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## **Effect of Environmental Factors on Sulfur Gas Emissions from Problem Drywall**

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**Environmental Energy Technologies Division**

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## INTRODUCTION

Problem drywall installed in U.S. homes is suspected of being a source of odorous and potentially corrosive indoor pollutants. The U.S. Consumer Product Safety Commission's (CPSC) investigation of problem drywall incorporates three parallel tracks: (1) evaluating the relationship between the drywall and reported health symptoms; (2) evaluating the relationship between the drywall and electrical and fire safety issues in affected homes; and (3) tracing the origin and the distribution of the drywall. To assess the potential impact on human health and to support testing for electrical and fire safety, the CPSC has initiated a series of laboratory tests that provide elemental characterization of drywall, characterization of chemical emissions, and in-home air sampling.

The chemical emission testing was conducted at Lawrence Berkeley National Laboratory (LBNL). The LBNL study consisted of two phases. In Phase 1 of this study, LBNL tested thirty drywall samples provided by CPSC and reported standard emission factors for volatile organic compounds (VOCs), aldehydes, reactive sulfur gases<sup>1</sup> (RSGs) and volatile sulfur compounds<sup>2</sup> (VSCs). The standard emission factors were determined using small (10.75 liter) dynamic test chambers housed in a constant temperature environmental chamber. The tests were all run at 25 °C, 50% relative humidity (RH) and with an area-specific ventilation rate of ~1.5 cubic meters per square meter of emitting surface per hour [ $\text{m}^3/\text{m}^2/\text{h}$ ]. The thirty samples that were tested in Phase 1 included seventeen that were manufactured in China in 2005, 2006 and 2009, and thirteen that were manufactured in North America in 2009.

The measured emission factors for VOCs and aldehydes were generally low and did not differ significantly between the Chinese and North American drywall. Eight of the samples tested had elevated emissions of volatile sulfur-containing compounds with total RSG emission factors between 32 and 258 micrograms per square meter per hour [ $\mu\text{g}/\text{m}^2/\text{h}$ ]. The dominant sulfur containing compounds in the RSG emission stream were hydrogen sulfide with emission factors between 17 – 201  $\mu\text{g}/\text{m}^2/\text{h}$ , and sulfur dioxide with emission factors between 8 – 64  $\mu\text{g}/\text{m}^2/\text{h}$ . The four highest emitting samples also had a unique signature of VSC emissions including > 40 higher molecular weight sulfur-containing compounds although the emission rate for the VSCs was several orders of magnitude lower than that of the RSGs. All of the high emitting drywall samples were manufactured in China in 2005-2006.

Results from Phase 1 provided baseline emission factors for drywall samples manufactured in China and in North America but the results exclude variations in environmental conditions that may exist in homes or other built structures, including various combinations of temperature, RH, ventilation rate and the influence of coatings such as texture and paints.

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<sup>1</sup> Throughout this document, “reactive sulfur gas” (RSG) includes hydrogen sulfide ( $\text{H}_2\text{S}$ ), carbonyl sulfide (OCS), sulfur dioxide ( $\text{SO}_2$ ), methyl mercaptan (MM), ethyl mercaptan (EM), dimethyl sulfide (DMS) and carbon disulfide ( $\text{CS}_2$ ).

<sup>2</sup> Volatile sulfur compounds (VSCs) include all sulfur containing compounds including mercaptans, sulfides and polysulfides eluting after  $\text{CS}_2$  in the under the chromatographic conditions applied in this project.

The objective of Phase 2 was to quantify the effect of temperature and RH on the RSG emission factors for uncoated drywall, and to measure the effect of plaster and paint coatings on RSG emission factors from drywall. Additional experiments were also performed to assess the influence of ventilation rate on measured emission factors for drywall.

## **METHODS**

All experiments performed in Phase 2 used the same small chamber emissions testing facility described in the Phase 1 report. The analysis focused on RSGs. The *in situ* solid phase micro extraction (SPME) method was used to sample the gas phase in the chambers and gas chromatography with sulfur chemiluminescence detection (SCD) was used to quantify the sulfur containing compounds. The *in situ* SPME sampling method and the analytical method were also described in detail in the Phase 1 report. This section briefly summarizes the testing methods and details the experimental design for measuring the effect of temperature, RH and coatings on emission factors for sulfur containing compounds or more specifically the RSGs. For further details on the chamber facility and the development of the analytical methods see Maddalena et. al. (2010).

### ***Overview of Experimental Approach***

All experiments followed the same general process to measure emission factors as described in the Phase 1 report. Individual six-inch square pieces of drywall were cut from the section provided to LBNL by CPSC. Edges of the test pieces were sealed with foil tape and the drywall was pre-conditioned at the target RH and room temperature prior to testing. Drywall samples were isolated continuously in the conditioning chambers, test chambers or foil wrapped in Ziploc bags to prevent cross contamination. Testing was conducted by installing the drywall sample into one of four test chambers mounted in a temperature controlled environmental chamber. The RH in each chamber was independently controlled and set to a predetermined level for testing. The samples were placed horizontally on a screen slightly below the mid-point of the chamber. Air samples were collected after at least six air changes to approximate steady-state concentrations. The measured steady-state concentrations were used along with material surface area, chamber volume, and chamber ventilation rate to estimate the emission factor for the given combination of drywall and environmental conditions.

### ***Material Handling and Preparation***

Drywall samples for the temperature and RH testing were selected from materials that were originally provided to LBNL by CPSC and used in the Phase 1 studies to measure the standard emission factors. The four highest emitting samples were selected along with one drywall sample that was manufactured in North America for the T/RH testing. These five materials were either stored in sealed stainless steel containers ventilated with carbon-filtered air or triple wrapped in foil and sealed in Ziploc bags between the Phase 1 and Phase 2 tests. Three identical samples from each material were cut to six-inch squares and the edges sealed with foil tape. Both the front and back faces were left exposed during the testing. The three samples were prepared to allow for simultaneous testing of each material at low, medium and high RH in the emission chambers for each

temperature as detailed later in this document. The fourth chamber was reserved for calibration measurements.

Additional drywall materials were collected by CPSC from homes reported by consumers to contain problem drywall and delivered to LBNL for use in the coating experiments. All materials were packaged, shipped and stored as described in the Phase 1 report. The additional samples were textured and painted when the drywall was originally installed in homes so the coatings on the front face of the drywall were fully cured prior to testing. For three of the drywall materials, the sections of drywall provided for testing were large enough to prepare four separate pieces cut into six-inch squares. Two pieces from each material were placed back-to-back with the coated faces exposed and the edges taped. The other two pieces were placed front-to-front with the unfinished faces exposed and the edges taped. This provided paired samples that were tested simultaneously under identical conditions. Two additional drywall samples were selected from the high emitters and used to create two additional paired samples with either the front (uncoated) or back faces exposed and edges taped.

### ***Material Conditioning***

All drywall samples were conditioned for a minimum of one week prior to testing. Stainless steel chambers described in the Phase 1 report were used to prepare drywall samples prior to testing. Carbon filtered house air was humidified to levels comparable to the test conditions and delivered at approximately 250 cubic centimeters (cc) per minute to each chamber using flow-control valves and taper-tube flow meters. The area specific flow rate is equivalent to  $0.375 \text{ m}^3/\text{m}^2/\text{h}$  for six-inch squares with two faces exposed.

### ***Material Testing***

The LBNL emissions testing approach, using small emission chambers, follows ASTM Standard Guide D-5116-97 (ASTM International, 2002) and California Specification 01350 (CDHS, 2004). The approach has been used for a wide range of building materials measuring both VOCs and carbonyls as described previously (Maddalena et.al., 2009), and for the sulfur containing compounds tested in Phase 1. The method is described in detail in the Phase 1 report.

