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Sent: Thursday, May 14, 2009 3:25 PM
To: McGeehin, Mike (CDC/CCEHIP/NCEH)
Subject: Fw: CPSC-LBNL wallboard IAG work plan
Attachments: CPSC Narrative Workplan 90427.doc

FYI
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Sent: Thu May 14 15:22:47 2009
Subject: CPSC-LBNL wallboard IAG work plan

Hi Gary. Here is the work plan that we developed for the CPSC IAG.

Best
Mike

1 **Background** - This work-plan responds to a need for measured emission factors
2 for sulfur containing compounds in gypsum board as outlined in the informal
3 description of emissions chamber studies provided by the Consumer Products
4 Safety Commission (CPSC) dated 4/9/2009 and subsequent conversations
5 between LBNL and CPSC.

6 According to the CPSC, "the purpose of the chamber studies is to provide
7 quantitative data on gas emissions from drywall." The emission factors need to
8 be presented in a way that is sufficient for deriving exposure concentrations in
9 dwellings and/or in confined spaces containing corrodible materials.

10 The proposed project includes two phases.

11 The objective of the first phase is to screen pristine (fresh) wallboard samples¹ to
12 1) identify the chemicals (primarily volatile sulfur constituents (VSCs) but also
13 VOCs) that are emitted from wallboard (no joint compound, no texture, and no
14 paint); 2) quantify emission factors for the main constituents in the emission
15 stream (reported as micrograms per square meter of material) and 3) calculate
16 and report steady-state indoor concentrations for the major constituents based
17 on archetypal home ventilation and wallboard loading factors per California
18 Specification 01350². An additional objective of Phase I is to provide a screening
19 assessment of the corrosiveness of the emissions from wallboard as it pertains to

¹ The wall board samples will be provided by CPSC.

² In the California Specification 01350 titled "Standard Practice for the Testing of Volatile Organic Emissions from Various Sources using Small-Scale Environmental Chambers" the measured emission factors derived from small chamber experiments are used to estimate steady-state building concentrations for comparison to a concentration of interest (i.e., chronic reference exposure levels, odor threshold, sensory irritation threshold, ...).

1 household components such as copper wires, receptacles, switches, electronic
2 boards, smoke detectors, gas lines and connectors.

3 The second phase of the study will focus on a limited number of higher emitting
4 materials identified in Phase I to characterize factors that may influence long-
5 term emissions such as temperature, moisture, ventilation, and wall coverings
6 (paint, joint compound, texture, paper) to support the reconstruction of chronic
7 exposure concentrations in both the ventilated and unventilated spaces in
8 dwellings.

9 **LBNL chambers** - LBNL has several existing test systems for characterizing
10 material specific emission factors. These include four small (10.5 L) stainless
11 steel chambers housed in a temperature controlled environment; a medium sized
12 (395L) continuous stirred emission chamber constructed from low sorption
13 materials; a room-scale (20 m³) stainless steel test chamber for standardized
14 material testing; and a room-scale "real room" test chamber for characterizing
15 complete wall systems. Well established test protocols are available for all of the
16 chamber systems. Therefore, minimal effort is anticipated to bring the emission
17 chamber component of the study on-line. However, the reactive nature of many
18 of the reduced sulfur constituents of interest may require that the stainless steel
19 chambers and transfer lines be treated using Sulfinert[®] surface coating.

20 The small chambers provide the quickest experimental results because multiple
21 samples (up to four) can be tested simultaneously for a given temperature and
22 humidity setting. The medium chamber provides better air mixing control to
23 characterize the relationship between emissions and ventilation and can also be

1 loaded with more material to improve detection limits as needed. The medium
2 chamber may also provide a useful test system for exposing metal and electronic
3 samples to artificial emissions to characterize corrosion rates in-situ. The large
4 chambers provide room scale testing where field relevant loading factors and
5 ventilation rates can be simulated.

