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**The Thesis Committee for Jennifer Wang  
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**Assessing Sheep's Wool as a Filtration Material for the Removal of  
Formaldehyde in the Indoor Environment**

**APPROVED BY  
SUPERVISING COMMITTEE:**

**Supervisor:**

---

Richard L. Corsi

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Atila Novoselac

**Assessing Sheep's Wool as a Filtration Material for the Removal of  
Formaldehyde in the Indoor Environment**

**by**

**Jennifer Wang, B.S.**

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## **Dedication**

To my family and friends –  
thank you for all your unconditional love and support.

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## **Abstract**

### **Assessing Sheep's Wool as a Filtration Material for the Removal of Formaldehyde in the Indoor Environment**

Jennifer Wang, M.S.E.

The University of Texas at Austin, 2014

Supervisor: Richard L. Corsi

Formaldehyde is one of the most prevalent and toxic chemicals found indoors, where we spend ~90% of our lives. Chronic exposure to formaldehyde indoors, therefore, is of particular concern, especially for sensitive populations like children and infants. Unfortunately, no effective filtration control strategy exists for its removal. While research has shown that proteins in sheep's wool bind permanently to formaldehyde, the extent of wool's formaldehyde removal efficiency and effective removal capacity when applied in active filtration settings is unknown.

In this research, wool capacity experiments were designed using a plug flow reactor and air cleaner unit to explore the capacity of wool to remove formaldehyde given different active filtration designs. Using the measured wool capacity, filter life and annual costs were modeled in a typical 50 m<sup>3</sup> room for a variety of theoretical filter operation lengths, air exchange rates, and source concentrations. For each case, annual filtration costs were compared to the monetary benefits derived from wool resale and from the

reduction in cancer rates for different population types using the DALYs human exposure metric.

Wool filtration was observed to drop formaldehyde concentrations between 60-80%, although the effective wool removal capacity was highly dependent on the fluid mechanics of the filtration unit. The air cleaner setup yielded approximately six times greater capacity than the small-scale PFR designed to mimic active filtration (670  $\mu\text{g}$  versus 110  $\mu\text{g}$  HCHO removed per g of wool, respectively). The outcomes of these experiments suggest that kinematic variations resulting from different wool packing densities, air flow rates, and degree of mixing in the units influence the filtration efficiency and effective capacity of wool.

The results of the cost-benefit analysis show that for the higher wool capacity conditions, cost-effectiveness is achieved by the majority of room cases when sensitive populations like children and infants are present. However, for the average population scenarios, filtration was rarely worthwhile, showing that adults benefit less from reductions in chronic formaldehyde exposure. These results suggest that implementation of active filtration would be the most beneficial and cost-effective in settings like schools, nurseries, and hospitals that have a high percentage of sensitive populations.

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# **1 INTRODUCTION**

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## **1.1 Problem Statement**

Formaldehyde (HCHO) is one of the most common and ubiquitous chemicals found in the indoor environment, where we spend 90% of our time (Klepeis et al., 2001). The predominant source of formaldehyde indoors is from the off-gassing of engineered wood composites (U.S. EPA 1999; U.S. EPA 2007), which are popular low-cost alternatives to solid wood as building materials (Maloney, 1996). In the indoor environment, formaldehyde is also commonly found in carpet adhesives, insulation, furniture, cleaning products, textiles, and tobacco smoke (IARC, 2006). After Hurricanes Katrina and Rita in 2005, approximately 100,000 mobile trailers distributed by FEMA to displaced residents as temporary housing shelters caused adverse health consequences attributed to elevated formaldehyde concentrations due to the trailers' poor ventilation and overall construction from composite woods (CDC, 2008). Indoor concentrations of formaldehyde are typically an order of magnitude higher than outdoors (IARC, 2006) and also than the concentrations of other gaseous chemicals found indoors (Logue et al., 2012). The combination of strong indoor sources, development of increasingly tighter buildings with low air exchange rates (Weschler 2009), and the fact that we spend approximately 90% of our time indoors makes exposure to formaldehyde in the indoor environment a serious chronic health concern. Labeled by the U.S. EPA as a Group B1 probable human carcinogen (U.S. EPA IRIS, 1999) and the World Health Organization

as carcinogenic to humans (IARC, 2006), formaldehyde is also one of the most toxic chemicals found indoors.

Yet to date, there exist no widely-accepted, effective technologies or mechanisms for the control of formaldehyde, and conventional filtration methods are ineffective at its removal. Given formaldehyde's high vapor pressure (Howard, 1989), it is not very sorptive to surfaces and thus easily passes through the pores of activated carbon, which is considered the best method to remove VOCs and ozone indoors (Marsh, 2006).

However, formaldehyde is known to be highly reactive with amino acids (Puchtler et al., 1985; French et al., 1945), which are abundant in sheep's wool (Reddie et al., 1971). A few studies have investigated the use of wool in the context of indoor air quality (Zwiener et al., 1999; Wortmann et al. 2005, Curling et al., 2012; Huang et al., 2007), but no studies have tested wool in active filtration systems. If found to be efficient and cost-effective, wool filters could potentially be built into existing active filtration systems like personal air cleaners or HVAC and HEPA filtration units. This research explores the implementation of sheep's wool in active filtration designs to observe the wool's efficiency at removing formaldehyde, the extent to which indoor concentrations and cancer risk can be reduced, and the mass capacity and lifetime of a certain quantity of wool.

## **1.2 Research Objectives**

The principal goals of this research were to explore the potential of amino acids in wool to bond with and permanently sequester formaldehyde, given the fluid mechanics associated with active filtration systems, and to determine whether wool filtration could be cost-effective. The research was defined by the following objectives:

- 1) Design and develop a small-scale plug flow reactor to mimic active filtration and determine the capacity and efficacy of wool for removing formaldehyde
- 2) Assess the fraction of formaldehyde removed by wool that was chemically sorbed versus physically sorbed by running heated and non-heated desorption tests
- 3) Observe the capacity and efficacy of wool for removing formaldehyde via wool packed in a personal air cleaner in a room-scale environment
- 4) Perform a cost-benefit analysis of wool filtration for different age groups of occupants and different room environmental parameters

## **1.3 Scope**

Research objectives were completed under the following constraints:

- 1) The PFR capacity experiments were limited to one test for the 5 g PFR packed with wool and one test for the 10 g PFR packed with wool.
- 2) The PFR heated desorption experiments were limited to one test for the 5 g PFR packed with wool and one test for 10 g PFR packed with wool.
- 3) The PFR non-heated desorption experiments were limited to one test for the 5 g PFR packed with wool and one test for the 10 g PFR packed with wool.



- 4) The air cleaner capacity experiments were limited to two experiments with 550 g of packed wool.
- 5) No heated desorption experiments were run for the wool in the air cleaner.
- 6) One non-heated capacity experiment was run for the wool in the air cleaner.
- 7) Development of a filtration model to determine the filter life of 5.5 kg of wool was limited to a selection of room parameters and filter operation hours, as described in Section 5. The model was based off the air cleaner fluid mechanics, where breakthrough occurred at 90% of the 670  $\mu\text{g}$  HCHO / g wool capacity.
- 8) A cost-benefit analysis was conducted for wool filtration comparing total benefit from wool resale and reductions in cancer rates for 3 population types, with total wool filter and energy costs based on the filtration model iterations.

## **1.4 Overview of Thesis**

A literature review assessing the current knowledge regarding formaldehyde sources, properties, health effects, concentrations, and potential control strategies in the indoor environment as well as the characteristics of sheep's wool that make it reactive with formaldehyde is presented in Chapter 2. The capacity and desorption experimental design methods are described in Chapter 3, and results and discussion are presented in Chapter 4. Chapter 5 explains the filtration model and cost-benefit model criteria, including building parameter choices and human exposure metrics. Chapter 6 presents the model results and discussion, and Chapter 7 summarizes the overall results, relevance, and impact of this research, as well as potential routes for future investigation.

## 2 LITERATURE REVIEW

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### 2.1 Formaldehyde

#### 2.1.1 PROPERTIES

Formaldehyde (molecular formula: HCHO, systematic nomenclature: Methanal) is a clear, colorless gas at room temperature that is highly reactive (IARC 2006, WHO 1999, U.S. EPA 2007). As such, it is an important precursor to the formation of other chemicals and prone to spontaneous polymerization with other substances as well as with itself, with the ability to form polymer chains of up to 100 formaldehyde molecules (Walker, 1964). As a reactive volatile organic compound, formaldehyde has a short lifetime in the atmosphere of approximately 1 day (Seco et al., 2007) and only 4 hours with the interaction of photolysis processes (Atkinson et al., 2003). Formaldehyde has a dipole moment of 2.33 D (see Figure 1), which makes it a highly polar electrophile that is soluble in water, ethanol and chloroform, and miscible in acetone, ether and benzene (Lide, 2003). In liquid solution, it is typically distributed as formalin, which is comprised of 30-50% formaldehyde mixed with approximately 10% methanol to prevent polymerization (ATSDR 1999).

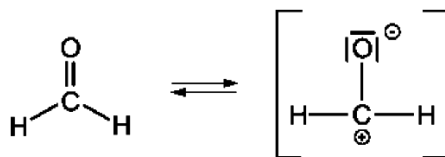


Figure 1: Resonance structure and polarity of formaldehyde (Salthammer et al., 2010)

Formaldehyde is distinguishable by its pungent, irritating odor (Reuss et al., 2003) and has a relatively low observed odor threshold of between 0.03 – 0.22 mg/m<sup>3</sup> (WHO,

2002) and a calculated theoretical standardized human olfactory threshold of 0.87 ppm or 1.07 mg/m<sup>3</sup> (Devos et al., 1992). It is also considered corrosive and flammable (ATSDR, 1999). Table 1 shows a summary of formaldehyde's physical and chemical properties.

Table 1: Physical and chemical properties of formaldehyde

Property		Reference
CAS	50-00-0	
Molecular Weight	30.03 g/mol	Lide 2003
Color	Colorless	Reuss et al., 2003
Physical State	Gas	Reuss et al., 2003
Odor	Pungent, suffocating and irritating odor	Reuss et al., 2003
Solubility	water, ethanol, chloroform, acetone, benzene, ether	Lide 2003
Density	0.815 at -20°C	Lide 2003
Melting Point	-92°C	Lide 2003
Boiling Point	-19.1°C	Lide 2003
Vapor Pressure	3,883 mm Hg at 25°C	Howard 1989
Henry's Law Constant	2.5 x 10 <sup>3</sup> M atm <sup>-1</sup> at 25°C	Seinfeld 2006
	3.27 x 10 <sup>-7</sup> atm-m <sup>3</sup> /mol at 25°C	Howard 1989
log(K <sub>ow</sub> )	0.35	Hansch et al. 1995
Absorption Spectrum	280-360 nm	Torres 2010
Conversion Factor	1 µg/m <sup>3</sup> = 0.816 ppb (at 295 K, 1 atm)	

Most relevant for the purposes of this study, formaldehyde is also well-known for its ability to bind with amino acids and proteins to form permanent cross-linking methylene bridges (Puchtler et al., 1985; French et al., 1945), which will be discussed further in Section 2.2.

### 2.1.2 MAJOR SOURCES AND APPLICATIONS

Formaldehyde is typically used as a preservative, disinfectant, and thermosetting agent or curing resin additive for adhesives. These formaldehyde-containing adhesives include urea, phenol, melamine and polyacetal resins, which are found in engineered wood-based products such as particleboard, plywood, high-density fiberboard (HDF) and medium-density fiberboard (MDF), as well as in insulation materials such as urea-formaldehyde foam, mineral wool and glass wool (Godish 2001). Other common applications include use in surface lacquers and coatings, paints, laminates, cleaning products, cosmetics, fertilizers, insecticides, embalming fluid, paper and textile treatment as anti-wrinkling agents, and curable molding compounds for electrical appliances and wiring (IARC 2006, Godish 2001, Salthammer et al. 2010).

Formaldehyde is also a significant industrial chemical intermediate used to synthesize other compounds like 1,4-butanediol, trimethylolpropane, pentaerythritol and hexamethylenetetramine, which are used in the manufacturing of polyurethane, plasticizers, oil lubricants, synthetic resin coatings, and explosives (IARC 2006, WHO 2002, Reuss et al. 2003). Formaldehyde can also be synthesized from the ozonolysis of unsaturated hydrocarbons and has been observed as a significant reaction byproduct of ozone chemistry with aircraft cabin materials, including deposited human skin oils comprised of squalene (Weschler et al., 2007; Wisthaler et al., 2005; Coleman et al., 2008; Petrick and Dubowski, 2009). It is also a byproduct of environmental tobacco smoke (Jenkins et al., 2000; Nazaroff and Singer, 2004), wood and biomass combustion

(Ezzati and Kammen, 2001), and residential cooking (Fortmann et al., 2001). Metabolic processes also generate formaldehyde, which has been measured in exhaled human breath at concentrations typically below 10 ppb (Moser et al., 2005).

In the ambient environment, formaldehyde exists naturally and is also produced anthropogenically, but typically at relatively low concentrations of  $\sim 3 \mu\text{g}/\text{m}^3$  (U.S. EPA, 2008) compared to indoor concentrations, which are  $\sim 10$  times higher (Health Canada and Environment Canada, 2001). Outdoor anthropogenic emissions mostly stem from formaldehyde manufacturing facilities and industries that use formaldehyde (e.g. adhesives, resin manufacturing), combustion processes: automobile exhaust, power plants, petroleum refineries, wood burning, and tobacco smoke, and photochemistry (ILSI, 2003; Possanzini et al., 2002; IARC, 2006; Salthammer et al., 2010). Seco et al., 2007 reported global observations of plant concentrations from 0.1-29 ppbv of formaldehyde, depending on the locale, atmospheric conditions and plant type. Although formaldehyde concentrations are generally low outdoors, as a significant combustion byproduct of vehicle exhaust (Wallington et al., 2006) and both a product and reactant in ozone photolytic chemistry (Stephens et al., 1961), formaldehyde can be generated in relatively high concentrations of 10-30 ppb in urban areas, especially during ozone-action days during summer months (Salas et al., 1986; Duan et al., 2008).

Of the various sources of formaldehyde, the indoor emissions from wood composites are by far the most substantial contributor. The following subsection discusses in further detail the chemistry, production, and emission parameters of wood composites, which are most relevant for indoor chronic exposures.

### 2.1.2.1 Engineered Wood Products

Formaldehyde is one of the most common, abundant, and well-documented chemicals in indoor environments due to its high prevalence in building materials and use as an adhesive resin in common engineered wood products (EWPs) like particleboard, plywood, and medium-density fiberboard. Since the 1950s, these wood composites have become popular, cheap substitutes for solid wood and are widely used as building materials (Maloney, 1996). These composites are mostly composed of wood scraps glued together with liquid resins, which often contain urea-formaldehyde.

While urea-formaldehyde is ideal for use as a wood adhesive because it is the most water soluble and fastest curing of the liquid resins, it is also the most highly emissive and reactive (Dunky, 1998). When water is present, dual hydrolysis reactions of the C-N bonds in urea-formaldehyde occur (see Figure 2), releasing two molecules of formaldehyde for each molecule of urea-formaldehyde (Roffael et al, 1993). Thus, formaldehyde emissions from wood composites are highly sensitive to relative humidity.

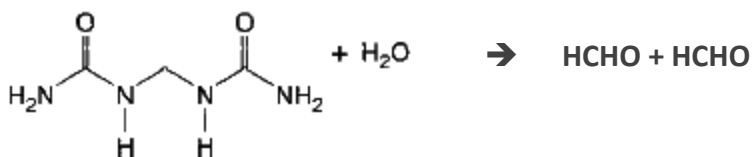


Figure 2: Hydrolysis reaction with urea-formaldehyde (modified from Salthammer et al., 2010)

In 2006, the global production of formaldehyde amounted to approximately 21 million tonnes (WHO, 2006), of which 4.65 million tonnes consisted of production in the

United States (IARC, 2006), with formaldehyde resin synthesis comprising over 65% of total resin synthesis (Tang et al, 2008). In the 1990s, formaldehyde ranked 24<sup>th</sup> in chemical production volume in the United States, and resin manufacturing comprised ~60% of total formaldehyde consumption (Foster, 1992). Table 2 shows the growth in formaldehyde production across several countries in the last few decades, up until 2000, based on the most current data available (Bizzari, 2000 as cited in IARC, 2006).

Table 2: Major formaldehyde production volumes in thousand tonnes (reproduced from IARC, 2006)

Country or region	1983	1985	1990	1995	2000
North America					
Canada	256	288	288	521	675
Mexico	79	106	118	139	136
USA	2520 <sup>a</sup>	2663	3402	3946	4650
Western Europe <sup>b</sup>	3757	3991	4899	5596	6846 <sup>c</sup>
Japan	1089	1202	1444	1351	1396

*From Bizzari (2000)*

<sup>a</sup> Data for 1980

<sup>b</sup> Includes Austria, Belgium, Denmark, Finland, France, Germany, Greece, Ireland, Italy, the Netherlands, Norway Portugal, Spain, Sweden, Switzerland and the United Kingdom

<sup>c</sup> Data for 1999

The demand for engineered wood products has rapidly increased over the last 50 years, with current consumption exceeding total production volumes, as shown in Tables 3 and 4. Total particleboard and medium-density fiberboard production in 2011 was ~3.75 billion ft<sup>2</sup>, and demand was ~4.68 billion ft<sup>2</sup>; compared to 10.6 billion ft<sup>2</sup> production and 12.7 billion ft<sup>2</sup> consumption for plywood (Howard et al., 2011).

Table 3: Particleboard and medium-density fiberboard production, imports, exports, and consumption, 1965-2011, 3/4-in. basis (Howard et al., 2011)

Year	Production				Exports Million square feet	Consumption	
	Total Million square feet	Particleboard Million square feet	Medium-density fiberboard Million square feet	Imports <sup>b</sup> Million square feet		Total Million square feet	Per capita Square feet
1965	828	753	75	4	<sup>c</sup>	832	4
1966	1,031	948	83	1	<sup>c</sup>	1,032	5
1967	1,167	1,074	93	1	2	1,166	6
1968	1,494	1,391	103	1	6	1,489	7
1969	1,796	1,682	114	12	14	1,794	9
1970	1,858	1,731	127	3	10	1,851	9
1971	2,500	2,359	141	8	20	2,488	12
1972	3,236	3,079	157	14	45	3,205	15
1973	3,634	3,460	174	17	77	3,574	17
1974	3,269	3,075	194	7	113	3,163	15
1975	2,718	2,503	215	16	84	2,650	12
1976	3,469	3,189	280	60	80	3,449	16
1977	4,010	3,569	441	158	63	4,105	19
1978	4,228	3,720	508	193	61	4,360	20
1979	3,883	3,376	507	221	84	4,020	18
1980	3,443	2,950	493	264	106	3,601	16
1981	3,385	2,869	516	254	117	3,522	15
1982	2,839	2,393	446	766	41	3,564	15
1983	3,613	3,009	604	994	47	4,560	19
1984	3,830	3,196	634	1,331	54	5,107	22
1985	4,016	3,331	685	1,335	59	5,292	22
1986	4,384	3,603	781	1,395	86	5,693	24
1987	4,605	3,706	899	1,550	113	6,042	25
1988	4,768	3,829	939	1,634	163	6,239	25
1989	4,828	3,858	970	425	333	4,920	20
1990	4,756	3,806	950	363	373	4,746	19
1991	4,730	3,772	958	293	369	4,654	18
1992	5,046	3,980	1,066	405	394	5,057	20
1993	5,402	4,241	1,161	572	318	5,656	22
1994	5,793	4,542	1,251	775	297	6,271	24
1995	5,307	4,200	1,107	840	319	5,828	22
1996	5,705	4,459	1,246	814	154	6,365	24
1997	5,916	4,531	1,385	963	188	6,691	25
1998	5,994	4,593	1,401	1,038	135	6,897	26
1999 <sup>f</sup>	6,229	4,816	1,413	1,221	135	7,315	27
2000	6,292	4,804	1,488	1,856	162	7,986	28
2001	5,480	4,096	1,384	1,936	192	7,224	25
2002	6,035	4,414	1,621	1,377	212	7,200	25
2003	5,592	3,984	1,608	1,574	194	6,972	24
2004	6,052	4,305	1,747	1,751	195	7,608	26
2005	5,951	4,111	1,840	1,571	199	7,322	25
2006	5,911	4,055	1,856	1,283	205	6,989	24
2007	5,432	3,543	1,889	1,241	328	6,345	21
2008	4,623	2,916	1,707	1,180	398	5,404	18
2009	3,865	2,194	1,671	1,144	338	4,671	15
2010	3,709	2,287	1,422	1,326	400	4,634	15
2011	3,750	2,290	1,460	1,333	407	4,676	15

<sup>a</sup>Composite Panel Association (15); U.S. International Trade Commission (84); U.S. Department of Agriculture, Foreign Agricultural Service (91). Data may not add to totals because of rounding.

<sup>b</sup>May contain significant volumes of waferboard and oriented strandboard products prior to 1989.

<sup>c</sup>Fewer than 500,000 ft<sup>2</sup>.



Table 4: Production, imports, exports, and consumption of structural panel products, 1980–2011  
(million square feet, 3/8-in. basis) (Howard et al., 2011)<sup>a</sup>

Year	Production			Imports			Exports			Consumption		
	Total	Softwood plywood	OSB	Total	Softwood plywood	OSB	Total	Softwood plywood	OSB	Total	Softwood plywood	OSB
1980	16,468	16,333	135	360	37	323	373	373	<sup>z</sup>	16,455	15,997	458
1981	17,023	16,752	271	349	30	319	686	686	<sup>z</sup>	16,686	16,096	590
1982	16,403	15,846	557	268	9	259	452	452	<sup>z</sup>	16,219	15,403	816
1983	20,821	19,480	1,341	423	18	405	574	574	<sup>z</sup>	20,670	18,924	1,746
1984	21,968	19,926	2,042	727	48	679	371	371	<sup>z</sup>	22,324	19,603	2,721
1985	22,838	20,169	2,669	848	54	794	321	321	<sup>z</sup>	23,366	19,903	3,463
1986	25,631	22,118	3,513	723	63	660	614	614	<sup>z</sup>	25,740	21,567	4,173
1987	26,975	22,899	4,076	889	129	760	796	796	<sup>z</sup>	27,068	22,232	4,836
1988	27,203	22,599	4,604	911	96	815	1,004	1,004	<sup>z</sup>	27,110	21,691	5,419
1989	26,490	21,385	5,105	1,160	49	1,111	1,442	1,442	<sup>z</sup>	26,207	19,991	6,216
1990	26,337	20,919	5,418	1,351	38	1,313	1,613	1,613	<sup>z</sup>	26,075	19,344	6,731
1991	24,265	18,652	5,613	1,016	28	988	1,379	1,322	57	23,901	17,358	6,544
1992	25,985	19,332	6,653	1,619	47	1,572	1,491	1,442	49	26,113	17,937	8,176
1993	26,317	19,315	7,002	2,203	41	2,163	1,470	1,409	60	27,051	17,946	9,105
1994	27,124	19,638	7,486	2,635	47	2,588	1,289	1,211	78	28,469	18,474	9,995
1995	27,270	19,367	7,903	3,274	60	3,214	1,348	1,267	82	29,196	18,160	11,036
1996	28,495	19,181	9,314	4,500	85	4,414	1,405	1,248	157	31,590	18,018	13,572
1997	28,497	17,963	10,534	5,376	104	5,272	1,715	1,548	167	32,158	16,519	15,639
1998	29,003	17,776	11,227	6,671	179	6,492	864	764	100	34,810	17,191	17,619
1999 <sup>f</sup>	29,428	17,816	11,612	7,659	309	7,350	960	781	179	36,127	17,344	18,783
2000	29,381	17,475	11,906	8,030	408	7,622	914	735	179	36,498	17,148	19,350
2001	27,653	15,121	12,532	8,755	665	8,090	681	514	167	35,727	15,272	20,455
2002	28,626	15,200	13,426	9,368	907	8,461	634	439	195	37,360	15,668	21,692
2003	28,321	14,706	13,615	10,386	1,306	9,080	567	410	157	38,140	15,602	22,538
2004	28,936	14,665	14,271	11,870	2,023	9,847	685	492	193	40,120	16,196	23,924
2005	29,315	14,330	14,985	12,965	2,421	10,544	580	411	169	41,700	16,340	25,360
2006	28,388	13,428	14,960	11,986	1,848	10,138	603	424	179	39,771	14,852	24,919
2007	27,006	12,243	14,763	7,916	1,087	6,829	817	553	264	34,105	12,777	21,328
2008	23,240	10,237	13,003	4,425	759	3,666	1,071	621	450	26,594	10,375	16,219
2009	18,206	8,608	9,598	3,372	616	2,756	653	473	180	20,915	8,741	12,174
2010	19,430	9,131	10,299	3,266	439	2,827	1,074	795	279	21,622	8,775	12,847
2011	19,019	8,980	10,039	3,406	478	2,928	1,079	740	339	21,346	8,718	12,628

<sup>a</sup>American Plywood Association (11,12,13); US International Trade Commission (83, 84); Data may not add to totals because of rounding.