The test conditions for the temperature and RH tests were as follows. The chamber temperature,  $T$  ( $^{\circ}\text{C}$ ), was set to 25, 32 and  $41^{\circ}\text{C}$  and the RH was set to ~5, 50 and ~90% resulting in a  $3 \times 3$  experimental matrix for each of the five materials tested. The inlet flow,  $F$  (in liters per minute of carbon-filtered, preconditioned air) to each chamber was generally run at 1 liter per minute (LPM) but for some experiments was varied between 0.250 and 1 LPM. The inlet flow was supplied continuously to each test chamber and the exhaust flow from each chamber was vented to a fume hood. The desired RH was achieved by mixing streams of carbon/HEPA filtered air that was either dry or water-saturated through a bubbler. The emitting surface area of the tested materials, including the front and back faces,  $A$ , was approximately  $0.04 \text{ m}^2$  (6-inch-square pieces of drywall), resulting in a loading factor,  $L$ , of  $3.7 \text{ m}^2/\text{m}^3$  and an area-specific air flow rate of  $1.5 \text{ m}^3/\text{m}^2/\text{h}$  for each sample at 1 LPM ventilation rate. The ventilation rate in the chambers was approximately 5.6 air changes per hour (ACH).

The collection of air samples for measuring chemical emissions was initiated after the sample was loaded into the test chamber and kept there for a minimum of one hour to

allow time for conditions to stabilize and the chemical concentrations to reach steady state.

### ***Air Sampling and Analysis***

The *in situ* SPME sampling method followed directly by a gas chromatography sulfur chemiluminescence analysis (SPME-GC/SCD) was used to quantify reactive sulfur gases. The method was described in detail in the Phase 1 report (Maddalena et al., 2010). Some minor changes were made to the method for Phase 2 as summarized here. Polydimethylsiloxane (PDMS) with Carboxen fiber has been found to achieve the best sensitivity for most reduced sulfur compounds (Pandey and Kim, 2009). Ras et al. (2008) found that analytes reached equilibrium conditions at 45 minutes (min) with SPME. In our initial experiments we used a 50-min sampling period but subsequently found that 30 min was sufficient to get consistent and reliable results for the RSGs. After sampling directly from the chamber, the SPME fiber was retracted then immediately transferred to the hot (200 °C) injector, and the fiber was extended into the injector in splitless mode for 3 min followed by a 50-milliliter per minute (mL/min) purge for 1 min, and then a 15-mL/min purge for the rest of the run. The fiber remained in the inlet for at least 10 min before retracting the fiber and transferring the SPME to the front inlet at 300 °C with purge flow of 50 mL/min. Two SPME samplers were used alternately allowing the extracted SPME to condition for at least one hour between uses. The column flow in the GC during analysis was 2 mL/min and oven start temperature was -50 °C held for 2 min, then increased first to 250 °C at 10 °C/min and held for 2 min.

### ***Data Analysis***

In the Phase 1 report, all emission factors were given in terms of sulfur equivalent mass per unit area of emitting surface per hour and an equation was provided for converting the units to the mass of chemical per unit area of emitting surface per hour. In this report, all emission factors are reported as  $\mu\text{g}/\text{m}^2/\text{h}$  where the  $\mu\text{g}$  refers to the mass of the individual chemical being emitted. Emission factors were calculated from the measured steady-state concentration in the chamber. Under steady state conditions, the concentration in the chamber is constant so 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 factors,  $EF$  ( $\mu\text{g}/\text{m}^2/\text{h}$ ), in a well-mixed system is:

$$EF = \frac{F \times (C - C_B)}{A} \quad (1)$$

Where  $F$  ( $\text{m}^3/\text{h}$ ) is the ventilation flow rate;  $A$  ( $\text{m}^2$ ) is the exposed surface area of the test material;  $C$  ( $\mu\text{g}/\text{m}^3$ ) is the measured steady state concentration in the chamber; and  $C_B$  ( $\mu\text{g}/\text{m}^3$ ) is the background or blank concentration in an empty chamber.

### ***Sulfur Dioxide Artifacts in the SPME Sampling Approach***

In Phase 1 of this project, we observed sulfur dioxide in the calibration gas when using the SPME PDMS/Carboxen fiber (Maddalena et al., 2010).  $\text{SO}_2$  was not in the mix of calibration gas so there was an apparent conversion taking place either in the chamber, the sampling fiber or the GC inlet. Residence time in the chamber and GC inlet are relatively short and the concentrations low compared to in the SPME fiber so we

suspected an oxidation reaction catalyzed by the Carboxen was taking place in the fiber. Several experiments were conducted to identify the source of SO<sub>2</sub>. A comparison of SPME chromatograms of the calibration gas measured when the chamber was ventilated with carbon filtered house air versus nitrogen as shown in Figure 1 indicates that the production of SO<sub>2</sub> is accompanied by a loss of hydrogen sulfide (also shown in the figure) and methyl mercaptan (not shown) which indicates oxidation in the presence of air.

When observing only the instrument response, we see that at 25 °C, 50% RH and 1 LPM ventilation rate, the loss of hydrogen sulfide and methyl mercaptan accounts for ~ 83% of the total gained response for sulfur dioxide and a second peak that was tentatively identified as isopropyl mercaptan. For measurements collected in air with the PDMS/Carboxen coated SPME fiber, we cannot distinguish between SO<sub>2</sub> emitted directly from the material and SO<sub>2</sub> generated as a breakdown product of H<sub>2</sub>S and/or methyl mercaptan. However, the methyl mercaptan is generally much lower in concentration relative to the H<sub>2</sub>S so formation of SO<sub>2</sub> is likely to follow the oxidation of H<sub>2</sub>S following the reaction



The implication of this observation is that some fraction of the emissions reported as SO<sub>2</sub> when experiments are performed in air may in fact be H<sub>2</sub>S that has been oxidized on the SPME fiber during sampling.

#### ***Temperature/Relative Humidity Experimental Design***

The temperature/relative-humidity experiments were carried out using nitrogen to ventilate the chambers. Nitrogen was used to reduce the SPME fiber artifacts described above. Emission factors were measured for each material in a 3 × 3 experimental matrix that included low, medium, and high temperature and low, medium, and high RH resulting in nine different measurements for each material. The temperature of the incubator housing the chambers was set to the first temperature level and the RH in chambers 1, 3 and 4 were adjusted to approximately 5%, 50% and 90%, respectively by adjusting the relative air flow through the wet and dry supply lines for each chamber. Chamber 2 was used for calibration measurements at the different RH and temperature settings to compensate for changes in the SPME sampling rate under the different conditions. The calibration levels were prepared by diluting a standard gas containing 10 ppm each of hydrogen sulfide, carbonyl sulfide, methyl mercaptan, dimethyl sulfide and carbon disulfide in the calibration chamber. Calibration levels were obtained by adjusting the flow of the calibration gas and/or the ventilation rate in the chamber.

To start the experiment, the first RSG calibration gas flow rate, ventilation rate and RH settings were established in the calibration chamber (empty) and the three prepared and conditioned drywall subsamples for the first drywall panel were installed in the three remaining chambers. Each drywall subsample was pre-conditioned at the target RH (low, medium or high) so equilibration of the RH in the chamber was achieved within an hour of installation. While the drywall subsamples were equilibrating in the test chambers, a SPME measurement was collected from the calibration chamber. After measuring the concentration in the calibration chamber, we adjusted RH to the next RH setting without changing the gas flow or ventilation flow. SPME measurements were then collected from

each test chamber while the calibration chamber stabilized. When testing of the drywall subsamples for the first drywall panel was completed, the subsamples were removed and the chambers were allowed to purge for one hour before loading the next set of three drywall subsamples from the second drywall panel. While the test chambers were purging, we collected the second calibration measurement and then changed the RH setting in the calibration chamber to the third setting, again without changing the calibration gas flow or ventilation rate.

Alternating between calibration measurements and drywall measurements continued until each drywall sample was tested. Each time we completed a set measurements for a given calibration level and temperature for each of the three RH settings, the gas and/or ventilation flow rate was adjusted to provide the next calibration level and the process repeated. In this way we were able to construct calibration curves for the SPME fiber as a function of both temperature and RH simultaneously with the collection of the emission factor measurements for the drywall samples.

