Assessment of Ozone Initiated Chemistry in Portable Classrooms

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5/4/2018

Executive Summary

The Issue

The average American spends 87% of their life indoors (Klepeis et al., 2001). Some people spend even more time inside, including those that are more susceptible to respiratory infections and complications, such as chronically ill patients, elderly, or infants. (Allen et al., 2004; Wallace et al., 2006; Wheeler et al., 2011). Cases of respiratory complications, such as asthma and allergies, have also been increasing in the past decades (Centers for Disease Control and Prevention 2011). The increase in these cases and the popularity of the indoors have been primary factors for the rising concern from the public regarding school classroom environments. Long-term exposure to indoor air contaminants can cause an array of adverse health effects in populations, ranging from eye and throat irritation to serious respiratory disease, and even cancer (Blue Point Environmental 2005). As a result, the quality of the indoor air environment has been an area of important research interest.

One contaminant of particular interest is tropospheric ozone, a ground-level pollutant. Ozone has been known to cause adverse health effects in humans, and numerous research teams have reported information on the matter. When ozone is inhaled, it reacts with epithelial cells of the lungs and polyunsaturated fatty acids within tissues. This creates by-products and increases the permeability of the epithelial lining fluid (ELF), causing increased transportation of pollutants from the lungs into the bloodstream, making occupants more susceptible to sickness and infection (Levy et al., 2001; Mudway and Kelly et al., 2000; USEPA, 2006).

Ozone also has a great effect on indoor air chemistry. When ozone reacts with chemicals in the indoor environment it is known to create undesirable by-products. Highly occupied spaces pose a unique area of interest for research due to the potential amount of heterogeneous (surface) reactions that can occur. Little research has been done to analyze indoor air chemistry in classrooms. The resulting data in this report offers potential concentrations of various reaction by-products within portable classrooms. Some of these products are known to cause adverse pulmonary complications, respiratory irritation, and even cancer (*EPA* 2006). The four by-products that were analyzed include: formaldehyde (HCHO), secondary organic aerosols (SOA), 4-oxopentanal (4-OPA), and 6-methyl-5-hepten-2-one (6-MHO).

Approach

A model was developed to predict estimates of reaction by-products in two cases. One case was based on average indoor ozone and limonene concentrations from a larger study conducted in school portable classrooms (base-case), and the other case was based on the highest recorded indoor ozone and limonene concentrations in the same study (worst-case). Indoor pollutant concentrations of these classrooms were assumed to be at steady-state and well-mixed. Details that outline the design of the model are discussed and explained in section 2 of this report.

Major Findings

Tables ES-1 to ES-3 summarize estimates of by-product concentrations for each case, as well as their maximum value ratios. Discussions of these results are found in Section 4.

Table ES-1. Maximum and Minimum by-product concentrations (base-case)

	HCHO (ppb)	**SOA (µg/m^3)**	**6-MHO (ppb)**	**4-OPA (ppb)**
Maximum	0.40	8.91	95.5	80.7
Minimum	0.015	0.34	3.93	3.3
Average	0.13	2.9	27.3	23.0

Table ES-2. Maximum and Minimum by-product concentrations (worst-case)

	HCHO (ppb)	**SOA (µg/m^3)**	**6-MHO (ppb)**	**4-OPA (ppb)**
Maximum	3.3	74.6	307.6	259.8
Minimum	0.10	2.2	2.2	11.2
Average	0.82	18.3	84.2	71.1

Table ES-3. Ratios of base-case and worst-case maximum concentrations

	Formaldehyde (ppb/ppb)	SOA ($\mu g/m^3/\mu g/m^3$)	6-MHO (ppb/ppb)	4-OPA (ppb/ppb)
Ratio (worst-case/ base-case)	8.3	8.4	3.2	3.2

The primary findings of this study suggest that formaldehyde (HCHO) concentrations derived from ozone chemistry levels under these conditions are not a concern. When compared with typical concentrations found in offices and schools of 15-30 ppb, the reaction-derived HCHO estimates should not raise concern (Weschler et al., 2000). Even though its worst-case maximum concentration was 8.3 times higher than its base-case condition, the highest theoretical value of 3.3 ppb is still well below the average for most indoor environments. However, concentrations of secondary organic aerosols (SOA), 4-oxopentanal (4-OPA), and 6-methyl-5-hepten-2-one (6-MHO) were high enough to pique interest into their effect on the classroom environment. When comparing their base-case conditions with their worst-case conditions, worst-case SOA maximum concentrations were almost 8.4 times higher than base-case conditions. The average SOA concentration of 18.3 $\mu g/m^3$ was above the average value recorded for fine particulate matter in indoor environments by the USEPA's National Ambient Air Quality Standard of 15 $\mu g/m^3$ (EPA, 2016). The highest maximum worst-case concentration of 308 ppb was for 6-MHO, and an average of 84.2 ppb. This is significantly higher than steady-state values of 2.3 ppb reported in an occupied aircraft cabin (Wisthaler et al., 2009). The model also resulted in relatively high concentrations of 4-OPA, with its maximum worst-case level at 260 ppb and mean level of 71 ppb. This is also well above the steady-state value reported in (Wisthaler et al., 2009). While the resulting data does not suggest HCHO as a compound of particular interest to portable classrooms, worst-case and average concentrations of SOA, 6-MHO, and 4-OPA propose that more research should be conducted on their effects in highly occupied indoor environments.

Table of Contents

1. Introduction

Potential concentrations of by-products driven by chemical reactions involving ozone in high school classrooms are presented in this study. These by-products, along with high indoor concentrations of ozone itself, can lead to health concerns for occupants. This section presents common concerns related to ozone and its reaction products, as well as the objectives of this study. The model used in this report is described in Section 2. The results of the model applications are discussed in Section 4 and compared with common concentrations found in other studies.

1.1 Concerns Related to Ozone

The effects of ozone on human health have been researched and are well known. Empirical studies on the subject have confirmed the negative impacts that ozone can have on people. The primary concern with ozone comes from its tendency to readily break down unsaturated organic molecules. As a result of this property, ozone can degrade important compounds for cell growth and sustainability. The break-down of epithelial cells in the lungs and respiratory tract can cause irritation in these areas that leads to coughing, pain, and irritation during respiration (California Air Resources Board, 2005).