<sup>b</sup>Based on Canadian export data. Industry sources estimate that about 95% of Canadian exports are to U.S. markets.

<sup>f</sup>Revised.

<sup>z</sup>Not available.

Urea-formaldehyde bonded emissions from EWPs can persist for months and even years (Brown et al., 1999; Zinn et al, 1990). However, emission rates do decrease over time based on various factors such as emission strength, product thickness, presence of various sources and chemicals, occupant behavior, and environmental parameters such as temperature, relative humidity and airflow rates (Godish, 1989).

The following chamber studies present evidence of formaldehyde emissions reduction over long-term periods. Brown et al. (1999) showed using chamber studies that formaldehyde emission factors for all wood-based panels dropped from 300-400  $\mu\text{g}/\text{m}^2\text{h}$  in the first few weeks of product manufacture to 80-240  $\mu\text{g}/\text{m}^2\text{h}$  after 6-10 months. Chamber studies conducted by Haneto et al (1986) showed that particleboard emissions were reduced by 50% across an 8-9 month timeframe; whereas Matthews et al (1983) showed that plywood emissions were reduced by 50% across an 11-month time frame, and medium-density fiberboard emissions were reduced by 50% across a 20-month time frame. Figure 3 illustrates particleboard emission degradations over the course of 5 years (Kazakevics et al, 1984).

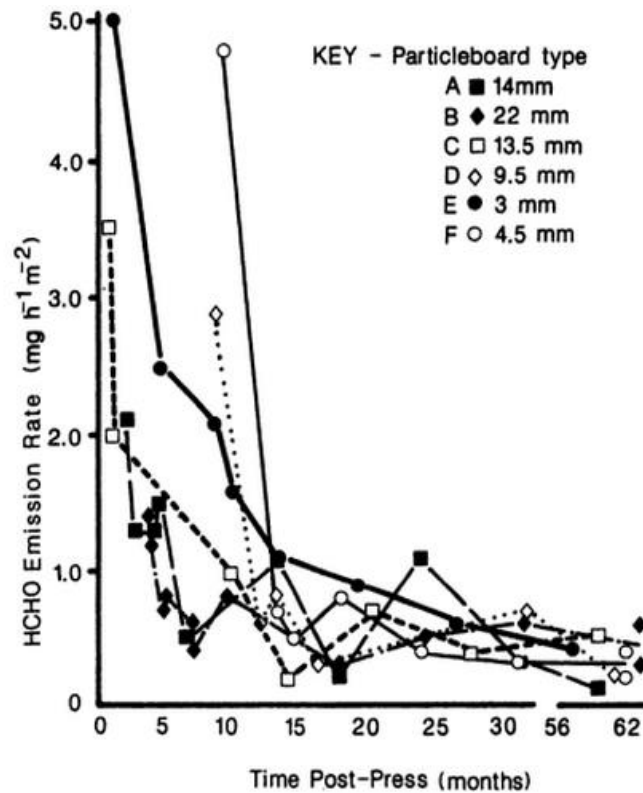


Figure 3: Time-dependent particleboard formaldehyde concentrations over 5 years (Kazakevics et al, 1984)

Numerous researchers have also documented the complex impact of environmental parameters like temperature, relative humidity and air velocity on the rate of VOC emissions (Wolkoff et al., 1998; Haghghat et al., 1998; Lin et al., 2009). Van Netten et al. (1989) showed specifically for formaldehyde that emission rates double with a 7 °C temperature increase, which corroborated the Andersen et al. (1975) chipboard emissions study, which also found a doubling of formaldehyde emission rate with every 7 °C increase from 14-35 °C. More recently, Zhang et al. (2007) showed that a temperature increase from 18 °C to 50 °C resulted in a 5 times greater diffusion coefficient but ¼ of the original partition coefficient for formaldehyde from wool-based panels, which was

then developed into an effective model of formaldehyde concentrations over time. Wiglusz et al. (2002) showed that formaldehyde emissions from laminate flooring heated to a consistent 50 °C resulted in initially elevated emissions an order of magnitude higher than at 23 °C and 29 °C, which then decayed over time to an order of magnitude lower levels as, presumably, the available formaldehyde mass decreased. This study's continual heating concept was used as a basis for the heated desorption experiments described in Section 3.2.1. Myers (1985) also reported that emission rates are exponentially affected by temperature (see Figure 4), but linearly by relative humidity and formaldehyde concentration (Myers, 1985).

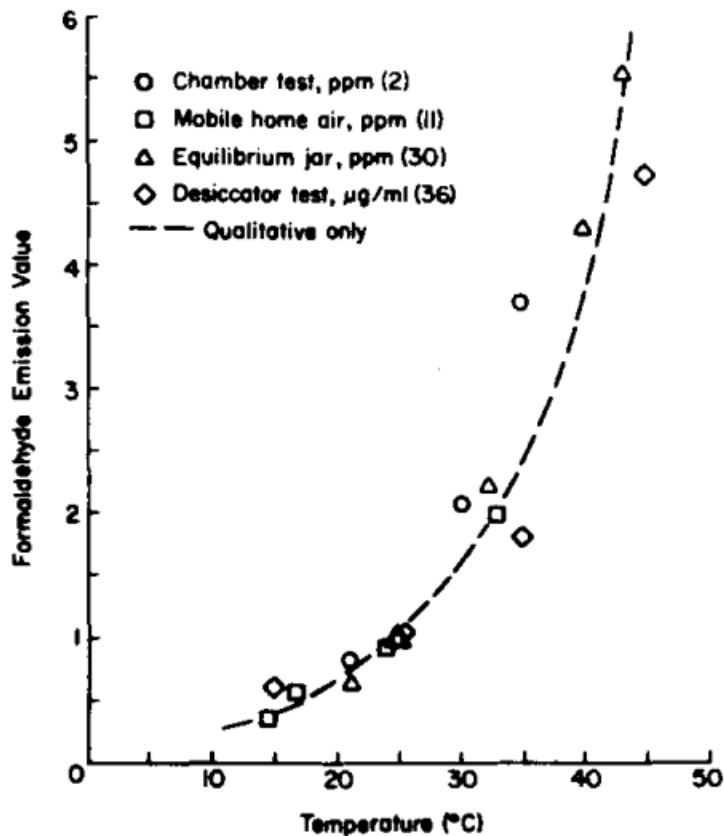


Figure 4: Nonlinear, exponential temperature dependence of formaldehyde emissions (Myers et al., 1985)

Jing et al. (2008) showed in application that increases in relative humidity significantly increased formaldehyde uptake in activated carbon modified with organosilane. Van Netten et al. (1989) and Andersen et al. (1975) showed that formaldehyde emissions doubled with a relative humidity increase from 30 to 70% when temperature was held constant at 22°C. In reverse, a drop in humidity from 70% to 30% resulted in approximately a 40% reduction of formaldehyde concentrations in a controlled study in mobile homes (Godish and Rouch, 1986). In a study of 20 sampled homes, Arundel et al. (1992) found a positive correlation between the relative humidity and formaldehyde concentrations.

Pickrell et al (1984) noted that increased product loading, or greater surface area to volume ratio in the small environmental chamber, dampened the impact of mass emission rate when temperature and relative humidity increased, seeing no appreciable changes in formaldehyde concentrations, which is especially important and relevant for this study's short-term experiments, which requires steady concentrations. Based on Fick's First Law of Diffusion,  $J = -D * dC/dx$ , the diffusion flux J, or mass emission rate per unit area, increases with increasing concentration gradient between the source and surrounding environment and decreases with increasing path length or thickness (Pickrell et al, 1982). Compared to ambient air placement of EWPs, in controlled chamber studies where the source is enclosed with high product loading ratios, thus maintaining high chamber concentrations, emission degradation will be slower because the concentration gradient between the EWP and the chamber air is reduced. Salthammer et al. (1995) also

concluded that of all environmental parameters, air exchange rate contributed most significantly to indoor concentrations.

These overall considerations were accounted for in this study's source chamber design in order to achieve steady concentrations over a short-term period by using high product loading ratios within the sealed environmental chamber, along with keeping relative humidity, temperature, and air exchange constant.

### 2.1.3 CONCENTRATIONS IN THE INDOOR ENVIRONMENT

#### 2.1.3.1 Guidelines for Formaldehyde Exposure Limits Indoors

For reference, The California Environmental Protection Agency, Office of Environmental Health Health Hazard Assessment (CA OEHHA) sets 8-hr and chronic recommended exposure limits of formaldehyde at  $9 \mu\text{g}/\text{m}^3$  (7.3 ppb) and an acute recommended exposure limit at  $55 \mu\text{g}/\text{m}^3$  (45 ppb). The National Institute of Occupational Safety and Health (NIOSH) sets a 10-hr reference exposure limit (REL) at  $19.6 \mu\text{g}/\text{m}^3$  (16 ppb) for a 40-hr workweek and a 15-min acute exposure limit at  $123 \mu\text{g}/\text{m}^3$  (100 ppb), and the California Air Resources Board (CARB) sets an 8-hr REL at  $32 \mu\text{g}/\text{m}^3$  (26 ppb). In comparison, the World Health Organization (WHO) guideline exposure limit is  $0.1 \text{ mg}/\text{m}^3$  (81 ppb) for a 30-min exposure duration. Table 5 presents a summary of the above recommended exposure limits for formaldehyde.

Table 5: Recommended exposure limit guidelines for formaldehyde

<i>Agency Guideline</i>	<i>REL (ppb)</i>	<i>REL (<math>\mu\text{g}/\text{m}^3</math>)</i>
CA OEHHA, 8-hr chronic	7.3	9
CA OEHHA, acute	45	55
NIOSH, 10-hr TWA for 40-hr workweek	16	19.6
NIOSH, 15-min acute	100	123
CA ARB, 8-hr	26	32
WHO, 30-min	81	100

### *2.1.3.2 Occupational Exposures*

A study of indoor occupational exposures to formaldehyde at seven U.S. resin manufacturing plants observed overall mean concentrations ranging from 0.03-30.45 ppm, with most individual plant measurements having mean concentrations between 0.2-0.6 ppm (Stewart et al., 1987; IARC, 2006). The same study reported a plywood manufacturing plant with average concentrations of 0.2 ppm. Another study by the World Health Organization reported average concentrations of 1.3 ppm in buildings being insulated with urea-formaldehyde foam insulation (UFFI), relevant for workplace exposures in the construction industry (WHO, 2002). One Taiwanese study of five office buildings reported 8-hr average concentrations ranging from 140-1190  $\mu\text{g}/\text{m}^3$  (Wu et al., 2003). These measured mean concentrations were well above the reference exposure levels set by various agencies as health guidelines, referenced in section 2.1.3.1.

### *2.1.3.3 Mobile Trailer Exposures*

With the occurrence of Hurricanes Katrina and Rita in 2005, over 200,000 homes were damaged or permanently destroyed, displacing over one million people from their homes (U.S. HUD, 2006; Hori et al., 2009). These natural disasters led to the widespread distribution of approximately 100,000 mobile trailers by the Federal Emergency Management Agency (FEMA) to serve as temporary housing shelters (CDC, 2008). However, the trailers were constructed predominantly of formaldehyde-emitting particleboard and other wood composites, leading to elevated formaldehyde levels.



Dingle et al. (2000) reported mobile home caravan trailers constructed with a high product loading ratio of approximately  $1.4 \text{ m}^2/\text{m}^3$  particleboard surface area to trailer volume, compared to a total loading factor of approximately  $0.37 \text{ m}^2/\text{m}^3$  in single-family, detached residences (CARB, 2007; Hun et al., 2010). The high wood composite product loading of trailers paired with relatively low air exchange rates, reported by Maddalena et al. (2008) to be between 0.15/hr and 0.39/hr, exacerbated concentrations within the trailers by preventing the influx of fresh air to flush out and dilute high concentration emissions. In comparison, the typical residential air exchange in the United States lies between 0.5/hr and 1.0/hr (Murray and Burmaster, 1995).

In a study commissioned by the U.S. Centers for Disease Control and Prevention after occupants reported adverse health symptoms associated with formaldehyde exposure, Murphy et al. (2013) sampled the air quality of 519 random FEMA trailers distributed after Hurricanes Rita and Katrina, reporting formaldehyde concentrations ranging from 3-590 ppb with a geometric mean of 77 ppb. The mean concentration exceeds most federal 8-hr exposure guidelines and exceeds or approaches most occupational thresholds for acute, short-term exposure limits. At the time of FEMA's purchase of the trailers for distribution, the U.S. Environmental Protection Agency had previously documented that travel trailers emitted relatively high concentrations of formaldehyde, reporting that of 470 trailers manufactured between 1966-1984, the mean concentration of formaldehyde measured was 70 ppb, and 31% of the trailers exhibited levels exceeding 100 ppb (Sexton et al., 1989).

#### *2.1.3.4 Residential Exposures*

Concentrations of formaldehyde in indoor air are often an order of magnitude higher than outdoor concentrations (IARC, 2006), and elevated formaldehyde concentrations are not only concerns in occupational or manufactured trailer environments, but also residential spaces. Since the 1950s, the trend in the building industry has been to tighten up homes to prevent energy losses from heating, cooling and ventilation (Weschler, 2009), especially for newer homes constructed in the last few decades (Weisel et al., 2005). The geometric mean for typical residential air exchanges across various seasons and climactic regions in the United States is approximately 0.5/hr-1.0/hr (Murray and Burmaster, 1995). Tighter homes may lead to problematic concentration levels if highly emissive materials are present.

However, in the last few decades, conscious effort has been made by manufacturers to not only minimize formaldehyde emissions from urea resins but to also use alternative resins in the wood curing process (Weschler, 2009; IARC, 2006). Extremely emissive materials like urea-formaldehyde foam insulation (UFFI) were also banned and removed from homes in the 1980s (CPSC, 1982). For these reasons, current residential formaldehyde concentrations tend to be more moderate overall relative to the aforementioned trailer and workplace environments. Even so, the mean concentrations reported by several research sampling studies still exceed long-term (8-hr, 10-hr) and chronic exposure recommendations listed in section 2.1.3.1.

For instance, in two studies conducted by Hodgson et al. (2000, 2002), 4 manufactured houses in Florida had an average concentration of 34 ppb, with a sampling range of 21-47 ppb; 7 site-built houses had an average concentration of 36 ppb, with a sampling range of 14-58 ppb; and one newly manufactured house had a concentration of 94.9  $\mu\text{g}/\text{m}^3$  three months after installation. An earlier study conducted by Sexton et al. (1986) measured formaldehyde concentrations in 51 residences in the San Francisco Bay Area, yielding an average of 41 ppb in the kitchen and 36 ppb in the main bedroom. In comparison, Shah and Singh (1988) reported an average of 44  $\mu\text{g}/\text{m}^3$  in a sample of 273 residences across the United States. The recent comprehensive RIOPA residential exposure study conducted in 2007 for 353 measurements in 234 U.S. homes reported median formaldehyde concentrations of 20.1  $\mu\text{g}/\text{m}^3$  and 95<sup>th</sup> percentile concentrations of 32.5  $\mu\text{g}/\text{m}^3$  (Liu et al., 2007; Hun et al., 2010). One residential study conducted in Louisiana involved 419 air samples in 53 homes and uncharacteristically high levels of formaldehyde at a mean concentration of 460  $\mu\text{g}/\text{m}^3$  – an order of magnitude higher than the other studies (Lemus et al., 1998).

#### *2.1.3.5 Exposure in Schools*

Formaldehyde is also the most commonly found volatile organic compound (VOC) pollutant in schools, and while measured concentrations typically fall below existing workplace exposure guidelines, there may be potential long-term cancer risk from prolonged exposures (Daisey et al., 2003) and increased risk of sensitization to

allergens even at low concentrations (Garrett et al., 1999). One study reported that the average concentration of formaldehyde in mobile trailer-style buildings of a daycare (0.35ppm) was five times higher than the average concentration found in permanent buildings of the same daycare (0.065ppm); and eye, nose and throat irritation symptoms were three times more common in staff of mobile buildings (Olsen and Dossing, 1982).

California's comprehensive study on environmental health in portable classrooms, found that of approximately 50% of portable classrooms sampled (mean = 32 ppb) compared to 29% of traditional classrooms sampled (mean = 24 ppb) in each of 644 randomly selected schools statewide measured formaldehyde concentrations exceeding the Indoor REL of 27 ppb, which was the CA OEHHA 8-hr guideline at the time of the study by the Air Resources Board (Jenkins et al., 2004). In a second phase of the study during cooler weather and when ventilation rates had been adjusted and possibly increased prior to sampling, only 4% of the portable classrooms sampled (mean = 15 ppb) and 3% of the traditional classrooms sampled (mean = 12 ppb) in each of 135 randomly selected schools statewide measured formaldehyde concentrations exceeding 27 ppb. It is important to note that since 2008, the CA OEHHA 8-hr guideline has been reduced to a more stringent standard of 7.3 ppb, so a greater percentage of schools overall would have been found to be in exceedance.

Such environmental health reports are concerning as mobile trailers become increasingly common in schools, with one-third of children in California learning in portable classrooms and with there being a scarcity of formaldehyde monitoring data in those environments aside from the CARB study (Shendell et al., 2004).

#### 2.1.4 HEALTH EFFECTS

Formaldehyde is classified by the World Health Organization International Agency for Research on Cancer as carcinogenic to humans (IARC, 2006) and by the U.S. Environmental Protection Agency as a Group B1 probable human carcinogen (U.S. EPA IRIS, 1999). On the short-term acute exposure scale, formaldehyde causes irritation of the eyes, skin, nose and throat, respiratory ailments like sneezing and coughing, and at extreme exposures, nausea and death (WHO, 2002). Because formaldehyde is highly soluble in water, with a Henry's law constant ranging from approximately  $2.5 \times 10^3$  -  $3.0 \times 10^3$  M atm<sup>-1</sup> at 25°C (Seinfeld et al, 2006; Betterton et al, 1988), its high solubility increases body absorption rates, especially through the lung and mucous membranes (Salthammer et al., 2010).

Formaldehyde's chronic exposure cancer risk assessments are predominantly based on non-human testing. For example, increases in nasal squamous cell carcinoma were observed in rats due to long-term formaldehyde exposure (Monticello et al., 1996; Kerns et al, 1983). A study by Soffritti et al. (2002), also conducted on rats, found that formaldehyde ingestion via drinking water resulted in a significant increase in malignant tumors and lesions in the mammary, stomach and intestine organs as well as testicular interstitiae cell adenomas and hemolymphoreticular neoplasias. However, the Nielsen et al. (2013) and Nielsen and Wolkoff (2010) reviews found that at lower exposures at 0.7 ppm, no gene mutations, changes in gene expression, or increases in cytotoxicity-induced cell proliferation – key precursors to nasal cancer – were observed in rats. The

researchers also reported that lymphohematopoietic malignancies were only reported in epidemiological studies with peak exposures above 2 ppm and average exposures above 0.5 ppm; and that nasopharyngeal cancer in humans was only reported above peak exposures of 4 ppm and average exposures above 1 ppm.

In the last decade, however, several human exposure studies have explored formaldehyde carcinogenicity in humans, specifically with respect to nasopharyngeal cancer and leukemia. Analysis of the largest U.S. cohort study of industrial workers exposed to formaldehyde found a statistically significant number of excess deaths compared with the national population due to nasopharyngeal cancer directly attributed to the degree of formaldehyde exposure (Hauptmann et al., 2004). Two separate case-control studies for workers exposed to formaldehyde found a significant association between longest exposure duration and incidence of nasopharyngeal cancer, but no significant association between maximum cumulative exposures and nasopharyngeal cancer incidence (Vaughan et al., 2000; Hildesheim et al., 2001). Nielsen et al. (2013) found that continuous exposures between 0.5-1 ppm in humans neither increased cell micronucleus formation in human buccal cells or nasal tissue nor caused *in vivo* genotoxicity in peripheral blood lymphocytes, but that these positive associations did occur at higher occupational exposures.

A new study of leukemia case-control exposure assessments conducted for funeral embalmers yielded positive associations of elevated mortality from myeloid leukemia for those who performed embalmings for extended exposure durations (over 34 years or over 3068 embalmings), or whose cumulative formaldehyde exposure exceeded 9253 ppm-hr,

compared with other subjects who performed less than 500 embalmings (Hauptmann et al., 2009). No positive associations were found with other types of lymphohematopoietic malignancies or brain cancer. According to a study by Coggon et al. (2014) on over 14,000 industrial workers in Britain, however, no excess mortality for myeloid leukemia, nasopharyngeal carcinoma, or other upper airway tumors was found for workers exposed to formaldehyde, even amongst the two highest exposure categories.

Researchers have also reported that residential and domestic exposure to formaldehyde in homes leads to increased risk of allergy sensitization and asthma in children (Garrett et al., 1999; Rumchev et al., 2002; Krzyzanowski et al., 1990). Garrett et al. (1999) found that low-level exposure to indoor formaldehyde in homes with a median concentration of 15.8  $\mu\text{g}/\text{m}^3$  (12.6 ppb) was associated with an increase in children's risk of allergy sensitization to common allergens. Rumchev et al. (2002) found that six times greater formaldehyde exposure of 60  $\text{mg}/\text{m}^3$  resulted in a 39% increase in the odds of children having asthma compared to an exposure of 10  $\text{mg}/\text{m}^3$ , and each 10  $\text{mg}/\text{m}^3$  increase in exposure resulted in a 3% increase in asthma risk. However, these exposure concentrations are much higher than typically observed in domestic indoor settings.

