CPSC Staff Preliminary Evaluation
of Drywall Chamber Test Results
Reactive Sulfur Gases[1]

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Executive Summary

U.S. Consumer Product Safety Commission (CPSC) staff contracted with Lawrence Berkeley National Laboratory (LBNL) for measurement of chemical emissions from 30 samples of drywall products obtained as part of an investigation of imported (Chinese) drywall. In this report, non-Chinese drywall is referred to as North American or NA.

The objectives of this preliminary evaluation are to:

(1) Evaluate chemical emissions from Chinese drywall and from drywall from other sources

(2) Identify the possible differences in chemical emissions between the two sources of drywall products

(3) Evaluate the possible chemical exposures in homes that contain either of these two sources of drywall.

The LBNL data contained measures for the following reactive sulfur compounds - hydrogen sulfide, sulfur dioxide, carbon disulfide, methyl mercaptan, dimethyl sulfide, and carbonyl sulfide.

CPSC staff used the LBNL reported emission rates in a mathematical model to estimate the concentrations of the chemicals in the indoor air of a home that might result from the presence of drywall. A simple one-zone model was used to estimate concentrations of reactive sulfur gases. The model accounted for factors, such as air exchange rate and room volume, which impact the concentrations of chemicals in the indoor air. It was assumed that the ceilings and walls of all rooms in the home were covered with drywall. In addition, the model includes reactive decay rates to account for the chemical reaction between the reactive gases and surfaces in the room, such as furniture and carpeting.

There are a number of uncertainties that limit the ability of the model to accurately estimate the levels of sulfur gases in actual homes. The tested wallboard samples were from a warehouse, where the stacking may have limited emissions of the sulfur compounds during storage and increased the tested chamber emissions relative to drywall that had been installed in homes. The tested drywall samples were not painted or otherwise coated, which likely increased drywall emissions relative to drywall installed in a home. Homes may have drywall from multiple manufacturers and sources. There is a general lack of data on reactive decay rates for the sulfur gases. The decay factors used in the model are estimates based on our professional judgment and it is unknown whether they may over or under-predict results in actual homes.

The top ten reactive sulfur emitting drywall samples are from China. The patterns of reactive sulfur compounds emitted from drywall samples show a clear distinction between the Chinese drywall samples manufactured in 2005/2006 and NA drywall samples, with the exception of two Chinese samples C14 and C15, which have similarities to the NA emission profile. The newer Chinese samples (manufacture date of 2009) demonstrate a marked decrease in sulfur emissions as compared to the 2005/2006 samples, and in some cases are similar to those of the NA samples.

While the data provided by LBNL to date are limited and the sample size is small, these data provide important information about chemicals that may be emitted from older Chinese drywall but are not released from NA drywall. Based on these preliminary results, the most salient difference between older Chinese and NA drywall is in the number and amount of reactive sulfur compounds emitted.

The data and analysis presented here are preliminary. This evaluation on reactive sulfur compounds will be followed by a more comprehensive exposure study once additional chamber data become available. CPSC staff will also continue its evaluation of possible health effects by comparing the concentrations measured in the chamber studies and the Environmental Health and Engineering (EH&E) 51-home study with concentrations of compounds known to result in health effects as noted in the scientific literature.

Introduction

The U.S. Consumer Product Safety Commission (CPSC) has received more than 3000 consumer complaints reporting health effects and corrosion of metal components in both newly built homes and homes renovated during the years 2001 through 2008. A spectrum of health effects has been reported by residents including recurrent headaches, irritated and itchy eyes and skin, difficulty in breathing, persistent cough, runny noses, sinus infections and congestion, sore throats, frequent nosebleeds, and asthma attacks. Frequently, consumers note that affected homes have an offensive or unpleasant odor. Drywall imported from China has been implicated as the probable underlying cause of reported problems, but it should be noted that other home materials and furnishings have not been ruled out as primary or contributing causes.

In an effort to address increasing consumer concerns about imported drywall and health, CPSC staff has undertaken a multi-track test program to evaluate the possible relationship between drywall and the health symptoms reported by affected homeowners. The specific elements of this test program include laboratory elemental characterization of drywall and raw materials, chamber testing of domestic and imported drywall emissions, and in-home air sampling.

This report is an evaluation of preliminary data from the drywall chamber testing being conducted at Lawrence Berkeley National Laboratory (LBNL)(CPSC, October 2009). The purpose of the laboratory chamber tests is to separate and isolate the drywall's chemical emissions from those of other products that can be found in the home (*e.g.*, wood products, carpets, cleaners, paint, adhesives, and beauty products) so that a determination may be made as to what gases are emitted from each drywall sample. It is important to be able to understand whether reported health-related symptoms might be related to the drywall, to other environmental factors or contaminants in the home, other home materials and furnishings, or to combinations or interactions amongst any of these factors.

The focus of this report is on the reactive volatile sulfur chemicals detected in the LBNL chambers.[2] Data received from LBNL are reported as emission rates (units of chemical mass per unit area of emitting surface per unit time). CPSC staff used the chamber emissions data to conduct mathematical exposure modeling to estimate sulfur gas concentrations (*e.g.*, hydrogen sulfide, sulfur dioxide, and carbon disulfide) which could be found in a home with suspected problem drywall. These estimates derived from modeling of potential home concentrations can then be compared to those measured in the Environmental Health and Engineering 51-home study (EH&E 2010) and can be used to evaluate the possibility of health risks from exposure to these compounds.

Methodology

Emissions Studies
Drywall samples provided to LBNL by CPSC were collected by CPSC staff from manufacturers, drywall suppliers and storage warehouses. North American (NA) drywall

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[2] The October 2009 CPSC evaluation reported preliminary results for both total volatile organic compounds (VOC) and total organic sulfur compounds (CPSC 2009).

samples[3] were manufactured in 2009 while Chinese drywall samples were manufactured from 2005 through 2009 (Appendix B). These 30 drywall samples were not obtained from individual homes, and were unfinished (*i.e.*, no paint, plaster or other modification had been applied).

LBNL measured emissions from a 6-inch square cut from the CPSC supplied 12x12 inch piece of drywall. The drywall cut edges were filed smooth and sealed with low VOC aluminum tape leaving both the front and back paper faces of the drywall exposed. The total exposed areas were measured and then each sample was placed in an individual conditioning chamber where it remained until testing. The conditioning chambers were supplied with a continuous stream of clean humidified air. Emissions from the preconditioned samples were measured in 10.5 L chambers with a ventilation rate of approximately 0.5 L/minute, at 25 ℃ (77 ℉) and 50% relative humidity.[4] All internal surfaces in the emission chambers and sampling lines were either treated with low sorption coating (Sulfinert®) or constructed from low sorption materials (Teflon®). Air samples were collected directly from the chambers after emission concentrations achieved a steady-state condition. LBNL analyzed the emissions using a range of methods, depending on the target chemical class (Appendix A). The measurements were used along with known ventilation rates, chamber volume and projected material surface areas to calculate the material-specific emission rate for each chemical. Emissions rates were presented as micrograms emitted per total sample area per hour ($\mu g/m^2/h$). It is important to note that the compounds measured by LBNL may be direct emissions from the drywall and/or from chemical reactions occurring amongst the emitted chemicals within the chamber.