High ozone concentrations have been linked to increased respiratory-related morbidity and premature mortality (e.g., Bell et al., 2005; Gryparis et al., 2004; Ito et al., 2005; Jerrett et al., 2009; Parodi et al., 2005). Some studies have shown that subjects with pre-existing respiratory issues are more susceptible to irritation and inflammation when exposed to ozone (Jorres et al, 1996; Holz et al, 2002 (224, 285). High levels of ozone have also been correlated to higher diagnoses of children with asthma as well as higher amounts of hospital emergency room visits among children and elderly (McConnell et al., 2002).

Long-term exposure to high ozone concentrations can have significantly negative effects on human health. Speculation has been made about the connection between long-term ozone exposure and increased mortality rates from cardiovascular and respiratory complications, but studies have only identified significant correlations between ozone and respiratory complications (Jerrett et al., 2009). Additionally, short-term exposure to high ozone concentrations, and even long-term exposure to low concentrations, can cause an increase in mortality (Bell et al., 2006).

Ozone enters the indoor environment through a few ways. An intentional supply of ozone can be produced by ozone generators. Passive infiltration of ozone from the outdoor environment occurs unintentionally through gaps in windows and openings. A third supply of indoor ozone is by the production of ozone emitted by machines such as copiers, printers, etc. (Ewers et al., 2006).

Due to its high reactivity, ozone concentrations are generally lower indoors than outdoors. This could be perceived as beneficial to the air quality of the space since high ozone concentrations pose concern for health. However, when the concentration of ozone decreases in an indoor environment, it is known to have reacted with molecules in the air as well as on indoor surfaces such as desks, tables, room decorations, and even human skin.

When ozone reacts, it creates oxidized products from heterogeneous and homogeneous reactions. Heterogeneous reactions are those that occur when ozone contacts chemicals on the surfaces of walls, stationary objects, people, etc, and homogeneous, or gas-phase, reactions occur when ozone interacts with reactants in the air (Fan et al., 2003; Long et al., 2000; Wainman et al., 2000; Sarwar et al., 2003 and 2004; Waring et al., 2011; Weschler and Shields, 1999), leading to a range of gaseous oxidized products (Destaillats et al., 2006; Weschler et al., 1992a; Singer et al., 2006; Weschler and Shields, 1996 and 1997; Sarwar et al., 2002). While both of these types of reactions do reduce the concentration of ozone, they have the potential to yield undesirable by-products. The indoor environment will typically contain higher by-product concentrations than the outdoor environment primarily due to the high concentrations of reactants that contribute to ozone-initiated chemistry, and that are found in building materials, consumer products, furnishings, and occupants. Another reason is due to the fact that indoor surface-to-volume ratios tend to be 300 times larger than ratios of the outdoor environment (Weschler 2006). This greatly increases the surface chemistry indoors, leading to much higher concentrations of by-products. Four chemicals that are known to form from ozone initiated chemistry and have been known to cause adverse health effects are described in the following section.

1.2 Concerns Related to Homogeneous Reaction By-Products

Two pollutants produced from homogeneous reactions are formaldehyde (HCHO) and secondary organic aerosols (SOAs).

Formaldehyde has long been a concern to human health beginning in the 1850's (Salthammer et al., 2010). Many building materials and engines have been known to produce undesirable levels of formaldehyde, exposing discomforting and dangerous concentrations to workers (Salthammer et al., 2010). Lower levels of formaldehyde, though, have also been known to cause sensory irritation and respiratory complications. Chronic exposure to low concentrations of formaldehyde has even been hypothesized to cause negative neuropsychological complications (Williams et al., 1998). Formaldehyde becomes detectable due to its strong odor at concentrations of 0.1 to 1 ppm. Pulmonary edema and fatalities have been reported to occur at concentrations above 100 ppm (Williams et al., 1998). Kaden (2010) provides a comprehensive list of indoor formaldehyde concentrations for various environments, including offices and schools. Concentrations in these environments ranged between 15 to 30 $\mu g/m^3$. Sensitization and irritation studies have analyzed the different levels of formaldehyde at which discomfort, irritation, and even fatalities have occurred. High levels of formaldehyde, ranging between 3.1 to 5.3 ppm, have been linked to significantly suppressed respiration due to throat irritation (Salthammer et al., 2010). The lowest levels of observable irritation for humans ranged from 0.4 ppm to 3 ppm, with eye irritation being the most sensitive parameter (Salthammer et al., 2010). Precautionary indoor concentrations have been set to 0.1 ppm as the standard for health concerns (Golden et al., 2011). Average indoor concentrations of up to 30 ppb have been reported (Weschler et al., 2000).

Secondary Organic Aerosols (SOA) are reaction products that contribute to fine particulate matter found in air pollution. SOA is made up of chemical components that are still being researched and identified. They are produced from natural as well as man-made sources (EPA, 2017). These products have been known to cause sensory irritation, specifically in the eyes and respiratory tract (Kleno and Wolkoff et al., 2004; Pope et al., 2002). An increase in mortality has even been linked with higher SOA concentrations (Baltensperger et al., 2008).

1.3 Concerns Related to Heterogeneous Reaction By-Products

Two known by-products of heterogeneous reactions with human skin oils are 6-methyl-5-hepten-2-one (6-MHO) and 4-oxopentanal (4-OPA).

6-MHO is derived from unsaturated volatile compounds such as lycopene, the primary pigment in red tomatoes, and squalene, a primary chemical found in skin oil (Sandrine et al., 2009; Wisthaler et al., 2009). At high concentrations, it has been known to cause pulmonary irritation, sensory irritation, and airflow limitation. (Wolkoff et al., 2013). In one study, mice were exposed to elevated concentrations of 6-MHO (Wolkoff et al., 2013). The resulting reference values for sensory irritation and airflow limitation values were determined to be 0.3 and 0.5 ppm, respectively. Steady-state indoor classroom concentrations have also been recorded to be around 0.6 ppb, and a study using an occupied aircraft cabin has reported 2.3 ppb steady-state values (Liu et al., 2016; Wisthaler et al., 2009).