Krzyzanowski et al. (1990) conducted an asthma risk study observing lung function at more realistic indoor concentrations, showing that the prevalence of asthma and chronic bronchitis were significantly greater in children who lived in homes with 60-120 ppb formaldehyde compared with < 60 ppb, especially in children also exposed to environmental tobacco smoke. The researchers also found that asthmatic children

exposed to low levels of HCHO < 50 ppb experienced stronger symptomatic responses than healthy children. In adults, however, the sensitivity to elevated formaldehyde concentrations > 40 ppb were only observed in the morning and predominantly in smokers. This study showed that children's respiratory systems are more sensitive than adults to formaldehyde exposure. Another study reported a reduction in respiratory symptoms when children were transferred from schools with formaldehyde concentrations of 43-75 ppb to schools with concentrations of 23-29 ppb (Wantke et al., 1996).



### 2.1.5 CONTROL STRATEGIES

Conventional indoor air cleaners and filtration devices are ineffective at removing formaldehyde (Tseng et al., 2005). Activated carbon filtration units target most VOCs and ozone (U. S. EPA, 1999), and HEPA and HVAC filtration units target particulates (Fisk et al., 2002), but none of these cleaners were designed to or are able to remove formaldehyde due to its high vapor pressure and low sorptivity. Thus, in order to increase deposition, the surfaces of the filter itself must be highly reactive with formaldehyde.

Some potential strategies associated with formaldehyde control involve chemically doping the surfaces of activated carbon with polar compounds to increase reactivity with formaldehyde, which also exhibits strong polarity (see Section 2.1.1). Several of these techniques include using potassium permanganate impregnated activated carbon (Sekine & Nishimura, 2001), polyacrylonitrile-based activated carbon (Lee et al., 2013), sulfuric acid and nitric acid- treated activated carbon (Tanada et al., 1999; Agarwal et al., 2011), organosilane-modified activated carbon (Jing et al., 2008), zeolites with  $\text{Co}^{2+}$  ions (Góra-Marek & Datka et al., 2007), and composite zeolite- $\text{TiO}_2$  sheets (Ichiura et al., 2001). Other alternative strategies involve exploring the adsorption properties of heat-treated rice husks (Kumagai et al., 2008), karamatsu tree bark (Takano et al., 2008), and  $\text{ZnCl}_2$ -impregnated nitrogen-treated activated carbon prepared from coffee residue (Boonamnuayvitaya et al., 2005). However, these designs have only been tested in small-scale passive laboratory settings and have yet to be implemented in room-scale testing at representative indoor concentrations. Furthermore, chemical doping of

activated carbon is typically expensive and non-regenerative (Marsh & Rodriguez-Reinoso, 2006).

The most well-established techniques to decrease indoor emissions are to: 1) limit the use of urea-formaldehyde resins at the manufacturer end by choosing alternative, less emissive resins like melamine and phenol-formaldehyde (Dunky, 1998), and 2) set building material emission limits and conduct materials emission testing in environmental chambers prior to distribution.

One preliminary study that fortified urea-formaldehyde resins with melamine to prevent emission release by obstructing the hydrolysis reaction yielded promising results, but the efficacy was highly dependent upon a narrow range of resin pH levels (Paiva et al, 2012). Another study showed that soy protein additives may decrease the reactivity of urea-formaldehyde resins, but this result is only relevant for pre-cured UF resins, which does not apply to engineered composite woods (Lorenz et al., 1999).

The emission limitation guidelines set by the United States Code of Federal Regulations (U.S. CFR, 1984) prevent formaldehyde concentrations from exceeding certain levels in various manufactured homes by monitoring the allowable emissions from plywood and particleboard. Based on modified small-chamber air emissions testing in accordance with the ASTM E1333-10 Standard Test Method for Determining Formaldehyde Levels from Wood Products under Defined Test Conditions Using a Large Chamber (ASTM, 2006), using product loading ratios of  $0.29 \text{ ft}^2/\text{ft}^3$  and  $0.13 \text{ ft}^2/\text{ft}^3$  for plywood and particleboard, respectively, the allowable emissions may not lead to a concentration that exceeds 200 ppb for plywood and 300 ppb for particleboard. More

recently, the California Air Resources Board (CARB) Phase 2 restrictions took effect starting January 1, 2011, stating that formaldehyde concentrations for particleboard cannot exceed 0.09 ppm (90 ppb) and for medium-density fiberboard cannot exceed 0.11 ppm (110 ppb) (CARB, 2007). However, these allowable concentrations are still at least double the recommended indoor concentration guidelines designated by various government agencies, as delineated in Section 2.1.3.1, which means that products may still emit at elevated levels when utilized downstream.

## **2.2 Sheep's Wool**

### **2.2.1 COMPOSITION AND CHEMICAL PROPERTIES**

Sheep's wool is primarily composed of keratins, or fibrous structural proteins that are the main component of hair and nails (Rippon, 2013). These keratins make up approximately 97% of the wool by mass (Zwiener et al., 1999; Wortmann et al., 2005) and contain an abundance of amino acids, as depicted in Table 6 (Rippon, 2013). By measuring the initial masses of amino acids in wool and the final masses post-formaldehyde treatment (Table 7), Caldwell and Milligan (1972) determined that 7 amino acids present in wool (i.e. Lysine, Arginine, Asparagine, Glutamine, Glycine, Cystine, and Proline) are significantly reactive with formaldehyde. These 7 amino acids make up approximately 50 mol% of the amino acids in wool (Table 6) (Rippon, 2013). Wortmann et al. (2005) also suggests that the side chains of histidine, tyrosine, and tryptophan are reactive with wool, which then yields a total of approximately 60 mol% of reactive amino acids in wool.

Table 6: Structure and amount of major amino acids in wool (Rippon, 2013)

Amino Acid	Structure <sup>(a)</sup>	mol%		Nature of Side Chain
		[13]	[14]	
Glycine		8.6	8.2	Hydrocarbon
Alanine		5.3	5.4	Hydrocarbon
Phenylalanine		2.9	2.8	Hydrocarbon
Valine		5.5	5.7	Hydrocarbon
Leucine		7.7	7.7	Hydrocarbon
Isoleucine		3.1	3.1	Hydrocarbon
Serine		10.3	10.5	Polar
Threonine		6.5	6.3	Polar
Tyrosine		4.0	3.7	Polar
Aspartic acid <sup>(b)</sup>		6.4	6.6	Acidic
Glutamic acid <sup>(c)</sup>		11.9	11.9	Acidic
Histidine		0.9	0.8	Basic
Arginine		6.8	6.9	Basic
Arginine		6.8	6.9	Basic
Lysine		3.1	2.8	Basic
Methionine		0.5	0.4	Sulphur-containing
Cystine <sup>(d)</sup>		10.5 <sup>(e)</sup>	10.0 <sup>(e)</sup>	Sulphur-containing
Tryptophan		See text		Heterocyclic
Proline		5.9	7.2	Heterocyclic

<sup>(a)</sup>Shading indicates identity of side chain.

<sup>(b)</sup>Includes asparagine residues (see text).

<sup>(c)</sup>Includes glutamine residues (see text).

<sup>(d)</sup>Includes oxidation byproduct, cysteic acid.

<sup>(e)</sup>Values are for half-cystine (see text).

Table 7: Amino acid analyses of wool before and after treatment with formaldehyde (reproduced from Caldwell & Milligan, 1972)

Amino Acid	Untreated Acid hydrolysate (μmole/g)	Formaldehyde-treated Enzyme hydrolysate (μmole/g) <sup>a</sup>
Lys	256	198
His	67	69
Arg	606	489
Cys/SCMC	1086	605
Asp	588	74
Glu	1034	291
Pro	646	350
Gly	776	453
Ala	471	464
Val	517	524
Met	38	40
Ile	274	284
Leu	687	677
Tyr	335	359
Phe	240	230

<sup>a</sup> Normalized to Leu + Ile = 961 μmole/g

The side chains of each amino acid, which are highlighted in Table 6, bind with formaldehyde to form a methylene bridge cross-link product in a stable and irreversible chemical reaction called *chemisorption*, which ensures that formaldehyde can never be reemitted (Rippon, 2013). Figure 5 shows the chemical process, including the intermediate reaction, that forms the methylene bridge (Curling et al., 2012), in which a reactive hydrogen atom attaches to the carbonyl double bond of a formaldehyde molecule, resulting in the formation of an amino-methylol derivative, with the methylol group reacting with one of the amino acid side chain groups (Zwiener et al., 1999).

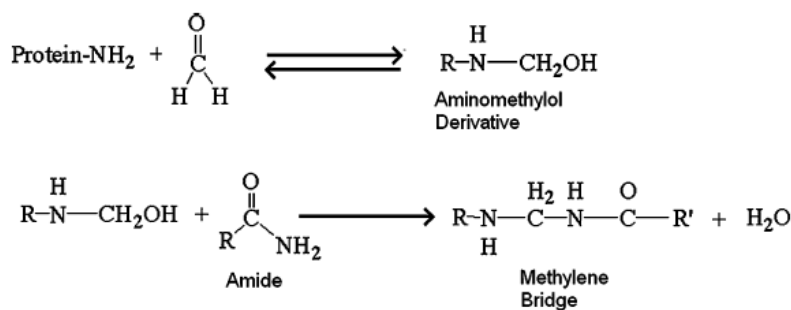


Figure 5: Reaction schematic of formaldehyde with proteins, including intermediate reaction (Curling et al., 2012)

Researchers have studied the chemisorption process by submerging wool in liquid formaldehyde solvent at various environmental conditions and concentrations. Reddie and Nichols (1971) found that the pH of the solution, the concentration of formaldehyde, and the treatment time and temperature have a significant impact on formaldehyde adsorption, and also that the presence of different types of salt in the solution has some effect on formaldehyde uptake. The researchers also found evidence of gradual re-emission over time, showing that not all formaldehyde adsorbed undergoes the permanent chemical bonding process.

For gaseous formaldehyde, Curling et al. (2012) reported that approximately one-third of the formaldehyde adsorbed in wool is only physically deposited, in a process known as *physisorption*. The physically sorbed formaldehyde is not permanently deposited and can potentially be offgassed with changes in environmental conditions like relative humidity and temperature, and changes in mass concentration gradients between the wool and ambient air. It is important to note that these experiments, described further in Section 2.2.2, were conducted on a very small scale, using only 10 mg of wool.

### 2.2.2 INDOOR AIR APPLICATION

Several researchers have conducted preliminary investigations on the capacity of wool to adsorb gaseous formaldehyde. Zwiener et al. (1999) and Wortmann et al. (2005) conducted batch reactor testing of 14 g of wool in a sealed 250 L glass chamber with no airflow by injecting single doses of formaldehyde into the chamber to generate an initial concentration of 300 ppm. The researchers observed resulting concentrations between 0.1-0.77 ppm across 10 days, finding consistently that over 97% of formaldehyde was adsorbed. This 97% adsorption equates to a capacity of approximately 6400  $\mu\text{g}$  HCHO removed / g wool. Huang et al. (2007) conducted similar batch reactor testing of 31.67 g of wool in a well-mixed 96 L chamber, observing a 70% concentration reduction from 1 ppm to 0.3 ppm across 3 hours, but did not carry out the experiment longer to observe full capacity. This 70% reduction equates to approximately 23.5  $\mu\text{g}$  HCHO removed / g wool during the 3 hour timespan. Neither experiment was carried out until wool saturation, and both studies were conducted at very high concentrations, but Wortmann et al. observed especially high sorption capacity for a 10-day period.

Curling et al. (2012) conducted a very small-scale observation in a sealed chamber using 10 mg of wool fiber saturated over a micro-balance pan filled with diluted formaldehyde solvent, at which point the wool was removed from the source and underwent moisture cycles of 0%, 90%, 0%, 90%, etc. relative humidity to observe the total amount of formaldehyde that desorbed due to elevated moisture content.

While these exploratory studies have begun to observe the application of wool as a filter for gaseous formaldehyde, no research thus far has observed wool capacity in active flow settings like a plug flow reactor (PFR) or continuous stirred-tank reactor (CSTR), or implemented wool experimentation in filtration systems in room-sized settings at typical domestic concentrations.



### 2.2.3 ABUNDANCE OF WOOL

Wool as a resource is plentiful in the U.S. and globally. According to the United States Department of Agriculture (USDA) Sheep and Lambs Inventory (2007) and an updated 2011 report, there are approximately 5.5 million sheep in the U.S. (USDA, 2011). This estimate roughly equates to 20 households supplied per sheep if all 115 million households in the U.S. (U.S. Census Bureau, 2013) implemented filtration. Figure 6 shows U.S. sheep density in 2007, as provided by the USDA 2011 report.



Figure 6: U.S. sheep density (USDA, 2011)

Globally, sheep are also quite abundant and are found at higher densities in other continents than in North America, according to the 2005 mapping report by the Food and Agriculture Organization (FAO) of the United Nations. The FAO map of global sheep density is shown in Figure 7.

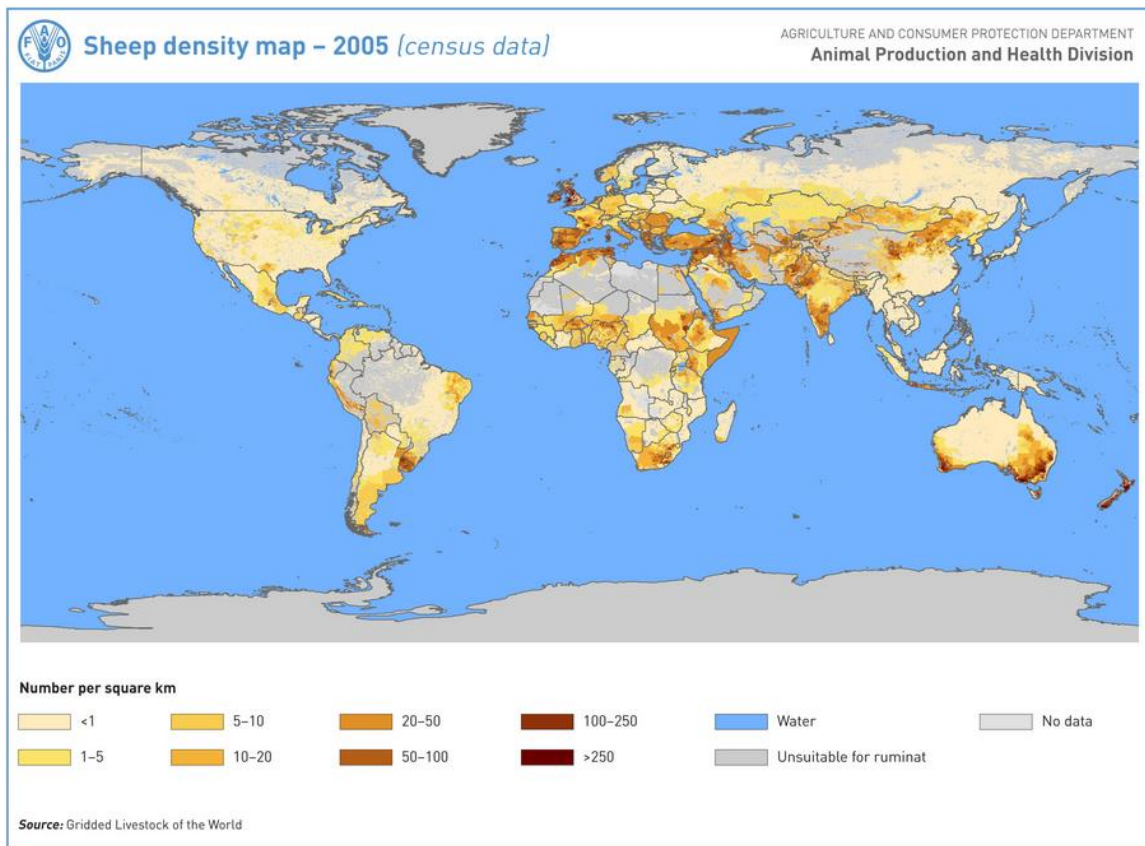


Figure 7: Global sheep density (FAO, 2005)

### 3 EXPERIMENTAL METHODOLOGY

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#### 3.1 Plug Flow Reactor (PFR) Setup

A plug flow reactor experimental setup was designed to mimic active filtration, as shown in the laboratory schematic (Figures 8 and 9). All materials and apparatus in contact with the flow stream were either composed of stainless steel or Teflon – materials chosen for their non-reactivity and minimal surface sorption behavior with formaldehyde. Tubing connections were composed of flexible ¼ -in OD PFA Teflon, and the Swagelok tubing fittings and valves were composed of stainless steel. All chambers were sealed and operated according to the ASTM D5116-10 and ISO 16000-9 experimental standards for small chamber emissions classification.

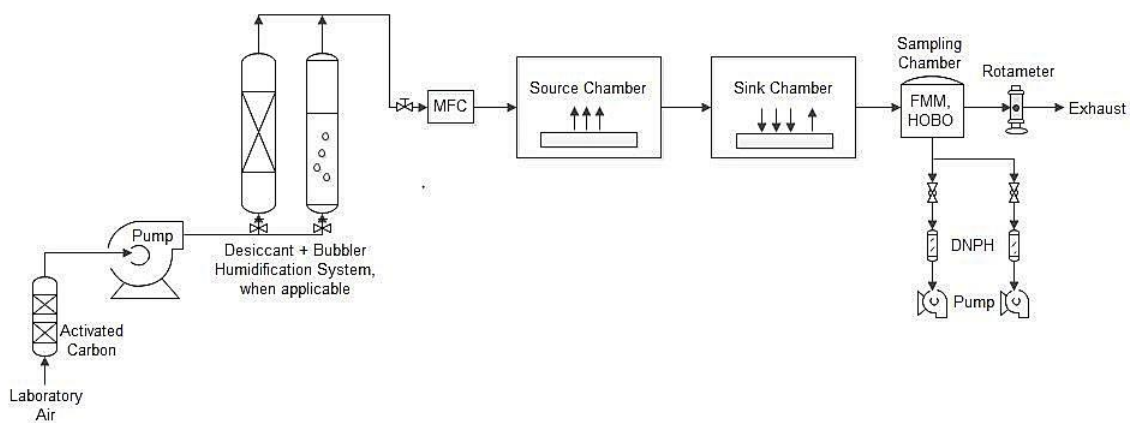


Figure 8: Plug flow reactor experimental design schematic

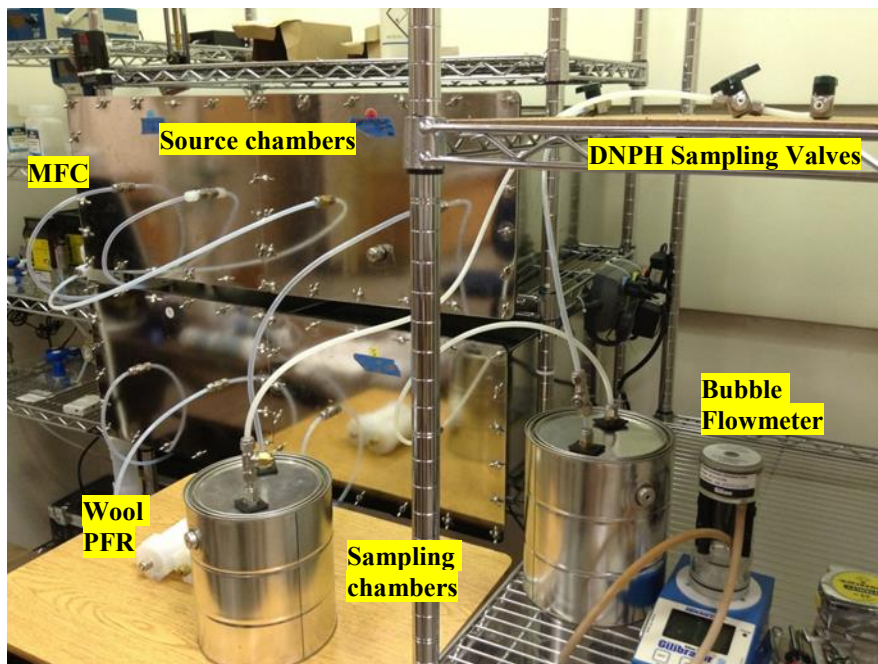


Figure 9: Experimental setup diagram

Laboratory air was pumped through the system using a compression pump (Thomas, Model 607CA220) at a controlled rate of 800 mL/min using mass flow controllers (MFCs) (Aalborg GCF17) to yield 1 air change/hour of air movement through 48 L stainless steel chambers. The air exchange rate of 1/hr was chosen to mimic the airflow conditions of a typical indoor room environment.

Laboratory air was first passed through two Savillex Teflon PFA columns packed with activated carbon (AC) mat granules to remove ozone and VOCs from laboratory supply air. Since formaldehyde is highly reactive, this initial filtration ensured that the air stream was free of other chemical contaminants. Desiccant and humidification columns were also included in the setup as potential controls; however, they were not necessary

for controls in the experiments presented in this research as the laboratory environmental conditions remained constant with the chamber set-up placed in a walk-in fume hood.

The filtered laboratory supply air was passed through an electro-polished stainless steel source chamber with 48 L of internal volume. Two perforated stainless steel tubes extended into the chamber to enhance mixing and distribute air uniformly. The left steel tube provided inlet air to the chamber while the right steel tube exhausted air from the chamber. The source chamber was filled with varying surface area slabs of medium-density fiberboard (MDF) to generate formaldehyde concentrations. Targeted concentrations were high, ideally above at least 80-100 ppb because laboratory background concentrations fluctuated between 10-20 ppb, and any drops in concentration achieved with the wool needed to be statistically significant relative to background levels.

When sealed in the chambers, the MDF slabs were shown to produce steady concentrations across day- and week-long sampling periods. While the individual emission rates of the slabs varied, the steady-state concentrations achieved in the source chamber for a given set of slabs under the specified fluid mechanics settings remained relatively steady overall, even with slight fluctuations due to diurnal changes in temperature and relative humidity. To dampen these diurnal fluctuations, which impact formaldehyde emission and uptake, the entirety of the experimental setup was enclosed within a walk-in fume hood that kept temperature and relative humidity stable at  $T = 22.5 \pm 0.5^{\circ}\text{C}$  and  $\text{RH} = 65 \pm 10\%$ .

At 1 ACH passing through the chambers, the back-of-the-envelope calculation to reach 95% steady-state once the chambers were loaded and sealed (assuming perfect mixing) was approximately 3 hours, as shown in Equation 1.

$$C = C_0 e^{-\lambda t}$$

$$\frac{C}{C_0} = e^{-\lambda t}$$

$$0.05 = e^{-\lambda t}$$

$$t = -\frac{\ln(0.05)}{\lambda} \approx \frac{3}{\lambda} \quad (1)$$

where:

C = Final Concentration [ppb or  $\mu\text{g}/\text{m}^3$ ]

C<sub>0</sub> = Initial Concentration [ppb or  $\mu\text{g}/\text{m}^3$ ]

$\lambda$  = Air Exchange Rate ( $\text{hr}^{-1}$ )

t = Time (hr)

For each experimental run and each time a new set of slabs were sealed in the chambers, the source chamber airstream initially bypassed the sink chamber (i.e., the PFR) and was first connected to a small 3.78 L (1 gallon) stainless steel sampling chamber downstream to measure the source concentration achieved. The large 48 L source chamber was allowed ~3 hours to come to steady-state before the FMM was placed in the small sampling chamber for data collection.

