specific surface area (m <sup>2</sup> g <sup>-1</sup> )	50.20	73.87	83.81	76.42	71.25	78.54	90.81
<i>t</i> -plot total surface area (m <sup>2</sup> g <sup>-1</sup> )	55.94	81.60	83.81	86.33	79.09	88.68	90.81
<i>t</i> -plot surface area (m <sup>2</sup> g <sup>-1</sup> )	51.94	75.00	78.78	82.80	72.38	82.92	85.78
Monolayer volume (cm <sup>3</sup> g <sup>-1</sup> , STP)	11.53	16.97	19.25	17.55	16.36	18.04	20.86
Micropore surface area (m <sup>2</sup> g <sup>-1</sup> )	4.00	6.60	5.03	3.53	6.71	5.76	5.03
Micropore volume (10 <sup>-3</sup> cm <sup>3</sup> g <sup>-1</sup> )	1.13	2.06	1.15	0.51	2.17	1.53	1.26
The total pore volume (cm <sup>3</sup> g <sup>-1</sup> ) ( <i>P</i> <sub>4</sub> / <i>P</i> <sub>0</sub> = 0.9814, adsorption)	0.152	0.270	0.228	0.205	0.252	0.248	0.234

<sup>a</sup> A = anatase.

Table 3.3.1: Crystal Parameters and BET data of TiO<sub>2</sub> and Ln<sup>3+</sup> - TiO<sub>2</sub> Catalysts

In some instances, values almost doubled for certain parameters listed above, and these translated to improved efficiency in removing contaminants (as shown in Figure 3.3.1 and Figure 3.3.2).