4-Oxopentanal (4-OPA) is formed by the ozonolysis of squalene, a primary human skin oil, and other compounds of high-volume production that are commonly found indoors (Anderson et al., 2012). 4-OPA has a structure similar to diacetyl, the chemical used for artificial butter popcorn flavoring, and has been reported to cause serious lung issues for factory workers (Weschler et al., 2009). 4-OPA causes adverse effects on pulmonary and dermal exposure in murine models and has been identified as a known sensitizer and irritant (Anderson et al., 2012). According to (Wolkoff et al., 2012) it can cause pulmonary irritation, airflow limitation, and sensory irritation. These effects by 4-OPA are hypothesized to be a result of inflammatory reactions, specifically its effect on messenger RNA expression of various inflammatory mediators (Anderson et al., 2007; Anderson et al., 2010). In an experiment involving 4-OPA exposure to dermal and pulmonary tissues it was reported to cause nonspecific airway hyperreactivity, increased amounts of associated lymphocytes and neutrophils, and increased interferon production by lung-associated lymph nodes (Anderson et al., 2012). Airflow limitation values from a study on the effects of volatile compounds on mice concluded to be 0.3 ppm (Wolkoff et. al., 2013).

1.4 Study Objectives

Little research has been done to analyze ozone-initiated indoor air chemistry in classrooms. This paper serves to provide insight into this issue and create a reference for the potential concentrations of various reaction by-products. In this project, existing data were used as related to indoor air quality of portable school classrooms. The data were used as input to a model outlined in section 2 to calculate concentrations of reaction by-products formed and driven by the concentrations of ozone in a set of seven classrooms in one school district in Texas.

Specific objectives:

1. To determine ozone concentration ratios between indoor portable classroom environments and their respective outdoor environments.
2. Develop a mass balance model to explore the extent of ozone initiated chemistry in portable classrooms located in Central Texas.
3. To use the model with existing data as parameter inputs to predict the extent of ozone initiated chemistry and chemical reaction products for reactions that occur in classroom air and on classroom surfaces.

1.5 Scope of Research

This analysis is limited to seven portable high school classrooms in Central Texas. Each classroom was sampled four separate days over a period of two years. One visit was conducted each school semester (fall and spring). The analysis is limited to only certain compounds that are known to react readily with ozone.

Data from the larger study was applied to the models in an effort to produce theoretical by-product concentrations. A well-mixed classroom at steady-state was assumed. Two scenarios, a base-case and worst-case, were simulated. In the base-case analysis, ozone concentrations were average values from each event, and in the worst-case analysis the concentrations were taken as the maximum recorded value during events.

2. Model Development

A model was developed to predict reaction by-product concentrations for two different cases. The details and assumptions of each case are outlined in this section, along with the model design and development.

2.1 Base-Case Scenario

The indoor air environment of each portable classroom under base-case conditions was considered to be well-mixed and to have reached a steady-state pollutant concentration. The concentration of limonene, the primary reactant for formaldehyde (HCHO) and secondary organic aerosol formation, was taken as an average of the existing data for each classroom. The ozone concentrations used for base-case conditions were average one-day values from the existing classroom data (UT Austin, 2017).

2.2 Worst-Case Scenario

The worst-case indoor air environment was also assumed to be well mixed and have reached a steady-state pollutant concentration. The limonene concentrations for each classroom were maximum values (UT Austin, 2017). The ozone concentrations were also the maximum values of each class.

2.3 Model Design and Equations

Steady-state mass balance models were developed to estimate indoor concentrations of ozone and reaction products in portable classrooms. Resulting mass balance equations are provided in this section.

<u>Indoor and Outdoor Ozone Concentration Ratio:</u>

- $R = \frac{C_{ozone\_inside}}{C_{ozone\_outside}}$ (2-1)

Formaldehyde:

- $C_p = \frac{(C_j * k_b * y_j) * C_{ozone}}{\lambda}$ (2-2)

Secondary Organic Aerosol:

- $C_p = \frac{(C_j * k_b * y_j) * C_{ozone} * \alpha}{\lambda}$ (2-3)

6-MHO:

- $C_p = \frac{(y_j * (k_{dep\_total} - k_{dep\_background}) * C_{ozone}}{\lambda}$ (2-4)

4-OPA:

- $C_p = \frac{(y_j * (k_{dep\_total} - k_{dep\_background}) * C_{ozone}}{\lambda}$ (2-5)

Parameters & Units:

- R= indoor/outdoor ozone concentration ratio [-]
- C_{ozone_inside}= concentration of ozone inside the classroom [ppb]
- $C_{ozone\_outside}$=concentration of ozone outside the classroom [ppb]
- C_p= concentration of by-product [ppb]
- C_j= concentration of limonene [ppb]
- y_j= molar yield of by-product p from reactant j
- α= constant, unit converter from ppb to $\mu g/m^3$ [$(\mu g/m^3)/ppb$]
- λ= air exchange rate [hr^{-1}]
- k_b= bi-molecular reaction rate constant for ozone [$ppb^{-1}hr^{-1}$]
- $k_{dep\_background}$= reaction rate constant for ozone with background surfaces, e.g. walls, desks, posters, etc. [hr^{-1}]
- k_{dep_total}= reaction rate constant for ozone with background surfaces and people [hr^{-1}]

3. Parameter Estimation

Model parameters and their application to the study are outlined below.

3.1 Classroom Characteristics

Each portable classroom contained numerous surfaces with different materials. Each contained wood paneling on the interior walls, carpeted floors, an average of 25 student desks, one or two printers and computers (all assumed to be kept off during analysis and thus neglected as a source of ozone), wall decorations and posters, and other school and work supplies. The classrooms contained windows but all are assumed to have been closed. The rooms were also assumed to be kept at a consistent temperature range from 20 to 22 °Celsius. The volumes and parameters for each room are listed in Table 3-1.