The smaller sampling chamber was used to achieve greater sensitivity to concentration changes. In the small chamber, it took only a residence time of 4.7 minutes for a given parcel of air to pass through and only 15 minutes for the chamber

concentrations to reach steady-state given an air exchange of 12/hr at the air flowrate setting of 800 mL/min (Equation 1). Because the formaldehyde monitor placed in the sampling chamber read continuous 30-minute averages of formaldehyde concentration, use of a smaller chamber ensured that concentration changes were well-mixed and uniformly distributed within the sampling period.

Once steady-state source concentrations were measured, the sink chamber (i.e., wool plug flow reactor) was connected to the system between the source chamber and the sampling chamber. The reactor vessel consisted of a Savillex Teflon® PFA fluoroplastic 150 ml column component segment with 1-1/2" MNPT, capped on both ends with a 58 mm transfer closure, (1) 1/4" OD tube port with 1-1/2" FNPT threads. Two capacity experiments were conducted in which the PFR was filled with 10g and 5g of wool, respectively. The sheep's wool used in this research was white, raw, untreated wool purchased from Oregon Shepherd Natural Wool Insulation®.

Once the PFR was connected, the concentrations measured in the sampling chamber were from the airstream exhausted from the PFR. In this system, the steady-state source concentration entering the PFR was known and assumed to be constant from preceding measurements, and the concentrations measured in the sampling chamber indicated the effective concentration reduction over time using the wool filter.

To ensure that flow rates between each consecutive chamber were relatively constant at 800 mL/min and that overall losses between chambers were less than 10% (in alignment with ASTM D5116-10 and ISO 16000-9 small-chamber experimental protocol), a Gilian bubble flow calibration meter was used to check flow rates after each

consecutive chamber (e.g. after mass flow controller, source chamber, PFR, and sampling chamber). If overall losses exceeded 10%, chambers fittings and tubing connections were retightened and checked for potential leakages.

The Shinyei FMM was also calibrated against the U.S. EPA TO-11a standard protocol for formaldehyde sampling, which uses 2,4-Dinitrophenylhydrazine (DNPH) sorbent tube sampling with high-performance liquid chromatography (HPLC) analysis. To conduct the DNPH sorbent tube sampling simultaneously with the FMM readings, a needle valve was connected downstream of the small sampling chamber. A personal air pump downstream of the SKC Inc. 226-119 Formaldehyde Sorbent Tube extracted air at approximately 225 mL/min from the sampling chamber for 2 hours. The mass collected across the known period of time and known volume of air yielded an average formaldehyde concentration across those 2 hours that was compared with an average of the 4 FMM readings taken in the same 2-hour period. At high concentrations, the FMM readings were slightly misaligned from DNPH concentrations, so all FMM concentrations above 60 ppb were adjusted according to the calibration curve generated (shown in Appendix A). No adjustments were made for concentrations measured below 60 ppb, as several researchers (Nirlo et al., in progress; Carter et al., 2013; Hun et al., 2013) had conducted low-concentration calibration curves showing a 1:1 relationship between the FMM + DNPH methods. Additional information about the Shinyei FMM as well as the QA/QC sampling protocol and results are provided in Appendix A.

Due to the complex impacts of environmental parameters on both formaldehyde emissions and uptake, this capacity study recognized that short term emissions within the



span of several hours or a day would incorporate minor diurnal spikes due to natural changes in relative humidity or temperature of ambient laboratory air. However, by keeping environmental conditions relatively stable, it was possible to observe overall long-term trends in concentration changes over several days as the filter material approached likely saturation capacity.

### **3.2. Desorption Experiments in the PFR**

Controlled laboratory small-chamber experiments by Curling et al. (2012) showed using a humidification method that approximately one-third of the formaldehyde sorbed onto wool was physically deposited and could be offgassed. If saturated wool were to be reused, buyers would need assurance that the physically deposited portion had been completely removed prior to resell and that any future depositions would not lead to elevated concentrations at typical room conditions.

The goal of this experiment was to determine the degree of desorption for two cases: 1) heated settings to force off all non-bonded formaldehyde, and 2) non-heated settings to observe natural desorption at standard room conditions. The purpose of the heated desorption was to determine the percentage of formaldehyde removed and whether the forced desorption process via a heating method could be feasible for real-world implementation (i.e. achieve full desorption within a short time span). The purpose of the non-heated desorption was to determine whether wool would re-emit above background concentrations at room conditions. All desorption tests were run within a day of disconnecting a given saturated wool sample. The PFRs were capped for the time in between disconnection and reconnection, and the wool in the air cleaner was kept in an airtight container until the environmental chamber returned to steady-state room conditions.

### 3.2.1. HEATED DESORPTION IN THE PFR

Based off the observation that every 7°C of temperature increase doubles formaldehyde emission rates (Van Netten et al., 1989), the wool PFR was heated to elevated temperatures to force desorption of all the physically-sorbed formaldehyde in the saturated wool. A Calorique Radiant Heating Panel was wrapped twice around the plug flow reactor and used to heat both the wool and ambient air passing through the 150mL PFR to induce desorption and to maintain a stable temperature during and after the desorption process.

Temperature controls were dependent on the combination of a Variac Variable Voltage Regulator to control the power supply of the Calorique heating panel and a one-inch thick layer of fiberglass insulation wrapped around the heating panel to prevent heat loss. The voltage regulator was used to limit the power supply of the heating panel. Based on the Calorique panel specifications of 240 V and an approximation of laboratory electrical current running at 1.5 A, the total power available for heating was approximately 360 W, much higher than the 150 W required to raise the temperature of the air flowing through the wool by approximately 25°C above room temperature (see Equations 2 and 3). Thus, the voltage regulator was set to 100 V (see Equation 4). Variations between temperatures in different experiments were due to the tightness of the wrapped fiberglass, which affected how well heat was being insulated within the PFR.

$$Q \text{ (kW)} = P = VI \quad (2)$$

$$= 240 \text{ V} * 1.5 \text{ A}$$

$$= 360 \text{ W} = 0.36 \text{ kW}$$

$$Q \text{ (kW)} = mc\Delta T = \rho Vc\Delta t \quad (3)$$

$$= 1.2 \text{ kg/m}^3 * 300 \text{ mL/min} * 1 \text{ L} / 1000 \text{ mL} * 1 \text{ min} / 60 \text{ s} * 1 \text{ kJ}/(\text{kg} * \text{K}) * (25 \text{ K})$$

$$= 0.15 \text{ kW}$$

$$V = P / I \quad (4)$$

$$= 150 \text{ W} / 1.5 \text{ A}$$

$$= 100 \text{ V}$$

During the desorption experiments, the clean ambient airstream was directly connected to the PFR at a reduced flowrate of 300 mL/min equivalent to 2 air exchanges per minute through the column to ensure that reemitted concentrations would not be diluted by high airflow streams and that air within the PFR volume had a long enough residence time to be heated to desired temperatures (Equation 3).

Since formaldehyde concentrations were measured in a separate downstream sampling chamber, air temperatures measured downstream were not an effective or accurate indicator of the wool temperature itself, which determines formaldehyde desorption. By the time the air reached the sampling chamber, it had cooled to ambient temperatures (approximately 22°C). In order to measure wool temperature, a 4700Ω thermistor was embedded within the center of the wool and connected to the ISO-9001 certified InstruNet Analog/Digital Input/Output System to record temperatures measurements every minute.

### **3.2.2 NON-HEATED DESORPTION IN THE PFR**

Desorption at non-heated, background conditions were also measured to determine whether emission levels of the physically deposited formaldehyde would elevate concentrations above background levels. All flow settings and connections were the same as described in Section 3.2.1, including the thermistor and Instrunet setup to measure actual wool temperatures, but the heating elements (i.e. Calorique panel, voltage regulator, and fiberglass insulation) were removed.

### **3.3 Air Cleaner Setup**

#### **3.3.1 CAPACITY EXPERIMENTS IN AIR CLEANER**

A modified personal air cleaner unit was placed in a 13.8 m<sup>3</sup> (2.4m x 2.4m x 2.4m) stainless steel environmental chamber to test wool capacity. The chamber contained a pump to bring in laboratory air and an exhaust fan to withdraw air. The pump and exhaust fan were each connected to a Variac Variable Voltage Regulator, set to 80V and 5V, respectively, to ensure a positively pressurized chamber. These settings resulted in an air exchange rate through the chamber of approximately 1.4/hr, which was measured by injecting CO<sub>2</sub> concentrations above background levels, removing the CO<sub>2</sub> source, and observing concentration decreases over time in the room chamber. The AER results are shown in Figure 10 below. Chamber pressure was measured using a Energy Conservatory DG-500 Pressure Gauge to take differential pressure measurements inside and outside of the closed chamber to ensure flow settings were under positive pressurization.

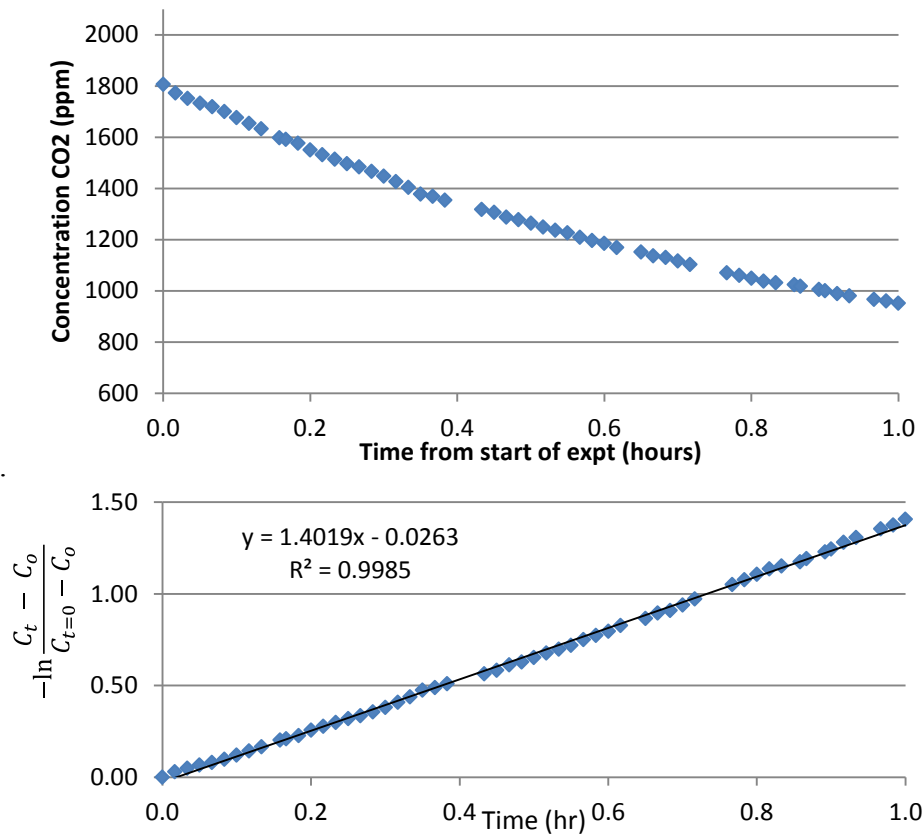


Figure 10: Air exchange rate analysis in 13.8 m<sup>3</sup> environmental chamber

The room chamber setup is depicted in Figure 11 below. The apparatus included: a solvent source to generate formaldehyde, a digital scale to measure the mass of solvent source remaining over time, a fan placed in the corner of the chamber to circulate air, an air cleaner filled with wool to conduct active filtration, and a Shinyei FMM to measure HCHO concentration. The intake and exhaust locations are also shown. During “source only” conditions, the air cleaner was not located in the chamber. Only after chamber concentrations had reached steady-state was the air cleaner with wool added to the chamber and turned on.

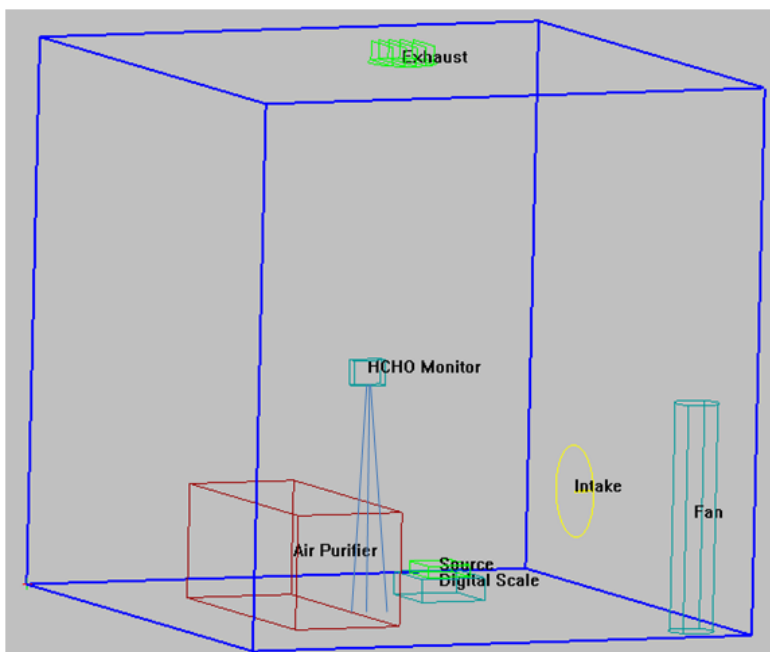


Figure 11: Setup of air cleaner in well-mixed CSTR environmental chamber

Formaldehyde concentrations were generated within the chamber by using the vaporization at room temperature of liquid formalin (Sigma Aldrich, 37% formaldehyde with 10-15% methanol as a stabilizer to prevent polymerization) diluted to 0.005% its original concentration. The diluted solvent, held in a flat 9.5"x13" tray, was placed on a scale to ensure a constant evaporation rate, observed to be an average of approximately  $10 \pm 1$  g/hr. The emission rate generated by the liquid solvent source was stable based on experimental results; however, concentrations generated using the vaporization method were high, approximately 300-400 ppb. Future experiments could involve optimizing the dilution to generate a lesser intensity emission source.



Once emission concentrations had stabilized within the chamber, the air cleaner filled with wool was added to the setup to begin filtration for the capacity experiment (Figure 12). The air cleaner vessel involved the modification of a personal air filtration device shell (Amaircare Airwash Whisper AWW200) by connecting a 100 L white diffuser container filled with ~550 g of wool to the unit. The fan located in the unit shell (green container) circulated air at approximately 120 cfm, or 200 m<sup>3</sup>/hr. Pressure losses through the operating unit, measured using the Energy Conservatory DG-500 Pressure Gauge, was approximately 10 ± 5 Pa. Unlike the PFR, which had only one inlet and outlet, the white diffuser container was perforated to draw in air along all its sides, which potentially resulted in increased mixing and decreased short-circuiting. However, fluid mechanics optimization for active filtration design was not considered in the scope of these experiments.

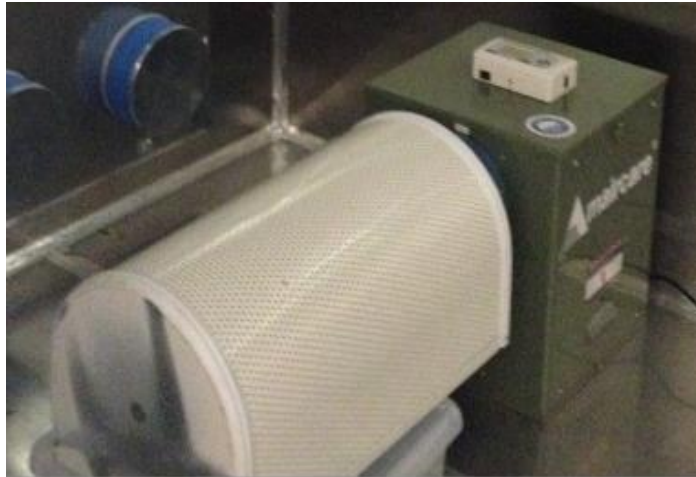


Figure 12: Modified air cleaner device

Once the air cleaner was turned on, the FMM measured the resulting reduced HCHO concentrations. Measurements continued after wool saturation occurred to ensure that starting source concentrations matched final source concentrations, showing that the source was constant throughout the capacity experiment and that the chamber was well-mixed at a stable air exchange rate.

### **3.3.2 NON-HEATED DESORPTION IN AIR CLEANER**

Desorption in the air cleaner was measured after eliminating the formaldehyde source and allowing chamber conditions to return to background levels. The air cleaner was turned off, and concentrations were measured in the chamber to determine whether desorption yielded elevated concentrations in typical room settings.

### 3.3 Mass Uptake Calculation

Mass uptake was measured by integrating over each time point for the reduction between the inlet source concentration and the effective filtration concentration, using Equation 5:

$$mass = \int_0^t Q(C_{source} - C_i)dt \quad (5)$$

where:

mass = mass uptake [ug]

Q = flow rate through the filtration unit [m3/hr]

$C_{source}$  = source concentration [ug/m3], assumed to be constant

$C_i$  = effective filtration concentration [ug/m3]

dt = 0.5 hr, for each 30-min sampling point

## 4 EXPERIMENTAL RESULTS AND DISCUSSION

### 4.1 Capacity Results

#### 4.1.1 PLUG FLOW REACTOR

The two plug flow reactor experiments yielded the same capacity; when the amount of wool placed in the plug flow reactor was doubled, the mass of formaldehyde captured also doubled. The capacity measured (see Equation 5) for both experiments in the plug flow reactor was  $110 \mu\text{g HCHO} / \text{g wool}$ : with  $545 \mu\text{g HCHO}$  sorbed in  $5 \text{ g wool}$  and  $1085 \mu\text{g HCHO}$  sorbed in  $10 \text{ g wool}$  (Figure 13).

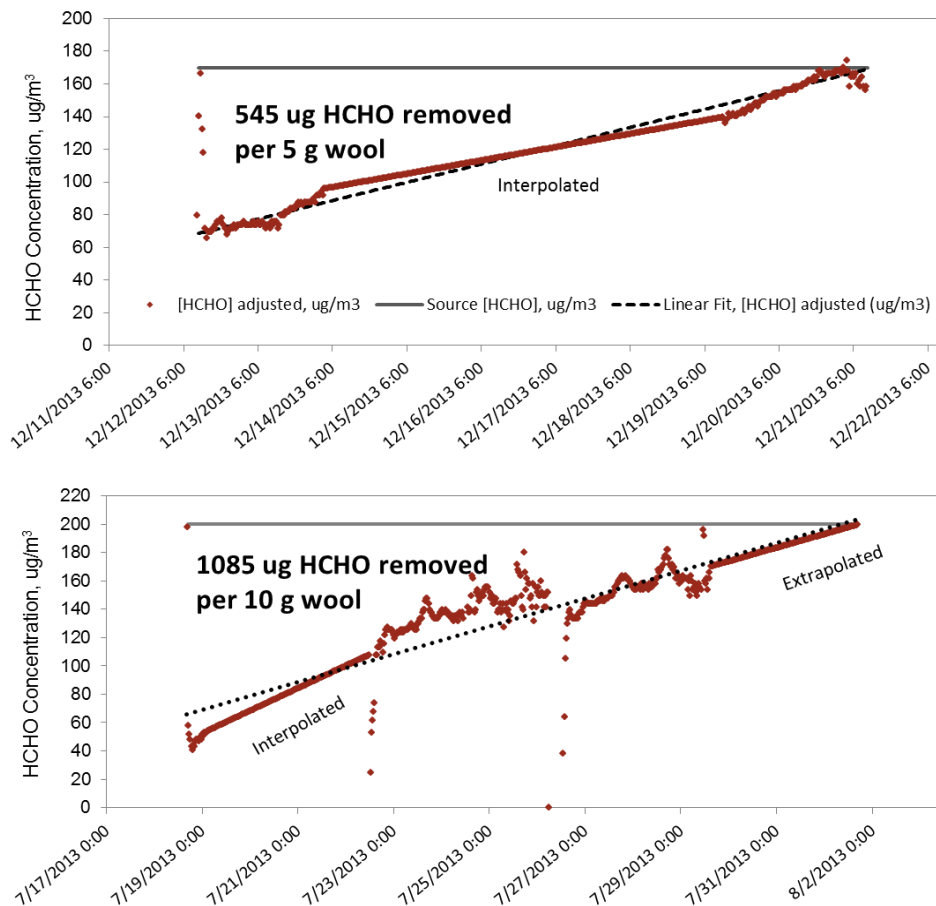


Figure 13: Capacity experiments in the plug flow reactor setup where: a) PFR filled with 5g of wool, and b) PFR filled with 10g wool

Breakthrough in the PFR lead to a gradual linear reduction in filtration efficiency as physi- and chemi-sorption sites were consumed. This result is evident from the gradual concentration rise over time.

#### 4.1.2 AIR CLEANER SETUP

The two capacity results measured in the air cleaner setup were approximately six times greater than observed in the PFR design – averaged to be approximately 670  $\mu\text{g}$  HCHO / g wool. Figure 14 below presents the experimental results from the first capacity test in the air cleaner. At the breakthrough point, the wool was calculated to be 90% saturated by taking the ratio between the mass uptake up to the breakthrough point when concentration began to rise and the overall mass uptake across the entire test. The brief concentration drop shown was likely due to a temporary mechanical error in the FMM.

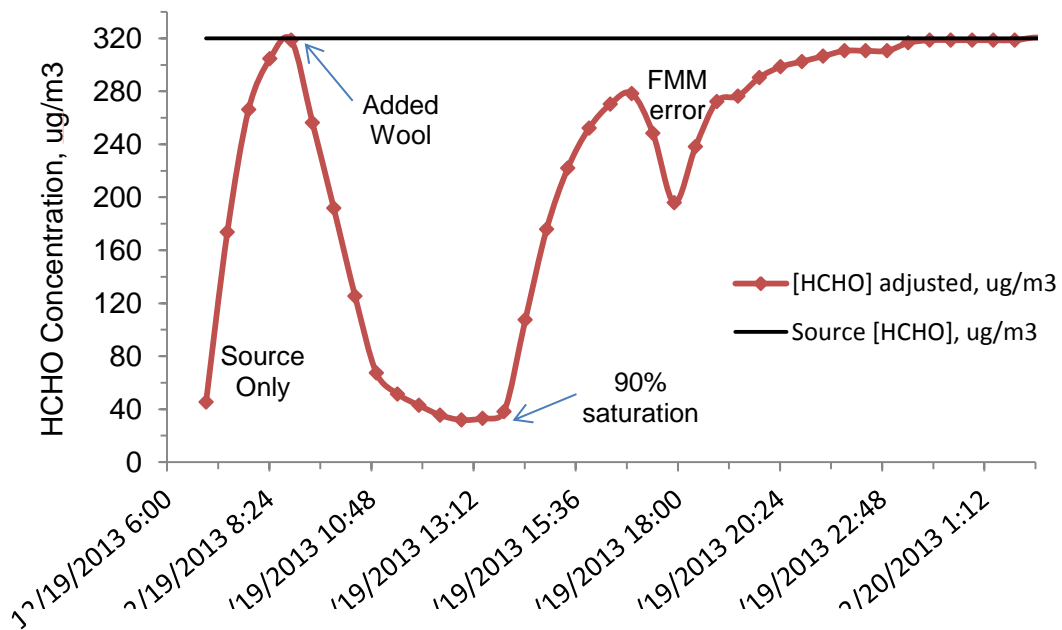


Figure 14: Experimental results in air cleaner placed in well-mixed CSTR environmental chamber - trial 1, breakthrough 1

The initial “source only” portion of the graph shows concentration rise over time once the constant source was placed in the room chamber. Once concentrations reached steady-state, the air cleaner containing wool was added to the system. Concentrations dropped and remained steady until the wool filter reached 90% of saturation, at which point breakthrough occurred and filter efficiency began to rapidly decrease. In this case, capacity was measured to be 700 µg HCHO / g wool.