### ***Coating Experimental Design***

The coating experiments were run at 32 °C, 50% RH and 1 LPM ventilation flow using carbon filtered house air to ventilate the chambers. Emission factors were measured for the coated ( $EF_{front}$ ) and uncoated ( $EF_{back}$ ) faces for the paired samples harvested from problem homes (5462, 1396 and 2542) as described above, and the emission factors from the front and back were compared to estimate the influence of coatings. To assess possible differences between the front and back face, independent of coating, two additional materials (1379 and 7339) were included and prepared in a manner similar to the coated samples but with neither the front face nor the back face having coating. This provided a comparison to assess differences between front and back faces. The relative difference ( $RD$ ) between the EFs measured for the front and back of each sample was calculated as

$$RD = \frac{(EF_{front} - EF_{back})}{(EF_{front} + EF_{back})} \times 2 \quad (3)$$

The remaining drywall samples that were harvested from problem homes and provided by CPSC were tested under the same conditions as the coating experiments but with only the coated face exposed to determine field relevant emission factors for these samples.

## **RESULTS AND DISCUSSION**

### ***Emissions Variation with Temperature and RH***

A complete set of measured emission factors for five drywall samples tested during the temperature and RH experiments are summarized in Table 1 along with the relevant test conditions. The samples are identified by a four-digit CPSC material tracking number followed by an LBNL sample number. Both temperature and RH show strong positive correlations with the natural log of the emission factors as shown in Figure 2 for RH and Figure 3 for temperature. In both figures, the regression lines are exponential and the  $R^2$  is reported for each chemical ranging from 0.71 to 1.00 for temperature effect and between 0.85 and 0.99 for the RH effect.

Previous work measuring the temperature and RH dependence of formaldehyde emissions from building materials found that a linear regression model using the natural log of the percent RH and the inverse temperature as independent variables provides a good fit with experimental data (Parthasarathy et.al., 2011). Both Parthasarathy et.al, (2011) and Meyers (1985) assume an exponential relationship between concentration or emission factors and the inverse of temperature following the Arrhenius relationship. The same relationship is used here to evaluate the effect of temperature and RH on emission factors.

A multivariate linear regression model was constructed for each combination of drywall and RSG using data from the  $9 \times 9$  experimental matrix for each of the five drywall materials. The regression model statistics and model variable values are listed in Table 2. The model fit for all materials combined is illustrated in Figure 2 for each of the seven RSGs. The figure compares the natural log of the measured emission factors to the predicted values using the chemical specific multivariate regression values from Table 2.

The regression models in Table 2 are specific to the individual drywall samples that were tested. To generalize the regression modeling, the data were normalized to the standard emission factor (SEF), defined as the emission factor measured at 25 °C and 50% RH, by using the multivariate regressions in Table 2 to predict the SEFs and then calculating the ratio of the predicted EFs to the SEFs. The regression variables and statistics for the generalized model are reported in Table 3. This generalized model can be used, given an estimate or measurement of the chemical specific SEF for a drywall, to predict the EF that would result from a change in T and/or RH.

To simplify the results even further, the multivariate regression in Table 3 was used to construct curves of EF as a function of temperature with RH held constant at 50% and then EF as a function of the natural log of RH with temperature held constant at 25 °C. The slope of these two lines for each drywall and chemical combination are reported in Table 4. The coefficients can be used to approximate the effect of temperature and RH on emissions. For example, the temperature coefficient for H<sub>2</sub>S emitted from drywall sample 8357 is 0.21 indicating that for a 10 degree Celsius rise in temperature, the emission rate of H<sub>2</sub>S will approximately double (i.e., 10 degree rise in temperature  $\times$  0.21= a factor of 2.1 increase in the EF). Several of the coefficients in Table 3 indicate either a very small slope or a negative slope. These are mostly associated with the carbonyl sulfide that typically had very low emission factors for all drywall types, and for the domestic drywall sample that had low emission factors for most of the RSGs. The lack of temperature dependence for the RSGs from the domestic board indicates that the emission factors were contributed by background and/or carryover in the chambers.

For most of the drywall materials, the emission factors for SO<sub>2</sub> were highest in the tests conducted at 50% RH. This pattern was independent of temperature. In each case the emission factor for SO<sub>2</sub> increased between the low and medium RH and either stayed relatively constant or dropped between the medium and high RH. Although not correlated, the drop in SO<sub>2</sub> when RH was increased from medium to high was accompanied by a relatively large increase in CS<sub>2</sub>. At all three temperature settings, the CS<sub>2</sub> increased by a factor of between 1.25 and 5 when the RH was increased from low to medium. CS<sub>2</sub> increased by a factor of between 3 and 9 when the RH was increased from

the medium setting to the highest setting. It is unclear whether these two changes are related. The behavior of the SO<sub>2</sub> at the highest RH may be due to transformation to H<sub>2</sub>SO<sub>4</sub> by the reaction



even though the experiments were run under nitrogen so oxygen would be limited. The higher humidity may also slow or stop reaction shown in Equation 2, but there was not a correlated increase in H<sub>2</sub>S so that pathway is also unlikely.

Table 5 includes results from additional experiments using drywall samples 7339 and 9672 that were completed several weeks prior to the experiments reported in Table 1. The earlier experiment in Table 5 found higher emission rates compared to the later experiments, but the data are incomplete. The two materials were only tested at 25 °C before an instrument malfunction stopped the experiment. The results in Table 5 are included to provide additional information on the trend of emission factors as a function of temperature and RH but also on the possible trend in emission factors as a function of conditioning time. For reference, the emission factors measured for materials 7339 and 9672 during Phase 1 of the study are also included in Table 5 along with the date that the samples were tested. The results indicated a decrease in emission rates for all chemicals over time.

#### *Coatings effect on emissions*

All of the tests measuring standard emission factors for drywall in Phase 1 of this study and the temperature and RH experiments described above were conducted with uncoated and never-installed drywall samples. The edges were sealed as described in the methods section but both the front and back of the unfinished drywall samples were exposed during testing. We assumed that the front and back of a board would emit at the same rate and that the emission rates measured with uncoated drywall would be relevant to the conditions found in homes.

To test this assumption, paired samples were prepared for both coated and uncoated drywall and tested to determine if there were differences between the faces or differences caused by the coating. A description of the drywall samples used in the coating experiment is provided in Table 6 and the measured emission factors for each sample is listed in Table 7. The EF values are compared by plotting the relative difference between EF measured for the front and the back faces of each paired sample. Three of the samples had the front face coated to test the effect of coating and two of the samples were uncoated on both faces to assess differences between the front and back. The relative difference in EF for each of the RSGs is plotted in Figure 5 where each curve is centered on a grid-line representing the point where the emission factors are equal.

The results do not show any consistent difference between the front face and back face nor is there a difference between the coated face and uncoated face. Figure 6 is provided to show the average EF for the ten samples tested in the coating experiment. The apparent larger deviation for dimethyl sulfide in the uncoated samples is likely due to the very low level EF for this chemical.

## Conclusions

This is the second report of a two-phase project characterizing chemical emissions from problem drywall. The first report described the development of a small chamber method and *in situ* SPME sampling method for measuring emission factors for RSGs and reported standard emission factors for 30 drywall samples. This report extended that work by characterizing the effect of temperature and RH on the EFs and assessing the influence of coatings and differences between emissions from the front and back faces of drywall panels.

While preparing for the Phase 2 experiments, we determined the source of SO<sub>2</sub> in the calibration gas used in this study to be from oxidation on the PDMS/Carboxen SPME fiber. It was not possible to determine how much H<sub>2</sub>S and mercaptan was lost and what fraction of the SO<sub>2</sub> in the original study was from oxidation but clearly there was loss of H<sub>2</sub>S and mercaptan when samples are collected in air as compared to nitrogen. To determine the temperature and RH effect, five drywall samples were tested in a 3×3 experimental matrix based on temperature and RH. The results show a strong positive correlation between the EFs and both temperature and RH although the temperature effect was found to be most significant. The relationship was expressed as a multivariate linear regression for the natural log of EF as a function of inverse temperature and the natural log of RH. These regression models were further processed to allow the estimation of fractional change in the standard emission factor as a function of temperature and RH.