Table 3-1. Classroom Characteristics

School	Classroom	Volume (m^3)	Avg λ (hr^-1)	Avg Lim. Conc. (ppb)	Max Lim. Conc. (ppb)	Avg Ozone Conc. (ppb)	Max Ozone Conc. (ppb)
CR	P5A	156	0.9	0.96	1.49	7.89	33.2
CR	P8B	163	0.3	10.91	24.61	5.74	21.3
MN	P2A	156	0.28	0.32	0.8	7.98	25.7
MN	P6B	156	1.65	3.68	6.31	5.8	19.6
SP	P2A	163	0.39	3.47	6.81	14.35	35.7
WW	901	163	0.63	5.59	5.79	6.24	14
WW	915	183	0.63	7.9	13.59	4.99	16.5

3.2 Classroom Air Exchange Rate (λ)

The air exchange rates for each classroom are provided in table 3-1. The values ranged between 0.3 hr^{-1} and 1.65 hr^{-1}.

3.3 Surface Reaction Rate Constant for Ozone (k_{dep})

The ozone decay rates for surface reactions (k_{dep} in equations 2-5 and 2-6) were adopted from a larger study conducted by the University of Texas at Austin. In the equations, k_{dep_total} refers to the deposition velocity of ozone while students occupied the classroom, and the $k_{dep\_background}$ refers to the deposition velocity of ozone in unoccupied classrooms. The resulting difference between these two values yields a deposition velocity associated with students occupying the classrooms. The k_{dep_total} values ranged from 9.6 hr^{-1} to 24.4 hr^{-1}, with an average of 13.7 hr^{-1}. The $k_{dep\_background}$ values ranged from 2.6 hr^{-1} to 7.2 hr^{-1}, with an average of 3.9 hr^{-1}.

3.3 Molar to Mass Yield Conversion (α)

For secondary organic aerosols, a unit converter was required to change the concentration of limonene from units of ppb to $\mu g/m^3$. The value for α was determined to be 5.75 ($\mu g/m^3$)/ppb based on the ideal gas law and molecular weight of limonene.

3.4 Bi-Molecular Reaction Rate Constant (k_b)

The bi-molecular reaction rate constants adopted in this study have units of ($ppb^{-1}hr^{-1}$) at a temperature of 20 °C. The value of k_b for limonene reactions with ozone was taken to be $k_b = 1.84x10^{-2}$ (Nazaroff and Weschler, 2004).

3.5 Molar Yields

The molar yields for formaldehyde (y_j in equation 2-3) tend to vary with the specific chemical that reacts with ozone. For this report, limonene was used as the chemical reactant. The molar yield associated with the ozone and limonene reaction is 0.1 moles/mole reaction for formaldehyde (Grosjean et al.,1993). The molar yields for 6-methyl-5-hepten-2-one (6-MHO) and 4-oxopentanal (4-OPA) were determined based on data reported by C.J. Weschler in 2016. The molar yields for 6-MHO and 4-OPA were 0.145 moles of product/mole ozone consumed and 0.122 moles of product/mole ozone consumed, respectively.

3.6 Mass Yields

The respective mass yield of secondary organic aerosols (SOA) associated with the ozone and limonene reaction was assumed to be 0.39 based on an average of three experiments conducted (Hoffmann et al., 1997).

3.7 Limonene Concentrations

Average and maximum limonene concentrations were used for each classroom. Averages ranged from 0.32 to 10.9 ppb. Maximum concentrations ranged from 0.80 to 24.6 ppb. Average and maximum values for each classroom are listed in table 3-1.

4. Results and Discussion

This section provides the results of field data analysis and model applications.

4.1 Indoor/Outdoor Ozone Concentration Ratios

The concentration gradient found in portable classrooms in Central Texas were determined. Specifically, one-day average indoor and outdoor ozone concentrations were used to calculate an indoor/outdoor ozone concentration ratio (I/O). The concentrations were recorded simultaneously on the date noted in Table 4-1. None of the ratios exceeded 0.45, which is typical for closed spaces and normal air exchange rates (Weschler et, al. 2000).

Table 4-1. Ozone Concentration Ratio Data

Classroom	Sample Date	λ (hr^-1)	Indoor (ppb)	Outdoor (ppb)	I/O Ratio
WW 915	10/6/15	0.60	7.9	47.9	**0.16**
WW 901	2/21/17	0.65	4.5	25.7	**0.17**
MN P2A	10/20/15	0.28	15.6	46.9	**0.33**
MN P6B	10/20/15	1.65	10.9	46.9	**0.23**
CR P5A	11/3/15	0.90	8.3	42.2	**0.20**
CR P8B	11/3/15	0.30	3.5	42.2	**0.08**
SP P2A	10/27/15	0.39	16.4	37.1	**0.44**
				Average	**0.23**