The “source only” portion of the graph as well as the breakthrough curve were compared with model predictions of concentration increase over time given a room modeled as a well-mixed CSTR with a steady emission source using Equation 6:

$$C(t) = C_{t=0}e^{-\lambda t} + (C_0 + \frac{E}{\lambda V})(1 - e^{-\lambda t}) \quad (6)$$

where:

$C_{t=0}$  = initial concentration [ug/m<sup>3</sup>]

$\lambda$  = air exchange rate [hr<sup>-1</sup>]

$E$  = emission rate [ug/(m<sup>3</sup>-hr)]

$C_0$  = ambient concentration [ug/m<sup>3</sup>]

$V$  = room volume [m<sup>3</sup>]

Model results are presented in Figure 15.

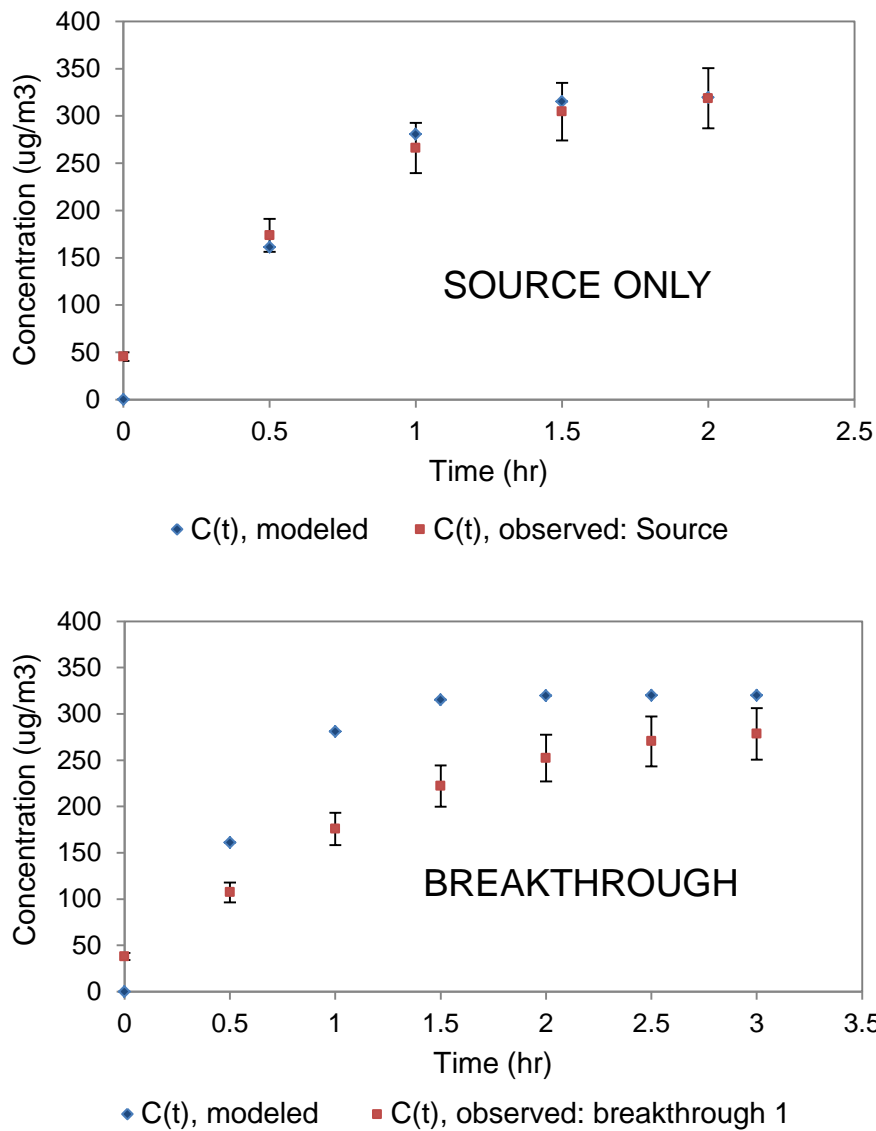


Figure 15: Observed vs. modeled concentrations when: a) only the source is present and b) when breakthrough occurs – trial 1, breakthrough 1

The source only experimental results corroborated well with the CSTR model at the following measured conditions:  $E = 6180 \text{ ug}/(\text{m}^3\text{-hr})$ ,  $\lambda = 1.4/\text{hr}$ ,  $C_0 = 0 \text{ ug}/\text{m}^3$ , and  $C_{t=0} = 0 \text{ ug}/\text{m}^3$ . This result demonstrated that the experimental room chamber was indeed

at well-mixed, CSTR conditions and could thus be modeled using the mass balance under these ideal assumptions.

The breakthrough experimental results were also modeled using the CSTR model. If breakthrough began to occur when the wool had reached complete saturation, filtration would no longer be occurring, and the experimental and modeled results should match as they do for the source only condition. However, because the observed concentrations were lower than the model predictions for a saturated filter/source only scenario, the results showed that there was still some filtration occurring at breakthrough. Thus, breakthrough does occur when the wool is nearing saturation rather than at full saturation, which corroborates the calculation from the mass uptake model that breakthrough occurs when the wool reaches approximately 90% saturation.



Figure 16 depicts a second capacity measurement in the air cleaner setup. The data collection in this scenario began once concentrations had already dropped to the effective filtration concentration. The observed result match the first case scenario, with breakthrough also occurring at approximately 90% saturation, determined in the same manner as the first experiment. In this case, the measured capacity was approximately 640  $\mu\text{g HCHO} / \text{g wool}$ . The applied CSTR model also confirmed that breakthrough began to occur while there was still some filtration occurring, albeit a minimal amount (Figure 17).

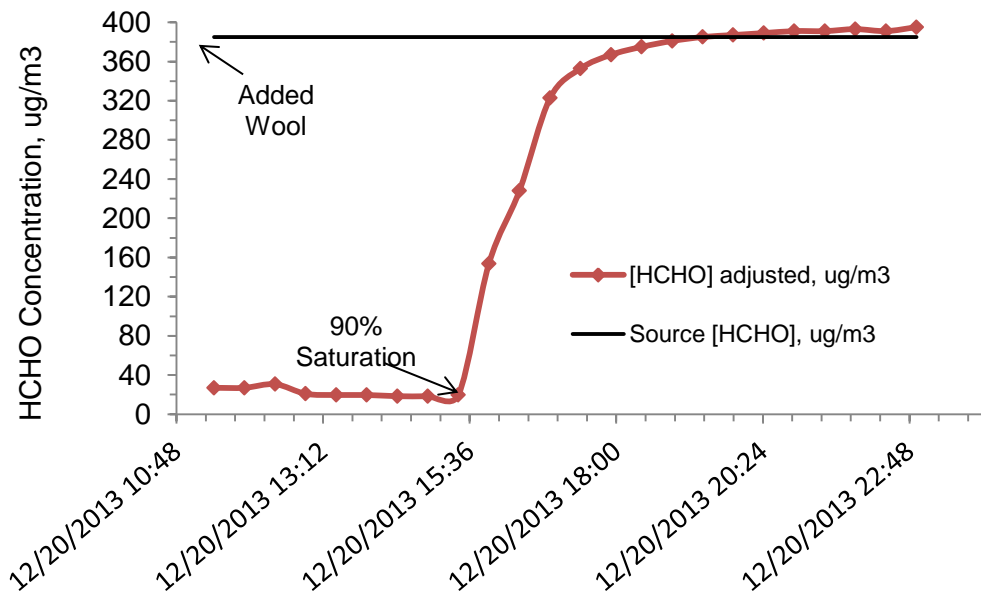


Figure 16: Capacity experimental results in air cleaner placed in well-mixed CSTR environmental chamber - trial 2, breakthrough 2

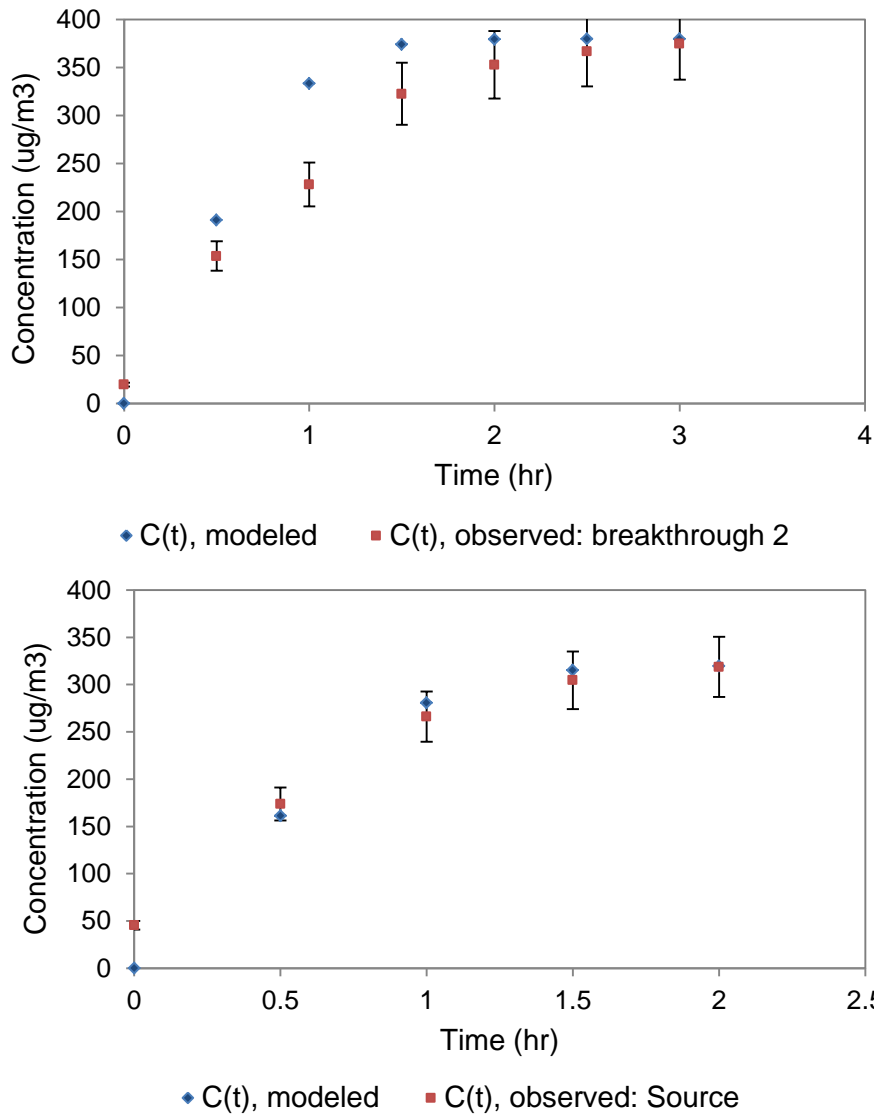


Figure 17: Observed vs. modeled concentrations when: a) only the source is present and b) when breakthrough occurs – trial 2, breakthrough 2

According to the capacity discrepancies between the plug flow reactor results and the air cleaner results, it appears that flow rate of air through the chamber or vessel, wool packing density, etc., and thus contact time with the wool, may have a significant impact

on sorption capacity. Thus, the “capacity” observed is not the absolute capacity of the wool, but rather a condition-specific capacity, or the amount of uptake that can be achieved under the given fluid mechanic circumstances.

#### 4.1.3 COMPARISON BETWEEN PFR AND CSTR RESULTS

Table 8 lists the experimental conditions for the three different setups, which may shed light on the differing capacity results. One hypothesis is that short-circuiting in the PFR may have limited the number of accessible reaction sites with which the formaldehyde air stream was making contact. The short-circuiting could be attributed to the wool in the PFR being packed 6-12 times more densely than the wool in the air cleaner and the air velocities in the PFR being ~6 times faster, increasing pressure drop across the bed and thus potential for short-circuiting.

Table 8: Experimental conditions for PFR vs. air cleaner

	<b>PFR Column – 5g</b>	<b>PFR Column – 10g</b>	<b>Air Cleaner Vessel</b>
<b>Volume</b>	150 mL	150 mL	100 L
<b>Flowrate</b>	815 mL/min	815 mL/min	120 cfm = 200 m <sup>3</sup> /hr
<b>Air Velocity</b>	1.3 m/s	1.3 m/s	0.2 m/s
<b>Residence Time</b>	11 seconds	11 seconds	1.8 seconds
<b>Mass of Wool</b>	5 grams	10 grams	550 grams
<b>Wool Density</b>	66 g/L	33 g/L	5.5 g/L

## **4.2 Desorption Results**

The degree of desorption was measured for the PFR filled with 10g of wool and 5g of wool in both heated and non-heated background conditions. The degree of desorption was experimentally measured for the air cleaner in non-heated background conditions.

### **4.2.1 PLUG FLOW REACTOR, FORCED DESORPTION UNDER HEATED CONDITIONS**

Using heated conditions to force formaldehyde desorption, the 10g of wool desorbed ~7% of the total mass of formaldehyde uptake into the wool, and the 5g of wool desorbed ~4% of the total mass of formaldehyde uptake into the wool (Figures 18 and 19). The amount of mass desorbed was measured by integrating between the observed concentration curve and an assumed 20 ppb background concentration using a similar process as described in Section 3.3. The 20 ppb background concentration is a conservative high-end estimate, as Figure 31 in Appendix A shows lab background concentrations typically fall between 10-15 ppb and do not exceed 20 ppb.

Full desorption occurred within 12 hours of heating for both scenarios, although the heating patterns fluctuated slightly due to experimental conditions. Concentrations spiked initially until full desorption occurred, at which point measured concentrations fell to background laboratory levels between 0-20 ppb while high temperatures were maintained. Concentrations never again rising above background levels even while wool temperatures remained elevated indicated that full desorption had occurred. Therefore,

heating wool to concentrations around 40°C is a quick, effective and feasible method to release the physically-sorbed portion of formaldehyde in a short period of time.

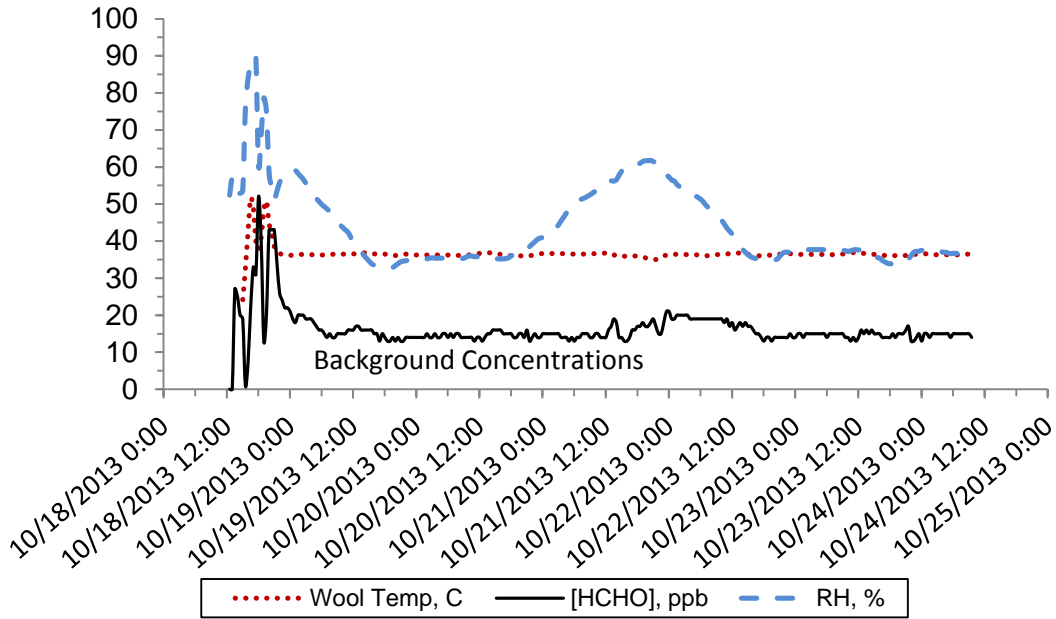


Figure 18: Heated desorption, 10g wool in PFR

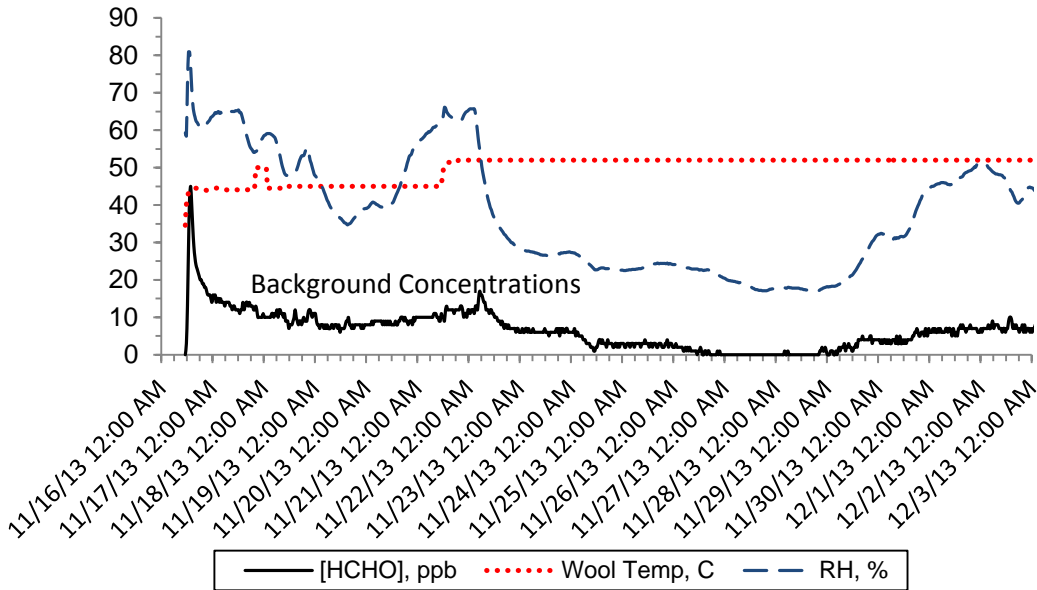


Figure 19: Heated desorption, 5g wool in PFR

#### 4.2.2 PLUG FLOW REACTOR, DESORPTION AT NON-HEATED, BACKGROUND CONDITIONS

Desorption at non-heated, background conditions for the PFRs filled with 10g and 5g of wool did not result in elevated concentrations above normal laboratory background levels (Figures 20 and 21) at steady room temperatures of  $23\pm 1^\circ\text{C}$ . The results show that in typical room conditions, the physically-sorbed portion of formaldehyde is not expected to desorb rapidly and thus does not elevate human exposure.

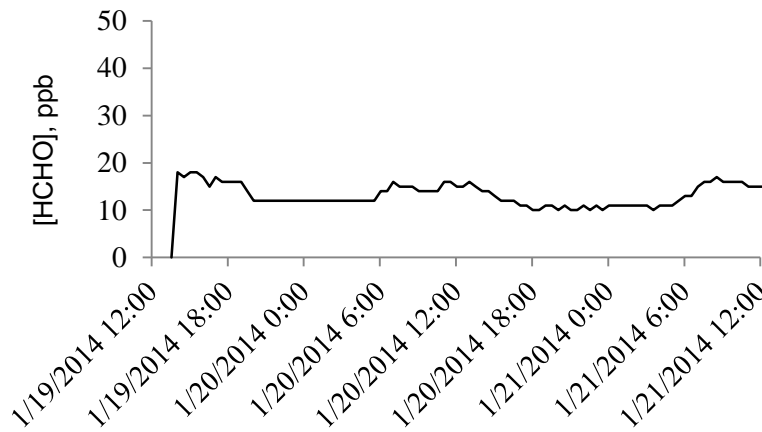


Figure 20: Non-heated desorption, 10g wool in PFR

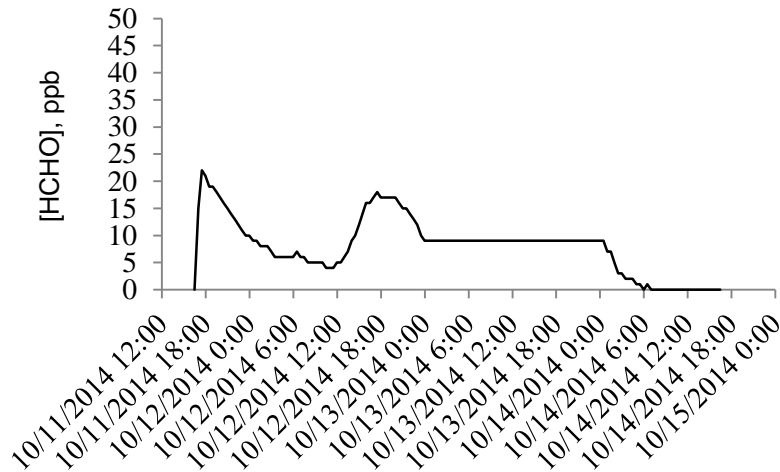


Figure 21: Non-heated desorption, 5g wool in PFR

### 4.2.3 AIR CLEANER, DESORPTION AT NON-HEATED, BACKGROUND CONDITIONS

Desorption at non-heated, background conditions for the air cleaner filled with 550 g of wool did not result in elevated concentrations above normal laboratory background levels (Figure 22) at steady room temperatures of  $23\pm 1^\circ\text{C}$ . The results show that under typical room conditions, the physically-sorbed portion of formaldehyde is not expected to desorb and thus does not elevate human exposure.