Indoor Air Modeling

Indoor concentrations were estimated with a simple one-zone mass-balance model. A single-zone model is justified in this case, in part, because the homes of interest generally have central air conditioning, which leads to rapid mixing of the air between rooms. In the absence of rapid mixing, pollutant levels are expected to be slightly greater in smaller rooms. A single-zone model is also justified because drywall is typically present in every room. Steady-state conditions were assumed, because drywall is an integral part of the residence and the source appears to emit at a steady rate such that consumers are exposed for many months. The steady-state indoor concentration is given by:

$$C = \frac{E \cdot \left(\frac{S}{V}\right) + a \cdot C_0}{a + k} \tag{1}$$

> where: C, concentration, $\mu g/m^3$; E, emission rate, $\mu g/m^2/h$; C_0, ambient concentration, $\mu g/m^3$; *a*, air exchange rate, h^{-1}; k, decay rate, h^{-1}; S/V, surface area-to-volume ratio (surface area of the source/volume of the house), m^2/m^3.

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[3] Non-Chinese drywall is referred to as North American or NA.
[4] In the October 2009 CPSC evaluation, emissions were measured at 35℃ (95 ℉) and 80% relative humidity in an attempt to maximize emissions.

Modeling Input Parameters

Emission rates were measured by LBNL (Table 1, Figure 1). For samples where a given sulfur gas was not detected, the emission rate was assumed to equal half the method detection limit.[5]

S/V is the ratio of the drywall surface area to the house volume. From a national survey of the U.S. housing stock (Persily *et al.* 2006), S/V was calculated from floor plans for selected small, medium, and large homes (Table 2). Drywall was assumed to cover all internal walls and ceilings. Surface area was not adjusted for the presence of doors and windows. Therefore, the S/V was determined to be approximately 1.6 m^2/m^3 for a small home and 1.2 m^2/m^3 for medium and large homes. In the 51-home indoor air study, the average floor area of homes associated with drywall-related complaints ("complaint homes") was approximately 3,000 ft^2 (EH&E 2010), which suggests an S/V estimate of 1.2 m^2/m^3 (large homes) is appropriate for use in the model. This parameter was held constant for probabilistic calculations.

Data on air exchange rates was obtained from two sources: (1) the distribution of air exchange rates in the U.S. housing stock as estimated by Murray and Burmaster (1995) from perfluorocarbon tracer data of Koontz and Rector (1993) (Table 3) and, (2) air exchange rates measured in the EH&E 51-home study (Table 4). Air exchange rates in the EH&E study homes (a mean of 0.22) were generally lower than in the general housing stock (a mean of 0.76), which is typical of newer homes. An air exchange rate of 0.35 air changes per hour (ACH), a value which falls between the U.S. housing stock and what was measured in the EH&E home study, was utilized for the modeling.

Values for ambient pollutant levels, C_0, which would be reflective of the U.S. states most impacted by problem drywall, were obtained from the EH&E 51-home study. Data for hydrogen sulfide and sulfur dioxide for all homes (complaint homes and non-complaint homes) were used (Table 5). CPSC staff used the sum of the hydrogen sulfide and sulfur dioxide as an estimate of total sulfur gases since the other reactive sulfur compounds (*e.g.*, methyl mercaptan, dimethyl sulfide and, carbonyl sulfide) were not measured in the EH&E home study. Similarly, carbon disulfide was not detected in the EH&E home study; therefore C_0 for carbon disulfide was set to zero. Median values reported in the EH&E study were used as values for C_0 in the model.

In contrast to the approach presented in the CPSC October 2009 report, this model also includes decay rates (also known as sink effects); which are the effects of various conditions and contents of a room through which chemicals may be removed from the air due to adsorption or reaction with surfaces in the room, such as furniture and carpeting. By reacting with components in the home, compounds are less available for human exposure. If decay factors are not taken into account, then estimated room concentrations would be higher than that which would be encountered in an actual occupied home. Actual data on decay rates of the sulfur gases are generally lacking in the scientific literature. The U.S. Environmental Protection Agency (EPA 2009) estimated the sulfur dioxide decay rate in residences and other settings, from published chamber experiments

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[5] Treating non-detect values as half the method detection limit is a standard approach used by CPSC staff and other agencies.

with a variety of materials (Grøntoft and Raychaudhuri 2004). These chamber experiments were performed at medium (50%) and high (90%) relative humidity. EPA used probabilistic methods to estimate the distribution of the decay rate at both levels of humidity. The two distributions were described by a geometric mean, geometric standard deviation, minimum, and maximum, as indicated in the following table.

Sulfur Dioxide Decay Rates (EPA 2009)				
Relative Humidity	Geometric Mean	Geometric Standard Deviation	Minimum	Maximum
50%	3.14	1.11	2.20	5.34
90%	13.41	1.11	10.31	26.96

The distributions were modeled by EPA as truncated lognormal distributions ("lognorm2" in @Risk). Lognorm2 was used because EPA reported the geometric mean, rather than the arithmetic mean.

Decay rates for the other sulfur gases were not available. The transport-limited decay rate can be regarded as the upper bound decay rate for reactive gases. Cano-Ruiz *et. al.* (1993) estimated the transport-limited decay rate for reactive gases to be roughly 0.2 cm/sec. Converting units and multiplying this value by a typical surface-to-volume ratio of 3.4 m^2/m^3 (Hodgson *et. al.* 2004) gives a value of about 25 h^{-1}. For this calculation, the surface area includes all surfaces in the homes, including ceilings, walls, floors, and all objects in the room. In the absence of data on decay rates for the sulfur gases, the decay rate 10 h^{-1} was chosen to estimate indoor air concentrations from the LBNL chamber data.

Results

Emission Rates

The top ten reactive sulfur emitting samples are drywall samples from China. The pattern of reactive sulfur compounds emitted from drywall samples, as measured by LBNL, show a clear distinction between the Chinese drywall samples manufactured in 2005/2006 and NA drywall samples, with the exception of Chinese samples C14 and C15 which have similarities to the NA emission profile (Table 1, Figure 1). The newer Chinese samples (manufacture date of 2009) demonstrate a marked decrease in sulfur emissions as compared to the 2005/2006 samples, and in some cases are similar to those of the NA samples.

Estimated Concentrations of Reactive Sulfur Gases

Accurate modeling of reactive gases requires data on their decay rates in residences under typical conditions. Decay rates generally depend on the total surface area in the residence, the materials present, and the relative humidity. Decay rates for the sulfur gases are generally unknown, except for sulfur dioxide. Figures 2, 3 and 4, show the effect on estimated indoor concentrations of using decay rates from 0 to 10 h^{-1} for the five

drywall samples with the highest hydrogen sulfide emissions (Figure 2), sulfur dioxide emissions (Figure 3), and total sulfur emissions (Figure 4). The decay rate 10 h^{-1} was used in subsequent modeling.

The estimated average indoor concentrations of the sulfur gases are markedly larger for the majority of the 2005/2006 Chinese drywall (7 out of 9) than for NA drywall. Estimated concentrations were approximately a factor of ten greater for the 2005/2006 Chinese samples than for the NA samples (Figure 5).

It may be informative to compare the concentrations of sulfur gases estimated from the LBNL emission rate measurements to the levels measured in the EH&E 51-home study. Table 6 shows that the estimated median (50th percentile) hydrogen sulfide concentration in modeled homes with NA drywall (0.16 µg/m^3) is half the level measured in the EH&E study non-complaint homes (0.32 µg/m^3) and one-third the level in complaint homes (0.82 µg/m^3). In contrast, the model's estimated hydrogen sulfide concentrations for Chinese samples C1 through C5, in homes with Chinese drywall (10.7 µg/m^3), is more than 10-fold greater than the levels measured in the EH&E home study.