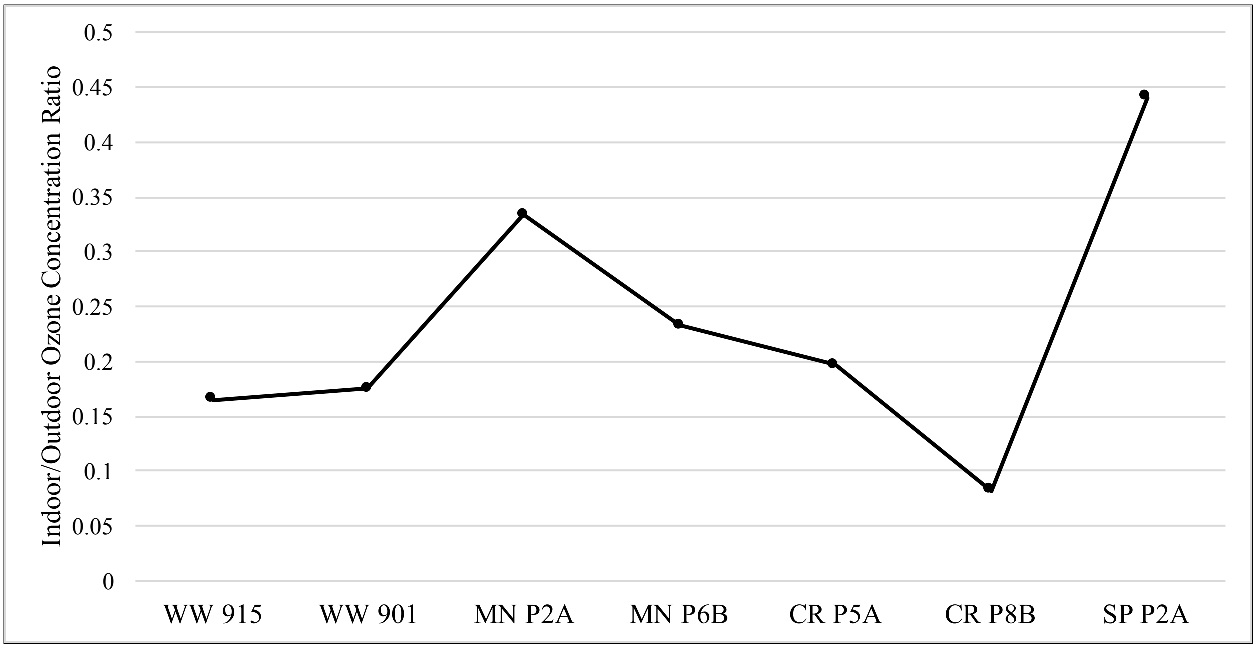

Figure 4-1. Indoor/Outdoor Ozone Concentration Gradients Plot

Typical I/O concentration ratios for schools have been reported to be 0.3 to 0.7 (Weschler *et al*., 2000). In comparison, the Indoor/Outdoor ozone concentration ratios observed in this study were relatively low, with an average of 0.23. This difference could be due to a number of factors, including air exchange rates being (λ) lower for portable classrooms in this study or higher reactivity of ozone with surfaces in the classrooms.

4.2 Base-Case and Worst-Case By-Product Concentrations

The maximum and minimum by-product concentrations determined from the base-case model are displayed in Table 4-2.

Table 4-2. Maximum and Minimum by-product concentrations (base-case)

	Formaldehyde (ppb)	SOA ($\mu g/m^3$)	6-MHO (ppb)	4-OPA (ppb)
Maximum	0.40	8.91	95.5	80.7
Minimum	0.015	0.34	3.93	3.3
Average	0.13	2.9	27.3	23.0

The maximum and minimum by-product concentrations determined from the worst-case model are displayed in Table 4-3.

Table 4-3. Maximum and Minimum by-product concentrations (worst case)

	Formaldehyde (ppb)	SOA ($\mu g/m^3$)	6-MHO (ppb)	4-OPA (ppb)
Maximum	3.3	74.6	307.6	259.8
Minimum	0.10	2.2	2.2	11.2
Average	0.82	18.3	84.2	71.1

The maximum concentration of the worst-case was divided by the maximum concentration of the base-case to produce the ratios listed in Table 4-4. The largest difference between the two cases can be seen in the formaldehyde (HCHO) and SOA concentrations, with each of their respective worst-case conditions yielding concentrations of 8.3 and 8.4 times the concentrations found in the base-case model. The ratios for 6-MHO and 4-OPA were found to be less, both showing worst case concentrations 3.2 times those of their base-case concentrations.

Table 4-4. Ratios of base-case and worst-case maximum concentrations

	Formaldehyde (ppb/ppb)	SOA ($\mu g/m^3/\mu g/m^3$)	6-MHO (ppb/ppb)	4-OPA (ppb/ppb)
Ratio (worst-case/ base-case)	8.3	8.4	3.2	3.2

Table 4-5. Formaldehyde concentration results

Experiment	Base-Case (ppb)	Worst-Case (ppb)
WW 915(1)	0.14	0.79
WW 915(2)	0.10	0.57
WW 901(1)	0.11	0.25
WW 901(2)	0.10	0.22
MN P2A(1)	0.018	0.15
MN P2A(2)	0.016	0.13
MN P6B(1)	0.024	0.14
MN P6B(2)	0.023	0.14
CR P5A(1)	0.016	0.10
CR P5A(2)	0.015	0.10
CR P8B(1)	0.40	3.33
CR P8B(2)	0.38	3.22
SP P2A(1)	0.23	1.15
SP P2A(2)	0.24	1.18

