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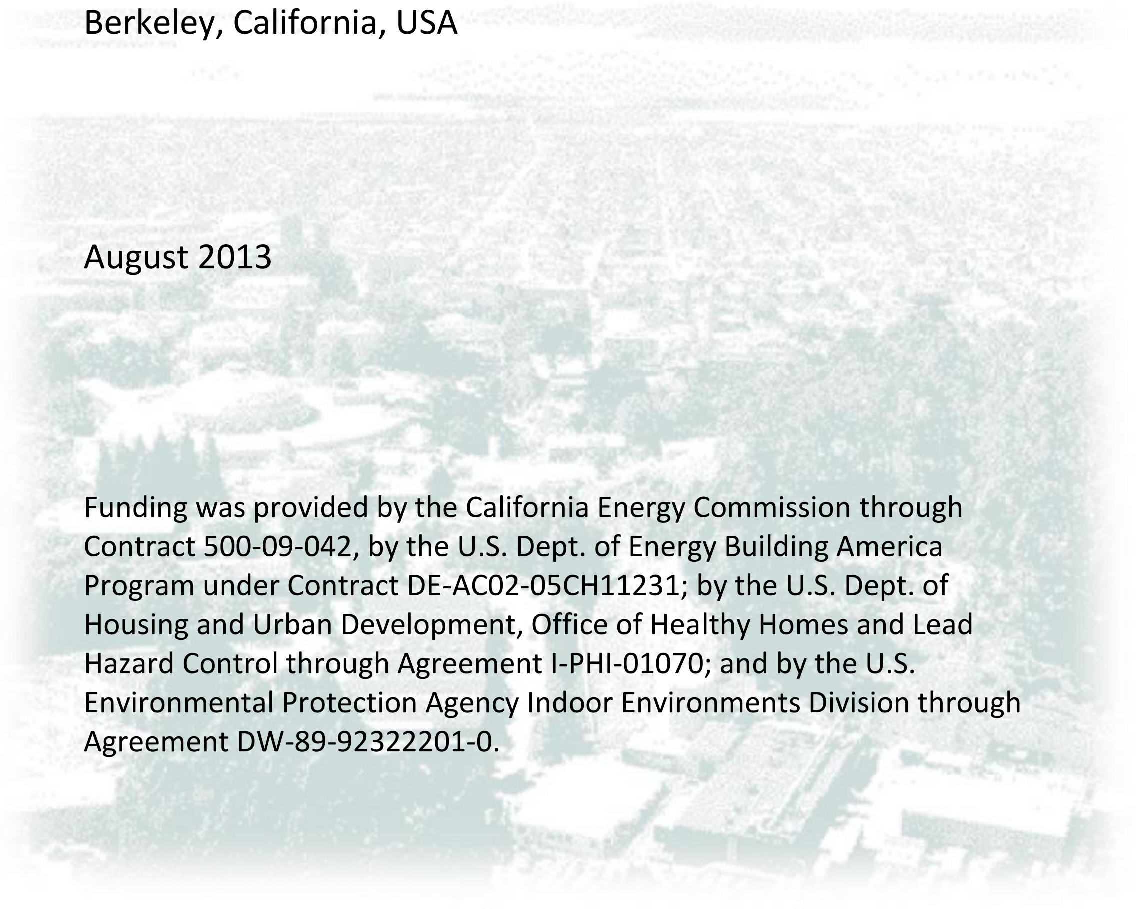

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Investigation of Formaldehyde and Acetaldehyde Sampling Rate and Ozone Interference for Passive Deployment of Waters Sep-Pak XPoSure Samplers

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Abstract

This study investigated formaldehyde and acetaldehyde passive sampling rates and ozone interference for the DNPH-based Waters Sep-Pak XPoSure sampler. Previous studies have shown that ozone interferes with active sampling by this cartridge. Our study included one laboratory and six field experiments conducted in Northern California homes. Passive sampling rates of 1.10 ± 0.09 and 0.86 ± 0.10 mL/min determined for formaldehyde and acetaldehyde are lower than previously reported. In a controlled laboratory experiment there were small, statistically insignificant impacts of subsequent ozone exposure on formaldehyde and acetaldehyde mass passively collected on the samplers. This sampler is inexpensive, easy to deploy and to transport by mail, and has a high sampling capacity when used passively; it is suitable for a wide-range of monitoring applications. However, the passive sampling rate remains in question given the internally consistent, but different results obtained in our study and the previous study.