Discussion

The purpose of this preliminary evaluation was to evaluate emissions of specific sulfur gases from NA and Chinese drywall, and estimate the possible exposures of sulfur-containing compounds in homes that contain either of these two sources of drywall. The estimated indoor levels may be used to estimate any possible health risks associated with these gases.

The results of the LBNL chamber studies demonstrated considerably higher emission rates from Chinese drywall samples manufactured in 2005-2006 compared to samples from North America. When these values are introduced into indoor air models, the differences in emission rates are reflected in the differences in estimated indoor concentrations.

Estimated hydrogen sulfide levels were compared to the hydrogen sulfide levels measured in the EH&E study. Hydrogen sulfide was chosen for comparison because there was a statistically significant difference between measured ambient (outdoor) and indoor levels in the EH&E home study. The hydrogen sulfide levels estimated by our model for homes with NA drywall were one-half to one-third the actual levels measured in the EH&E study. The reasons for the lower estimated levels are likely complex and not yet completely understood, but may be due to the lower air exchange rates in the study homes (mean = 0.22 h^{-1}), as compared to U.S. housing stock (mean = 0.76 h^{-1}; Murray and Burmaster 1995). In addition, a broad distribution of decay rates was used, because decay rate data for hydrogen sulfide were not available. A lower air exchange rate and lower decay rate would lead to higher estimated (modeled) hydrogen sulfide levels in a home.

The estimated hydrogen sulfide levels in homes with Chinese drywall were more than 10-fold greater than the actual levels measured in the EH&E study, including complaint homes. The reasons for this difference are not yet completely understood but may reflect

the complex chemical reactions that are likely occurring in homes. The LBNL chambers were designed to be non-reactive so that the emitted compounds would not react with chamber components prior to being detected. Certain factors that might also be expected to significantly influence the emissions, such as drywall treatment (*e.g.,* paint and other finishing methods), were not included. In addition, it was assumed in the model that the ceilings and walls of all rooms in the home were covered with drywall (either Chinese or NA). It is also possible that the tested Chinese drywall samples have unusually high emissions, resulting in higher estimated (modeled) room concentrations. Alternatively, it is possible that emission rates decline with time after drywall is installed in homes.

Estimates of indoor air concentrations of the sulfur gases are limited by several factors including the lack of data on decay rates for all sulfur compounds, as well as the lack of information on the effect of paint coatings or other wall coverings on emission rates.

The EH&E data were collected in homes where the chemistry of the indoor air is very complex; identifying and quantifying these compounds with models and air measurements is challenging. This is because in the actual home environment organic and inorganic chemicals from the drywall itself or from other home furnishings or products may react with sulfur compounds from the drywall to create complex mixtures that analytical methods utilized in the EH&E study (or any indoor air study) could not necessarily account for. These factors could result in total measured concentrations of sulfur compounds that are lower than expected in homes that contain imported drywall. Additionally, method detection limits for many of the measured compounds in the EH&E study were relatively high. Furthermore, sulfur compounds from drywall might also adsorb onto and react with metal surfaces. While these reactions could potentially lead to the observed corrosion of certain metallic elements in homes (EH&E 2010), the compounds would not necessarily be present in the indoor air at a high enough concentration for detection and quantitation.

As with any mathematical model-based exposure assessment, there are numerous assumptions, limitations, and sources of uncertainty that should be further explored. For example, the model employed in this analysis and with the CPSC October 2009 total sulfur and VOC analysis is a commonly used indoor air model for estimating indoor air concentrations of chemicals released from materials in homes. Other models for estimating indoor air concentrations exist (*e.g.*, NIST's CONTAM, EPA's MCCEM) and could provide more or less conservative estimates of chemical concentrations. In all cases though, the result of the estimation is dependent on the quality of the input parameters. This evaluation on reactive sulfur compounds will be followed by a more comprehensive exposure study once additional chamber data become available. CPSC staff will also continue its evaluation of possible health effects by comparing the concentrations determined in the chamber studies and the EH&E 51-home study with concentrations of compounds known to result in health effects as noted in scientific literature.

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Table 1. Emission rates of sulfur gases (μg/m^2/h) [a]

Sample [b]	Hydrogen Sulfide	Sulfur Dioxide	Carbon Disulfide	Methyl Mercaptan	Dimethyl Sulfide	Carbonyl Sulfide	Total Sulfur [c]
C 1	118.83	36.09	2.44	0.93	0.40	1.35	132.3
C 2	22.04	8.13	1.08	0.27	0.31	--	25.6
C 3	123.16	44.60	2.70	1.33	0.44	--	140.3
C 4	185.14	64.36	3.67	1.47	0.36	0.87	209.4
C 5	24.75	10.25	1.21	0.10	0.29	0.66	29.5
C 6	3.18	--	--	--	0.91	--	3.5
C 7	3.36	--	--	--	0.94	--	3.8
C 8	--	--	--	--	0.94	--	0.9
C 9	15.43	2.91	--	--	0.87	--	16.4
C 10	4.99	--	--	--	0.88	--	5.3
C 11	10.88	--	--	--	0.89	--	10.8
C 12	8.58	--	--	--	0.95	--	8.7
C 13	--	--	--	--	0.90	--	0.9
C 14	1.04	--	--	--	0.86	--	1.5
C 15	4.15	--	--	--	0.85	--	4.4
C 16	67.11	1.53	--	--	0.87	--	64.3
C 17	203.27	13.44	0.28	--	0.89	--	198.3
NA 1	--	--	0.45	--	0.18	--	0.3
NA 2	3.99	4.24	0.72	--	0.24	--	6.3
NA 3	--	1.36	0.48	--	0.23	--	1.0
NA 4	--	--	0.69	--	0.18	--	0.4
NA 5	--	2.00	0.67	--	0.31	--	1.4
NA 6	0.12	--	0.36	--	0.16	--	0.4
NA 7	2.39	--	0.48	--	0.15	--	2.5
NA 8	--	4.11	0.53	0.15	0.31	1.12	3.1
NA 9	3.32	2.53	0.59	--	0.38	--	4.8
NA 10	--	4.99	0.13	--	--	--	2.6
NA 11	1.74	2.54	0.49	--	0.16	--	3.2
NA 12	--	0.61	0.54	--	0.19	--	0.6
NA 13	--	--	--	--	0.90	--	0.9
LOD	0.60	0.40	0.60	0.10	0.02	--	--

[a] Measured by LBNL.

[b] C, China; N, North America; LOD, LBNL limit of detection.

[c] Calculated by converting to the mass as total sulfur and then summing the emission rates.

Table 2. Surface-to-Volume Ratios of Selected Homes

Home [a]	Floor Area (ft^2)	Floor Area (m^2)	Volume (m^3)	Drywall Area [b] (m^2)	S/V (m^2/m^3)
DH-A(2)	1152	107	261	410	1.6
DH-B(2)	1942	180	440	545	1.2
DH-C(1)	2966	276	672	832	1.2

[a] Persily *et al.* 2006.

[b] Assumes all interior walls and ceilings are covered with drywall.

Table 3. Distribution of air exchange rates in the U.S. housing stock (Murray and Burmaster 1995).