Several of the drywall samples included in the temperature and RH experiments were included in the original experiments measuring standard emission factors. These samples had aged both in isolated storage (foil wrapped) and in conditioning cans with and without air flow and the result was a marked decrease in the EFs measured in the Phase 2 experiments relative to the original measurements collected approximately one year earlier.

The coating experiments showed no significant effect of plaster and paint on the EFs for the RSGs. Nor did they show any difference between the front face of uncoated drywall and the back face. The emission factors reported in this project are relevant to modeling chemical concentrations in either the living space or the wall cavities.

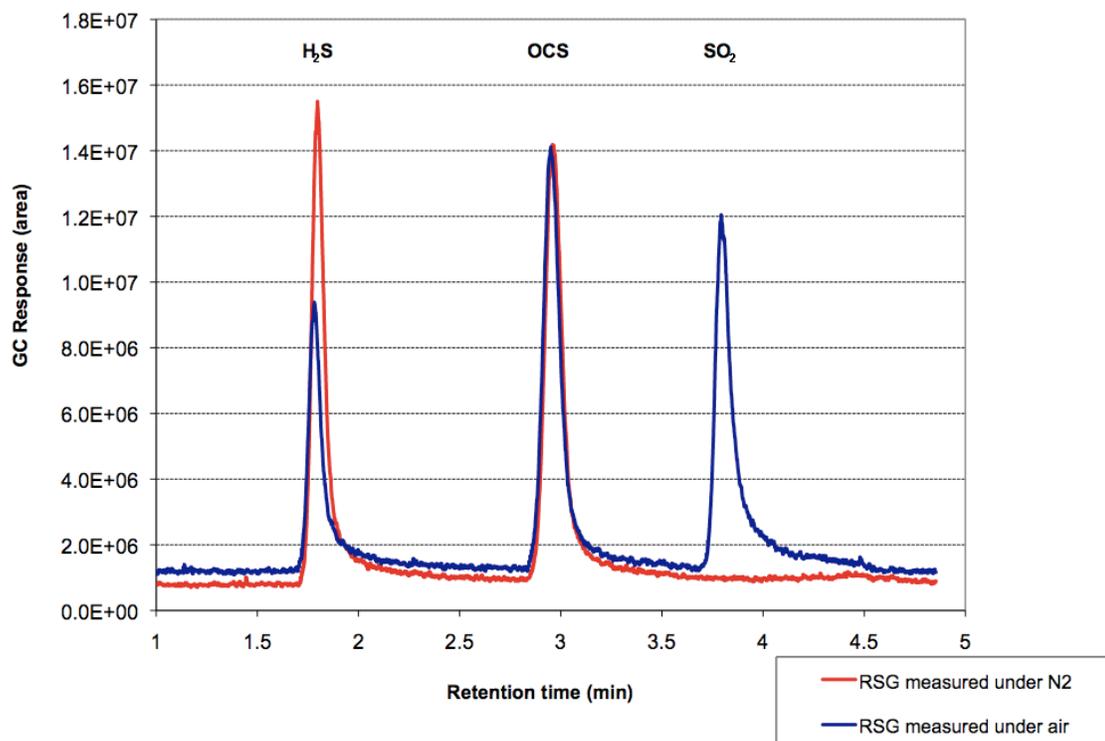


Figure 1: Sulfur chemiluminescence response overlay of calibration gas sampled with SPME using PDMS/Carboxen fiber with chamber ventilated using air (blue curve) or nitrogen (red curve) showing a drop in H<sub>2</sub>S response concurrent with an increase in the SO<sub>2</sub> response. There is a similar drop in methyl mercaptan when sampled under air and an increase of a second peak that is tentatively identified as isopropyl mercaptan.

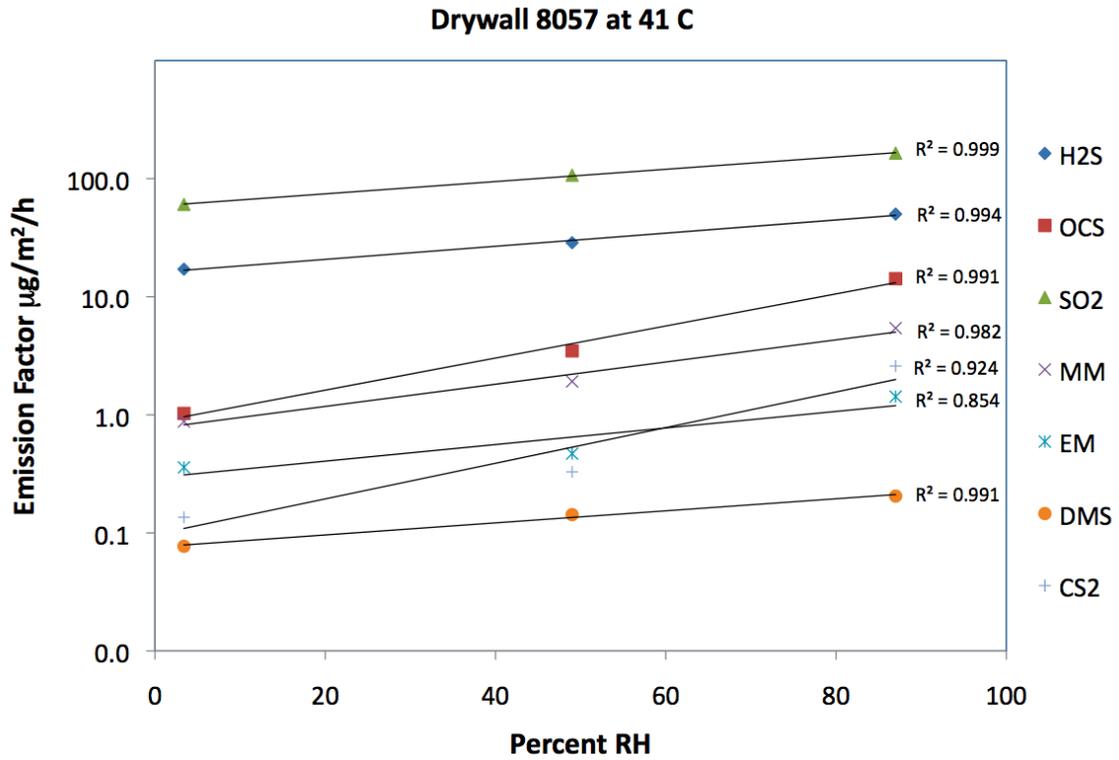


Figure 2: The emission factors for seven chemicals measured at 41 °C and three different RH levels showing the correlations between RH and emissions.