1. Introduction

Formaldehyde and acetaldehyde are ubiquitous air pollutants that are commonly present in homes at concentrations exceeding health-based exposure guidelines (Logue et al., 2011). A commonly used method to measure formaldehyde and acetaldehyde concentrations in homes is to collect the compounds onto samplers coated with 2,4-dinitrophenylhydrazine (DNPH), extract with acetonitrile, and quantify the derivative compounds by high performance liquid chromatography (CARB 430, EPA 0011). This approach is suitable for active or passive air sampling and there are many commercially available samplers that utilize this chemistry, as summarized in Table 1.

Other formaldehyde samplers that have been described in the literature are not currently available as commercial products. These include samplers leveraging aldehyde reactions with DNPH (Grosjean and Williams, 1992; Gillett et al., 2000), $NaHSO_3$ (Geisling et al, 1982), O-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine (Tsai and Hee, 1999), and dansylhydrazine (Zhang et al., 2000). Some of these samplers have been validated for collection of other aldehydes (Grosjean and Williams, 1992; Tsai and Hee, 1999; Zhang et al., 2000).

Active sampling requires a pump with a consistent and measured flow rate. Active sampling enables short duration sampling and provides a more precise and consistent measurement than passive samplers. Passive sampling is more flexible and less expensive to conduct since it requires no pump or power, makes no noise, and allows longer sampling durations. The ideal passive sampler for residential applications is inexpensive, deployable by an untrained layperson, and validated over a wide range of sampling durations. Few currently available passive aldehyde samplers achieve all these objectives. The capacity of the UMEx and Sigma-Aldrich samplers may be inadequate for continuous sampling beyond one week. The Sigma-Aldrich sampler requires deployment in a particular orientation, which may not be amenable to deployment by untrained persons. The 3M and Radiello samplers cost 1.5-2 times more than other samplers (USA prices, March 2013).

In addition to those listed in Table 1, a DNPH-Silica cartridge designed for active sampling (Waters Sep-Pak XPoSure, part # WAT047205) was shown to be suitable for passive sampling with sampling rates of 1.48 mL/min for formaldehyde and 1.23 mL/min for acetaldehyde (Shinohara et al., 2004). The unit cost of these samplers is among the lowest of those that are currently commercially available (USA prices, March 2013). The manufacturer reports an active sampling capacity of 70 μg of formaldehyde. Studies have shown that active sampling with these cartridges in the presence of ozone results in biased low measurements (Sirju and Shepson, 1995; Kleindienst et al., 1998). The manufacturer has developed an ozone scrubber to precede the cartridge for active sampling. We found no published information on sampling capacity or the effect of ozone when the XPoSure cartridge is used passively. Although there is no holder for deployment provided by the manufacturer, we fabricated two holder designs using inexpensive parts. One design utilized a small tool holder (McMaster Carr #1723A63) and the other a nickel-plated luer lock with female tube coupler on one end and a threaded male fitting on the other (McMaster Carr #51465K161).

In this work, we present the results of one laboratory and six field experiments designed to examine acetaldehyde and formaldehyde sampling rates, and the influence of ozone, when the XPoSure sampler is used passively.