Percentile	1	5	10	20	25	30	40	50	60	70	75	80	90	95	99
ACH (h^{-1})	0.08	0.15	0.21	0.28	0.32	0.35	0.41	0.51	0.61	0.77	0.87	1.00	1.48	2.19	4.76

N = 2844; Mean = 0.76 h^{-1}; Standard Deviation = 0.88 h^{-1}.

Table 4. Measured air exchange rates (h^{-1}) in EH&E study homes (EH&E 2010).

0.22	0.23	0.19	0.24	0.19	0.15	0.13	0.32	0.19	0.16
0.20	0.16	0.20	0.33	0.19	0.06	NA	0.18	NA	0.13
0.28	0.13	0.26	0.05	0.10	0.09	0.14	0.12	0.14	0.12
0.19	0.13	0.24	NA	0.23	0.17	0.46	0.63	0.18	0.20
0.18	0.28	0.08	NA	0.80	0.27	0.12	0.20	0.42	0.16
0.46									

N = 51; Mean = 0.22 h^{-1}; Standard Deviation = 0.14 h^{-1}.

Table 5. Ambient levels of sulfur gases in EH&E study homes (EH&E 2010)

Hydrogen Sulfide (µg/m^3) [a]

0.29	0.27	0.28	0.29	0.29	0.29	0.29	0.31	0.31	0.31
0.31	0.32	0.32	0.32	0.34	0.36	0.39	0.40	0.40	0.40
0.43	0.43	0.56	0.59	0.61	0.63	0.64	0.67	0.77	0.82
0.82	0.88	0.89	1.0	1.12	1.13	1.14	1.19	1.20	1.23
1.26	1.31	1.32	1.37	1.41	1.65	1.78	2.05	2.54	3.11
3.11									

N	Mean	Median	SD[6]
51	0.87	0.63	0.69

Sulfur Dioxide (µg/m^3) [b]

1.92	1.77	1.77	1.78	1.80	1.80	1.87	1.87	1.88	1.88
1.90	1.90	1.90	1.90	1.90	1.90	1.90	1.90	1.90	1.90
1.90	1.91	1.91	1.91	1.93	1.93	1.93	1.94	1.94	2.02
2.02	2.02	2.04	2.04	2.04	2.04	2.04	2.04	2.05	2.05
2.05	2.05	2.06	2.06	2.06	2.08	2.18	2.20	2.20	2.40
2.41									

N	Mean	Median	SD
51	1.97	1.92	0.14

Total Sulfur (µg Sulfur/m^3) [c]

2.22	2.04	2.05	2.07	2.09	2.09	2.16	2.18	2.19	2.19
2.21	2.22	2.22	2.22	2.24	2.26	2.29	2.30	2.30	2.30
2.33	2.34	2.47	2.50	2.53	2.55	2.56	2.61	2.71	2.84
2.84	2.90	2.93	3.03	3.16	3.17	3.18	3.23	3.25	3.28
3.31	3.36	3.38	3.43	3.47	3.73	3.96	4.25	4.74	5.51
5.52									

N	Mean	Median	SD
51	2.84	2.55	0.82

[a] Converted from parts-per-billion (ppb) to µg/m^3

[b] Converted from parts-per-billion (ppb) to µg/m^3

[c] Sum of hydrogen sulfide and sulfur dioxide.

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[6] SD = standard deviation

Table 6. Comparison of modeled and measured hydrogen sulfide concentrations ($\mu g/m^3$).

Source	Modeled Concentrations[a]		Measured Concentrations[b]	
	China	North America	Complaint	Non-Complaint
Mean	13.4	0.28	0.92	0.63
5th/Minimum[c]	1.8	0.03	0.27	0.28
25th	3.1	0.07	0.40	0.31
50th/Median	10.7	0.16	0.82	0.32
75th	17.3	0.36	1.23	0.39
95th/Maximum[c]	35.6	0.85	3.11	3.11

[a]The values are for samples C1 through C5, the imported drywall most frequently reported by consumers.

[b]EH&E 51-home study (EH&E 2010), ppb values converted to $\mu g/m^3$.