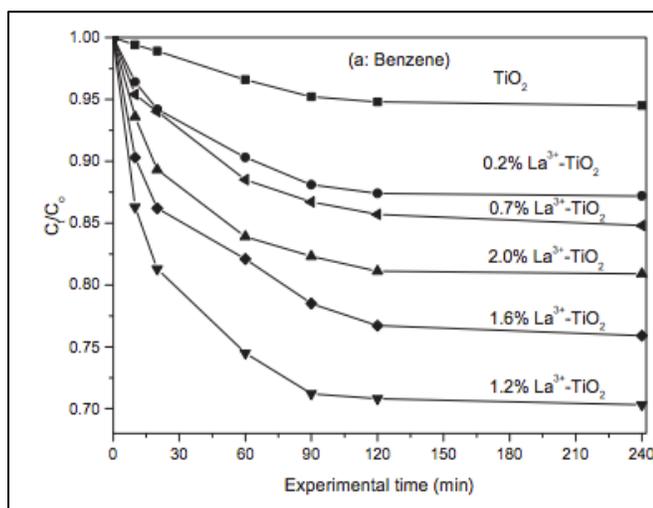


Figure 3.3.1: PCO Degradation of Benzene

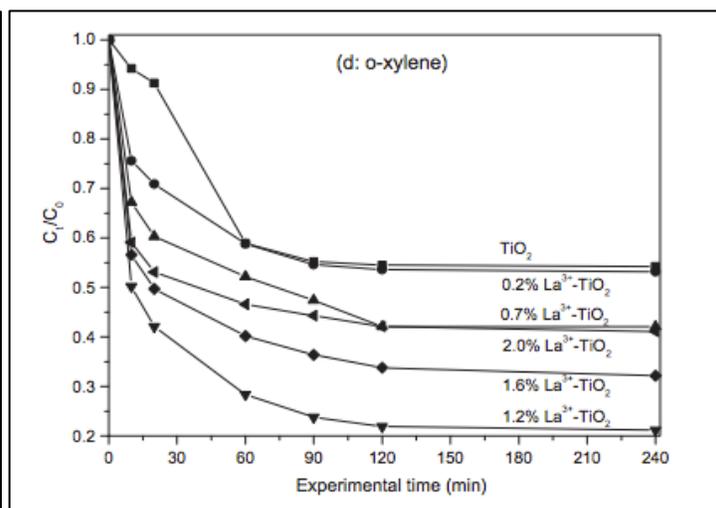


Figure 3.3.2: PCO Degradation of *o*-xylene

These figures show a large improvement in pollutant removal with *o*-xylene being removed at higher levels than Benzene. Both toluene and ethylbenzene showed improvements as well and had removal efficiencies in between those of the contaminants shown. It should be noted that the 1.2% doped catalyst proved to have the highest removal capacity although the 0.7% catalyst showed the highest surface micropore surface area and pore volume. This can be interpreted to mean that the photocatalytic activity of the 1.2% doped catalyst (separating electron-hole pairs more efficiently) had a larger impact than the larger adsorption capacity of the 0.7% doped catalyst. It was also determined that an increase in humidity level corresponded to a decrease in removal efficiency while an increase in NO concentration corresponded to an increase in efficiency. This is believed to be caused by the fact that at higher humidity levels, water can outcompete VOCs for the active sites on the TiO<sub>2</sub> surface while photodegradation of NO led to the formation of more free radicals and thus further removal of BTEX.

### **3.4 Case Study 2: Indoor Air Purification by Photocatalyst TiO<sub>2</sub> Immobilized on an Activated Carbon Filter Installed in an Air Cleaner [28]**

Much research has been done on the ability of activated carbon (AC) to adsorb VOCs and AC is currently ubiquitously used for this purpose. However, one of the main issues with the technology is that contaminants are solely transferred from one phase to another and then further treatment and/or disposal are required. This paper focuses on pairing both AC and PCO to improve the removal and eventual degradation of harmful contaminants (mainly toluene and NO in this study). Using TiO<sub>2</sub> immobilized on an

activated carbon ( $\text{TiO}_2/\text{AC}$ ) filter improved the removal efficiencies of both NO and toluene. Research shows that the activated carbon provides a larger adsorption capacity, and the adsorbed NO on this filter is then transferred to the photocatalyst for photodegradation [28].

Gas cylinders containing both NO (50ppmv) and toluene were used as the contaminants and their removal efficiency was recorded. Figure 3.4.1 shows the experimental design.

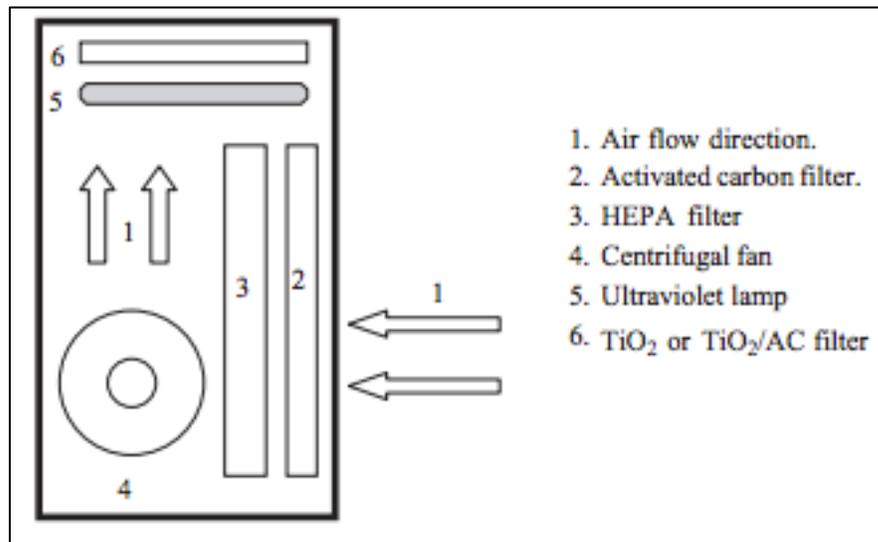


Figure 3.4.1: Schematic Diagram of Air Cleaner

A high-efficiency particulate air filter (HEPA) and an activated carbon filter (AC) were both used prior to oxidation, and contaminants can be stored in the filters and then later degraded leading to improved air quality. The centrifugal fan draws air from the filters and flows it towards the UV lamp and photocatalyst. Figure 3.4.2 and Figure 3.4.3 show the differences between the photocatalyst alone and the photocatalyst paired with an AC filter for both NO and toluene.