2. Methods

2.1 Laboratory experiment

In an experiment conducted at Lawrence Berkeley National Laboratory in 2010, nine XPoSure samplers were placed in a 39.5 L Teflon chamber for 98 hours. An inlet stream of purified house air was supplied to the chamber at 7.6 x10^3 mL/min, resulting in an air-exchange rate of 11.5 h^{-1}. The chamber was mixed continuously with a large impeller. A thermistor-based data logger (onsetcomp.com) confirmed that temperature (T) and relative humidity (RH) were maintained at a mean ± standard deviation of 21.3 ± 0.5˚C and 48.1 ± 5.1%. An NE-4000 model syringe pump (New Era Pump Systems, syringepump.com) and a Gerstel (gerstelus.com) Tube Spiking Apparatus were used to inject an aqueous solution into the chamber via a 500 μL glass syringe at a rate of 0.012 μL/min and a T of 100 ºC. The aqueous mixture included formalin (Sigma part # 252549, 37% in water, stabilized with 10% methanol) and an acetaldehyde standard (Sigma part # 402788, 99.5% in water) dissolved in deionized water to a final concentration of 200 mg/mL for each analyte and 5-8% methanol. Concentrations of formaldehyde and acetaldehyde in the chamber were measured by active sampling with a peristaltic pump (Cole Parmer Master Flex). Two 40 to 50 L samples were collected at 750 mL/min once during each day of the 4-day experiment. The active sampling indicated average concentrations of formaldehyde and acetaldehyde in the chamber of 58 and 53 ppb, respectively. After exposure, three of the samplers were stored in the freezer to await analysis and the remaining six were divided between two 10 L Siltek-coated stainless steel chambers. Both chambers were maintained between 22.8 and 23.5 ˚C and 48% to 50% RH, and were supplied with 1.0 LPM of purified house air. A stream of ozone was supplied to one of the chambers at a rate of 56.5 mL/min via a Teflon tube attached to one of the chamber ports, maintaining an average concentration of 70 ppb. Ozone was generated using a Stable Ozone Generator (Model S0G-2, UVP LLC, uvp.com), and monitored using a Teledyne API (teledyne-api.com) Model 400E UV Absorption ozone analyzer. The other chamber was maintained as an ozone free environment. After 76 hours, all samples were extracted with high purity acetonitrile and analyzed by HPLC.

2.2 Ten day field experiment

A 10-day field experiment was conducted during March 2012 in the great room of a single-family home with a floor area of 93 m^2 and built in 1944. Samplers were set-up in the corner of a half-wall separating the kitchen and living room. On the first day of the experiment, fourteen samplers were deployed; twelve sampled passively and two sampled actively. An average 10.3 mL/min of room air was pulled through the active samplers using a peristaltic pump. Figure 1 shows a photograph of the fourteen samplers. Every two days, the two active samplers were removed, sealed in airtight bags and replaced with two new samplers. This step was repeated every two days of the 10-day sampling period, until five contiguous pairs of continuous two-day active samples had been collected. On Day 4, three of the passive aldehyde samplers were removed and packaged in airtight bags, but were *not* replaced. Every two days following Day 4, three more passive samplers were removed, until the final triplicate was removed on Day 10. The schedule of samples for the10-day experiment is shown in Table 2.

2.3 Six-day field experiment

Six-day experiments were conducted in five homes from June through August 2012. On Day 1 of these experiments, three passive and two active samplers were set-up in the home. Roughly 10 mL/min of room air was pulled through the active samplers using a peristaltic pump. The airflow rate was measured roughly once a day. On Day 6, the five samplers were removed from the home and returned to the lab for analysis. The six-day experiments were conducted in homes in multiunit buildings. Two of the buildings were less than 10 years old (H3, H6), while the remaining four were more than 30 years old. One of the homes had a floor area of roughly 140 m^2 (H5), while the remaining five had floor areas of less than 70 m^2. At one of the homes (H5), the samplers were set-up in a kitchen that had been renovated with a new wood floor and wood cabinets within 3 months prior to the experiment. Placement of the samplers in H5 is shown in Figure 2.

2.4. Passive sampling rate calculation

If the mass of pollutant sampled remains well below the cartridge capacity, and the collection efficiency remains constant during sampling, the ratio of mass simultaneously sampled passively (M_P) and actively (M_A) is expected to vary linearly according to the relationship described by Equation 1.

$$\frac{M_P}{Q_P t} = \frac{M_A}{Q_A t} = \overline{C} \qquad (1)$$

In this equation, Q_P and Q_A are the passive and active sampling rates, t is the duration of time over which sampling occurs, and $\bar{C}$ is the average concentration of the pollutant in the sampled air. This equation can be rearranged to obtain the expression for passive sampling rate shown in Equation 2.

$$Q_P = Q_A \frac{M_P}{M_A} \tag{2}$$

Since Q_A is the measured pump flow rate and M_P and M_A are the mass quantities measured by HPLC, Q_P is the only unknown parameter.

2.5 Quality assurance for HPLC Analysis

The analytical limit of detection (LOD) and limit of quantitation (LOQ) were calculated by analyzing seven injections of a certified liquid standard of 2,4-dinitrophenylhydrazone derivatives of formaldehyde and acetaldehyde by HPLC. The LOD was calculated as the standard deviation of the seven injections multiplied by the students' t-value corresponding to a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom, according to US EPA procedure (Title 40 Code of Federal Regulations Part 136, Appendix B, revision 1.11). The critical t-value was 3.143. The LOQ was calculated as ten times the standard deviation of the seven analyzed samples. The resulting LOD and LOQ values were 3.48 $\times 10^{-3}$ and 1.11 $\times 10^{-2}$ μg for formaldehyde and 7.77 $\times 10^{-3}$ and 2.47 $\times 10^{-2}$ μg for acetaldehyde. Assuming sampling occurs for six days at the passive sampling rates reported in this paper, the LOD and LOQ would be equivalent to air concentrations of 0.3 and 0.9 ppb for formaldehyde and 0.6 and 1.8 ppb for acetaldehyde.