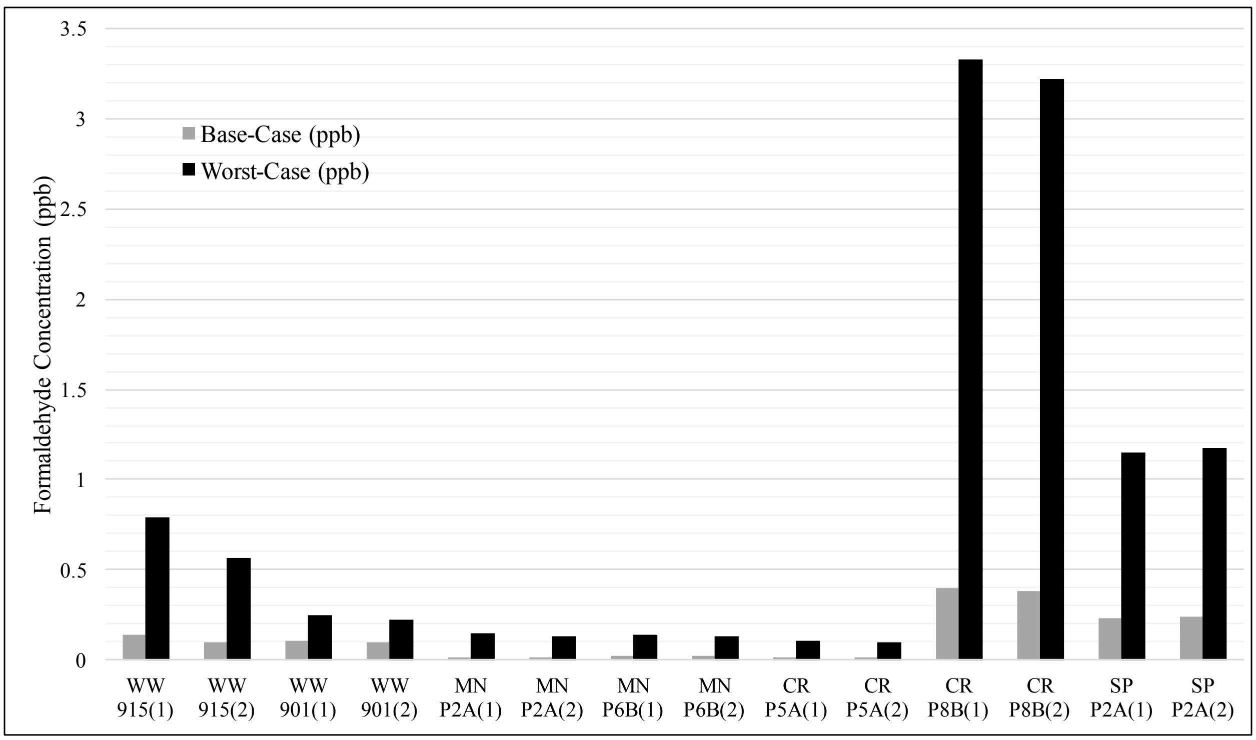

Figure 4-2. Formaldehyde by-product concentrations for base-case and worst-case scenarios.

Typical indoor concentrations of formaldehyde average around 30 ppb (Weschler *et al*, 2000). The values for the base-case analysis of formaldehyde were significantly lower than this, with average and maximum values of 0.129 and 0.397 ppb, respectively. The worst-case values were also lower, with an average of 0.818 ppb and maximum of 3.32 ppb. Relative to the rest of the results, this worst-case maximum value in classroom P8B was significantly different from the rest of the concentrations yielded by the model. This is most likely due to the unusually high peak levels of limonene (24.6 ppb), as well as the low air exchange rates of 0.29 and 0.3 hr^{-1}.

Table 4-6. Secondary Organic Aerosols concentration results

Experiment	Base-Case (µg/m3)	Worst-Case (µg/m3)
WW 915(1)	3.1	18
WW 915(2)	2.2	13
WW 901(1)	2.4	5.7
WW 901(2)	2.1	5.0
MN P2A(1)	0.41	3.3
MN P2A(2)	0.36	2.9
MN P6B(1)	0.55	3.2
MN P6B(2)	0.52	3.0
CR P5A(1)	0.36	2.3
CR P5A(2)	0.34	2.2
CR P8B(1)	8.9	75
CR P8B(2)	8.6	72
SP P2A(1)	5.3	26
SP P2A(2)	5.4	26

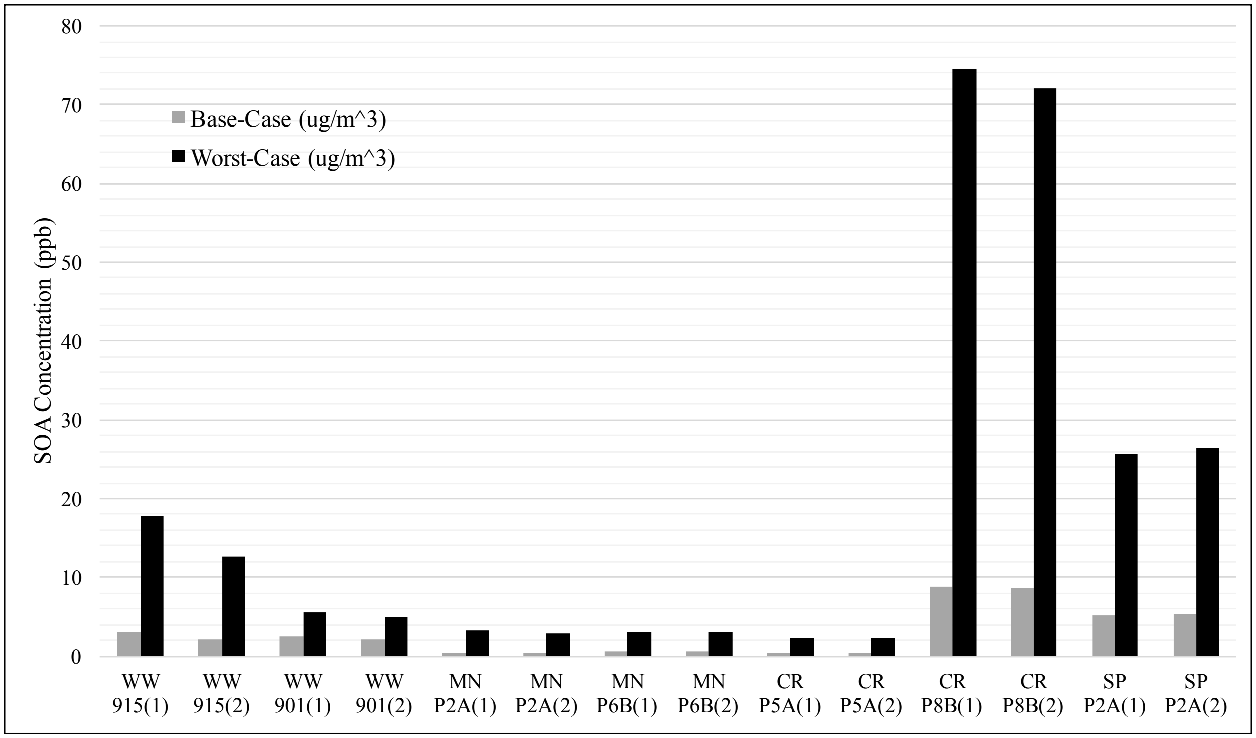

Figure 4-3. Secondary Organic Aerosol (SOA) by-product concentrations based on base-case and worst-case scenarios.

Weschler (2016) reported that typical indoor concentrations of secondary organic aerosols range from 0.1 to 4.2 µg/m^3. The concentrations determined in this study appear to be consistent with this range, save for a few outliers. The base-case average concentration was 2.9 µg/m^3 while the average value for the worst-case concentration was 18.3 µg/m^3. The classrooms P8B and P2A yield significantly higher predicted by-product concentrations than the rest of the rooms. For P8B this could be due to the unusually high levels of limonene recorded in the data samples, as well as its low air exchange rate of 0.3 hr^{-1}. Classroom P2A had the highest indoor/outdoor concentration ratio of 0.44, leading it to have a much higher concentration of ozone to react homogeneously with the indoor environment.