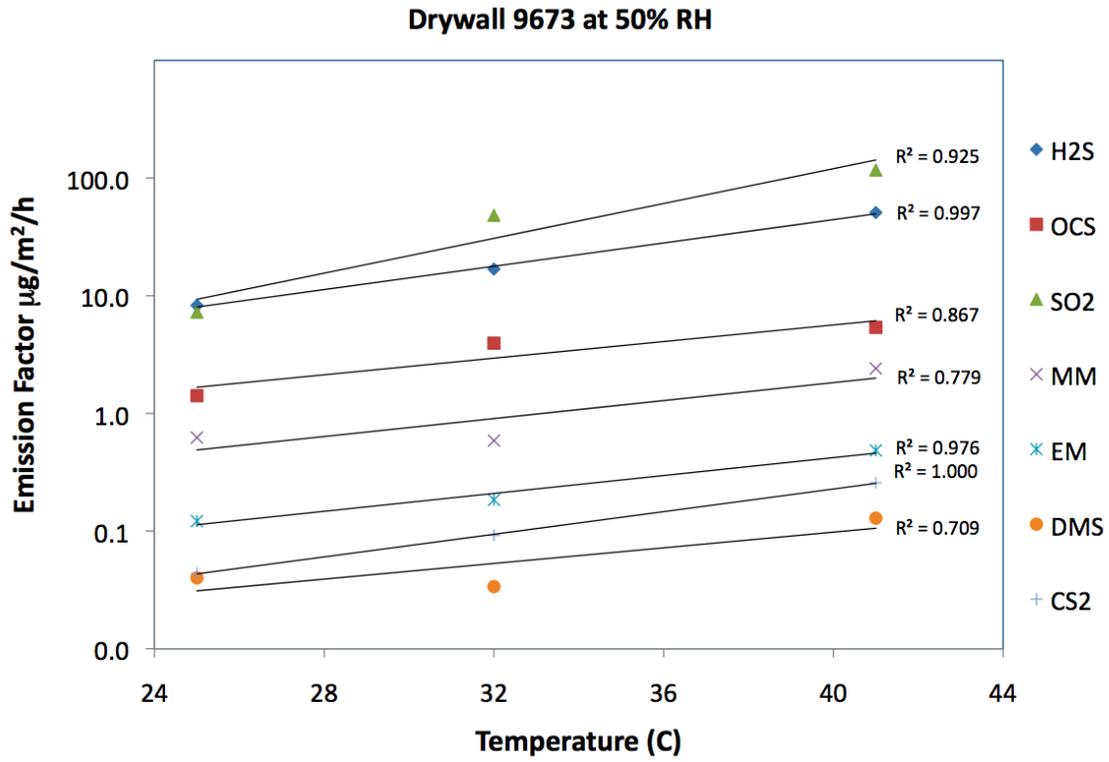


Figure 3: The emission factors for seven chemicals measured at 50% RH and three different temperature levels showing the correlation between temperature and emissions.

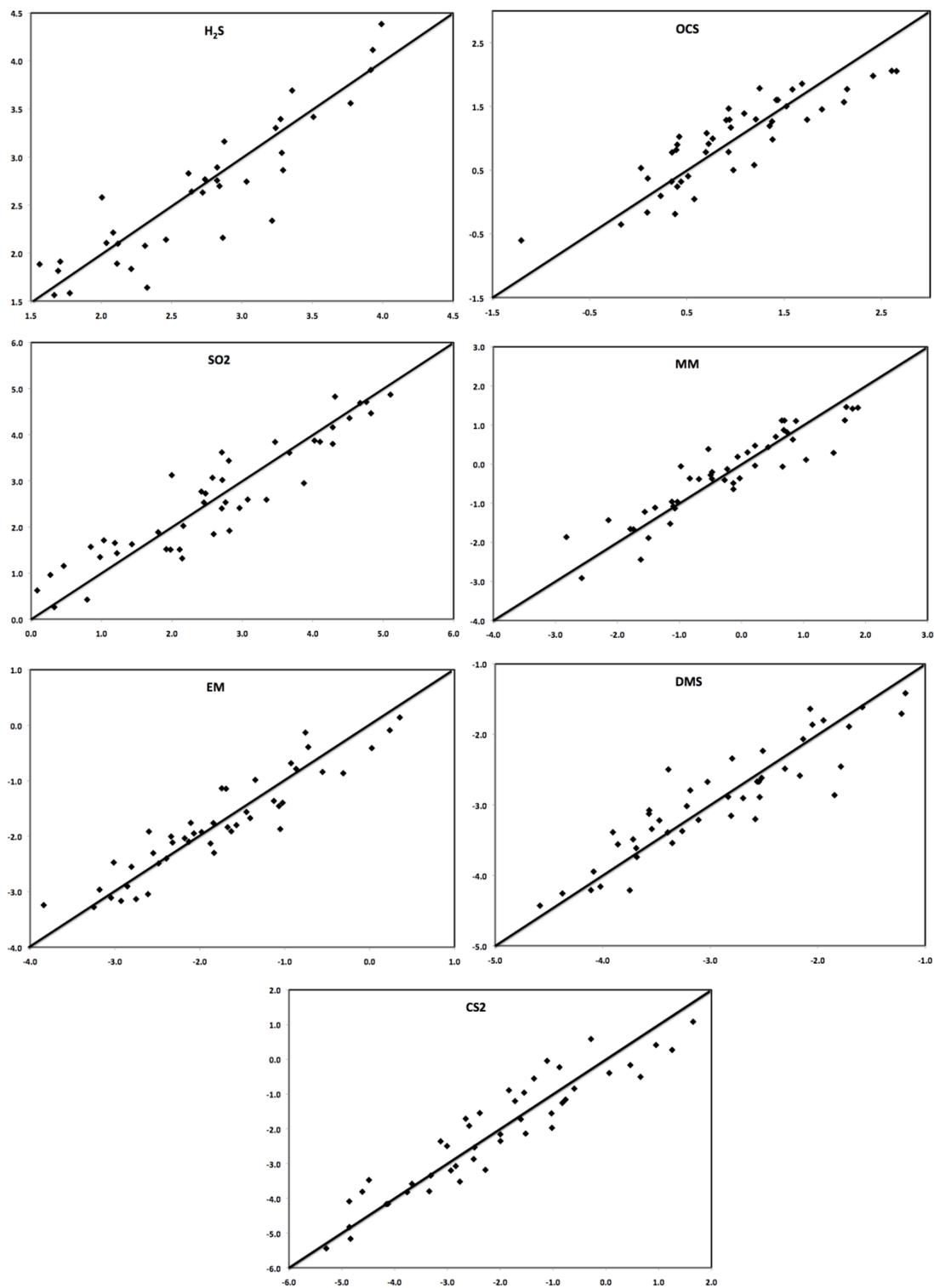


Figure 4: Comparison of the natural log of predicted and measured emission factors for RSGs using model parameters given in Table 2. The natural log of the measured EF is on the x-axis and the predicted values are plotted on the y-axis. The diagonal line is the 1:1 relationship.

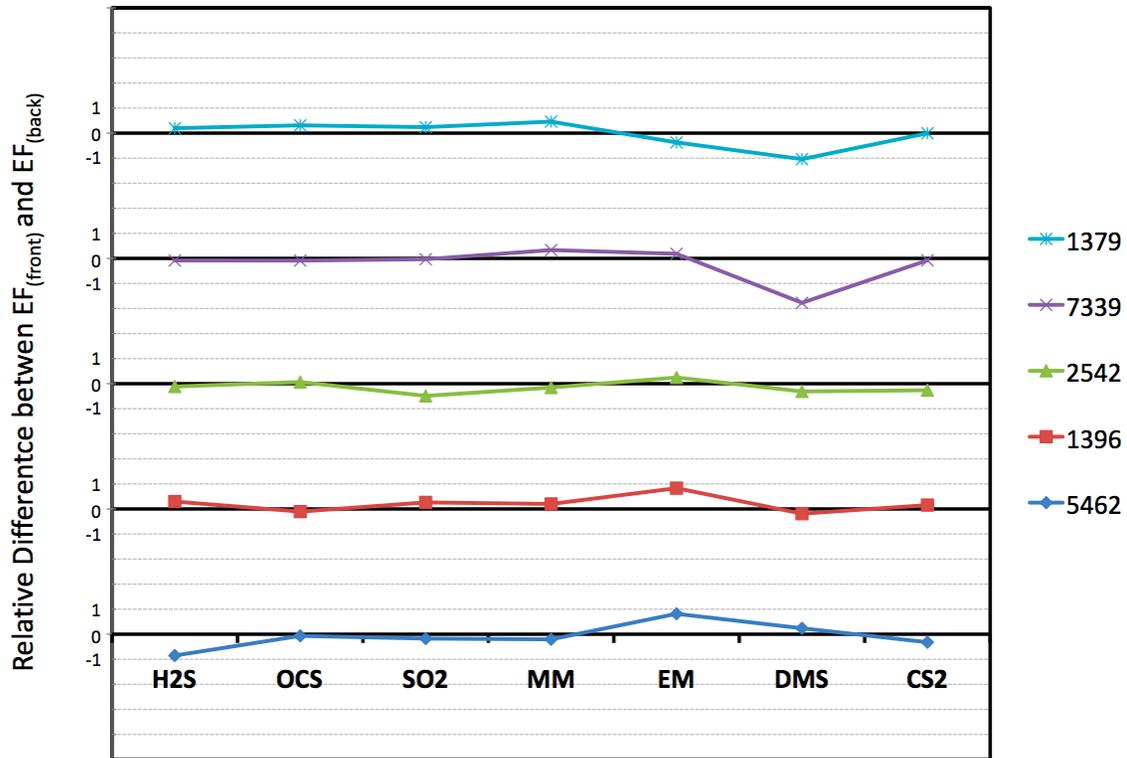


Figure 5: The relative difference of the EF between the front and back of drywall panels where 1379 and 7339 were uncoated on both sides while the other three drywall samples, which were collected from homes, were coated on the front face and uncoated on the back face. Each line is the relative difference  $(EF_{front} - EF_{back}) / \text{average}(EF_{front}, EF_{back})$  for the drywall panel and the solid grid-line represents perfect agreement. The dashed minor grid-lines are 1 unit apart.