Eight laboratory blank samples were included in HPLC analysis of field samples and produced mean ± standard deviation formaldehyde and acetaldehyde masses of 6.4 ± 9.2 $\times 10^{-3}$ μg and 3.5 ± 0.9 $\times 10^{-2}$ μg. Five of the samples had formaldehyde concentrations of zero, thus contributing to the high standard deviation. The masses measured on samples collected from the field and laboratory experiments were adjusted by subtracting the mean mass collected on blanks. The uncertainty associated with exposed samples was determined by taking the square root of the sum of squared uncertainties associated with the masses measured on blank and replicate exposed samples. All exposed samples exceeded the LOQ, even after blank subtraction and within the calculated range of uncertainty.

3. Results

3.1 Influence of ozone on passive sampling rate

The amounts of formaldehyde and acetaldehyde collected on samples in the laboratory chamber are shown in Table 3. The average mass of formaldehyde collected by cartridges that were exposed to ozone following aldehyde exposure was 4% lower than the mass collected by cartridges not exposed to ozone. Conversely, the mean mass of acetaldehyde collected by cartridges exposed to ozone was 7% higher than cartridges not exposed to ozone. Applying the Mann-Whitney test (two-tailed) indicates that these groups were indistinguishable, based on $p<0.1$ (Table 4). The most significant difference was observed between the acetaldehyde mass measured by the cartridges immediately analyzed and those that were exposed to ozone ($p=0.2$). However, this difference was not in the direction expected, and the difference between the cartridges exposed to zero air and those exposed to ozone was not significant ($P=0.4$). There was a progressive increase in the standard deviation of the three groups for both formaldehyde and acetaldehyde, suggesting that the delay in analysis and/or ozone exposure may have had an influence on the precision of measurements. However, the standard deviations of all groups were small relative to the mean (3-15% of mean value).

Overall, these results suggest that ozone does not interfere with passive sampling of formaldehyde and acetaldehyde by the Sep-Pak DNPH cartridges. One hypothesis for this result is that, when sampling passively, ozone reacts only with DNPH derivatives at the face of the cartridge, whereas active sampling pulls ozone deeper into the sampling medium. However, more data are needed to test this hypothesis.

3.2 Passive sampling rate

Results from field experiments to determine passive sampling rates are presented in Table 5. The laboratory experiment conducted in 2010 yielded sampling rates of 1.24 and 0.97 mL/min for formaldehyde and acetaldehyde based on the six samplers not exposed to ozone. Results from the five six-day experiments and the six-, eight- and ten-day passive samples from H1 yielded mean ± one standard deviation passive sampling rates of 1.09 ± 0.08 and 0.84 ± 0.09 mL/min for formaldehyde and acetaldehyde. The four-day passive samples from H1 were excluded, because the mass of acetaldehyde collected was only 2.2 times the mean mass measured on laboratory blanks. The combined sampling rates calculated from both field and lab experiments were 1.10 ± 0.09 and 0.86 ± 0.10 mL/min for formaldehyde and acetaldehyde.

There was no detectable influence of sampling duration on the formaldehyde passive sampling rates calculated from the experiment at H1. However, there was an apparent increase in the acetaldehyde passive sampling rate between 6 and 8 days; however, a two-tailed t-test for independent groups indicates that the difference between the two rates is not significant ($p= 0.16$). It should also be noted that the mass of acetaldehyde collected on the four- and six-day samples were only 2.2 and 2.7 times the mean mass measured on blanks, respectively, increasing the relative uncertainty of the result.