Table 4-7. 6-MHO concentration results

Experiment	Base-Case (ppb)	Worst-Case (ppb)
WW 915(1)	7.8	25.7
WW 915(2)	5.6	18.4
WW 901(1)	17.5	39.2
WW 901(2)	15.0	33.6
MN P2A(1)	95.5	307.6
MN P2A(2)	87.3	281.0
MN P6B(1)	3.9	13.3
MN P6B(2)	4.3	14.5
CR P5A(1)	8.9	37.6
CR P5A(2)	8.7	36.5
CR P8B(1)	22.7	84.2
CR P8B(2)	22.1	81.9
SP P2A(1)	28.9	71.8
SP P2A(2)	53.6	133.3

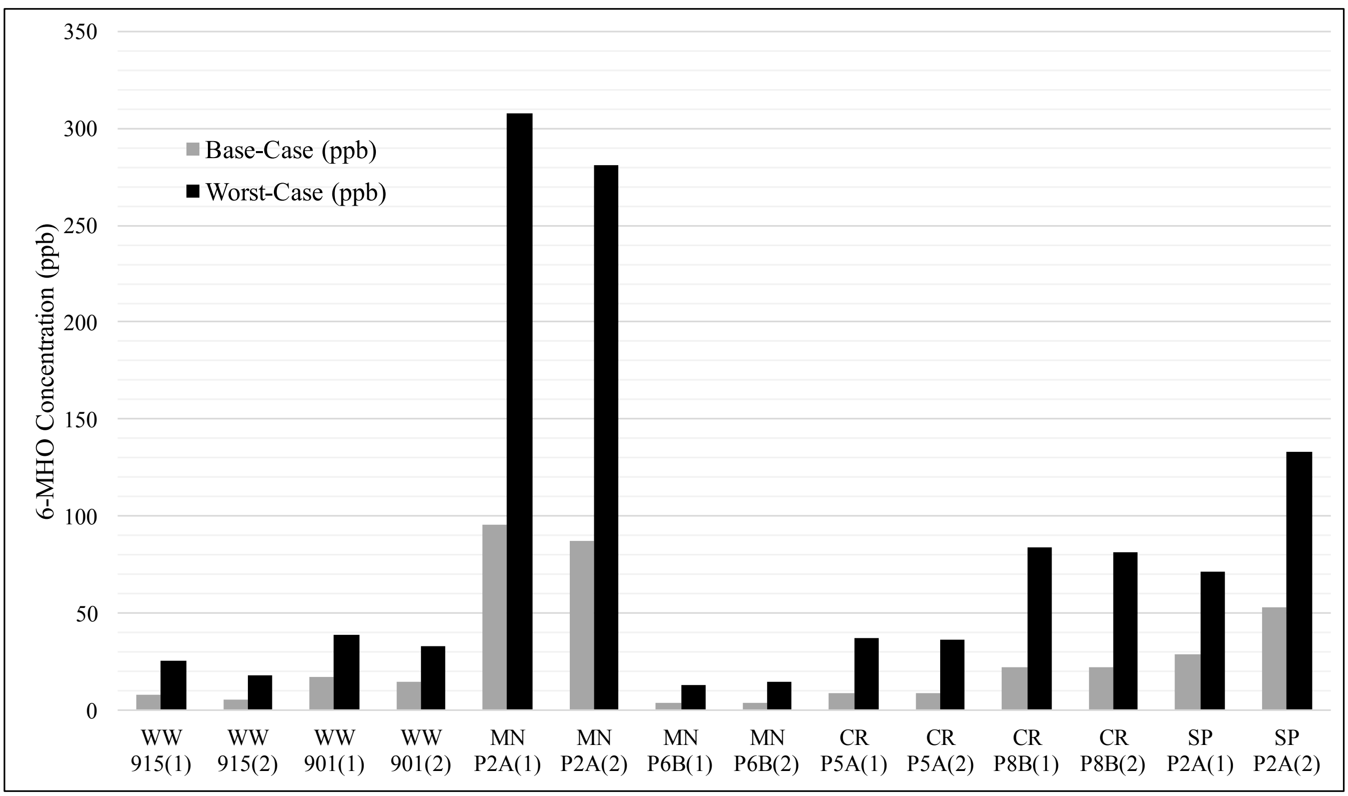

Figure 4-4. 6-methyl-5-hept-2-one (6-MHO) by-product concentration results from base-case and worst-case models.

Weschler (2016) reported steady-state concentrations values of 6-MHO of 2.3 ppb with occupants in an aircraft cabin. The theoretical values determined from the model in this study were far greater than this value, averaging 27.2 ppb and 84.1 ppb for the best- and worst-case analyses, respectively. In one classroom, P2A, estimated 6-MHO concentrations were much higher than the average, with base-case and worst-case maximum values of 96 ppb and 308 ppb, respectively. This classroom had a relatively high indoor/outdoor ozone concentration ratio compared to other rooms, and the lowest air exchange rate with values of 0.26 and 0.29 hr^{-1}.