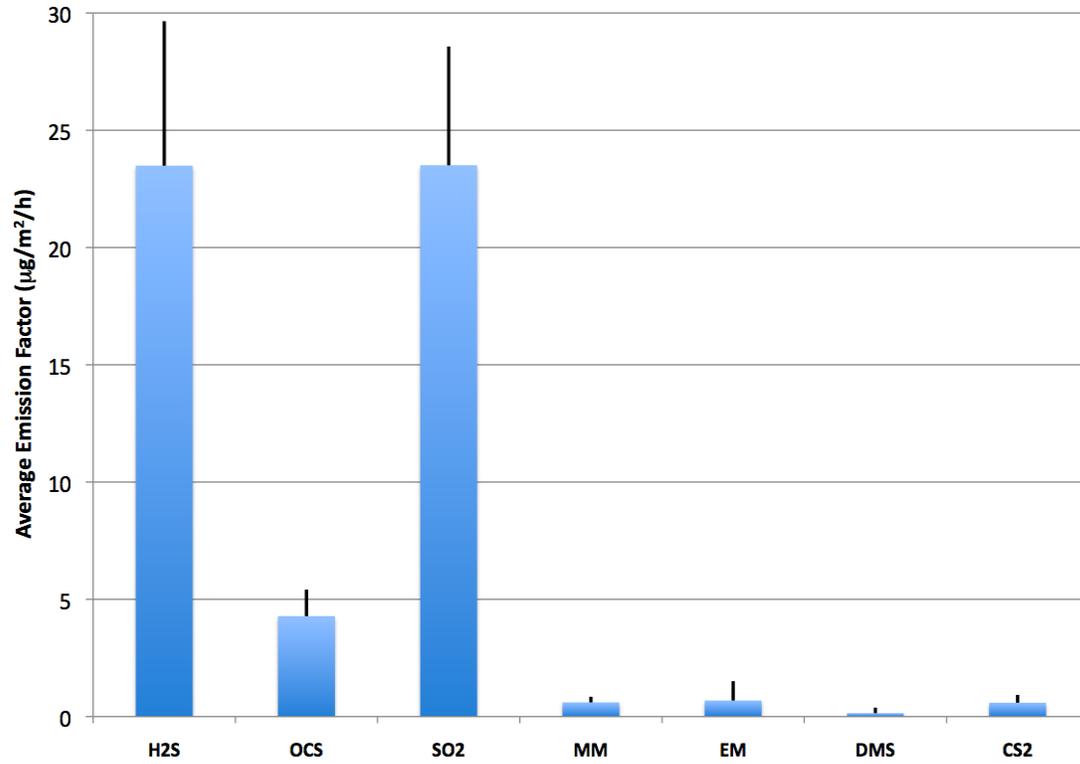


Figure 6: Average EFs for each chemical including both sides of all five drywall samples tested (n=10) in the coating experiment. The bar indicates one standard deviation.

Table 1: Experimental conditions and emission factors from T/RH experiments

Sample	Temperature (°C)			RH (%)			Emission Factors (µg/m <sup>2</sup> /h)						
	25	32	41	3.4	49	87	H <sub>2</sub> S	OCS	SO <sub>2</sub>	MM	EM	DMS	CS <sub>2</sub>
7339-01	x			x			5.29	1.49	3.29	0.32	0.04	0.02	0.05
7339-02	x				x		8.32	1.52	13.36	0.62	0.11	0.03	0.16
7339-03	x					x	8.04	3.86	6.07	0.80	0.19	0.04	1.07
7339-04		x		x			7.67	2.66	15.82	0.36	0.08	0.03	0.08
7339-05		x			x		14.05	2.47	11.91	0.94	0.23	0.04	0.42
7339-06		x				x	16.83	6.60	11.22	1.54	0.32	0.08	3.51
7339-07			x	x			15.44	1.48	39.17	0.61	0.20	0.06	0.20
7339-08			x		x		25.52	4.13	72.50	1.98	0.26	0.12	0.76
7339-09			x			x	33.37	8.55	31.99	5.30	0.42	0.18	5.22
8037-10	x			x			1.17	0.30	1.39	0.08	0.04	0.01	0.01
8037-11	x				x		2.63	1.10	1.59	0.12	0.05	0.02	0.01
8037-12	x					x	1.76	3.29	2.66	0.25	0.16	0.04	0.04
8037-13		x		x			0.70	1.46	2.22	0.20	0.05	0.02	0.01
8037-14		x			x		4.98	2.53	8.55	0.33	0.08	0.03	0.01
8037-15		x				x	5.91	2.15	8.24	0.88	0.15	0.06	0.06
8037-16			x	x			2.02	1.55	1.09	0.06	0.06	0.02	0.01
8037-17			x		x		4.77	2.55	6.82	0.50	0.12	0.03	0.01
8037-18			x			x	11.71	4.58	2.81	1.94	0.14	0.08	0.10
8357-19	x			x			2.33	0.84	2.33	0.17	0.09	0.01	0.02
8357-20	x				x		3.67	1.49	19.29	0.38	0.18	0.02	0.07
8357-21	x					x	24.87	2.59	28.29	4.42	0.73	0.08	0.44
8357-22		x		x			9.14	1.78	21.67	0.34	0.13	0.04	0.06
8357-23		x			x		13.73	3.35	16.57	1.24	0.40	0.05	0.21
8357-24		x				x	26.65	8.28	15.01	2.08	1.03	0.10	1.93
8357-25			x	x			17.12	1.03	60.53	0.88	0.36	0.08	0.14
8357-26			x		x		28.68	3.48	106.97	1.92	0.47	0.14	0.33
8357-27			x			x	50.14	14.22	164.56	5.42	1.43	0.21	2.59

Table 1: Experimental conditions and emission factors from T/RH experiments (continued)

Sample	Temperature (°C)			RH (%)			Emission Factors (µg/m <sup>2</sup> /h)						
	25	32	41	3.4	49	87	H <sub>2</sub> S	OCS	SO <sub>2</sub>	MM	EM	DMS	CS <sub>2</sub>
9672-28	x			x			3.79	1.26	3.38	0.22	0.07	0.02	0.02
9672-29	x				x		5.52	2.02	16.72	0.43	0.07	0.03	0.05
9672-30	x					x	10.09	5.67	8.68	1.24	0.24	0.07	0.22
9672-31		x		x			5.44	1.67	11.63	0.21	0.06	0.02	0.03
9672-32		x			x		7.43	2.97	15.11	1.10	0.10	0.17	0.08
9672-33		x				x	20.75	4.20	7.37	2.29	0.16	0.08	0.36
9672-34			x	x			15.19	2.00	55.97	0.76	0.02	0.08	0.08
9672-35			x		x		26.43	4.87	91.96	2.00	0.10	0.13	0.18
9672-36			x			x	43.44	11.17	124.85	6.54	0.35	0.31	0.55
9673-37	x			x			0.62	1.10	1.31	0.18	0.05	0.03	0.02
9673-38	x				x		8.26	1.41	7.24	0.62	0.12	0.04	0.04
9673-39	x					x	17.52	3.97	4.18	2.84	0.34	0.16	0.36
9673-40		x		x			10.24	1.41	14.99	0.33	0.06	0.03	0.04
9673-41		x			x		16.84	3.96	48.17	0.59	0.18	0.03	0.09
9673-42		x				x	17.72	2.53	13.14	1.74	0.57	0.06	0.47
9673-43			x	x			26.89	2.06	72.52	0.97	0.21	0.11	0.14
9673-44			x		x		50.86	5.38	116.94	2.41	0.49	0.13	0.26
9673-45			x			x	54.10	13.54	74.91	6.00	1.27	0.30	1.59