The passive sampling rates determined from both laboratory and field experiments in this study were 25-30% below the rates of 1.48 and 1.23 mL/min for formaldehyde and acetaldehyde reported by Shinohara et al. (2004). There are a few possible explanations for this result. First, sampling in the Japanese homes was conducted for periods ranging from 12 hours to 14 days, with a mean duration of 65 hours. In addition, the mean mass of formaldehyde sampled actively and passively in the Japanese homes was 30x and 2x higher, respectively, than the mean sampled in the California homes, though both studies confirmed that the mass sampled was neither below the detection limit nor above the sampling capacity. It is conceivable that the passive sampling rate varies under different loading conditions, as is the case with the UMEx 100 passive sampler (see Table 1). Second, environmental factors such as T and RH affect the aldehyde sampling rate. Specifically, an increase in T increases diffusive transport into the sampler (Brown, 2000), and sampling in very low RH environments may decrease collection efficiency (Otson et al., 1993). T and RH were not reported for experiments conducted by Shinohara et al. (2004) and not measured in three of the experiments in the present study (see Table 5). In the four deployments in which T and RH were measured, the sampling rates did not clearly vary as expected. A third possible source of error is ozone interference with the concentrations determined by active sampling, since an ozone scrubber was not used for active sampling in either study. Elevated ozone levels could result in biased low active measurement, thus causing over prediction of the passive sampling rate (see Equation 2). Unfortunately, ozone concentrations were not measured in either study. Sadanaga et al. (2012) reported that, in 2005, the average ozone concentration in Tokyo calculated from 23 monitoring sites was roughly 30 ppb in the fall and winter and 60 ppb in the spring and summer. Ozone concentrations measured at central monitoring sites located 3 - 7 km from the homes in the present study ranged from 17- 31 ppb, with a mean of 22 ppb. The fraction of outdoor ozone that penetrates and persists indoors typically ranges from 0.2 – 0.7 (Weschler, 2000). Past studies have indicated that the percent decrease in measured formaldehyde resulting from ozone exposure depends on both the ozone and formaldehyde concentrations (Sirju and Shepson, 1995; Kleindienst et al., 1998). Thus, as the concentrations of the two pollutants vary, the relative bias is also expected to vary. However, in both the present study and the study in Japan, a regression of the active and passive sampling results does not exhibit the variability that would be expected if ozone interference were significant.

It is not uncommon for the uptake rate of passive samplers to vary with experimental design and environmental conditions (Bhangar et al., 2013; Delgado-Saborit and Esteve-Cano 2006; Mason et al. 2011). In this case, there is insufficient information to identify the exact cause of the difference in results between these two studies. More research is needed to assess the sensitivity of the XPoSure cartridge passive sampling rate to factors such as sampling duration, sampling load, T and RH.

4. Conclusions

The objectives of this study were to measure the passive sampling rate and assess possible ozone interference of a commercially available aldehyde sampler intended for active sampling. We measured passive sampling rates of 1.10 ± 0.09 and 0.86 ± 0.10 mL/min for formaldehyde and acetaldehyde, respectively, in Northern California homes. These rates are lower than previously reported by Shinohara et al. (2004). The cause of this difference is unclear. Results from the ozone exposure experiment indicate that ozone does not significantly interfere when deploying the XPoSure cartridge for passive sampling of aldehydes.

5. Acknowledgements

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Table 1. Characteristics of some commercially available passive aldehyde samplers utilizing derivitization with DNPH.

Sampler [a]	Capacity [b]	Sampling rate [b]	References [c]
UMEx 100 Passive Sampler	19.2 ppm-h	20.4 mL/min [d]	skcinc.com/prod/500-100.asp (Levin et al., 1986) (Levin and Lindahl, 1989) (Lindahl et al., 1996)
Assay Tech - 571	100 ppm-h	13.1 mL/min	assaytech.com/571_sales2.htm (Andersson et al., 1979) (Levin et al., 1985)
Sigma-Aldrich DSD-DNPH	28.2 ppm-h	71.9 mL/min	Uchiyama et al., 2004 (Uchiyama and Hasegawa, 1999)
3M-3721B monitoring badge	72 ppm-h	61.4 mL/min	OSHA methods ID-205 [e] (Kennedy and Hull, 1986)
Radiello – RAD1234	54.2 ppm-h	99 mL/min	radiello.it/english/download_en.htm (Mason et al., 2011)

[a] All samplers, excluding 3M-3721B, can reportedly sample multiple aldehydes.

[b] Formaldehyde sampling capacity and rate reported by manufacturer (assumed 25 °C and 1 atm).

[c] All websites accessed in March 2013.

[d] Sampling rate for a 7 day period. For 15 min to 8 h periods, sampling rate of 28.6 mL/min is specified.