Table 4-8. 4-OPA concentration data

Experiment	Base-Case (ppb)	Worst-Case (ppb)
WW 915(1)	6.6	21.7
WW 915(2)	4.7	15.5
WW 901(1)	14.8	33.1
WW 901(2)	12.6	28.3
MN P2A(1)	80.7	259.8
MN P2A(2)	73.7	237.3
MN P6B(1)	3.3	11.2
MN P6B(2)	3.6	12.2
CR P5A(1)	7.6	31.8
CR P5A(2)	7.3	30.9
CR P8B(1)	19.1	71.1
CR P8B(2)	18.6	69.1
SP P2A(1)	24.4	60.7
SP P2A(2)	45.3	112.6

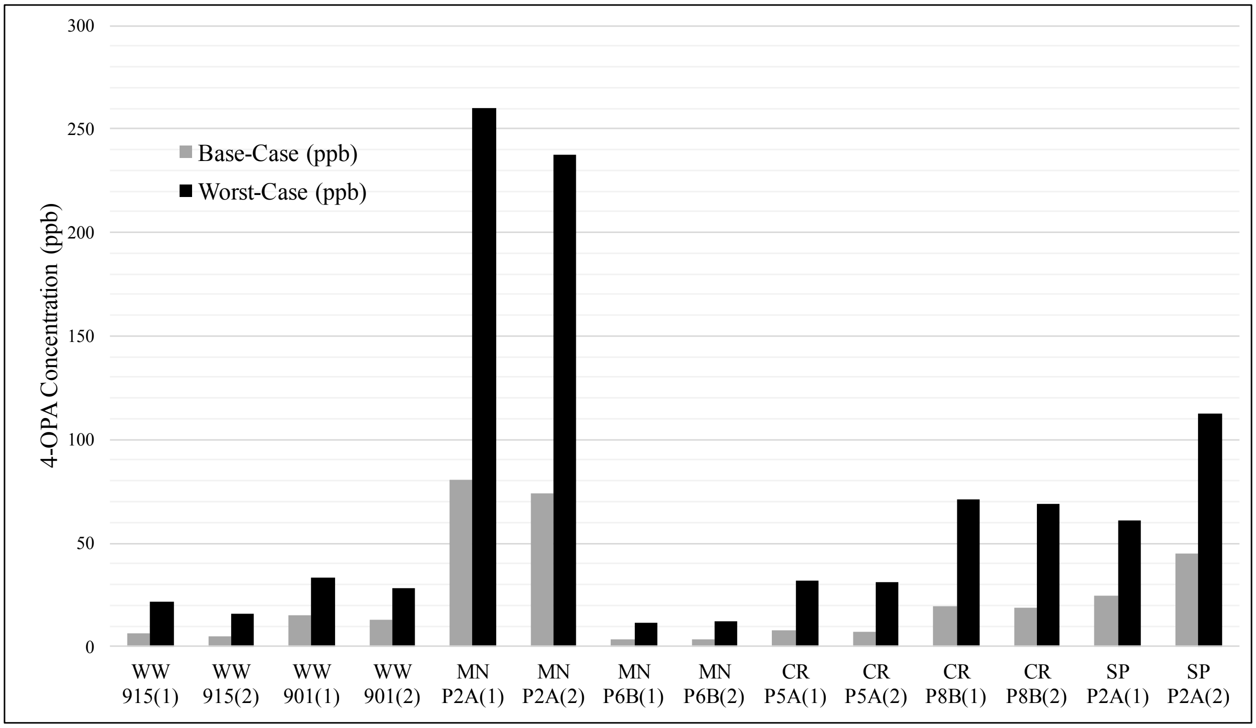

Figure 4-5. 4-Oxopentanal (4-OPA) by-product concentration results from base-case model.

Weschler (2016) reported steady-state concentrations of 4-OPA around 2.0 ppb with occupants in an aircraft cabin. The theoretical values determined from the model in this study were far greater than this value, averaging 23.0 ppb and 71.1 ppb for the best- and worst-case analyses, respectively. Again, in the P2A classroom there is a significant difference in the concentrations predicted here as opposed to other rooms. This could also be due to the high indoor/outdoor concentration ratio of the classroom, as well as its low air exchange rates.

While some of the by-product values were relatively small compared to standard concentrations, there were plenty of alarmingly high results found in this study. The potential for these high levels of secondary organic aerosols, 6-methyl-5-hepten-2-one, and 4-oxopentanal should raise concern for highly populated indoor environments such as classrooms. Efforts to prevent and reduce these levels are explored below.

4.3 Quenching Indoor Chemistry

Methods to reduce indoor ozone and by-product concentrations have been researched. One cause of these large by-product concentrations are artificial scenting agents used in body sprays, candles, and aerosol sprays. Concentrations of up to several hundreds of ppb of limonene or linalool (another highly reactive molecule with ozone) have recorded immediately after use of fragrance products (Singer et al., 2006; Wainnman et al., 2000). Thus limiting, or even prohibiting, the use of these agents in schools would reduce the levels of by-products found in classroom environments. Another solution that has become increasingly popular is the use of activated carbon filters (Aldred et al., 2016). These filters contain heated or treated charcoal that increase its adsorption capacity. Millions of pores within the charcoal are able to catch gases that would otherwise slip through normal sized filters (Aldred et al., 2016). Studies have shown that these filters can remove volatile organic compounds, such as the by-products discussed in this report (Sidheswaran et al., 2011). Other studies have shown that clay is a viable substance for reducing indoor air pollution (Darling et al., May 2016; Darling et al., October 2016). Clay has the ability to catalyze ozone, which allows it to reduce indoor ozone concentrations, and effectively reduce potential by-products made from its chemistry. The implementation of clay-based materials has shown to reduce indoor concentrations of ozone and improve the overall air quality of the environment (Darling et al., May 2016). Another study analyzes the effects on indoor air chemistry of clay-based paints and plaster over a period of six months (Darling et. al., October 2016). The results further suggest that clay-based materials have the capability to improve indoor air quality and passively reduce ozone and formaldehyde concentrations.

4.4 Conclusion

In summary, a model was developed to predict concentrations of homogeneous and heterogeneous ozone initiated reaction by-products in portable classrooms. The resulting estimates offer reference values for highly occupied indoor environments. Indoor concentrations of formaldehyde (HCHO), 4-oxopentanal (4-OPA), 6-methyl-5-hepten-2-one (6-MHO), and secondary organic aerosols (SOA) were predicted based on various parameters of specific portable classrooms in central Texas. The results were not significant to raise concern for formaldehyde, but they did yield relatively high average and maximum concentrations of 4-OPA, 6-MHO, and SOA. While the health implications of SOA are more well known, less has been done to determine the toxicological effects of 4-OPA and 6-MHO. The results of this report indicate that more research should be conducted to better understand the effects of these compounds on the indoor environment, as well as human health.

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