[c]5th and 95th Percentiles are given for the modeled concentrations; the EH&E reported minimum and maximum values for the measured concentrations are placed in the same row as the modeled 5th and 95th Percentiles.
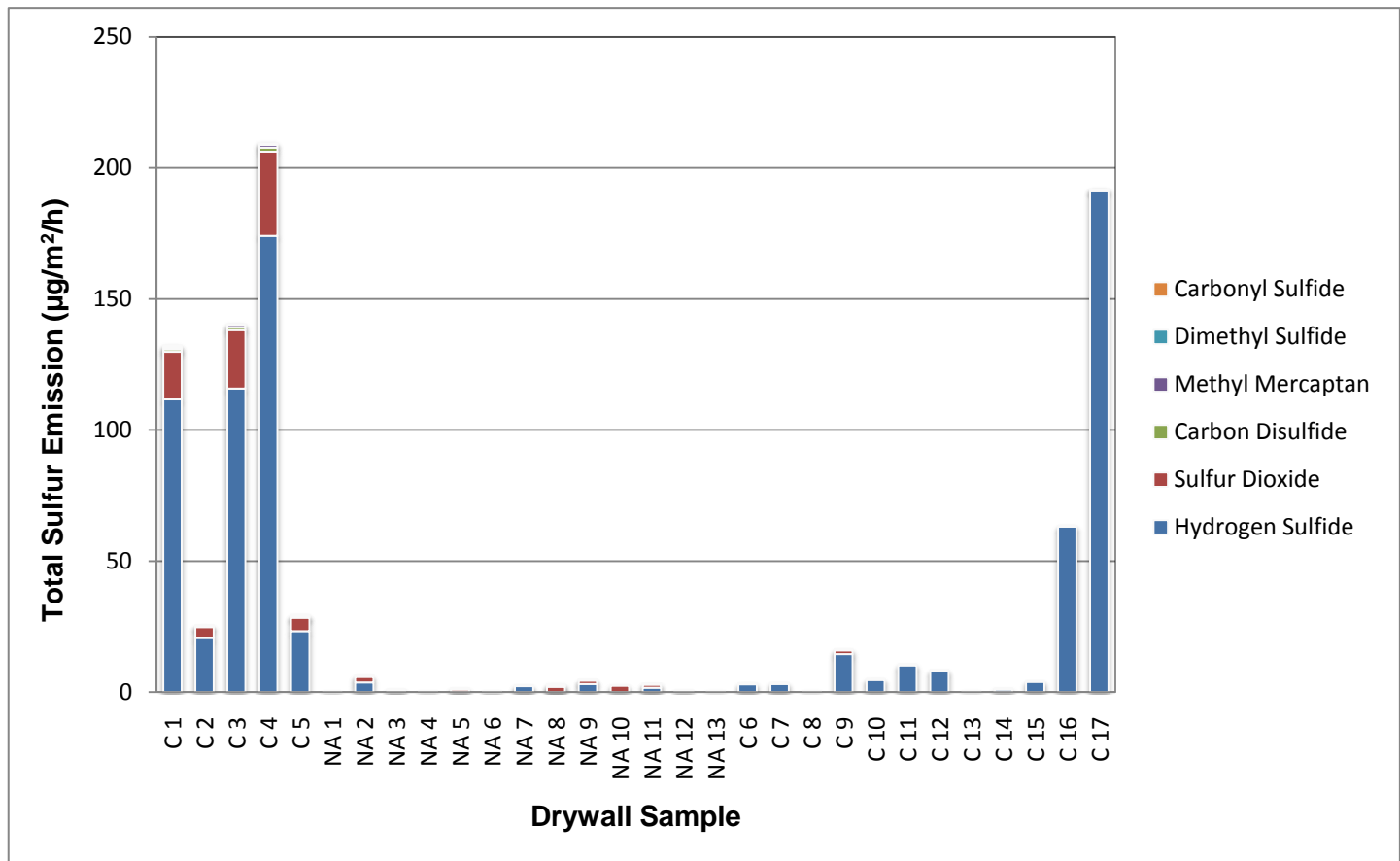
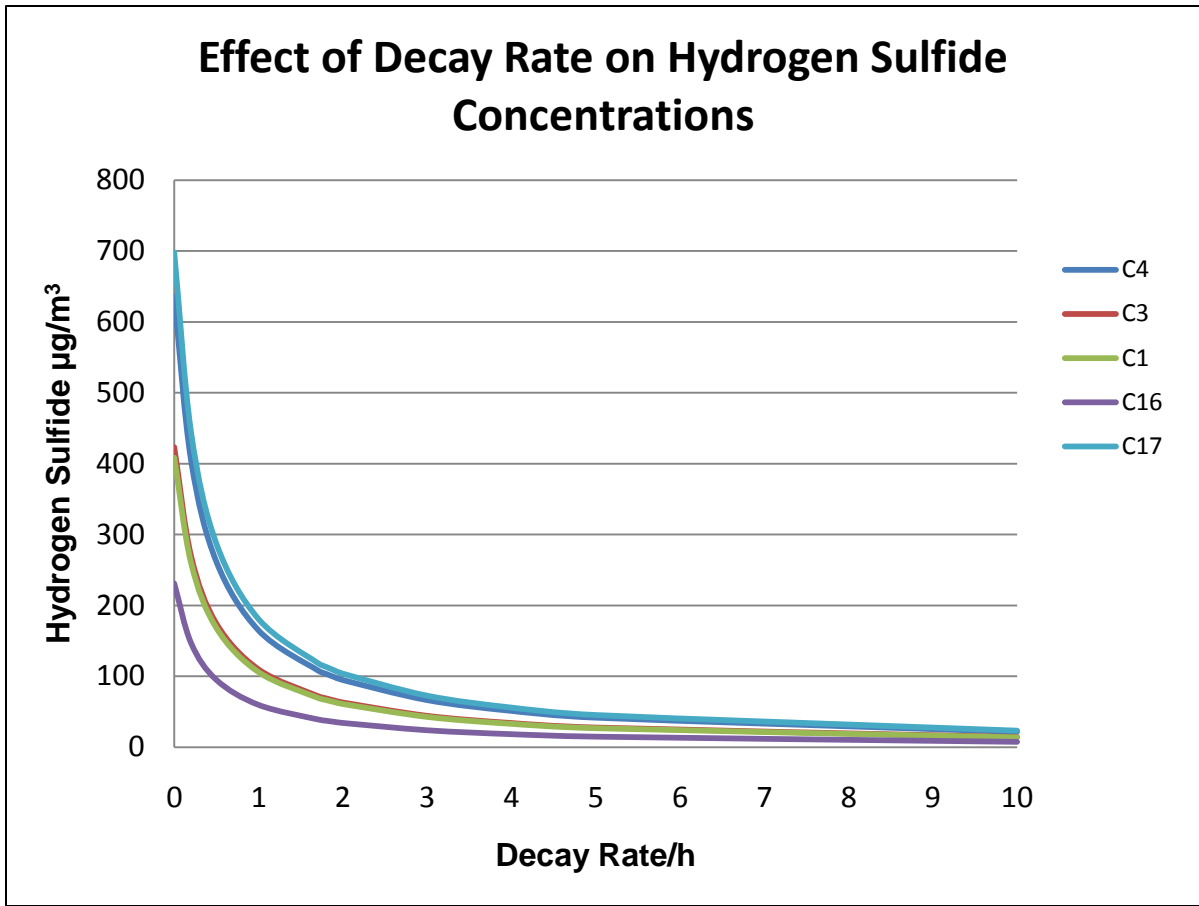**Figure 1**: Sum of the LBNL measured reactive sulfur gas emission rates as mass total sulfur.