6 Recommendation – Assuming we are able to achieve adequate detection limits
7 (see below), the preferred approach would be to use the small chamber system
8 to determine standard emission factors following established protocols. The need
9 for treating the chambers and sample handling components to reduce loss of
10 reactive sulfur constituents will be determined after the analytical methods are
11 established. Results from the small chambers will provide initial, and relatively
12 rapid (compared to the larger chambers) estimates for emission factors for all
13 samples. Single samples can be run first to identify potential high emitters with
14 follow-up experiments including replicates of samples that are found to have
15 higher emissions.

16 To improve sample throughput, it is anticipated that up to 16 pre-conditioning
17 chambers will be constructed to provide a controlled environment for bringing
18 fresh samples into equilibrium with test conditions prior to installation in the
19 emissions chambers. This is expected to increase sample throughput by
20 approximately a factor of four because the emission factors can be measured
21 from samples either the same day that they are installed or the following
22 morning. Without the pre-conditioning chambers it would be necessary to wait
23 several days to a week before fresh samples had equilibrated to the standard

1 temperature and humidity conditions used for testing. The pre-conditioning
2 chambers may also provide a testbed for assessing the rate and extent of
3 corrosion on household components exposed to the emissions from wallboard as
4 described below.

5 **LBNL sampling and analysis** - LBNL has well established methods for
6 collection and analysis of volatile organic chemicals, low molecular weight
7 aldehydes and organic acids, both in field samples and in experimental
8 chambers. However, we have not previously focused on the volatile sulfur
9 containing constituents that are of interest in this study. Therefore we will need
10 to identify appropriate methods and/or modify our existing methods to assure
11 adequate detection limits to meet the project objectives.

12 *Target experimental sensitivity* – To estimate the target detection limits, we note
13 that a report prepared by Unified Engineering Inc. for the Bureau of Community
14 Environmental Health, Florida Department of Health measured sulfur
15 components in headspace over gypsum and paper after the materials were
16 subjected to high humidity and found three primary sulfur containing chemicals –
17 carbonyl sulfide, hydrogen sulfide and trace amounts of carbon disulfide. These
18 chemicals are rarely measured in homes but when detected, the carbon disulfide
19 and carbonyl sulfide have been found to be approximately 5 ppb ($\sim 15 \mu\text{g}/\text{m}^3$)
20 (Larkin et al., 2008; Wiesel et al., 2008).

21 Assuming steady state conditions, only one source material, and no contribution
22 from outside air, the indoor concentration C_{ss} ($\mu\text{g}/\text{m}^3$) of a pollutant is related to
23 the material specific emission factor EF_i for material i ($\mu\text{g}/\text{m}^2/\text{h}$) as

1
$$EF_i = \frac{C_{ss} \times ACH}{L_i} \quad (1)$$

2 where L_i (m^2/m^3) is the loading factor or surface area of material per volume of
3 dwelling and ACH (h^{-1}) is the air exchange rate in the dwelling. The approximate
4 surface to volume ratio for gypsum board in homes is $1.2 m^2/m^3$ (Hodgson et al.,
5 2004) and a typical air exchange rate is $0.5 (h^{-1})$. Therefore, assuming gypsum
6 board is the primary source of sulfur containing compounds, the emission factor
7 that would result in a concentration of $15 \mu g/m^3$ is $6 \mu g/m^2/h$.

8 Applying this emission factor to a material in the small experimental chamber
9 with a material loading factor of approximately 2 and a ventilation rate of 5 would
10 result in a steady state concentration of $2.5 \mu g/m^3$, per Equation 1. For VOC
11 analysis, we typically sample up to 6 liters of air. Assuming we can achieve
12 acceptable collection efficiency and recovery, this sample volume would collect
13 15 ng of analyte, which is well within the typical range of quantification for other
14 VOCs. Therefore, we expect to be able to analyze carbon disulfide using a
15 modified version of our VOC method. However, carbonyl sulfide and hydrogen
16 sulfide have very low boiling points so may be difficult to collect on
17 thermodesorption tubes under ambient conditions. We will construct a
18 cryotrapping system to attempt to collect all analytes with the same sample but if
19 this is not successful, we will adapt an existing aldehyde method for collection
20 and analysis of carbonyl sulfide and apply OSHA Method 1008, which utilizes
21 silver nitrate coated silica gel for collection and analysis of hydrogen sulfide.