H<sub>2</sub>S=hydrogen sulfide; OCS=carbonyl sulfide; SO<sub>2</sub>=sulfur dioxide; MM=methyl mercaptan; EM=ethyl mercaptan; DMS=dimethyl sulfide; CS<sub>2</sub>=carbon disulfide

Table 2: Regression model variables and statistics for estimating emission factors<sup>a</sup>

Sample		H <sub>2</sub> S	OCS	SO <sub>2</sub>	MM	EM	DMS	CS <sub>2</sub>
7339	1/T	-7.1×10 <sup>3</sup>	-3.4×10 <sup>3</sup>	-1.1×10 <sup>4</sup>	-7.3×10 <sup>3</sup>	-6.2×10 <sup>3</sup>	-7.8×10 <sup>3</sup>	-8.6×10 <sup>3</sup>
	ln(RH)	0.20	0.29	0.07	0.43	0.35	0.31	0.87
	b	24.97	11.21	39.96	22.41	17.27	21.41	24.71
	r <sup>2</sup>	0.98	0.61	0.81	0.90	0.91	0.95	0.82
8037	X <sub>1</sub>	-5.9×10 <sup>3</sup>	-5.4×10 <sup>3</sup>	-2.1×10 <sup>3</sup>	-6.1×10 <sup>3</sup>	-2.2×10 <sup>3</sup>	-2.8×10 <sup>3</sup>	-3.6×10 <sup>3</sup>
	X <sub>2</sub>	0.45	0.37	0.34	0.56	0.30	0.33	0.51
	b	19.03	17.06	6.98	17.03	3.71	4.66	6.01
	r <sup>2</sup>	0.82	0.73	0.45	0.69	0.74	0.72	0.57
8357	X <sub>1</sub>	-9.2×10 <sup>3</sup>	-5.2×10 <sup>3</sup>	-1.3×10 <sup>4</sup>	-6.9×10 <sup>3</sup>	-5.9×10 <sup>3</sup>	-9.3×10 <sup>3</sup>	-9.8×10 <sup>3</sup>
	X <sub>2</sub>	0.37	0.47	0.32	0.60	0.47	0.33	0.79
	b	31.50	16.47	45.91	20.63	16.75	26.52	27.92
	r <sup>2</sup>	0.77	0.74	0.76	0.76	0.79	0.86	0.78
9672	X <sub>1</sub>	-8.7×10 <sup>3</sup>	-4.0×10 <sup>3</sup>	-1.4×10 <sup>4</sup>	-8.7×10 <sup>3</sup>	1.2×10 <sup>3</sup>	-8.7×10 <sup>3</sup>	-7.6×10 <sup>3</sup>
	X <sub>2</sub>	0.29	0.37	0.18	0.57	0.42	0.39	0.63
	b	29.94	13.13	49.15	26.51	-7.44	24.60	20.48
	r <sup>2</sup>	0.88	0.81	0.80	0.90	0.61	0.85	0.84
9673	X <sub>1</sub>	-1.3×10 <sup>3</sup>	-6.3×10 <sup>3</sup>	-1.9×10 <sup>4</sup>	-7.7×10 <sup>3</sup>	-8.0×10 <sup>3</sup>	-6.8×10 <sup>3</sup>	-1.1×10 <sup>4</sup>
	X <sub>2</sub>	0.47	0.35	0.21	0.55	0.53	0.27	0.67
	b	43.76	20.57	63.57	23.32	23.01	18.61	30.50
	r <sup>2</sup>	0.81	0.79	0.88	0.79	0.88	0.56	0.79

<sup>a</sup> the multivariate linear regression model takes the form  $\ln(\text{EF}) = X_1 \times 1/T + X_2 \times \ln(\text{RH}) + b$  where EF has units of  $\mu\text{g}/\text{m}^2/\text{h}$ , T is absolute temperature (K) and RH is given in percent.

Table 3: Regression model variables and statistics for estimating the ratio of EF/SEF<sup>a</sup>

Sample		H <sub>2</sub> S	OCS	SO <sub>2</sub>	MM	EM	DMS	CS <sub>2</sub>
7339	1/T	-1.2×10 <sup>4</sup>	-4.0×10 <sup>3</sup>	-3.4×10 <sup>4</sup>	-1.3×10 <sup>4</sup>	-9.5×10 <sup>3</sup>	-1.4×10 <sup>4</sup>	-1.8×10 <sup>4</sup>
	ln(RH)	0.33	0.29	0.23	0.59	0.44	0.49	1.04
	b	41.36	13.39	115.11	41.02	31.32	46.92	57.56
	r <sup>2</sup>	0.93	0.96	0.93	0.88	0.91	0.90	0.79
8037	X <sub>1</sub>	-8.9×10 <sup>3</sup>	-7.7×10 <sup>3</sup>	-2.2×10 <sup>3</sup>	-9.4×10 <sup>3</sup>	-2.3×10 <sup>3</sup>	-3.2×10 <sup>3</sup>	-4.3×10 <sup>3</sup>
	X <sub>2</sub>	0.51	0.42	0.29	0.60	0.27	0.30	0.43
	b	28.93	25.35	7.43	30.43	7.84	10.55	13.81
	r <sup>2</sup>	0.90	0.92	0.97	0.88	0.97	0.96	0.93
8357	X <sub>1</sub>	-1.9×10 <sup>4</sup>	-7.2×10 <sup>3</sup>	-4.5×10 <sup>4</sup>	-1.1×10 <sup>4</sup>	-8.8×10 <sup>3</sup>	-2.0×10 <sup>4</sup>	-2.3×10 <sup>4</sup>
	X <sub>2</sub>	0.67	0.49	1.03	0.68	0.53	0.62	1.14
	b	63.77	23.40	149.11	36.63	28.46	65.94	72.48
	r <sup>2</sup>	0.86	0.91	0.84	0.86	0.89	0.88	0.78
9672	X <sub>1</sub>	-1.8×10 <sup>4</sup>	-5.0×10 <sup>3</sup>	-5.7×10 <sup>4</sup>	-1.7×10 <sup>4</sup>	9.0×10 <sup>2</sup>	-1.8×10 <sup>4</sup>	-1.4×10 <sup>4</sup>
	X <sub>2</sub>	0.52	0.37	0.77	0.82	0.25	0.65	0.76
	b	58.40	16.49	187.17	56.03	-2.97	57.34	43.62
	r <sup>2</sup>	0.89	0.94	0.88	0.83	0.98	0.87	0.84
9673	X <sub>1</sub>	-4.2×10 <sup>4</sup>	-9.9×10 <sup>3</sup>	-1.3×10 <sup>5</sup>	-1.4×10 <sup>4</sup>	-1.5×10 <sup>4</sup>	-1.1×10 <sup>4</sup>	-2.6×10 <sup>4</sup>
	X <sub>2</sub>	1.29	0.46	1.64	0.71	0.72	0.40	1.15
	b	137.28	32.53	417.08	44.29	48.07	37.43	84.81
	r <sup>2</sup>	0.80	0.90	0.84	0.85	0.85	0.92	0.79

<sup>a</sup> the multivariate linear regression model takes the form  $EF/SEF = X_1 \times 1/T + X_2 \times \ln(RH) + b$  where EF/SEF is the ratio of the emission factor at T and RH to the standard emission factor at 25 °C and 50% RH

