Measured Concentrations of VOCs in Several Non-residential Microenvironments in the United States

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Supporting Information text includes further description of composite sampling and analysis methods, quality assurance and quality control, and detailed results on regression analysis for restaurants (pg. S1-S6)

Supporting Information

Details on composite sampling. We used two main composite designs. These designs were chosen as a balance between minimizing the standard errors for estimating the mean and variance, and logistical constraints. The first design is indicated in Figure 1 and was used, for example, in sporting goods stores. Four of the sampling tubes have two sites collected on each tube. These four samplers contain air from 4 different sites which were visited twice each. The repeated samples allow some estimation of the variation over time for sporting goods stores. The remaining three samplers contain air from three sites. The second design included one sample with 3 sites, two with 2 sites, and four with 1 site. The first design chosen was used if there was more heterogeneity in store characteristics among a particular store type (e.g. large differences in store sizes and configuration). The second was chosen if there was less heterogeneity – this generally was used for store types that were made up of more uniform chain stores.

Sample collection. Samples were collected using a personal sampler, which consisted of one VOC sorbent tube and DNPH aldehyde cartridge connected to a personal pump (BGI, AFC 400s) and battery (BGI 8x Sanyo HR 4/3 FAU), along with a temperature/relative humidity HOBO (Onset Computer), in a backpack. Flow rates depended on the sampling time and were adjusted to maintain a consistent target volume across samples of the same microenvironmental type. For composite tubes, approximately equal volumes of air were collected at each location. The initial target volume for sorbent tubes was 10 L to ensure detectable levels, but was reduced in the winter of 2005 to 2.5 L for logistical reasons. This reduction was not expected to affect our ability to detect any compounds, as concentrations in stores were much higher than

anticipated. The desired sampling volume for the DNPH cartridges was based on manufacturers recommended volume for the expected concentration range. The sampling volume was 200 L for samples three hours and over, but was reduced to 100 L due to pump flow constraints for samples less than three hours. The sampling volume in winter 2005 was reduced to 50 L.

Prior to going into the field, the samplers were set up to the sampling line in the lab and the flows were adjusted. The sampling lines were disconnected from the pump while being transported to, and where applicable, between, sampling locations in a sealed plastic bag with charcoal paper and dessicant. The sampling line was attached to the pump just prior to entering the sampling location and flows were measured and adjusted, if necessary. Flows were measured and the sampling line disconnected from the pump just after departure from the store or restaurant. The times varied from 1 hour per sample to 3 hours per sample for all sampling.

Sample analysis. Sampling for VOCs was done with stainless steel multi-bed sorbent tubes (Supelco/Perkin-Elmer) containing 200 mg of Carbopack B, 230 mg of Carbopack X and 170 mg of Carboxen 1001. The sampling and analytical methods are described in US EPA's Compendium Method TO-17 (1). Analysis of VOC tubes was carried out using a Perkin-Elmer Automatic Thermal Desorber (ATD), Model 400 connected to a Hewlett Packard (HP) 5890II GC/5971 MSD.

Aldehydes were sampled using cartridges containing 2,4-dinitrophenylhydrazine (DNPH) coated silica from Waters Chromatography. Cartridges were eluted using a

gravimetric feed of 5 mL acetonitrile and then analyzed using a high pressure liquid chromatograph (Hewlett Packard 1100) with a UV detector, set at 360 nm.

Pilot testing. We conducted substantial pilot testing, particularly for the triple desorption tubes, which had not been field tested. We conducted breakthrough testing in a busy bus depot and determined a safe sampling volume of 15 L or less, and set our actual sampling volume to be 10 L for the main sampling campaign. We tested the tubes with Summa Canisters which were analyzed by an outside laboratory. We also sampled triplicates of the thermal desorption tubes, with one set going to an outside lab and 2 sets analyzed at Harvard. We conducted a storage test at intervals with spiked tubes, covering a month-long period to determine the optimum storage time before significant losses, defined as 20% or more, occur. Storage time was limited by 1,3-butadiene, the most volatile compound, which could be stored refrigerated for up to 1 week before we saw greater than a 20% drop between spiked and stored compounds.

Quality Assurance / Quality Control. For quality assurance and quality control (QA/QC), 15% of all samples were duplicate samples to determine measurement and analytical precision over the course of the study. Duplicates were analyzed both at HSPH and at an outside lab. Field blanks are taken on 11% of the samples, with 2% going to an outside lab. Field blanks were opened and resealed in the lab and transported between the lab and field in the same way as the actual samplers. The mean of the field blanks for each compound analyzed at HSPH was compared to zero using a t-test. Those that were significantly above zero (at $\alpha = 0.05$) were blank corrected using the mean of the blanks. Formaldehyde, benzene, toluene, styrene, and the xylenes were blank corrected. The limit of detection was calculated by taking three times the standard deviation of the field

or lab blanks, whichever had the higher mean (Table 3). Most compounds had less than 10% non-detects, except for methylene chloride (24%), trichloroethene (15%), and 1,3-butadiene (11%). In this paper, we do not report 1,3-butadiene values from summer 2003, due to the high number of non-detects (76%) compared to winter 2004 (11%). The summer data was considered too uncertain, since about half the samples were stored for longer than a week, the maximum time for storage before a substantial amount of loss occurred.

Due to flow rates and pump loads, duplicate samples were taken with a separate pump and battery. Precision was checked each month using the average difference between each pair. Compound precisions for the study are reported in Table 3. In the data analysis, duplicate concentrations from samples analyzed at HSPH were averaged.