1 *Sampling and Analysis Method Development* – We will start by adapting and
2 optimizing our VOC method, which is based on EPA Method TO-17, for
3 quantification of volatile sulfur compounds. We will determine whether carbonyl
4 sulfide and hydrogen sulfide can be collected and quantified with the VOC
5 method. Analyzing the highly volatile and reactive sulfur constituents may require
6 a specially formulated GC column, inert surface treatment of transfer lines, ultra-
7 cold sample collection tubes and GC inlet, and a water management system for
8 cold trap sampling. We will test the use of cold trap conditions for sample
9 collection and the use of drying tubes or two-stage cold trap protocols to remove
10 water from the sample air stream. Having as many analytes included in the same
11 analysis stream is advantageous because it reduces labor and supply costs but if
12 we cannot analyze for all the volatile sulfur compounds (VSCs) using a modified
13 version of the TD-GCMS method then chemical specific methods will be applied.
14 For example, if we cannot achieve the desired detection limits for the carbonyl
15 sulfide and/or hydrogen sulfide using the modified VOC method, we will use an
16 existing aldehyde method with DNPH coated samplers that derivitize the
17 carbonyl compound which is then analyzed by HPLC. For the hydrogen sulfide,
18 we will evaluate the applicability of a test method based on OSHA method T-
19 1008 which uses silver nitrate coated silica gel to collect hydrogen sulfide. This
20 method is similar to our existing method for sampling and analysis of volatile
21 organic acid compounds. Once the appropriate method(s) are identified and
22 optimized, we will develop basic QA/QC criteria for collection efficiency, method
23 detection and quantification limits and analyte recovery.

1

2 **Measurements of emission factors** – Once the instrumental analyses are
3 optimized for the VSCs, we can proceed with emission testing. Using the small
4 emissions chambers we can process 12 samples per month for standard
5 emission factors if the small chambers are also used for pre-conditioning the
6 samples. Our small chamber protocol generally follows ASTM Standard Guide D-
7 5116-97 and CDHS 2004 “Standard Practice for the Testing of Volatile Organic
8 Emissions from Various Sources Using Small-Scale Environmental Chambers”.
9 The objective is to screen a large number of samples for material specific
10 emission factors so to increase sample throughput, a set of pre-conditioning
11 chambers will be constructed to allow samples to be brought to equilibrium with
12 environmental conditions prior to being installed in the emission chambers.
13 Previous work with building materials indicates that samples equilibrate within a
14 few days after chamber conditions are changed so if we use pre-conditioning
15 chambers before loading the materials then the air-sampling in the small
16 chambers can begin within approximately 6 air changes after installing the
17 material. This will allow us to process materials at a rate of four samples per day
18 (four days per week) or an average of 16 samples per week.

19 The tests will be conducted in four 10.5-L stainless steel chambers maintained at
20 23 ± 1 °C in a controlled environmental chamber. If necessary, the chambers will
21 be surface coated with Sulfinert[®] treatment prior to use to minimize surface
22 interactions with the reactive sulfur constituents. A 0.06-m³/h inlet flow of carbon-

1 filtered preconditioned air at $50\% \pm 5\%$ relative humidity³ will be supplied
2 continuously to each test chamber. The relative humidity within the test
3 chambers will be controlled by a flow of mixed streams of dry- and water-
4 saturated air. The RH can be adjusted over a wide range so the Phase I
5 experiments can be conducted at a selected RH based on needs of CPSC (i.e.,
6 conditions relevant to Gulf Coast states). The backs and raw edges of the
7 gypsum board samples will be sealed by pressing (snug fit) into stainless steel
8 trays and the samples will be placed face up on screens that rest slightly below
9 the center of the test chamber. For each material, the emitting area, A (m^2), will
10 be 0.023; the loading factor, L (m^2/m^3), will be 2.2; and the area-specific flow rate
11 ($m^3/m^2/h$) will be approximately 2.6 ($m^3/m^2/h$). The total sampling rate for all
12 samples collected from the chamber exhaust stream will be maintained at less
13 than 90% of the inlet air stream to prevent introduction of room air into the
14 samplers. These conditions may need to be adjusted depending on the final
15 analytical methods used but the values will be used to guide the initial setup of
16 the experiments.