Figure 2: Hypothetical effect of decay rate, at 0.35ACH, on indoor hydrogen sulfide concentrations for the top five emitters.
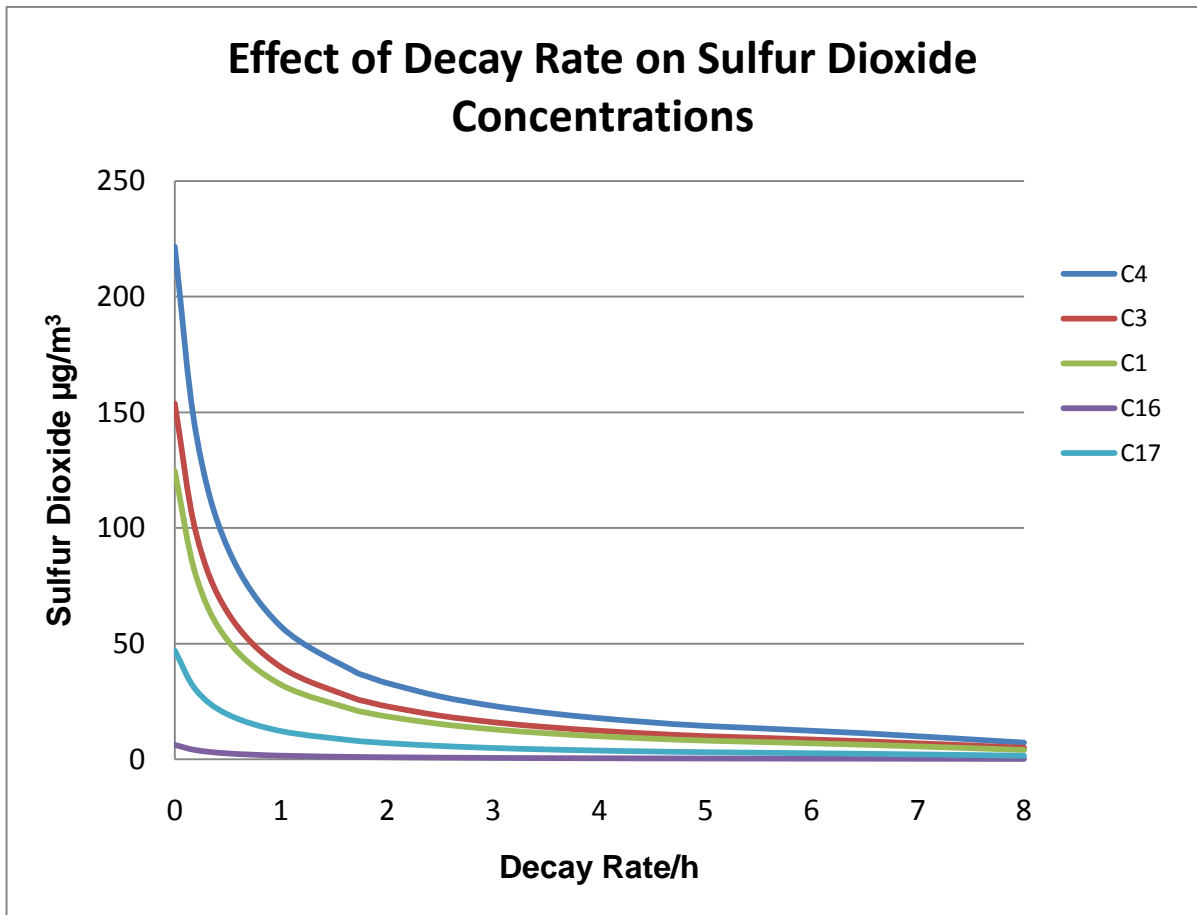
Figure 3: Hypothetical effect of decay rate, at 0.35ACH, on indoor sulfur dioxide concentrations for the top five emitters.
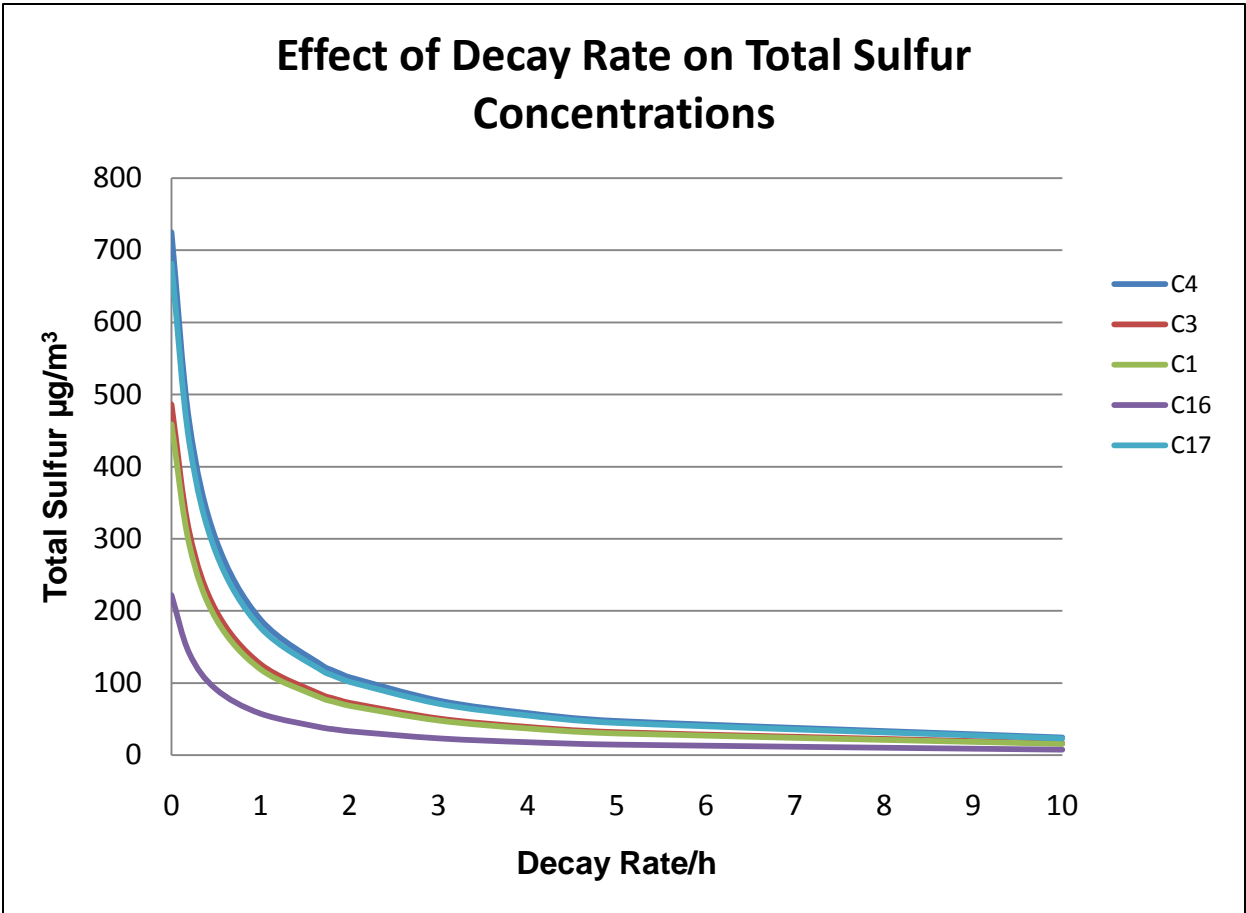
Figure 4: Hypothetical effect of decay rate, at 0.35ACH, on indoor total sulfur concentrations for the top five emitters.
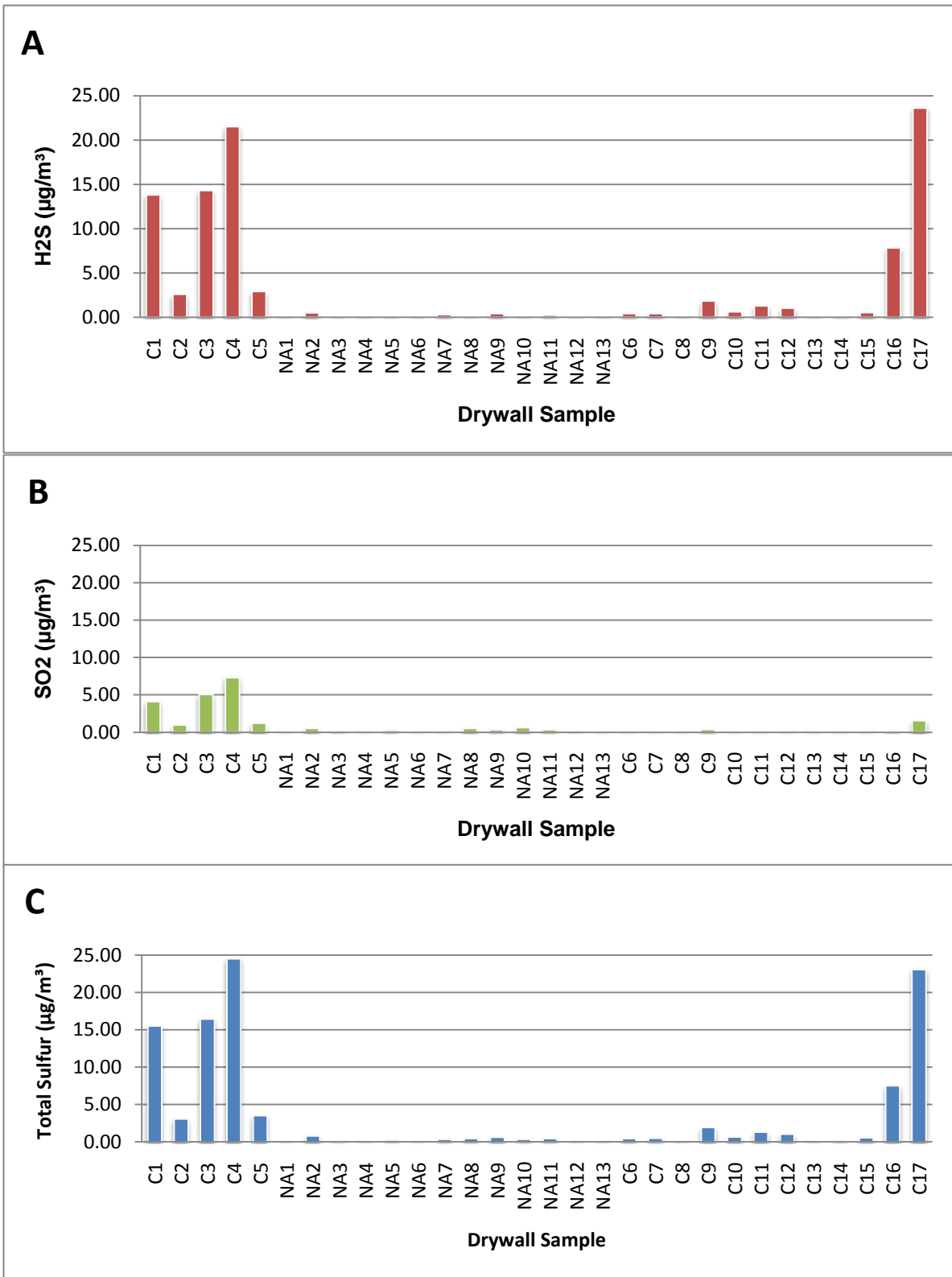
Figure 5: Estimated levels of sulfur gases in residents at 0.35ACH. (A) Hydrogen sulfide, k = 10/h (B) Sulfur dioxide, k = 3.1/h (C) Total sulfur gases, k = 10/h.