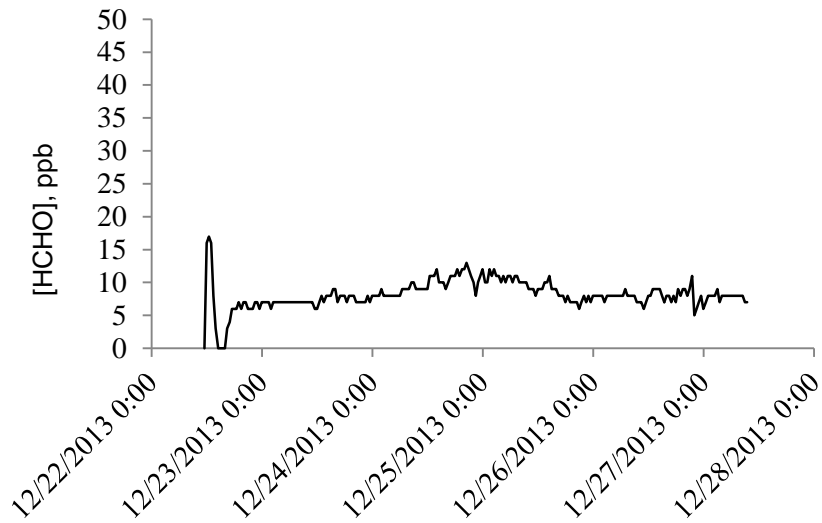


Figure 22: Non-heated desorption, 550 g wool in Air Cleaner

## 5 MODELING METHODOLOGY

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### 5.1 Filtration Model

Equation 7 is based on a mass balance for formaldehyde in a well-mixed room operating as a continuous stirred tank reactor (CSTR) with constant flow into and out of the system.

$$V \frac{dC}{dt} = QC_{in} - QC - Q_c \eta C + E - \beta C - \frac{dC}{dt} K_{eq} \frac{A}{V} - \sum k C C_j \quad (7)$$

where:

$V$	= chamber volume [m <sup>3</sup> ]
$\frac{dC}{dt}$	= change in HCHO concentration over time [ppb/hr]
$Q$	= airflow rate through the chamber [m <sup>3</sup> /hr]
$C$	= concentration of formaldehyde in the chamber [ppb]
$Q_c$	= airflow rate through the personal air filter [m <sup>3</sup> /hr]
$\eta$	= efficiency of personal air filter [--]
$E$	= source emission rate of formaldehyde in chamber [ppb*m <sup>3</sup> /hr]
$\beta C$	= removal due to heterogeneous surface deposition reactions [ppb*m <sup>3</sup> /hr]
$\frac{dC}{dt} K_{eq} \frac{A}{V}$	= removal due to sorption [ppb*m <sup>3</sup> /hr]
$\sum k C C_j$	= removal due to homogeneous reactions in the air [ppb*m <sup>3</sup> /hr]

Equations 8-10 describing the CSTR case with a constant emission source and filtration unit present is then derived assuming the following conditions:

- negligible heterogeneous surface deposition reactions
- negligible sorption onto the walls of the steel chamber and the air purifier vessel



- negligible homogeneous reactions in the air with other chemicals like ozone, hydroxyl radicals, nitrate radicals, etc., operating under the assumption that those concentrations should be relatively low in the environmental chamber

$$\frac{dC}{dt} = \lambda C_{in} - \lambda C - \frac{(CADR)*C}{V} + \frac{E}{V} \quad (8)$$

Assuming well-mixed, steady-state conditions:

$$0 = \lambda C_{in} - \lambda C - \frac{(CADR)*C}{V} + \frac{E}{V} \quad (9)$$

Solving for concentration at steady-state:

$$C_{ss} = \frac{\lambda C_{in} + \frac{E}{V}}{\lambda + \frac{(CADR)}{V}} \quad (10)$$

where the Clean Air Delivery Rate (CADR) [m<sup>3</sup>/hr] =  $Q_c * \eta$ .

For a typical particulate air filtration unit, the Clean Air Delivery Rate (CADR) is a function of both the filter efficiency and flow rate through the filtration unit. As particulate loading increases on the filter, the efficiency of the filter actually increases to a certain degree as there are fewer gaps for particles to pass through the unit. However, flow rate simultaneously decreases through the unit as the filter becomes increasingly obstructed. Thus, a fully clogged filter can be close to 100% efficient at removing all particles that pass through it, but if airflow through the unit is so obstructed that very few

particles have the opportunity to make contact with the filter unit, then the overall delivery rate of clean air is minimal.

In the case of a wool filtration unit, to remove formaldehyde as molecules that make contact with the wool's highly reactive amino acid surfaces, the chemical binding reaction that occurs does not alter the physical porosity of the wool in a degree that would noticeably reduce airflow rate. Therefore, the CADR of the wool filter is a direct function of the efficiency of the wool as a filter, or on a chemical level, when and how quickly the available amino acid reaction sites become consumed. When the mass fraction of saturation capacity reaches a certain point, eventually breakthrough begins to occur, where there are not enough reaction surfaces available for all the formaldehyde in a given airflow rate passing through the filtration unit to make contact with remaining sites. Based on the experimental results from the air filtration unit, the filtration efficiency remains effectively constant until saturation reaches approximately 90%, at which point breakthrough begins to occur and CADR drops proportionally with the remaining mass fraction of wool.

To determine the initial maximum CADR associated with a fresh wool filter where enough reaction sites remain to remove all formaldehyde passing through the system, the assumption is made that the initial concentration drop that occurs is maintained at a steady-state balance prior to breakthrough where wool filter efficiency begins to effectively depreciate.

Assuming ambient formaldehyde concentration is negligible relative to emissions, the steady-state source concentration with a filtration unit in operation during constant source emission is:

$$C_{ss,final} = \frac{E}{\left(\lambda + \frac{CADR}{V}\right) * V} \quad (11)$$

Equation 12 models the steady-state concentration from which the emission rate is determined. In this case where no air cleaner is present, the constant source emission rate is determined from the indoor formaldehyde source concentration prior to filtration.

$$C_{ss,initial} = \frac{E}{\lambda * V} \quad (12)$$

Taking the ratio of the initial steady-state formaldehyde concentration without a filter present (Equation 12) and the resulting initial steady-state source concentration with a filter present (Equation 11) yields a relationship between the concentration reduction and the Clean Air Delivery Rate (Equations 13, 14).

$$\frac{C_{ss,initial}}{C_{ss,final}} = \frac{\frac{E}{\lambda V}}{\frac{E}{\left(\lambda + \frac{CADR_{max}}{V}\right) * V}} \quad (13)$$

Rearranged to solve for CADR\_max:

$$CADR_{max} = \left[ \frac{C_{ss,initial}}{C_{ss,final}} - 1 \right] * \lambda V \quad (14)$$

The initial maximum CADR is determined by using observed experimental concentration decreases given a known emission rate (Equation 12). In the CSTR

scenario, the concentrations used to determine  $CADR_{max}$  were:  $C_{ss,initial} = 320 \text{ ug/m}^3$  as the steady-state emission concentration and  $C_{ss,final} = 40 \text{ ug/m}^3$  as the reduced concentration observed, which was assumed to be maintained at steady-state. The room volume was  $13.8 \text{ m}^3$ , and the ACH was 1.4/hr during these experimental conditions. This initial CADR value is calculated to be  $135 \text{ m}^3/\text{hr}$ . This value is then used in Equation 11 to determine the resulting concentration after filtration.

The initial CADR is maintained for each day until the filter reaches approximately 90% saturation, at which point the model assumes a reduction in CADR that is proportional to the remaining available sorption sites (Equation 15).

$$CADR_t = CADR_{t=0} \left( 1 - \frac{\Sigma mass_{HCHO, removed}}{mass_{HCHO, capacity}} \right) \quad (15)$$

The total mass capacity of the filter for formaldehyde depends on the size of the filter (in pounds) and the total capacity to sorb formaldehyde for that mass. The model was run using both the low-end capacity result ( $110 \text{ } \mu\text{g HCHO} / \text{g wool}$ ) as well as the high-end capacity result from the air cleaner unit ( $670 \text{ } \mu\text{g HCHO} / \text{g wool}$ ) to model results achievable given different filter densities, filtration rates, and filtration unit fluid mechanics.

The cumulative mass removed is determined by the concentration drop per day, the CADR for each time step (which is modeled as 1 day), and the amount of time the filtration unit is in operation per day, which allows adjustment of filtration for occupants that choose to reduce operating costs and operate the filter only during building occupancy hours (Equation 16).

$$\Sigma mass_{HCHO, removed} = CADR_t * \Delta C * t_{oper} \quad (16)$$

where:

CADR<sub>t</sub> = Clean Air Delivery Rate [m<sup>3</sup>/hr]

ΔC = Concentration reduction per time step [μg/m<sup>3</sup>]

t<sub>oper</sub> = Amount of time filter is in operation per day [hr]

Once the filter reaches 90% saturation, the remaining fraction of available reaction sites decreases, reducing the filter efficiency and CADR, which is calculated via Equation 15 per time step. Using the new CADR value for the current time step, the corresponding concentration that results is calculated using Equation 11. Iteration between Equations 15 and 11 occurs for each time step until the remaining 10% of the mass capacity is fully saturated and the saturation ratio of cumulative mass removed to total mass capacity = 1. The model determines the filter life given various input parameters to determine the number of filter changes required per year.

The iterations (described in Appendix B) varied the following parameters:

- Wool capacity:
  - Densely packed wool: 110 μg HCHO / g wool
  - Loosely packed wool: 670 μg HCHO / g wool
- Hours of operation per day: 24 hr, 12 hr, 8 hr
- Initial source concentrations used to determine the constant emission rate E:
  - 10 μg/m<sup>3</sup>, 20 μg/m<sup>3</sup>, 30 μg/m<sup>3</sup>, 40 μg/m<sup>3</sup>, 50 μg/m<sup>3</sup>, 60 μg/m<sup>3</sup>

- Filter replacement occurs at the 90% saturation point, when the concentration drop is no longer constant because CADR is substantially reduced.
- Air Exchange Rate (ACH) = 1/hr, 0.5/hr, 0.35/hr

The following parameters were assumed to be constant:

- Room volume = 50 m<sup>3</sup>
- Occupants per filtration unit = 4 people
- Filter Mass = 10 lb

At a constant CADR = 135 m<sup>3</sup>/hr and room volume = 50 m<sup>3</sup>, the concentrations during filtration varied depending on room air exchanges and initial indoor concentrations prior to filtration, which affected the extent of concentration reduction possible for each scenario. The post-filtration concentrations achievable are summarized in Table 9 below. All final concentrations post-filtration for a space with an air exchange of 1.0/hr meet the stringent CA OEHHA chronic exposure guideline of 9.0 µg/m<sup>3</sup>. The only cases that do not meet the CA OEHHA guideline are ACH=0.5/hr at 60 µg/m<sup>3</sup> and all ACH=0.35/hr cases above 40 µg/m<sup>3</sup>. However, every post-filtration concentration meets the second strictest emission limit guideline of 19.6 µg/m<sup>3</sup> set by NIOSH for a 40-hr workweek. (Section 2.1.3.1)

Table 9: Initial indoor concentrations prior to filtration and reduced indoor concentrations with filtration, given various air exchange rates

<b>ACH</b>	<b>Indoor Concentration, no filtration (<math>\mu\text{g}/\text{m}^3</math>)</b>	<b>Indoor Concentration, with filtration (<math>\mu\text{g}/\text{m}^3</math>)</b>
1	10	1.1
1	20	2.3
1	30	3.4
1	40	4.6
1	50	5.7
1	60	6.9
0.5	10	1.6
0.5	20	3.1
0.5	30	4.7
0.5	40	6.3
0.5	50	7.8
0.5	60	9.4
0.35	10	2.7
0.35	20	5.4
0.35	30	8.1
0.35	40	10.8
0.35	50	13.5
0.35	60	16.2

The model yields the number of filtration days achievable per filter prior to breakthrough at 90% saturation, when the indoor concentration sharply rises due to the filter rapidly losing efficiency and experiencing a drop in CADR, marking the point of filter replacement. The above parameters were varied for high and low wool capacity in 54 different iterations each to determine annual filtration cost for the cost-benefit analysis. An example iteration of a filtration model case scenario is presented in Tables 14 and 15 of Appendix B.

## 5.2 Cost-Benefit Analysis

A total of 324 cases were modeled for the cost-benefit analysis, with 54 different room scenarios (9 ACH + operation settings at 6 initial pre-filtration indoor concentrations) at 2 wool capacities for 3 population types (average population, children, and infants). The case descriptions and parameters are referenced in Appendix B.

### 5.2.1 TOTAL FILTRATION COST

Filtration cost was calculated on a yearly basis based on the number of filter unit replacements required and the total energy cost based on hours of operation per year. The market price for raw, unprocessed wool is currently \$6.60/kg (Oregon Shepherd, LLC – oregonshepherd.com), and each 4.5 kg filter costs \$30. Average power consumption for personal air filtration units is approximately 50 W (Amaircare – amaircare.com, Humanscale – humanscale.com), and the average residential retail prices of electricity in the US is \$0.1172/kWh (Energy Information Administration - EIA, 2011). Total Filter Costs were normalized for a population of 100,000 in order to compare with the DALYs metric per 100,000 people, assuming an occupancy of 4 users per filtration unit.

Total filtration cost (TFC) per year was calculated per 100,000 people (Equation 17):

$TFC = \text{Filter Cost} + \text{Energy Cost}$

$$TFC = \left[ \left[ \#Filters * Filter \$ \right] + \left[ P_{elec} * \frac{\$}{kWh} \right] \right] * \left[ \frac{100,000}{Occup.} \right] \quad (17)$$

where:

$TFC$  = Total filter costs or filtration costs per 100,000 persons per year [\$]



<i>#Filters</i>	=	Number of filter replacements required per year [--]
<i>Filter \$</i>	=	Cost per filter = \$10/filter [\$]
<i>P<sub>elec</sub></i>	=	Energy consumption per year running air cleaner [kWh]
	=	0.05 kW * hours operation / day * 365 days
<i>\$/kWh</i>	=	Electricity cost per kWh [\$/kWh] = \$0.1172/kWh
<i>Occup.</i>	=	Building occupancy [persons] = assumed to be 4 persons

### 5.2.2 FILTRATION BENEFIT

The monetary benefit derived from filtration is based on the DALYs saved for years of life lost associated with formaldehyde exposure concentration, assuming that the lowered effective filtration concentration remains constant at maximum filtration efficiency. The DALY model used for the benefit-cost analysis is explained in further detail in section 5.2.2. The dollar value assigned per DALY (year of life lost per 100,000 people per year) is taken from the literature (Lvovsky et al., 2000) and scaled for inflation and time value of money to 2014 dollars. This dollar value is then multiplied by the DALYs reduced after filtration to determine the overall benefit value of filtration.

An additional benefit utilized in the model is wool resale priced at \$4.40/kg. This resale value was assumed to be  $\frac{2}{3}$  the original wool buying price. Since filter saturation does not alter the physical properties of the wool, wool can be resold for use in textiles, insulation, furniture, etc. The \$4.40/kg resale value was assumed for the purposes of this model, deducting \$2.20/kg wool from the original wool value to account for transport, repackaging, and desorption costs of the physically-sorbed portion of formaldehyde.

## 5.3 Human Exposure Assessment

Based on formaldehyde concentration measurements in various indoor environments, a theoretical human exposure assessment was conducted for a range of hypothetical chronic indoor exposures based on empirical measurements from literature and typical environmental parameters observed. Two exposure metrics were used to quantify detriment to human life from formaldehyde exposure: Cancer Risk (CR) and Disability Adjusted Life Years (DALYs). DALYs were then used to determine the monetary benefit associated with reducing loss of life and incorporated into the cost-benefit analysis.

### 5.3.1. CALCULATING CANCER RISK

Cancer Risk designates the estimated number of cancer cases developed per year based on formaldehyde inhalation exposure in a typical residential environment. The oral ingestion route was deemed negligible and not included in the calculation. Cancer risk was calculated as follows in Equation 18:

$$CR = EC * IUR \quad (18)$$

where:

CR = cancer risk [number of individuals who develop cancer/1 million people]

EC = exposure concentration [ $\mu\text{g}/\text{m}^3$ ]

IUR = inhalation unit risk factor for cancer [number of excess cancer cases per million people per  $\mu\text{g}/\text{m}^3$  of exposure]

The inhalation unit risk factor (IUR) is a cancer potency value that describes the probability of cancer for a 70-year continuous exposure to  $1 \mu\text{g}/\text{m}^3$  of a given chemical, where 70 years represents the average adult lifetime (EPA, 2009). The IUR for formaldehyde is estimated by the CA OEHHA (2009) to be  $6 \times 10^{-6}$ , meaning that 6 excess cancer cases would be expected to develop for every 1 million people exposed constantly to a concentration of  $1 \mu\text{g}/\text{m}^3$  in air. Because the IUR assumes continuous exposure conditions for one's lifetime, it is important to note that the cancer risk derived represents an upper-bound measurement. Nevertheless, because the average person spends over 90% of their time indoors and over 70% in their residence (Klepeis et al., 2001), the upper-end cancer risk estimate may not be too far from actual exposure impacts specifically for indoor environmental exposures. Even so, the IUR is then scaled by the exposure concentration, which does account for overall lifetime exposure durations and adjusts the cancer risk to be representative of the environment in question.

The exposure concentration was calculated by scaling the observed air concentration by length of exposure (EPA, 2009), as shown in Equation 19:

$$EC = CA * \% \text{ Lifetime Exposure} = CA * ET * EF * ED / AT \quad (19)$$

where:

EC = exposure concentration [ $\mu\text{g}/\text{m}^3$ ]

CA = air concentration [ $\mu\text{g}/\text{m}^3$ ]

ET = exposure time [hours/day]

EF = exposure frequency [days/year]

ED = exposure duration [years]

AT = averaging time [days], # days across which exposure is averaged

For example, residential exposure accounting for 70% of the year across one's lifetime, which was assumed for this cancer risk model, results in the following relationship:

$$EC = CA * 0.70 \quad (20)$$

The cancer risk metric assumes that each unit of mass loading is equivalent regardless of exposure intensity (e.g. 25  $\mu\text{g}/\text{m}^3$  experienced for 2 hours is equivalent to 50  $\mu\text{g}/\text{m}^3$  experienced for 1 hour).

### **5.3.2. DISABILITY ADJUSTED LIFE YEARS (DALYS) CALCULATION**

Disability Adjusted Life Years (DALYs) serve as a metric for quantification of present-value health costs associated with years of life lost (YLL) from premature mortality and years of life lost from disability, disease and reduced health (YLD) (Logue et al., 2012; U.S. EPA, 2010). In other words, DALYs account for mortality and morbidity due to incremental exposure and mass intake of some chemical. DALYs are weighted for changes in life expectancy as a person ages and also for disease severity or degree of physical impairment (Murray, 1994).

For non-criteria pollutants like formaldehyde that do not have extensive human toxicity literature, the intake-DALY (ID) approach cited in Logue et al. (2012) was used to determine the health impact associated with exposure based on animal toxicity literature, from which cancer and noncancer potency values are derived (EPA, 2009; OEHHA, 2009). Huijbregts et al. (2005) calculated the DALYs lost per incidence of specific disease type from exposure to over 1,000 chemicals, deriving DALY factors that

describe the incremental change in DALYs per mass of chemical intake ( $\delta\text{DALY}/\delta\text{intake}$ ), or in other words, the incremental damage per mass of chemical inhaled by an individual across a given time frame. The DALYs calculated represent the number of years of life lost (YLL) amongst 100,000 people of a certain population type (infants, children, adults, or average population) across 1 year of exposure.

The ID approach modified from Logue et al. (2012) is presented in Equation 21. This modified version neglects the non-cancer DALY term because the incremental non-cancer mass intake-based DALY factor  $\left[\frac{\partial\text{DALYs}_{\text{non-cancer}}}{\partial\text{intake}}\right]_i$  is unknown for formaldehyde (Huijbregts et al., 2005).

$$\text{DALYs} = (\text{intake}) * \left[\frac{\partial\text{DALYs}}{\partial\text{intake}}\right]$$

$$\text{DALYs} = (C_i * V)(P)(\text{frac}_{\text{exp}}) * \left[\left[\frac{\partial\text{DALYs}_{\text{cancer}}}{\partial\text{intake}}\right]_i (\text{ADAF})\right] \quad (21)$$

where:

intake = annual pollutant intake of gaseous pollutant i per person in  $\left[\frac{\text{kg}}{\text{person-year}}\right]$

$C_i$  = exposure concentration of pollutant i  $\left[\frac{\text{kg}}{\text{m}^3}\right]$

$V$  = average air volume intake per person per year  $\left[\frac{\text{m}^3}{\text{person-year}}\right]$

$P$  = exposure population, typically 100,000 people for DALYs [people]

$\text{frac}_{\text{exp}}$  = fraction of year when exposure occurs [--]

$\left[\frac{\partial\text{DALYs}_{\text{cancer}}}{\partial\text{intake}}\right]_i$  = cancer intake factor for gaseous pollutant i  $\left[\frac{\text{year}}{\text{kg}}\right]$

ADAF = age dependent adjustment factor for cancer exposure [--]

For the DALYs calculation during filtration, the fraction of exposure and exposure concentration involved two sets of values because indoor exposure was assumed to account for only 70% of the day. Even if the filtration unit was operating 24 hrs/day, only 70% of that time would yield reduced DALYs. On the other hand, when the filter operated only 8 hr/day and 12 hr/day, the remainder of the time up to 70% of the day (16.8 hours) was considered to be at the original indoor source concentration prior to filtration. Therefore, total benefit was normalized out of the 70% exposure time to take into account the high and low concentrations that occurred when filtration hours of operation were < 70% occupancy duration. The effective exposure concentration was calculated and substituted for the values  $C_i * frac_{exp}$  in Equation 21.

The DALY value also accounts for differing impacts across differing populations, using an age-dependent adjustment factor (ADAF) and differing intake volumes based off varying breathing rates between age groups. The parameters used to calculate DALYs for various population types are presented in Table 10.

Table 10: DALYs parameters for various population types

Age (years)	Age Group	Air Intake (m <sup>3</sup> /day)	Intake Volume per year (m <sup>3</sup> )	ADAF	$\delta DALY_{scancer} / \delta Intake$ (95% CIs)
≤2	Infants	7	2,555	10	0.7600 (0.0292, 19.7600)
2-16	Children	13	4,745	3	0.7600 (0.0292, 19.7600)
≥16	Adults	15	5,475	1	0.7600 (0.0292, 19.7600)
Population Average	--	14.4	5,256	1.6	0.7600 (0.0292, 19.7600)

Source: Logue et al., 2012; Heijbregts et al., 2005

According to Logue et al. (2012), formaldehyde had the second highest DALYs lost out of an analysis of forty hazardous air pollutants: 46 years of life lost (95%

confidence interval of 0.2-14,000), an order of magnitude higher DALYs lost value than all the other chemicals assessed, and also a value higher than all the other chemicals' confidence interval upper bounds, except for ozone and acetaldehyde. It is important to note that this estimate was calculated using a relatively high concentration assumption for formaldehyde of  $69 \mu\text{g}/\text{m}^3$ .

However, for most homes, lifetime concentrations do not exist at such high continuous levels. The 2007 RIOPA residential concentration study for 234 U.S. homes reports a median concentration of  $20.1 \mu\text{g}/\text{m}^3$ , and the 1988 Shah and Singh study for 273 U.S. homes reports an average concentration of  $44 \mu\text{g}/\text{m}^3$ . The higher level used by Logue et al. is more representative of average concentrations measured in mobile trailers. Thus, for the filtration model used in this research, a range of concentrations from 10-60  $\mu\text{g}/\text{m}^3$  was used to represent a spectrum of most commonly observed concentrations in typical residential environments.

The goal of the DALYs benefit model was to predict the reduction in DALYs associated with the reduction in concentrations once filtration was implemented. Each DALY, or year of life lost, is associated with a monetary value estimated in literature, which is derived from the social and economic costs associated with a year of lost life but that represents one's willingness to pay to avoid a statistical premature death, rather than the actual valuation of a year of life. Using this method, Lvovsky et al. (2000) estimated that one DALY is equal to \$164,000 in year 2000 dollars (approximately \$271,700 in 2014 when adjusted for inflation). Although these monetary values are quantified on

subjective parameters, they are as of yet the most widely-accepted estimations in human exposure analysis.