[e] osha.gov/dts/sltc/methods/inorganic/id205/id205bkr.html .

Table 2. Schedule for 10-day aldehyde passive sampling rate field experiment.

	Sample Name	Day 1	2	3	4	5	6	7	8	9	10
Active Samples	ACT12-x	⬛	⬛								
	ACT34-x			⬛	⬛						
	ACT56-x					⬛	⬛				
	ACT78-x							⬛	⬛		
	ACT910-x									⬛	⬛
Passive Samples	PASS4-x	🟧	🟧	🟧	🟧						
	PASS6-x	🟧	🟧	🟧	🟧	🟧	🟧				
	PASS8-x	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧		
	PASS10-x	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧	🟧

Table 3. Mass of formaldehyde and acetaldehyde collected by cartridges in three different exposure groups.

	Immediate Analysis		3 days in zero air		3 days in ozone [b]	
	Mean [a]	*SD*	*Mean* [a]	*SD*	*Mean* [a]	*SD*
Formaldehyde (ng)	527	21	509	37	497	75
Acetaldehyde (ng)	546	21	546	35	584	36

[a] Mean of measurements made by three samplers

[b] Exposed to 70 ppb ozone for 76 hours

Table 4. P-value characterizing significance of the difference between mass measurements, based on Mann-Whitney non-parametric test (two-tailed).

	Immediate Analysis vs. Zero air exposed	Immediate Analysis vs. Ozone exposed	Zero air vs. Ozone exposed
Formaldehyde	0.70	0.70	0.70
Acetaldehyde	1.00	0.20	0.40

Table 5. Results from aldehyde passive sampling rate validation experiments.

ID	Sampling Duration (days)	Pump flow rate (mL/min, RSD)	Formaldehyde mass (μg) mean ± SD [b]	Acetaldehyde mass (μg) mean ± SD [b]	Formaldehyde sampling rate (mL/min, RSD) [d]	Acetaldehyde sampling rate (mL/min, RSD) [d]	T (°C), RH (%)[e]
L2	3.9	750[c]	0.54 ± 0.03	0.55 ± 0.03	1.24 (4%)	0.97 (4%)	21, 48
H1-4d[a]	4.1	10.4 (0%)	0.09 ± 0.01	0.04 ± 0.01	1.01 (10%)	0.65 (16%)	19, 62
H1-6d	6.0	10.2 (1%)[f]	0.12 ± 0.01	0.06 ± 0.01	0.99 (4%)	0.68 (6%)	19, 62
H1-8d	8.0	10.2 (1%)	0.16 ± 0.01	0.08 ± 0.01	1.02 (3%)	0.89 (11%)	19, 62
H1-10d	10.0	10.2 (1%)	0.20 ± 0.02	0.10 ± 0.01	1.08 (7%)	0.86 (10%)	18, 62
H2	6.1	10.3 (2%)	0.14 ± 0.01	0.09 ± 0.01	1.03 (8%)	1.04 (1%)	23, 46
H3	5.9	12.8 (2%)	0.50 ± 0.03	0.14 ± 0.01	1.16 (6%)	0.96 (7%)	25, 45
H4	6.0	11.2 (1%)	0.34 ± 0.04	0.14 ± 0.01	1.09 (11%)	0.90 (8%)	NA
H5	5.6	10.6 (4%)	1.32 ± 0.08	0.09 ± 0.01	1.09 (6%)	0.79 (8%)	NA
H6	5.9	13.6 (1%)	0.15 ± 0.03	0.06 ± 0.01	1.23 (16%)	0.81 (16%)	NA

[a] Passive sampling duration ranged from four and ten days at H1. At H2 to H6, the duration was six days.

[b] Mean and standard deviation of mass measured passively (after blank subtract) by triplicate samples.

[c] Unlike the field experiments, active sampling did not occur continuously in the lab experiment.

[d] Calculated by comparing mean of two active and three passive samples.

[e] Mean T and RH during aldehyde exposure period. Data not available for H4-H6.

[f] Relative deviation of flow measurements is provided for H1-6d, because there were only two readings.

Figure 1. Placement of the 12 passive samplers and two active samplers during the 10-day passive sampling rate field experiment. (Object in corner is a statue, not a live cat. Area is nook in L-shaped counter top; open just above top of photo.)

Figure 2. Placement of the three passive and two active samplers during the six-day passive sampling rate field experiment at site H5.