Table 4: Temperature and RH coefficients for increase in emission factors

Sample	Factor	Coefficient or slope of line relative to environmental factor						
		H <sub>2</sub> S	OCS	SO <sub>2</sub>	MM	EM	DMS	CS <sub>2</sub>
7339	T	0.14	<i>0.04</i>	0.38	0.14	0.10	0.16	0.20
	Ln(RH)	0.33	0.29	0.23	0.59	0.44	0.49	1.04
8037	T	0.10	<i>0.08</i>	<i>0.02</i>	0.10	<i>0.03</i>	<i>0.03</i>	<i>0.05</i>
	Ln(RH)	0.51	0.42	0.29	0.60	0.27	0.30	0.43
8357	T	0.21	<i>0.08</i>	0.50	0.12	0.10	0.22	0.25
	Ln(RH)	0.67	0.49	1.03	0.68	0.53	0.62	1.14
9672	T	0.19	<i>0.05</i>	0.62	0.19	<i>-0.01</i>	0.19	0.15
	Ln(RH)	0.52	0.37	0.77	0.82	0.25	0.65	0.76
9673	T	0.46	0.11	1.38	0.15	0.16	0.12	0.29
	Ln(RH)	1.29	0.46	1.64	0.71	0.72	0.40	1.15

Table 5: Results for drywall 7339 and 9672 from earlier experiments <sup>a</sup>

Drywall	Test date	Relative Humidity (%)			Emission Factors ( $\mu\text{g}/\text{m}^2/\text{h}$ )						
		3.4	49	87	H <sub>2</sub> S	OCS	SO <sub>2</sub>	MM	EM	DMS	CS <sub>2</sub>
7339-P1 <sup>b</sup>	12/03/09		x		131.2		89.33	2.00		0.85	6.41
7339-46	02/15/11	x			32.18	8.07	20.38	3.30	0.07	0.07	0.22
7339-47	02/15/11		x		60.61	7.05	113.00	8.03	0.35	0.09	0.47
7339-48	02/15/11			x	99.12	27.51	38.07	20.89	0.90	0.19	3.42
9672-P1 <sup>b</sup>	02/02/10		x		71.60	3.51	22.22	0.59		0.03	0.27
9672-49	02/16/11	x			12.63	2.52	15.23	1.74	0.07	0.11	0.14
9672-50	02/16/11		x		33.28	5.17	56.21	4.30	0.15	0.11	0.17
9672-51	02/16/11			x	85.91	14.37	121.33	14.44	0.27	0.20	0.51
9672-52	02/16/11			x	94.90	12.23	123.77	16.99	0.45	0.24	0.53

<sup>a</sup> All experiments in this table conducted at 25 °C

<sup>b</sup> Data extracted from Table 3 of Phase 1 report and converted from  $\mu\text{g-S}/\text{m}^2/\text{h}$  to  $\mu\text{g}/\text{m}^2/\text{h}$  and shown here for comparison purposes

Table 6: Description of drywall samples from field and coating experiment<sup>a</sup>

<b>Sample</b>	<b>Exposed face</b>	<b>Coating</b>
09-302-2543	Front	Smooth textured finish with flat paint
10-302-1266-01	Front	Sample from ceiling with roll-on medium texture and flat paint
10-302-1266-02	Front	Sample from closet wall with medium knock down texture and flat paint
09-302-2544	Front	Heavy spray on knock down texture with flat paint
10-302-1719	Front	Heavy knock-down texture or skip trowel texture with flat or possibly egg-shell finish
10-810-5462-02	Front	Medium spray on texture with flat paint
10-810-5462-02	Back	Unfinished
809-302-1396-15	Front	Smooth coat plaster with flat paint
809-302-1396-15	Back	Unfinished
09-302-2542-01	Front	Medium spray on texture with flat paint
09-302-2542-01	Back	Unfinished
810-7339	Front	Unfinished
810-7339	Back	Unfinished
1379-10	Front	Unfinished
1379-10	Back	unfinished
Empty chamber	Blank	Empty chamber

<sup>a</sup> Samples were tested as received. See methods for description of preparation of samples for coating experiment. No coatings were applied at LBNL.

Table 7: Emission factors ( $\mu\text{g}/\text{m}^2/\text{h}$ ) measured at 32 °C and 50% RH

CPSC Sample #	H <sub>2</sub> S	OCS	SO <sub>2</sub>	MM	EM	DMS	CS <sub>2</sub>
09-302-2543	12.77	7.34	32.79	0.90	0.55	0.06	0.16
10-302-1266-01	13.98	7.92	26.46	0.55	0.44	0.13	0.23
10-302-1266-02	9.05	6.40	22.09	1.04	0.22	0.10	0.34
09-302-2544	6.30	4.23	16.09	0.40	0.12	0.07	0.72
10-302-1719	7.81	4.68	11.90	0.36	0.10	0.05	0.89
10-810-5462-02	11.57	3.43	17.19	0.41	0.22	0.05	0.37
10-810-5462-02	28.69	3.66	20.44	0.50	0.09	0.04	0.51
809-302-1396-15	30.43	5.96	33.35	1.05	2.75	0.07	0.55
809-302-1396-15	22.58	6.62	25.63	0.86	1.14	0.09	0.47
09-302-2542-01	24.67	4.02	17.48	0.69	0.19	0.04	0.98
09-302-2542-01	27.63	3.76	28.70	0.80	0.14	0.05	1.28
810-7339	25.98	3.51	23.13	0.59	1.01	0.05	0.65
810-7339	28.21	3.83	23.90	0.42	0.84	0.79	0.70
1379-10	19.30	4.65	25.34	0.46	0.20	0.07	0.21
1379-10	15.85	3.40	19.93	0.29	0.29	0.23	0.21
Empty chamber	3.03	5.52	6.63	0.45	0.16	0.03	0.12

## REFERENCES

ASTM International (2002) “Standard Test Method for Determining Formaldehyde Concentration in Air from Wood Products Using a Small Scale Chamber. Designation: D 6007-02.

Baltussen, E., F. David, P. Sandra, and C. Cramers. 1999. *On the performance and inertness of different materials used for the enrichment of sulfur compounds from air and gaseous samples*. Journal of Chromatography A, 864: 345–350.

CDHS (2004) California Department of Health Services “Standard Practice for the Testing of Volatile Organic Emissions from Various Sources Using Small-Scale Environmental Chambers. Environmental Health Laboratory Branch. July 15, 2004.

Maddalena R., M. Russell, M. Melody and M. G. Apte (2010) *Small-Chamber Measurements of Chemical-Specific Emission Factors for Drywall*. Lawrence Berkeley National Laboratory. Report number LBNL-3986E.

Maddalena R., M. Russell, D.P. Sullivan and M.G. Apte (2009) *Formaldehyde and Other Volatile Organic Chemical Emissions in Four FEMA Temporary Housing Units* Environmental Science and Technology. 43:5626–5632.

Myers, G.E. (1985) *The Effects of Temperature and Humidity on Formaldehyde Emission from UF-Bonded Boards: A Literature Critique*. Forest Prod. J. 35: 20-31.

Pandey, S.K., and K.-H. Kim. 2009. *A review of methods for determination of reduced sulfur compounds (RSCs) in air*. Environmental Science & Technology, 43: 3020–3029.

Parthasarathy, S., Maddalena, R.; Russell, M.; Apte, M.G. 2011 *Effect of temperature and humidity on formaldehyde emissions in temporary housing units*. JAWMA. 61: 689-695.

Ras, M.R., F. Borrull, and R.M. Marcé. 2008a. *Determination of volatile organic sulfur compounds in the air at sewage management areas by thermal desorption and gas chromatography–mass spectrometry*. Talanta, 74: 562–569.

Ras, M.R., R.M. Marcé, and F. Borrull. 2008b. *Solid-phase microextraction—gas chromatography to determine volatile organic sulfur compounds in the air at sewage treatment plants*. Talanta, 77:774–778.