In the cost-benefit model, the reduced DALYs and the associated reduction in cost of life lost yields a monetary benefit that was then added to wool resale value and compared with filter costs to determine whether given scenarios for differing room environments, filtration operating times, and population types were cost-effective to implement as active personal air filtration systems.



## 6 MODEL RESULTS AND DISCUSSION

The cost-benefit analysis of wool filtration applied in a 50m<sup>3</sup> room at varying air exchange rates, hours of operation, and indoor concentration yielded variable results for filtration cost-effectiveness. The cost-effective scenarios were heavily dependent upon the above room parameter factors, type of population exposed, wool resale value, and whether the wool exhibited higher or lower capacity. Figure 23 illustrates the benefit-cost ratios for all the modeled scenarios, where each point refers to a single model iteration at the specified parameter sets. Each point represents an initial indoor concentration prior to filtration (designated by x-axis), an air exchange rate (designated by color), and the hours of filter operation per day (designated by shape).

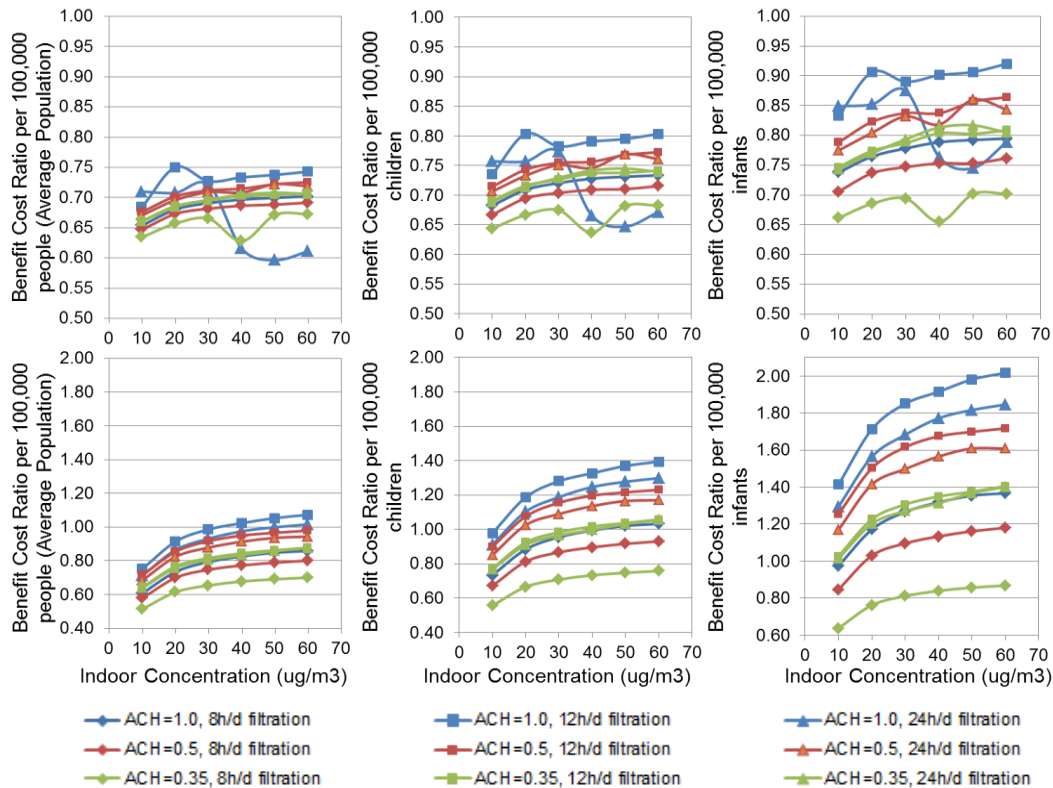


Figure 23: Annual cost-benefit values per 100,000 people (\$/year) for 54 case scenarios and three population types (average population, children, and infants). Top = low wool capacity. Bottom = high wool capacity

For the low capacity wool, filtration was never cost-effective, as none of the 54 iterations for any of the population types exceeded a benefit-cost ratio of 1.0. The B/C ratio is highly sensitive to the reduction in filter life at low wool capacity and higher concentrations. For example, when filter saturation occurred within 1 day, the associated incremental benefits from concentration reduction were minimal compared with the excessive costs required. The observed trend showed that above a certain concentration where filter life is drastically reduced, the B/C ratio may dip significantly, as was the case for the ACH=1.0, 8 h/d filtration scenario above concentrations of  $40 \mu\text{g}/\text{m}^3$ .

For the high capacity wool with approximately six times greater capacity, there were several cost-effective scenarios for average populations, but significantly more worthwhile cases for sensitive populations. For the average population, only the filtration scenarios for ACH=1.0 operating 12 h/d at initial indoor concentrations  $> 30 \mu\text{g}/\text{m}^3$  were cost-effective. For children, approximately half of the modeled cases were worthwhile. For infants, almost all of the modeled cases were worthwhile, with the exception of the case at the lowest air exchange rate and shortest filtration duration (ACH=0.35 operating 8h/d, for all concentrations  $10\text{-}60 \mu\text{g}/\text{m}^3$ ).

In general, the higher the air exchange rate, the higher the benefit-cost ratio. This result makes sense because higher ventilation enhances the rate that clean, ambient air is entering the room to dilute concentrations, which reduces filter burden and depletion. Another observed trend was that the B/C ratio increases across higher initial indoor source concentrations. This result is significant because it shows that even with higher filtration costs associated with having to reduce a larger concentration increment when

indoor concentrations are at higher levels, the associated monetary benefit offsets the greater filtration burden.

Filtration duration per day also was an important factor in terms of optimizing the B/C ratio. In this filtration model, it was assumed that occupants were present in a given room with filtration 70% of the day, or approximately 16.8 hours per day. Filtration operation varied between 24 h/d, 12 h/d, and 8 h/d. Operating a filter 24 hr/day, approximately 8 hours longer than the 70% of the time a person is indoors to be exposed to the chemical, yielded better cost-effectiveness than when the filter was only in operation 8 hr/day, approximately 8 hours shorter than the 70% of the time a person is exposed. In other words, it is not worthwhile to filter only part of the time that occupants are present. The results show that to optimize filtration cost-effectiveness, filtration should occur the entire time occupants are present. However, if a unit was accidentally left on 24 hr/day, the benefit derived from full filtration during occupancy still offsets the costs associated with excess filtration time for most of the room parameters. On the other hand, filtering only half the time while occupants are present exposes them to ~9 hours of elevated concentrations, in which case the minimal benefits achieved do not offset the costs.

Figure 24 shows that a drastic reduction in filter life leads to significant increases in cost. The steepness of cost primarily increases due to longer operation times per day, thus clustering the results into three sections. Sub-clusters within those sections also show that cost increases as air exchange decreases. Lower air exchange reduces the amount of fresh air that enters the space to flush out formaldehyde concentrations.

Therefore, in general, the higher the air exchange rate and the shorter the operation time, the longer the filter life and the lower the cost.

Filter life is also primarily influenced by operating time per day and secondarily by air exchange rate. Under the high capacity wool conditions, the 8 hour/day filtration scenarios are able to increase filter life to ~300-365 days/year at the lower end indoor source concentrations. However, shorter operating times yield minimal benefit because occupants are exposed to high concentrations when the filter is not in operation. Therefore, while the reduction of filtration time maximizes filter life and minimizes costs, these scenarios do not achieve the adequate benefit required for cost-effectiveness.

Filtration for 24 hours/day is significantly more costly. Although many of the 24 hour/day filtration cases for the high capacity scenario were cost-effective for sensitive populations, people may not be willing to pay \$600/year for filtration, especially when the monetary health benefits from reductions in chronic exposure and cancer risk are not immediately observable or tangible.

However, the optimal B/C ratio scenarios involving filtration at 12 hours/day (designated by square markers) yield filter life results that are reasonable compared to conventional air filter replacement. For example, at indoor source concentrations of  $40 \mu\text{g}/\text{m}^3$ , filter life lasts approximately 2 months with a total cost of ~\$200/year, and at indoor source concentrations of  $60 \mu\text{g}/\text{m}^3$ , filter life lasts approximately 1 month with a total cost of ~\$300/year. Therefore, although filter life drops exponentially with increasing concentrations, the aforementioned examples show that it is possible to achieve reasonable filter life and filtration costs given optimized filtration settings.

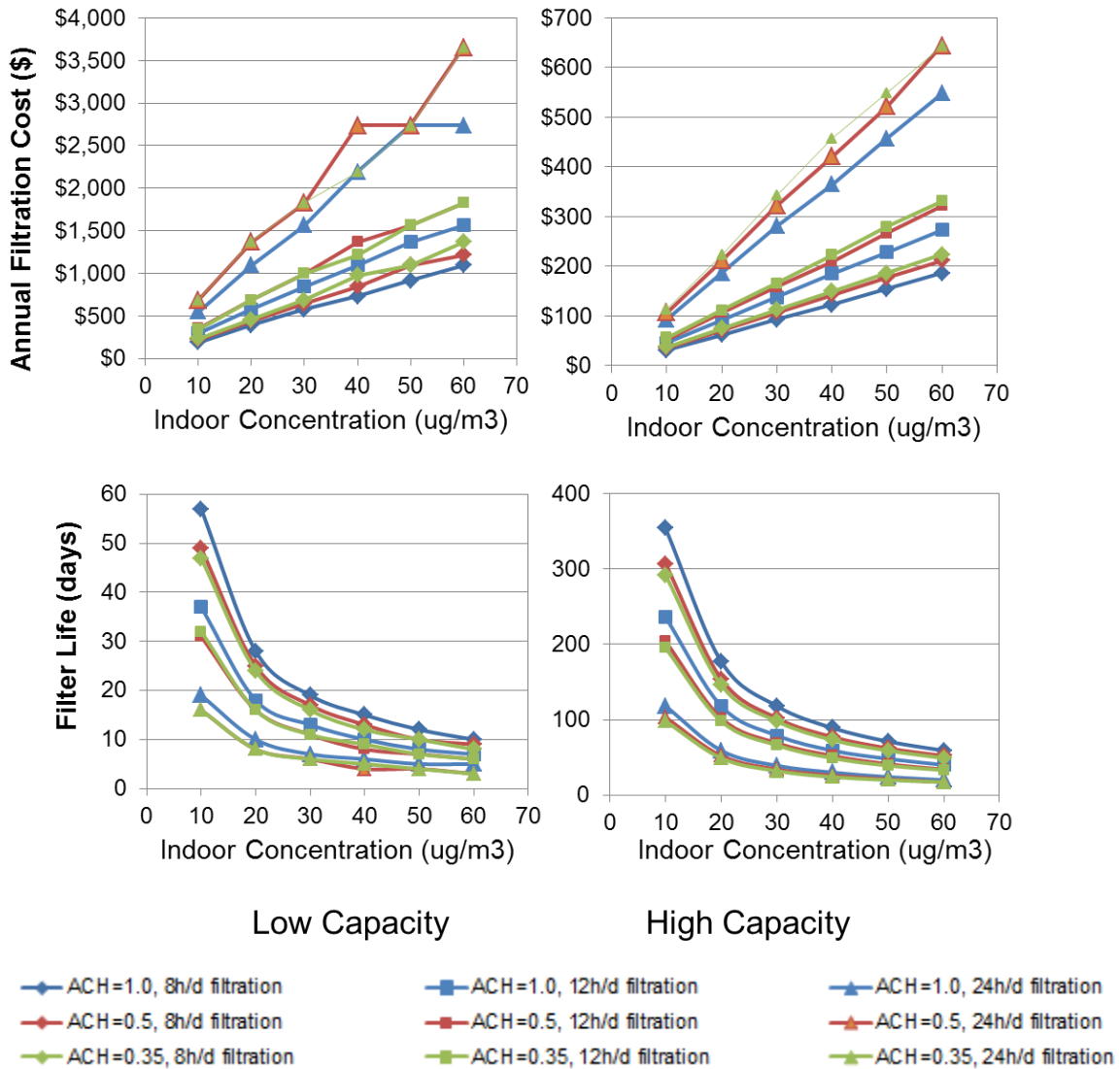


Figure 24: Annual filtration costs and filter life for 108 cases. Left = low wool capacity, Right = high wool capacity

Figure 25 shows the initial and final DALYs and Cancer Risks with no filtration as well as the reduced values given various filtration conditions. The higher the air exchange rate and the longer the filtration operation, the greater the reduction in years of

life lost. However, longer filtration operation increases costs associated with the number of filter changes required per year. The tradeoff that results determines whether the monetary benefits derived from the concentration reductions at longer filter operation are worth the additional incurred costs, noting that maximum benefit cannot exceed 70% exposure duration. For the DALYs or YLLs across various age groups, the severity of lives lost per 100,000 individuals of that population increases the more sensitive the population (i.e. the younger the age group). At the same time, the reduction in years of life lost also greatly improves with more sensitive populations. Overall, reduction in years of life lost increases with higher indoor source concentrations and operation time.

Cancer Risk (CR), although not included in the cost-benefit analysis, was another metric used in the overall population exposure analysis to measure the number of excess cancer cases that result per million people per year given a certain concentration and length of formaldehyde exposure. Overall, the general cancer risk trends and reductions regarding filtration time and source concentrations (Figure 25) align with the DALYs model.

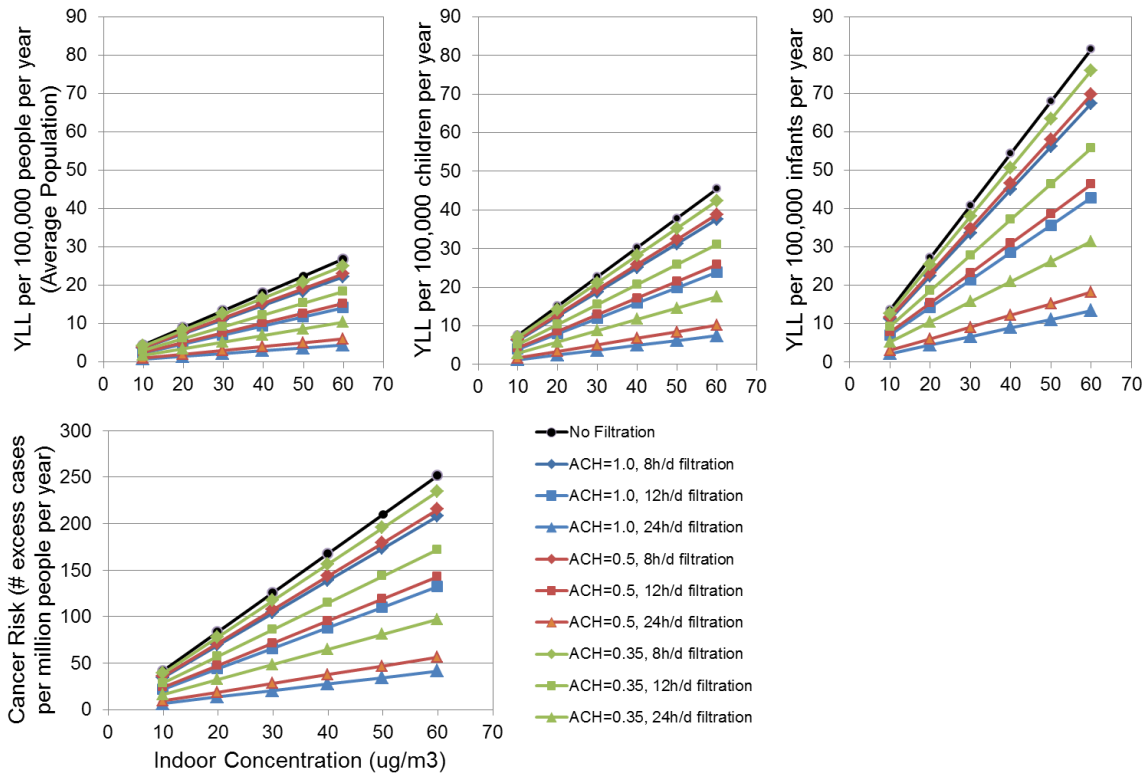


Figure 25: Original DALYs and cancer risk prefiltration & reduced DALYs and cancer risks postfiltration per population type

Table 11 displays the cancer risk results at various indoor concentrations prior to filtration and scales them for the entire U.S. population of 313.9 million people. At a chronic exposure concentration of 20  $\mu\text{g}/\text{m}^3$ , which is typical of the average residential setting, approximately 26,000 excess cancer cases in the United States are directly attributable to formaldehyde exposure. At a chronic exposure concentration of 60  $\mu\text{g}/\text{m}^3$ , which represents mid- to high-end exposure observed in mobile trailers and some highly emissive residences, approximately 79,000 excess cancer cases in the United States are directly attributable to formaldehyde exposure. For reference, Jemal et al. (2008) projected a total of 1.4 million cancer incidence cases in the United States. According to these conditional parameters, approximately 2-5% of cancer incidences in the United States are directly attributable to chronic formaldehyde exposure.

Table 11: Formaldehyde inhalation cancer risk, scaled for U.S. population

<b>Indoor Concentration, no filtration (<math>\mu\text{g}/\text{m}^3</math>)</b>	<b>Cancer Risk, no filtration (# cases / million people)</b>	<b>Cancer Risk, no filtration (# cases in US)</b>
10	42	1.3E+04
20	84	2.6E+04
30	126	4.0E+04
40	168	5.3E+04
50	210	6.6E+04
60	252	7.9E+04



## 7 CONCLUSION

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In active filtration systems, wool can effectively reduce formaldehyde concentrations between ~60-80%, depending on filtration fluid mechanics and room parameters. However, the effective capacity of the wool varies significantly depending on how airflow patterns through the filtration unit affect how formaldehyde in the air contacts reaction sites on wool. Design factors like wool packing density, degree of mixing in the unit, and intensity of air flowrate and velocity may influence whether short-circuiting occurs through the wool and thus what percentage of reaction sites are available for filtration. Therefore, the capacities observed for different filtration systems are not the absolute saturation capacities, but rather the effective capacities that can be achieved given the kinematic constraints.

Experimental results showed that the wool packed in the air cleaner yielded six times greater available capacity (670  $\mu\text{g}$  HCHO removed / g wool) than the wool packed in the PFR (110  $\mu\text{g}$  HCHO removed / g wool). Compared to a batch reactor study by Wortmann et al. (2005) which yielded a capacity of ~6400  $\mu\text{g}$  HCHO removed / g wool across 10 days, the wool in the air cleaner and PFR achieved ~10 times and ~60 times less wool capacity, respectively, than the wool in the sealed batch reactor.

The filtration efficiency of the wool is also dependent on the filtration fluid mechanics, as evidenced by breakthrough curves that yielded differing trends for the two filtration designs. In the plug flow setup, filtration efficiency gradually reduces as the available mass sites are taken up. However, in the air cleaner, filtration efficiency

remains at a maximum until ~90% of the available mass sites are taken up, at which point a rapid drop in efficiency occurs.

Because the filtration unit design and kinetics of airflow through the system greatly impact effective capacity, filtration efficiency, and thus effective filter life, future work may involve filtration optimization by investigating the ideal design settings to maximize the wool reaction sites available for filtration. In addition to optimizing wool filtration in personal air cleaners, it is also worthwhile to test the implementation of wool filtration in conventional HVAC systems. These future filtration optimization tests could also explore uptake efficiency at various temperature and relative humidity stresses.

A batch reactor design with no active airflow through the unit may also be used to determine the absolute saturation capacity of wool by eliminating the highly variable kinetic impacts that prevent full availability of wool reaction sites. This type of design would be more representative of passive filtration, where wool might be located directly in a room without any forced active airflow through it. Examples of passive filtration mechanisms include wool carpets, curtains, insulation, and mattresses and couches stuffed with wool instead of polyurethane foam. Passive filtration would eliminate the energy penalties associated with active filtration, although at the expense of filtration efficiency because air contact with the wool is not as rapid or extensive.

Overall, desorption of the physically-sorbed formaldehyde from the wool at typical room temperatures and relative humidity does not cause elevated concentrations (i.e. above background levels) of formaldehyde to be re-emitted. Forced desorption via heating the wool to above ~40°C is an effective mechanism to remove the physically

deposited portion of formaldehyde. Because this forced desorption process occurs rapidly and effectively (within half a day), it may feasibly be implemented for saturated wool filters, which would allow the wool to be recycled for reuse without concern of formaldehyde re-emission from the wool. The fact that wool has a resell value is crucial for offsetting filtration costs in the cost-benefit analysis. If wool were not resold post-filtration, the monetary health benefits alone would be insufficient to make wool filtration cost-effective in the technical sense.

Overall, the cost-benefit analysis showed that wool filtration yielded significant benefits in the reduction of morbidity and mortality for sensitive populations like children and infants. Nevertheless, in reality, the cumulative monetary health benefits derived across a lifetime of reduced chronic exposures are not as tangible as yearly filtration costs. An individual's willingness to pay for filtration may depend on personal sensitivity to formaldehyde and/or whether the concern for sensitive occupants is worth a few hundred dollars of annual investment. If so, future pilot studies could consider implementing wool filtration in settings like nurseries, hospitals, and schools where high percentages of sensitive populations are present.

## Appendix A: QA/QC

Appendix A provides additional background on the QA/QC tests conducted as well as on the Shinyei FMM continuous formaldehyde sampling technology.

The following quality assurance/quality control (QA/QC) experiments were conducted:

- 1) calibrating the FMM measurements against the established EPA TO-11a DNP + HPLC standard protocol for formaldehyde sampling
- 2) validating FMM precision chamber measurements by:
  - a. collocating different monitors
  - b. comparing source chamber and sampling chamber concentrations
  - c. testing background measurements

### SHINYEI FMM

Because the Shinyei Formaldehyde Multimode Monitor (FMM) continuous emission monitoring device is a novel sampling technology (Carter et al., 2013), it was especially important in this research to conduct a series of thorough QA/QC analyses in order to generate reliable, trustworthy measurements. The Shinyei FMM uses colorimetric passive sampling to determine 30-minute time averaged concentrations of formaldehyde uptake.

This passive sampling system measures a colorimetric change in absorbance across a sensor assay coated with  $\beta$ -diketone on a porous glass surface. As formaldehyde

reacts with the  $\beta$ -diketone, it forms a lutidine derivative that generates a yellow dye on the glass surface that darkens proportionally to formaldehyde concentration. Over each 30-minute exposure duration, the FMM measures relative changes in absorbance at a wavelength of 410nm corresponding to formaldehyde derivative mass increases. Each sensor typically has a sampling life of ~200 ppb across a 24 hour period before maximum absorbance changes have been observed and the sensor reaches saturation. (Shinyei Technology, 2011; Maruo et al., 2007)

The benefit of this monitoring system is that it allows the observation of time series concentration variations across 30-minute averages with a relatively wide detection range from 20-1000 ppb (Maruo et al., 2007). In contrast, the traditional formaldehyde measurement technique, DNPH sorbent tube sampling, while the most accurate and trusted method by the EPA, requires a minimum mass loading for detection that results in longer exposure durations on the order of several hours and therefore lesser ability to observe temporal fluctuations. For the purposes of this study, which was developed to observe relatively rapid changes in concentration, use of the FMM measurement device was optimal. However, it was important to adjust FMM concentrations to the calibration curve generated because at higher concentrations above ~60 ppb, the FMM underreported actual formaldehyde concentrations, as represented by the DNPH concentrations.