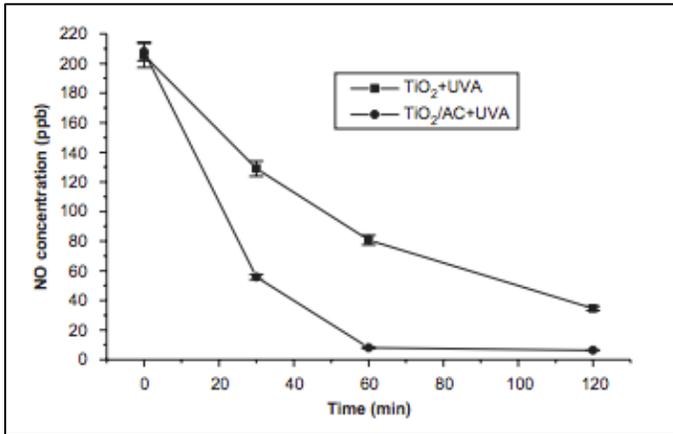


Figure 3.4.2: NO Removal via PCO

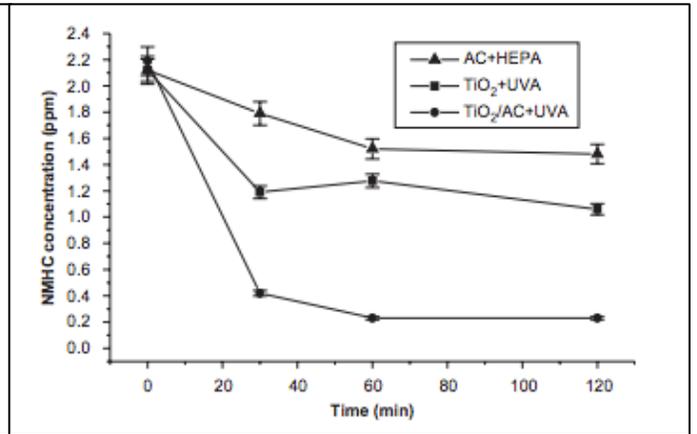


Figure 3.4.3: Toluene Removal via PCO

Both NO and toluene were removed at greater efficiencies when an AC filter was used in conjunction with the photocatalysis process. The NO concentration reached a steady state value at 60 min (AC) while it was still decreased when no AC filter was used. This small residence time and low NO concentration decrease the probability of NO contact with radicals. The AC filter increases the adsorption of NO and then transfers it to the photocatalyst (TiO<sub>2</sub>) where it is degraded. At lower concentrations of contaminants, the residence time is increased, which means there are fewer interactions between contaminants and radicals. By using an AC filter, these interactions are increased and the lower initial concentration, in theory, acts as a higher concentration [28].

Toluene was removed solely with a HEPA and AC filter (most likely due to adsorption of toluene on the activated carbon filter), but the largest removal efficiency was clearly with the photocatalyst and AC filter. While NO had a higher removal efficiency in general (97%), when compared to toluene (89.5%), the difference in removal efficiency (between TiO<sub>2</sub> and TiO<sub>2</sub>/AC) of toluene (49.5%) was much higher than that of NO (13.8%). This is most likely a function of the less photoreactive nature

of toluene, which corresponds to a greater enhancement effect of the TiO<sub>2</sub>/AC filter with toluene as opposed to NO [28].

Under low residence time, low pollutant concentration and high levels of relative humidity, the use of the TiO<sub>2</sub>/AC filter proved to be very effective in removing contaminants. However, as concentrations increase and humidity decreases, the use of an AC filter is of less importance and the contaminants do not need to be concentrated and transferred (they are already in high enough concentrations and interactions between radicals and contaminants are relatively high). However, with low residence times and few particle interactions, the AC filter is quintessential in concentrating pollutants and leading to a higher removal efficiency [28].

*The following two case studies involve new photocatalysts that are not TiO<sub>2</sub>*

### **3.5 Case Study 3: ZnO for Photocatalytic Air Purification Applications [29]**

Similar to TiO<sub>2</sub>, ZnO also has high photosensitivity, stability, a large band gap, strong oxidizing power, and is also non-toxic, making it another viable candidate for PCO. Research shows that ZnO can exhibit an even higher activity than titanium dioxide in the photodegradation of dyes, and this paper focuses on the air purification properties of ZnO coated textiles as well as nano and micro-structured ZnO coatings. ZnO was chemically deposited on to organic substrates and despite damage to these substrates during deposition; good adhesion resulted even after successive washings. Multiple substrates were tested including Organic Cotton, Silk+Viscose, Bambus, Tencel and Glass Fibers. Out of these substrates, the glass fibers were the most promising, as they

were able to sustain ZnO nanostructure growth, which is crucial for PCO. Figure 3.5.1 shows the ZnO nanostructure coating on the glass fibers [29].