APPENDIX A

The following are excerpts from a draft document prepared by LBNL. Upon receipt of the final LBNL report, full details of methodology will be made available.

Material Conditioning

The drywall collected for this study represented either domestic or imported stock and were collected directly from manufacturers, drywall suppliers and warehouses. It was important to fully condition the samples to allow potential contaminants that were not indigenous to the material to off-gas prior to testing. Further, it was important to provide a clean and controlled environment to allow the materials to equilibrate with the test conditions prior to transferring the material to the test chamber.

Sixteen individual conditioning chambers were constructed by LBNL using 6-liter air-tight stainless steel food grade containers. Each container was plumbed with a dedicated inlet and outlet line and mounted on a panel for easy access. Dry house air was passed through an activated carbon filter followed by a HEPA filter and then a portion of the air stream was passed through a bubbler containing deionized water. A small amount of activated carbon was placed in the bubbler reservoir. The wet and dry air streams were mixed to produce the desired relative humidity; the humidified air was delivered at approximately 250 cc/min (1.4 air exchange rates per hour, ACH) to each chamber using flow control valves and taper-tube flow meters.

The drywall samples were conditioned for a minimum of one week prior to initial emission testing but conditioning and testing continued for several months while analytical methods were optimized. Conditioning time is recorded for the individual materials as they were tested.

Material Testing

Emission testing generally followed ASTM Standard Guide D-5116-97 and California Specification 01350 using small emission chambers.

The emission testing apparatus consisted of four 10.75-liter stainless steel chambers that were treated with Sulfinert® coating (http://www.silcotek.com/) to minimize wall interaction for active compounds like hydrogen sulfide, sulfur dioxide and the low molecular weight mercaptans. The test materials were placed on a Sulfinert® treated screen resting slightly below the center of the test chambers and the chambers were sealed with clamp on lids. The chambers were mounted inside a controlled environment oven that was used to provide a constant temperature.

The test conditions were as follows: chamber temperature, T, (°C) was 25; the inlet flow, F, (L/min, LPM) of carbon filtered preconditioned air was maintained at 1 LPM and 50% relative humidity, was supplied continuously to each test chamber with the exhaust flow vented to a fume hood. The relative humidity was achieved by mixing streams of dry air

and water-saturated air as described for the conditioning chambers. The emitting area of the tested material, including both the front and back face, A, (m^2) was approximately 0.04, resulting in a loading factor, L, (m^2/m^3) of 3.7 and an area specific air flow rate (m^3/m^2/h) of 1.5 for each material. The ACH (1/h) within the chambers was 5.6.

The collection of air samples was initiated after at least one hour but typically at more than three hours from the time of loading to allow time for the conditions to stabilize after loading in the chamber. The samples were pre-conditioned at the target humidity so the emission rates are expected to be constant resulting in an approach to steady state concentration in the chamber that is exponential following the relationship

$$\frac{C_t}{C_{ss}} = 1 - \exp(-k \times t)$$

where C_t is the concentration (μg/m^3) in the chamber at a time t (h) after inserting the sample in the chamber, C_{ss} is the steady state concentration (μg/m^3) in the chamber, and k is the removal rate (h^{-1}) of the chemical from the chamber where the lower bound removal rate would be equivalent to the ACH for non-reacting chemicals. With an ACH on the order of 5.6 per hour, the time to reach 99% of steady state is approximately one hour.

Air Sampling and Analysis

In general, active samples were collected on thermodesorption tubes for volatile organic compounds (VOCs) and volatile sulfur compounds (VSCs), and on sorbent cartridges for aldehydes. The samples were drawn directly from the chamber. The sampling rate was maintained at less than 80% of the total flow through the chamber to prevent backflow of air into the test chamber. Reactive sulfur gases, collected using solid phase micro extraction (SPME), were collected directly from the chamber by inserting the SPME fiber through an access port in the lid of the chamber.

Four analytical methods were utilized to characterize chemical emissions from the drywall samples. These include (1) a thermodesorption gas chromatography mass spectroscopy (TD-GC/MS) method to identify and quantify the VOCs; (2) a thermodesorption gas chromatography sulfur chemiluminescence (TD-GC/SCD) method to quantify the VSCs; (3) a SPME gas chromatography sulfur chemiluminescence method (SPME-GC/SCD) to quantify the reactive sulfur gases; and (4) a derivitization based sampling followed by liquid extraction and high performance liquid chromatography with UV detection (HPLC-UV) method to quantify low molecular weight carbonyls.   Since this report is focused on the reactive sulfur compounds, the following details are provided for those methods employed by LBNL for detecting sulfur chemicals.

Volatile Sulfur Compounds

Samples were collected for the VSCs using the same tubes and sampling method described for the VOCs.

VOC samples were collected onto multibed sorbent tubes (P/N 012347-005-00; Gerstel or equivalent) with a primary bed of Tenax-TA® sorbent backed with a section of Carbosieve®. Prior to use, the sorbent tubes were conditioned by helium purge (~10 cc/min) at 280 °C for 60 minutes and sealed in Teflon capped tubes. VOC samples were focused directly onto the sampling tubes from the exit port in the small emission chamber. A variable speed peristaltic pump was used to pull air through the sample tubes at a sampling rate of approximately 200 cc/min. Flows were checked using either a bubble flow meter or a DryCal gas flow meter (BIOS, 500 cc/min) at least twice during each sampling period. Approximately 12 liters were collected from the emission chambers. A backup sampling tube was used periodically to check for breakthrough[‡‡]. After sample collection, the sorbent tubes were sealed with Teflon lined caps and either analyzed the same day or stored in a freezer until analysis. Samples were typically analyzed within one day of collection. Sample stability over freezer storage times of more than 2 months have been confirmed previously in our lab for a wide range of VOCs.

Sorbent tubes were thermally desorbed for analysis by TD-GC/MS using a thermodesorption auto-sampler (Model TDSA2; Gerstel), a thermodesorption oven (Model TDS3, Gerstel) and a cooled injection system (Model CIS4; Gerstel). Desorption was performed in splitless mode and the desorbed sample was refocused on the cooled injector in solvent vent mode with flow of 30 cc/min). Compounds were resolved on a GC (Series 6890Plus; Agilent Technologies) equipped with a 30 meter HP-1701 14% Cyanopropyl Phenyl Methyl column (Model 19091U-233; Agilent Technologies).