#### **DNPH VS. FMM CALIBRATION**

According to U.S. EPA Compendium TO-11a, DNPH measurements are considered the highest accuracy standard measurement protocol to observe formaldehyde

concentrations. To utilize the FMM measurements, quality assurance/quality control testing was conducted to calibrate the FMM measurements against the DNPH measurements for accuracy and precision.

Previous researchers had conducted congruent DNPH/FMM measurements for concentrations up to 50-60 ppb, categorizing calibration curves that showed approximately a 1:1 relationship between the two sampling techniques, given the +/- 10% error provided via the Shinyei FMM manufacturer specifications and +/- 7.5% error provided via the Bureau Veritas Laboratory high-performance liquid chromatography (HPLC) analysis for the DNPH sampling technique. Figure 26 shows calibration curves conducted by Nirlo et al. (in progress) and Carter et al., 2013. In both cases, the FMMs slightly underreported formaldehyde concentrations but remained within the 1:1 relationship given error bounds.

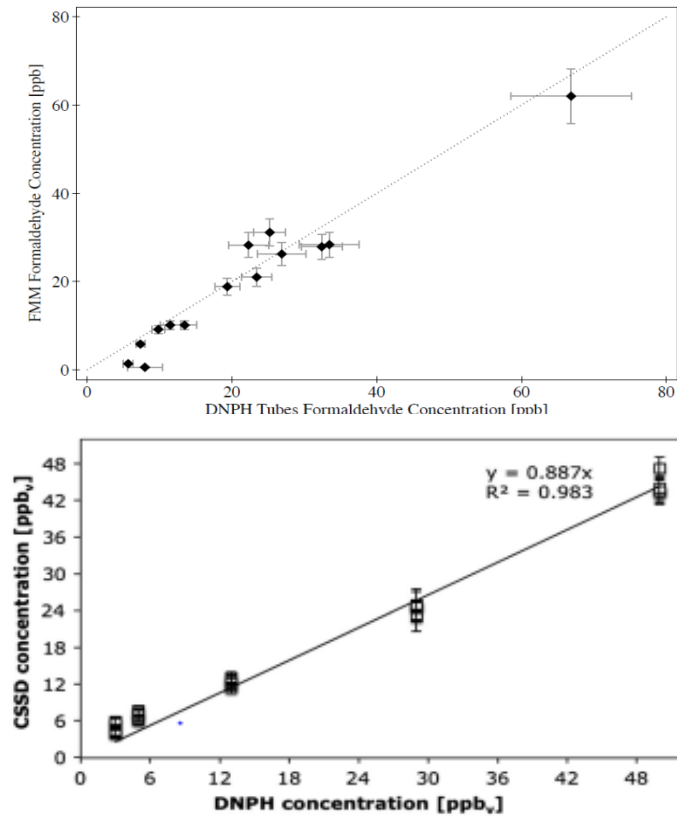


Figure 26: FMM v. DNP calibration curves 0-60 ppb (Nirlo et al. (i.p.); Carter et al., 2013)

However, for the purposes of the capacity experiments, which utilized concentrations in a higher range, a new calibration curve had to be determined for concentrations above 60 ppb to test how closely the FMM was measuring actual concentrations, as represented by the DNP measurements. Simultaneous measurements were taken using the DNP and FMM sampling methods described in Section 3.1 for a variety of source concentrations spanning 0-180 ppb. Several HPLC extractions were conducted by the Bureau Veritas lab, and several extractions were self-conducted according to the EPA TO-11a protocol. Table 12 presents a summary of the calibration

data, and Figure 27 plots the dataset with  $\pm 10\%$  error bars for the FMM data and  $\pm 7.5\%$  error bars for the DNPH+HPLC data in order to generate a calibration curve for the FMM measurements.

Table 12: DNPH v. FMM concentrations for various sources

Source Material in Steel Chamber	HPLC extraction	[DNPH], ppb	[FMM], ppb
Two 12"x12" MDF (replicate)	Mine	158	116
Two 12"x12" MDF (replicate)	Mine	177	116
Two 12"x12" MDF	Lab	180	125
One 12"x12" MDF (replicate)	Lab	74	56
One 12"x12" MDF (replicate)	Mine	75	56
One 12"x12" + One 4"x4" MDF (replicate)	Lab	110	72.4
One 12"x12" + One 4"x4" MDF (replicate)	Lab	120	72.4
Three 6"x6" MDF	Lab	150	89.25
Two 6"x6" MDF	Mine	87	60
One 6"x6" MDF	Lab	51	44
One 4"x4" MDF	Lab	21	32
Field Blank	Mine	0	BG

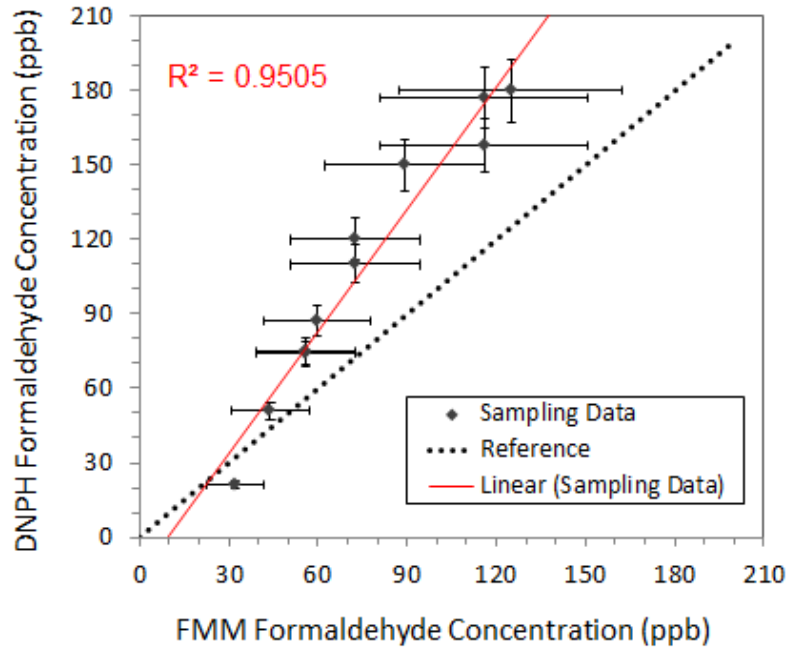


Figure 27: FMM v. DNPH calibration curve for  $[HCHO] > 60$  ppb



Running a linear regression analysis on the data, a positive correlation was determined between the DNPH concentration measurements and the FMM concentration measurements, with a value of  $R^2 = 0.9505$  and a p-value of  $3.54E-07$ . These results demonstrate a significant relationship between the sampling mechanisms; however, the relationship deviates from the reference 1:1 relationship in a higher concentration range.

The linear relationship generated was used to determine a calibration equation for concentrations above 60 ppb:  $[DNPH] = 1.6417*[FMM] - 15.863$ . For concentrations below 60 ppb, the reference 1:1 relationship was used because previous researchers had conducted extensive data sampling in those regions, whereas the above calibration curve only includes two data points lying below 60 ppb.

### **FMM QA/QC**

To test the precision of the FMM monitors, two monitors were collocated, or placed side by side within a 48 L stainless steel chamber filled with MDF as a formaldehyde source. Figure 28 shows that the concentrations measured by two different FMM monitors were equivalent, which shows that there are no discrepancies between different units.

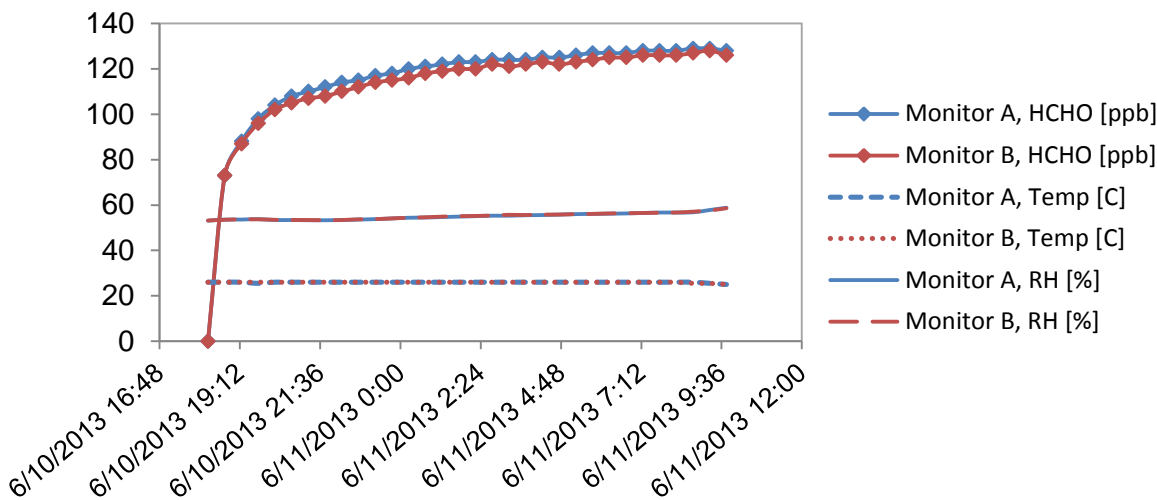


Figure 28: Collocated monitors in source chamber

Another important test was to determine the accuracy of measurements between the source chamber and sampling chamber. One FMM was placed in the 48 L chamber, and one monitor was placed in the sampling chamber. Figure 29 shows the comparison during the presence of a source, and Figure 30 shows the comparison at background levels. Both experiments showed that the two devices in separate chambers measured within the 10% error reported by the manufacturer.

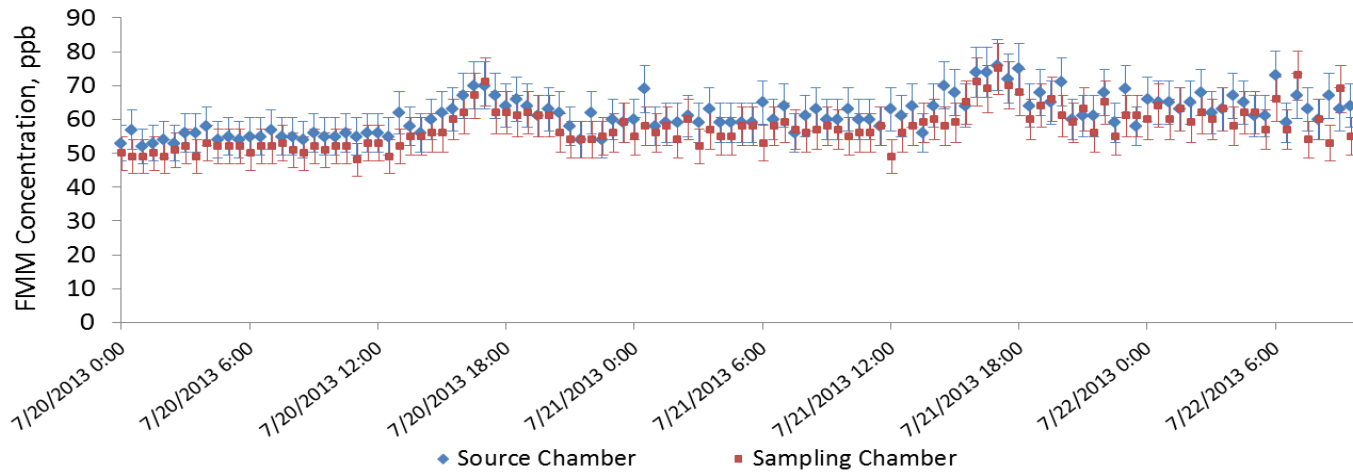


Figure 29: Concentrations measured in source chamber v. sampling chamber, source present

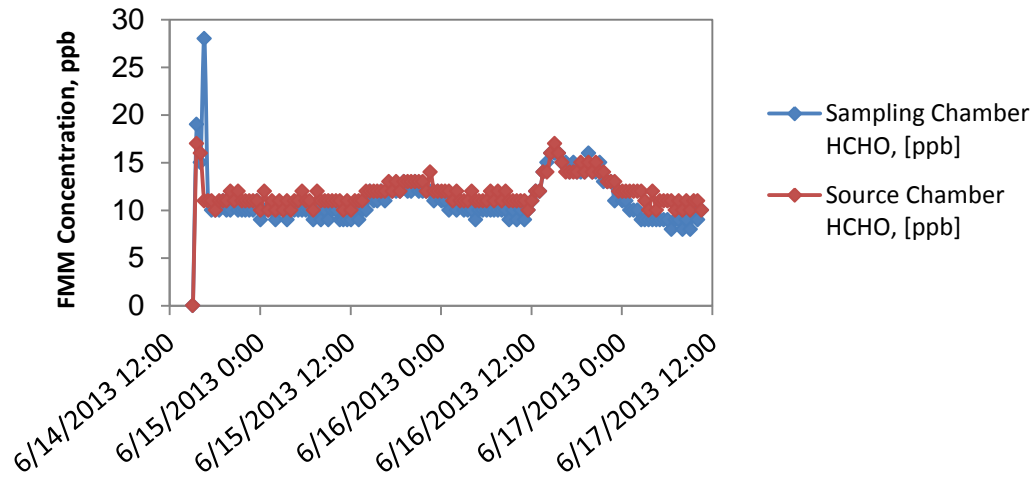


Figure 30: Concentrations measured in source chamber v. sampling chamber, no source present

### LABORATORY BACKGROUND CONCENTRATIONS

Background chamber concentrations were measured continuously across a two-week time frame, showing that concentrations averaged around 14 ppb and never exceeded 20 ppb, even with slight fluctuations with diurnal changes in relative humidity (Figure 31).

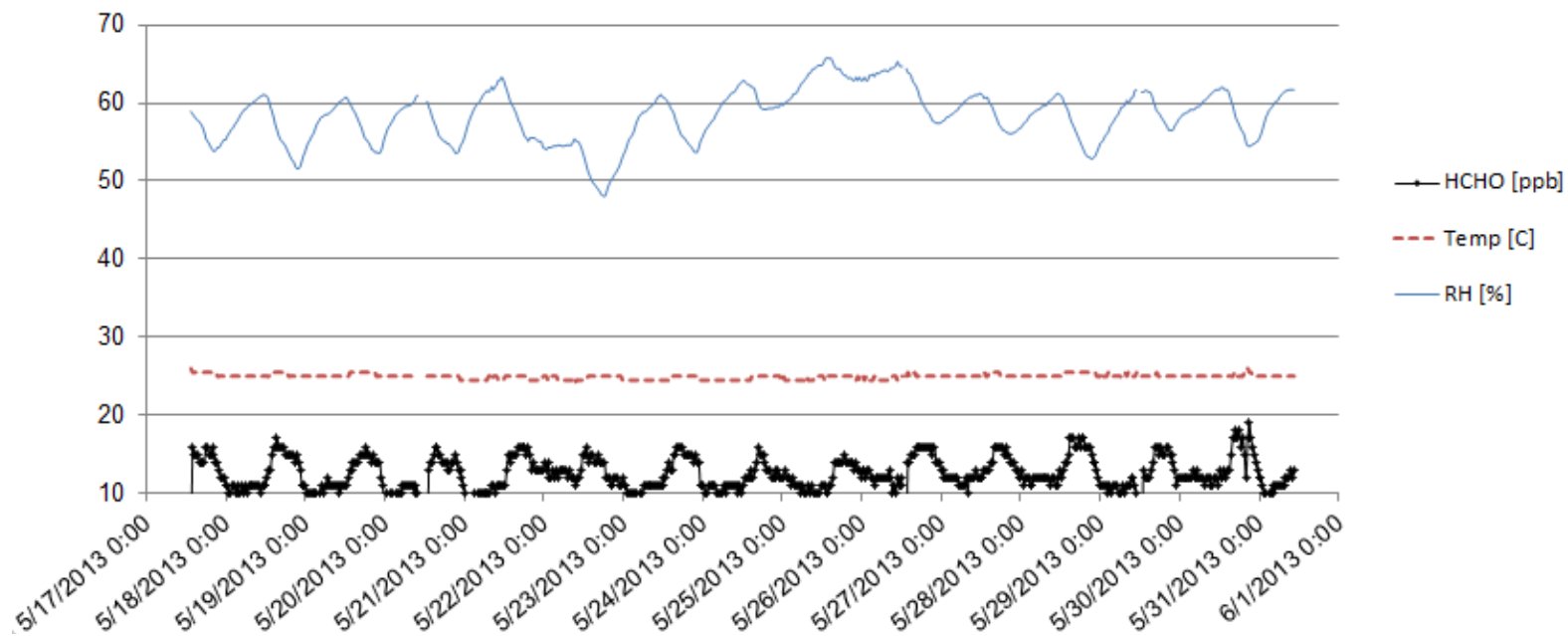


Figure 31: Background concentrations measured in 48 L steel chambers

## Appendix B: Model Iterations

Table 13: Summary of case scenarios

<b>Case</b>	<b>Filter Mass (lb)</b>	<b>Hours of Operation per day (hr)</b>	<b>ACH</b>	<b>Indoor Conc, no filtration (ug/m3)</b>	<b>Indoor Conc, w/ filtration (ug/m3)</b>	<b>Concentration Reduced (ug/m3)</b>
1	10	8	1.0	10	1.1	8.9
2	10	8	1.0	20	2.3	17.7
3	10	8	1.0	30	3.4	26.6
4	10	8	1.0	40	4.6	35.4
5	10	8	1.0	50	5.7	44.3
6	10	8	1.0	60	6.9	53.1
7	10	12	1.0	10	1.1	8.9
8	10	12	1.0	20	2.3	17.7
9	10	12	1.0	30	3.4	26.6
10	10	12	1.0	40	4.6	35.4
11	10	12	1.0	50	5.7	44.3
12	10	12	1.0	60	6.9	53.1
13	10	24	1.0	10	1.1	8.9
14	10	24	1.0	20	2.3	17.7
15	10	24	1.0	30	3.4	26.6
16	10	24	1.0	40	4.6	35.4
17	10	24	1.0	50	5.7	44.3
18	10	24	1.0	60	6.9	53.1
19	10	8	0.5	10	1.6	8.4
20	10	8	0.5	20	3.1	16.9
21	10	8	0.5	30	4.7	25.3
22	10	8	0.5	40	6.3	33.7
23	10	8	0.5	50	7.8	42.2
24	10	8	0.5	60	9.4	50.6
25	10	12	0.5	10	1.6	8.4
26	10	12	0.5	20	3.1	16.9
27	10	12	0.5	30	4.7	25.3
28	10	12	0.5	40	6.3	33.7
29	10	12	0.5	50	7.8	42.2
30	10	12	0.5	60	9.4	50.6

31	10	24	0.5	10	1.6	8.4
32	10	24	0.5	20	3.1	16.9
33	10	24	0.5	30	4.7	25.3
34	10	24	0.5	40	6.3	33.7
35	10	24	0.5	50	7.8	42.2
36	10	24	0.5	60	9.4	50.6
37	10	8	0.35	10	2.7	7.3
38	10	8	0.35	20	5.4	14.6
39	10	8	0.35	30	8.1	21.9
40	10	8	0.35	40	10.8	29.2
41	10	8	0.35	50	13.5	36.5
42	10	8	0.35	60	16.2	43.8
43	10	12	0.35	10	2.7	7.3
44	10	12	0.35	20	5.4	14.6
45	10	12	0.35	30	8.1	21.9
46	10	12	0.35	40	10.8	29.2
47	10	12	0.35	50	13.5	36.5
48	10	12	0.35	60	16.2	43.8
49	10	24	0.35	10	2.7	7.3
50	10	24	0.35	20	5.4	14.6
51	10	24	0.35	30	8.1	21.9
52	10	24	0.35	40	10.8	29.2
53	10	24	0.35	50	13.5	36.5
54	10	24	0.35	60	16.2	43.8

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Table 14: Example filtration model for parameters provided in Table 15

Day	Conc C (ug/m3)	Concentration Reduction ΔC (ug/m3)	CADR(t ) (m3/hr)	Mass Removed per day (ug) = CADR <sub>(t-1)</sub> * ΔC * #hrs operation/day	ΣMass HCHO removed (ug)	Total Mass Capacity (ug)	$\left( \frac{\Sigma mass_{HCHO, removed}}{Total\ mass_{HCHO, capacity}} \right)$
0	60.0	0.0	135	0.0E+00	0.0E+00	3.1E+06	0.0000
1	6.9	53.1	135	1.7E+05	1.7E+05	3.1E+06	0.0556
2	6.9	53.1	135	1.7E+05	3.4E+05	3.1E+06	0.1111
3	6.9	53.1	135	1.7E+05	5.2E+05	3.1E+06	0.1667
4	6.9	53.1	135	1.7E+05	6.9E+05	3.1E+06	0.2222
5	6.9	53.1	135	1.7E+05	8.6E+05	3.1E+06	0.2777
6	6.9	53.1	135	1.7E+05	1.0E+06	3.1E+06	0.3332
7	6.9	53.1	135	1.7E+05	1.2E+06	3.1E+06	0.3887
8	6.9	53.1	135	1.7E+05	1.4E+06	3.1E+06	0.4442
9	6.9	53.1	135	1.7E+05	1.5E+06	3.1E+06	0.4997
10	6.9	53.1	135	1.7E+05	1.7E+06	3.1E+06	0.5552
11	6.9	53.1	135	1.7E+05	1.9E+06	3.1E+06	0.6108
12	6.9	53.1	135	1.7E+05	2.1E+06	3.1E+06	0.6663
13	6.9	53.1	135	1.7E+05	2.2E+06	3.1E+06	0.7218
14	6.9	53.1	135	1.7E+05	2.4E+06	3.1E+06	0.7773
15	6.9	53.1	135	1.7E+05	2.6E+06	3.1E+06	0.8328
16	6.9	53.1	15	1.7E+05	2.8E+06	3.1E+06	0.8883
17	32.2	27.8	15	1.0E+04	2.8E+06	3.1E+06	0.8916
18	32.6	27.4	14	9.6E+03	2.8E+06	3.1E+06	0.8947
19	33.1	26.9	14	9.2E+03	2.8E+06	3.1E+06	0.8976
20	33.5	26.5	13	8.8E+03	2.8E+06	3.1E+06	0.9005

Table 15: Example parameters for filtration case modeled in Table 14

Parameters		
Mass Capacity	3.1E+05	ug HCHO/lb wool
Mass Wool	10	lb
C_init = C_max	60.0	ug/m3
E = C_start*λ*V	1050	ug/(m3-hr)
Q	17.5	m3/hr
V	50	m3
λ	0.35	/hr
Qc	200	m3/hr
# hrs operation/day	24	hr
Css,i_exp_CADR	320	ug/m3
Css,f_exp_CADR	40	ug/m3
V_exp_CADR	13.8	m3
λ_exp_CADR	1.4	/hr
Cost		
Power Consumption	50	W
Annual Energy Usage	438	kWh/yr
Energy Cost	0.1172	\$/kWh
<b>Total Energy Cost</b>	51	\$/yr
Filter Unit Cost	3	\$/lb
Cost/Filter	30	\$
Filter Replacement Conc	9	ug/m3
#Days/Filter	16.0	days/filter
#Filters/yr	22.8	filters/yr
<b>Total Filter Cost</b>	684.38	\$/yr
<b>Total Cost</b>	<b>736</b>	<b>\$/yr</b>



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