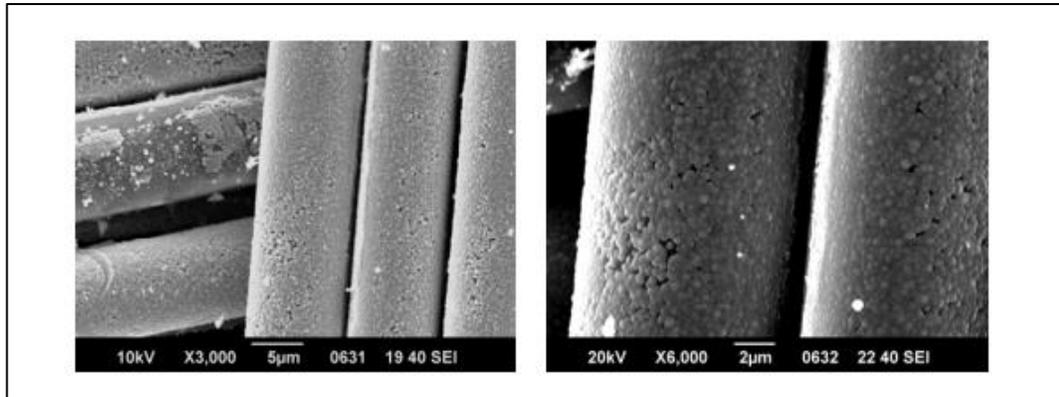


Figure 3.5.1: Nanostructured ZnO Coating onto Glass Fiber Substrates (SEM)

The 2-micron scale image clearly shows the ZnO particles, which are the essential catalyst for the PCO process. Other substrates (specifically organic) were not able to support ZnO nanoparticles and were normally degraded during deposition. SEM and XRD shows that highly crystalline ZnO growth occurs on different textile fibers with varying success. The nature of the substrate has implications for ZnO deposition and thus potential activity and removal potential for contaminants. Figure 3.5.2 shows methylene blue (MB) degradation using photocatalysis [29].

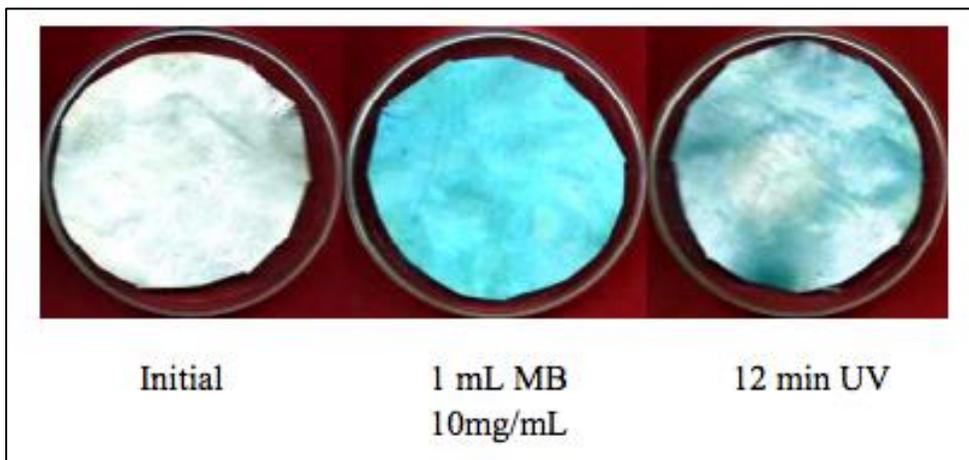


Figure 3.5.2: MB Discoloration onto ZnO onto Glass Fiber Substrate

The glass fiber coated with MB was shown to discolor after exposure to UV light as the deposited ZnO nanoparticles were able to photocatalytically degrade MB. Further research will include experiments relating to formaldehyde degradation using similar textile substrates and catalysts [29]. This work not only has implications in terms of creating a device that can purify indoor air, but it also can potentially lead to research involving textiles that people can wear that can actively degrade contaminants.