The resolved analytes were detected using an electron impact MS system (5973; Agilent Technologies). The MS was operated in scan mode. All compounds over the detection limit (< 1ng to several ng) were identified by library search using the National Institute of Standards and Technology (NIST) spectral library followed by comparison to reference standards as needed. Multipoint calibrations were prepared from pure standards for quantification. When pure standards were not used the analyte was reported in terms of toluene equivalence by comparing the instrument response for the total ion chromatogram for the chemical to a multipoint calibration of toluene. All pure standards and analytes were referenced to an internal standard (~120 ng) of 1-bromo-4-fluorobenzene that was added directly to the thermodesorption tube prior to analysis.

Initially the VOCs and the VSCs were to be analyzed in parallel with a new GC with parallel MS and sulfur chemiluminescence detectors. However, difficulties with the instrument necessitated the use of the instrument described above for VOCs and a new instrument to focus on the sulfur gases as described below. Thus, two independent samples were collected and analyzed separately for the VSCs and the VOCs.

[‡‡] Some of the earlier samples were collected at 100 cc/min but the higher flow rate of 200 cc/min provided better detection limits without resulting in breakthrough for either VOCs or VSCs so the final method utilized the higher sampling rate.

Sorbent tubes were thermally desorbed for analysis by TD-GC/SCD using a thermodesorption auto-sampler (Model TDSA2; Gerstel), a thermodesorption oven (Model TDS-G, Gerstel) and a cooled injection system (Model CIS4; Gerstel). The cooled injection system was fitted with a Tenax-packed glass liner (P/N 013247-005-00; Gerstel). TDS desorption was performed in splitless mode. The cryogenic inlet trap was held at -50°C throughout desorption phase and run in solvent vent mode with a vent flow of 30 cc/min. Following TDS desorption, the CIS was heated within 0.2 minutes to 270°C at a rate of 12°C/s, followed by a 3-minute hold time. Compounds were resolved on a GC (Series 7890A; Agilent Technologies) equipped with a 30 m × 0.32 mm DB1 column with 1 micron film thickness at an initial temperature of -10°C for 2 minutes then ramped to 250°C at 8°C/min holding for 5 minutes.

Initial identification of VSCs in the emission stream was accomplished using the GC described above but interfaced to a mass spectrometer (5875C intert; Agilent Technologies). A 12 liter sample was collected from a chamber containing three times the normal loading of a drywall that had previously been identified as emitting the highest levels and widest range of sulfur containing chemicals. Following initial identification by mass spectral library search, the sulfur chemiluminescence detector was installed and a second 12-liter sample was analyzed. The pattern of retention times and peak heights was used to identify the peaks in the SCD analysis and then a series of pure standards was run to positively identify chemicals where pure standards were available and to determine the relationship between chemical structure and retention time. The pure standards were run individually by injecting 1 μl of pure standard into a warm dilution bulb (2 L) containing several glass beads and allowed to rest in an oven at 70°C. An aliquot of the initial dilution was subsequently spiked into a second dilution bulb then transferred to a sampling tube for analysis. The results from the pure standards provide retention windows for a series of sulfides and disulfides of increasing symmetric alkyl number. The retention windows are used to qualitatively identify VSCs where the identification either by mass spectral match or by pure standard was inconclusive.

The sulfur gases are quantified by the sulfur chemiluminescence response. The SCD has a number of advantages for sulfur gas analysis over other detectors including a wide linear range and equimolar response for all sulfur compounds with very good sensitivity and selectivity (Xinewei, 2006). The equimolar response allows for the quantification of all analytes in the sample, even unknowns, based on a single standard calibration. Several pure standards were used to develop a multipoint calibration for sulfur gases. The initial work did not include an internal standard but the final method uses thiophene (CAS# 8014-23-1) generated in a diffusion oven and added to each sampling tube prior to analysis.

Reactive Sulfur Gases

A number of different active sampling methods were explored for quantifying the reactive sulfur gases including: (1) on-line cryogenic sampling where chamber air was drawn directly into a cryogenically cooled thermodesorption tube and desorbed into the cooled injection system; (2) on-line cryogenic sampling through a nafion$^{®}$ drying tube (http://www.permapure.com/) to provide a dry sample stream; and (3) direct large volume (1-5 cc) injection from chamber to cooled injection system. A number of sorbent

materials and temperature regimes were also tested. None of the conditions provided satisfactory results for the reactive ultra volatile sulfur gases. Therefore, LBNL elected to use a solid phase micro extraction method (SPME) sampled directly from the emission chamber as described below.

A Polydimethylsiloxane/Carboxen (PDMS/Carboxin) stationary phase (0.75 μm) installed in a manual SPME holder was conditioned in the GC inlet at 300°C with elevated purge flow for two hours prior to use. The holder was inserted through a sampling port mounted in the front of the emission chamber and the fiber was extended into the chamber for sampling. A 50 minute sampling period was found to provide adequate response for the range of sulfur gases. After sampling, the SPME was transferred directly to the hot (250°C) injector in splitless mode for two minutes followed by a 30 ml/min purge for 1 minute and then 15 ml/min purge for the remainder of the run. The fiber remained in the inlet for at least ten minutes before returning to the emission chambers to start collecting the next sample. The column and detector were as described for the VSC analysis. The SPME fiber was stored in the hot injector between sampling periods.

Data Analysis

The material specific emission rates were calculated by LBNL from measurements collected from the chambers at steady-state conditions, meaning that the concentration in the chamber is constant such that a simple mass balance can be used to estimate emission rates. The steady-state form of the mass balance equation for calculating area-specific emission rates, ER, ($\mu g/m^2/h$) in a well-mixed system is:

$$ER = \frac{F \times (C - C_0)}{A}$$

where F (m^3/h) is the ventilation flow rate, A (m^2) is the exposed surface area of the test material, C ($\mu g/m^3$) is the measured steady state concentration in the chamber and C_0 ($\mu g/m^3$) is the background concentration in the chamber. Air change rates in the chamber, ACH (1/h) is the ventilation rate divided by the volume (F/V) and the material loading factor is the exposed area of test material divided by the chamber volume. The above equation can be rearranged to the form

$$ER = \frac{ACH \times (C - C_0)}{L}$$

where L (m^2/m^3) is the loading factor for the material in the chamber.

APPENDIX B

Sample Identification Key

This table lists the sample identifiers used in this report with the associated brief CPSC sample identification number and the manufacture date for each drywall sample.

Sample	CPSC id	Country	Manufacture Date
C 1	1379	China	**2006***
C 2	7069	China	**2006***
C 3	7339	China	**2006***
C 4	8357	China	**2006***
C 5	9707	China	**2006***
C 6	1491	China	2009
C 7	1493	China	2009
C 8	2631	China	2009
C 9	2632	China	2009
C 10	2634	China	2009
C 11	2635	China	2009
C 12	2636	China	2009
C 13	2637	China	2009
C 14	7078	China	**2006**
C 15	9667	China	**2006**
C 16	9672	China	**2006***
C 17	9673	China	**2005***
NA 1	6226	North America	2009
NA 2	7639	North America	2009
NA 3	8036	North America	2009
NA 4	8037	North America	2009
NA 5	8213	North America	2009
NA 6	8235	North America	2009
NA 7	8236	North America	2009
NA 8	9139	North America	2009
NA 9	9175	North America	2009
NA 10	9858	North America	2009
NA 11	9961	North America	2009
NA 12	9962	North America	2009
NA 13	7932	North America	2009

*Samples emitting more reactive sulfur gases relative to other samples