17 **Assessing corrosiveness of emissions –**

18 The objective of the corrosiveness testing is to characterize the potential for
19 damage of household components exposed to the emissions from the wallboard.

20 The emissions testing will identify wallboard that has the highest emissions of
21 volatile sulfur chemicals as well as other volatile organic chemicals. Based on
22 these results, we will classify the wallboard as high, medium or low emitters.

³ Baseline conditions for humidity and temperature will be identified after consulting with the funding agency to insure the values are relevant to the conditions of interest.

1 Samples of these boards will be obtained from CPSC for use in the corrosion
2 testing. The premise is that the actual board will provide a more realistic and
3 relevant emission stream than a custom mixed gas stream designed to mimic the
4 emissions results. The material pre-conditioning chambers developed for the
5 emission testing provide a matrix of test containers that can provide a range of
6 controlled humidity and ventilation conditions. To provide an elevated source in
7 the chambers for accelerated corrosion conditions, four walls within each
8 chamber will be covered with the wallboard that is selected for testing. For a
9 chamber with dimensions of 12×12×18 inches, this results in a loading factor > 5
10 m²/m³, which is well above typical values in homes and comparable to what
11 would be expected in an unventilated wall cavity. If needed to accelerate
12 corrosion, we will identify options for installing the test chambers in a controlled
13 temperature environment.

14 Once the chambers are loaded with source materials, a set of sentinel materials
15 will be installed in each container. Sentinel materials include copper test strip,
16 silver test strip, or other metal alloys as requested by CPSC. The test strips will
17 be installed with test face oriented towards the open end of the chamber to allow
18 monitoring of corrosion. The open face of the chambers will be closed using a
19 transparent face material with clamping ring and the conditions in each chamber
20 will be adjusted to a predetermined combination of RH and ventilation. The
21 selection of conditions in the exposure chambers will result in a wide range of
22 humidity and chemical concentration values and at least one chamber will be run
23 without wallboard as a control and at least four chambers will be reserved for

1 installation of actual household components (i.e., receptacles, switches, smoke
2 detectors, ...).

3 The chemical concentration in each chamber will be periodically monitor for
4 target VSCs and VOCs . This will include at least thee different sampling times
5 over the course of the experiment. Corrosion on the test strips will be tracked
6 using high resolution images. The experiments are expected to run
7 approximately 30 days depending on the rate of corrosion observed. At the end
8 of the experiment, test strips will be remove and characterized by electron
9 microscopy depending on instrument availability or the test strips and household
10 components will be packaged and shipped to CPSC for further evaluation.

11 The experimental matrix will be repeated for at least two wallboard types (high
12 emitter and low emitter). An optional third experimental matrix would include the
13 range of wallboards tested for emission all run at the same conditions so a direct
14 comparison across boards can be made. An advantage of this approach is that it
15 uses real materials for the source of corrosive gas and uses standardized
16 materials as the corroding substrate. Each experiment provides a
17 multidimensional dataset including temperature, concentrations, ventilation and
18 corrosion, which could lead to a detailed semi-empirical model for translating the
19 results to field conditions.

20

21 **Phase II emission factor characterization –**

1 The work-plan to address Phase II objectives will be provided after initial results
2 are reported from Phase I. Phase II will likely use a combination of the small and
3 medium chambers to characterize environmental factors and long-term
4 emissions and possibly one or both of the larger chambers to explore the impact
5 of wall coverings and exposure of building materials that may enhance the
6 corrosiveness of the wallboard emissions.

7

8 **Estimated Cost**

9 See budget/proposal.

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DRAFT

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