### **3.6 Case Study 4: Facile Synthesis of in situ Phosphorus-doped g-C<sub>3</sub>N<sub>4</sub> with Enhanced Visible Light Photocatalytic Property for NO Purification [30]**

Photoactivity of catalysts is one of the greatest limitations of the PCO process and so new materials and doping strategies seek to improve removal efficiency. In this case, graphitic carbon nitride (g-C<sub>3</sub>N<sub>4</sub>) is used as it is metal free, easily synthesized, stable, has a suitable band gap and a unique electronic structure [30]. In contrast to these advantages, g-C<sub>3</sub>N<sub>4</sub> also has a low quantum efficiency, small surface area, low visible light utilization, and sub-par catalytic performance. However, both metal (Fe, Li, K) and non-metal (S, B, P) doping, micro-structural engineering (e.g. nanospheres or nanoflowers) and the construction of heterojunctions (e.g. g-C<sub>3</sub>N<sub>4</sub>/(BiO)<sub>2</sub>CO<sub>3</sub>) have been found to improve the overall photocatalytic capability of the substrate [30].

Previous studies have investigated carbon dots and nanocomposites, thermally induced copolymerization, and mesoporous doped substrates with nanoflowers as methods for phosphorus doping. However, in this study, a novel P-doped catalyst was formed by directly heating a mixture of thiourea and  $\text{Cl}_6\text{N}_3\text{P}_3$  in air. This phosphorus-doped catalyst showed substantial efficiency improvements over the pure sample [30] when exposed to NO concentrations. TEM was used to investigate the differences between these two samples showing the abundant pore structures and improved surface area of the doped catalyst. Table 3.6.1 shows a comparison of different catalysts with respect to both surface area and pore volume.

Samples	$S_{\text{BET}}$ ( $\text{m}^2 \text{g}^{-1}$ )	$V_p$ ( $\text{cm}^3 \text{g}^{-1}$ )
CN	13.49	0.11
CN-P-3	22.17	0.15
CN-P-5	23.80	0.17
CN-P-10	30.33	0.21

Table 3.6.1: Surface Area and Total pore Vol. of CN, CN—P-3, CN—P-5 and CN—P-10

The data shows an increase in both surface area and total pore volume due to phosphorus doping, with the largest values being for the CN—P-10 catalyst. The photocatalytic properties of these catalysts were evaluated by removal of NO in the gas phase. After 30min, the NO removal ratios of CN, CN—P-3, CN—P-5 and CN—P-10, were 28.7%, 37.7%, 42.3%, and 37.5% respectively, and this is shown in Figure 3.6.1.

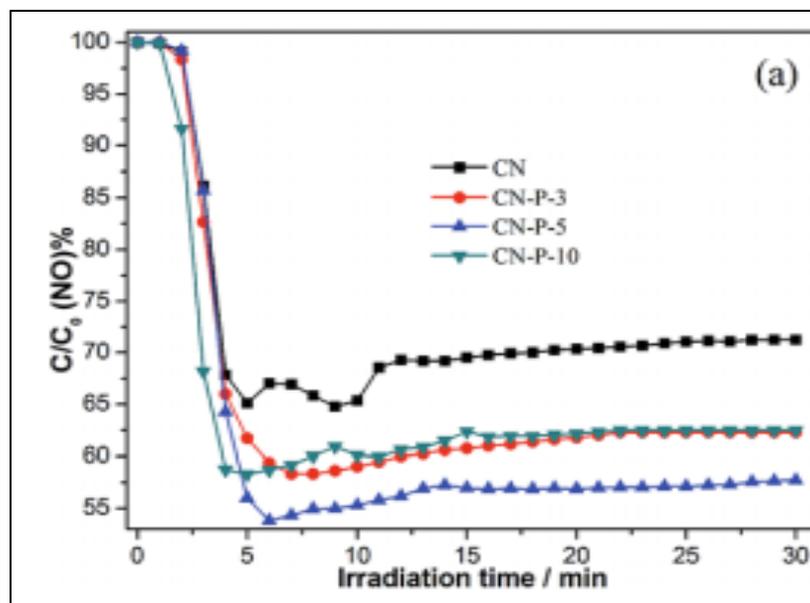


Figure 3.6.1: Photocatalytic Activity for the Removal of NO Under Visible Light Irradiation (420nm)

The CN—P-5 proved to be the best catalyst in removing NO mainly due to increased surface area and pore volume (promoting mass transfer and providing more active sites), its ability to separate and transfer photo-generated electrons and holes (thus increasing quantum yield and activity), and lastly, its down shift valence band-edge potential (increase in gap between VB and CB), which led to a stronger oxidation ability and thus improved removal efficiency [30]. The results suggest that phosphorus doping has serious implications on removal efficiency and critical effects on the physiochemical properties of catalysts.

### 3.7 Feasibility of Photocatalytic Oxidation

Overall, air purification via photocatalytic oxidation proves to be a viable method for removing low concentrations of volatile organic compounds, small bioaerosols, as

well as gases such as  $\text{NO}_x$ s. While  $\text{TiO}_2$  is the primary photocatalyst of choice in many applications, new research shows that the photocatalytic activity can be improved using  $\text{Ln}^{3+}$  and also by using PCO in conjunction with an activated carbon filter. Additionally, other materials, both organic (g- $\text{C}_3\text{N}_4$ ) and inorganic ( $\text{ZnO}$ ), also exhibit photocatalytic properties and have the potential to become viable alternatives to titanium and may in fact even improve overall removal efficiency. Case studies show that doping increases both the surface area and total pore volume of the material, consequently leading to higher removal efficiencies in multiple instances.

Improving indoor air quality represents a crucial facet of air quality engineering as people are spending more and more of their time indoors, and the EPA has reported that indoor air pollution poses a greater health risk than outdoor air pollution [31]. PCO, unlike many other technologies, degrades contaminants into innocuous products, mainly water and carbon dioxide and doesn't require further treatment. Further research in the field is leading to improved efficiencies and increasing the viability of the technology, making scaling up and economic profitability outcomes in the near future.

# Chapter 4

## Conclusion

Outdoor air quality can often overshadow indoor air quality concerns as pollutants such as carbon dioxide, greenhouse gases in general, ozone, sulfur dioxide, and particulate matter frequently represent areas of concerns and debate in the public sphere. However, as individuals are spending an increasing amount of time indoors, concerns regarding our indoor air environment are receiving more attention than ever. According to the EPA, humans spend over 90% of their time in indoor environments and as such, ensuring clean and contaminant free air is crucial for human health and wellness.

Many of the contaminants in indoor environments can be a product of external sources or outside air; however, there are also many sources of contaminants in both residential and non-residential facilities. Some of these contaminants may be natural, while others come directly from human use. Understanding sources of these contaminants, especially in our health facilities represents a quintessential factor in understanding how to contain, mitigate and avoid these pollutants altogether.

Health facilities not only represent facilities with large sources of indoor air contaminants, but these facilities in general can have higher standards for air quality than many residential or industrial locations. As such, high quality filters, ventilation systems and practices are put in place to ensure minimal exposure to these pollutants. However, these practices are not always completely effective. Healthcare workers and patients are

exposed to not only biological contaminants and particulate matter, but also VOCs in varying concentrations.

More than 40 VOCs have been measured in indoor environments and while these contaminants are below exposure limits in most cases, most sampling techniques do not allow for a true understanding of acute, cumulative or chronic exposure. While technologies such as activated carbon adsorption, and photocatalytic oxidation (PCO) exist to help combat these contaminants, these methods are not always feasible or effective in practice as they are in theory. While PCO definitely represents a viable option, there are undoubtedly limitations and challenges associated with scaling and implementation. Further studies not only investigating long term impacts of VOC exposure, but also involving more advanced and developed treatment technologies will prove helpful in providing a more complete understanding of the indoor environment and aid in improving our air.

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## Vita

Michael Celente was born on August 1<sup>st</sup>, 1994 in Parsippany, NJ to Albert and Nancy Celente (maiden name Lukert). He graduated from Newark Academy in 2012 where he was a recipient of an International Baccalaureate diploma. He then attended Lehigh University where he received a Bachelor of Science in Integrated Energy Engineering and Sustainable Development with a focus in Urban Environmental Studies through the IDEAS (Integrated Degree in Engineering Arts and Sciences) program. He graduated in 2016 Summa Cum Laude, a member of Phi Beta Kappa and attained the Presidential Scholarship. He was also heavily involved as an Orientation Leader and member of the Gryphon Society where he acted as both a Gryphon and Head Gryphon of Dravo House and Head Gryphon of Richards House. He is currently pursuing a Master of Science in Environmental Engineering at Lehigh and will graduate in May of 2017.

His research interests lie in both renewable energy and air pollution and the intersection of engineering, public policy and social justice. He is passionate about sustainable development, environmental justice and environmental stewardship in general.