Dining regression analysis. Predictor variables included smoking and open kitchen (binary), traffic (categorical), percent occupancy (continuous and binary), capacity and proximity to kitchen (continuous variables). Since capacity is a proxy for size, interaction terms were investigated between capacity and other variables. Variables with univariate regressions with a significance level of 0.20 or below were included in a multivariate model. Through backwards elimination, variables with p-values greater than 0.05 were removed. The regression analysis found that smoking and capacity were significant in the multivariate model for 1,3-butadiene and benzene, and that smoking was a significant predictor for toluene and styrene. The adjusted R-squared for the 1,3-butadiene and benzene models were 0.83 and 0.34, respectively. The effect was positive for smoking and negative for capacity (i.e. larger size, lower concentration). For toluene and styrene, the R-squared was 0.25 and 0.57, respectively. For chloroform, an open

kitchen, proximity to the kitchen, and occupancy (as a binary variable) were significant univariate predictors, but none were significant in the multivariate analysis. Adding interaction terms between smoking and capacity for 1,3-butadiene and benzene improved the adjusted R^2 of the model, but the terms were not all significant. For chloroform, the R^2 could similarly be increased by adding in all significant predictors including an interaction between capacity and open kitchen.

Table 1: Geometric means (µg/m^3) and coefficients of variation for retail stores

		Department	Drug Store	Electronics	Furniture	Grocery	Hardware	Home Store	Multipurpose	Sporting Goods	Transportation
Acetaldehyde	GM	7.22	13.34	2.69	10.86	19.01	14.98	14.34	9.12	11.81	4.21
	CV	0.96	0.91	2.10	1.29	1.12	0.74	0.63	0.63	0.41	0.50
Formaldehyde	GM	13.77	19.64	5.96	38.41	13.55	23.72	53.22	15.43	31.68	9.55
	CV	1.13	0.62	2.08	0.93	0.51	1.09	0.52	1.25	0.58	0.45
Benzene	GM	1.75	1.32	1.05	1.42	1.84	1.87	2.48	2.14	1.74	2.64
	CV	1.11	0.64	0.61	1.22	0.49	0.84	1.19	0.41	0.60	0.50
Toluene	GM	42.25	18.98	7.85	28.75	18.74	47.70	53.68	76.38	44.67	6.72
	CV	1.22	1.37	2.58	1.08	1.69	2.07	1.11	1.33	0.89	0.86
m,p-Xylene	GM	4.67	5.96	3.17	10.88	6.58	45.89	13.23	16.27	7.24	4.04
	CV	1.73	1.46	2.95	1.44	1.09	2.45	2.44	1.03	2.44	1.10
o-Xylene	GM	1.85	2.02	1.19	3.80	2.24	9.81	6.15	4.99	3.08	1.55
	CV	1.21	1.09	2.31	1.17	1.04	2.43	1.65	1.42	1.65	0.87
Ethylbenzene	GM	2.08	2.06	1.36	4.15	1.99	13.03	8.59	6.89	3.22	1.27
	CV	1.26	1.39	3.88	1.23	1.15	2.18	1.55	1.28	1.62	1.05
Perchloroethylene	GM	2.04	0.86	0.47	1.34	0.95	1.79	1.48	1.18	2.96	0.78
	CV	0.74	1.11	5.43	2.96	1.16	1.70	1.49	2.39	2.04	0.90
Trichloroethene	GM	0.35	0.29	0.03	0.71	0.28	0.58	1.10	0.51	0.50	0.14
	CV	1.66	1.53	107.75	62.46	0.79	6.38	1.46	1.08	1.81	0.32
Chloroform	GM	0.31	0.54	0.03	0.24	1.09	0.48	0.20	0.64	0.67	0.12
	CV	0.97	0.71	153.88	7.91	1.03	1.39	7.29	0.99	2.59	0.66
Carbon Tetrachloride	GM	0.72	1.15	0.27	0.87	1.19	1.22	0.84	0.97	0.89	0.60
	CV	0.46	0.68	3.63	0.42	0.39	1.06	0.74	0.41	0.51	0.85
Styrene	GM	2.13	1.90	1.18	2.33	1.68	6.44	10.19	4.81	1.42	0.60
	CV	1.09	0.63	10.35	1.03	0.98	1.95	1.29	1.13	4.38	0.79
Methylene Chloride	GM	1.26	2.31	1.06	1.19	1.19	11.12	1.09	3.97	1.56	0.57
	CV	2.53	1.08	2.14	5.27	1.54	2.07	1.46	0.64	2.11	0.62
1,4-Dichlorobenzene	GM	1.45	5.83	0.08	0.77	2.73	3.69	8.83	6.75	1.12	0.60
	CV	2.06	2.54	872.51	0.86	2.10	7.51	2.61	2.03	0.67	2.50
MTBE	GM	1.65	2.96	0.47	2.62	3.46	2.82	1.71	1.87	2.60	2.45
	CV	1.94	0.90	4.73	2.90	0.72	2.69	4.66	1.50	1.67	1.48

Table 2: Sample minimum and maximum values for each microenvironment ($\mu g/m^3$)

		Department	Drug	Electronics	Furniture	Grocery	Hardware	Home Stores	Multi-purpose	Sporting Goods	Dining	Transport-ation
Acetaldehyde	Min	3.02	3.26	0.97	5.81	10.7	5.49	9.18	5.47	8.92	1.16	1.85
	Max	18.6	26.5	8.75	30	71.7	40	37.9	26.4	18.2	184.8	9
Formaldehyde	Min	4.88	10.4	1.58	26.5	7.76	8.78	22.2	7.79	28.4	0.68	4.89
	Max	36.1	31.1	25.3	90.6	27	70	86.4	53.6	51.1	47.8	18.6
Benzene	Min	0.81	0.83	0.47	0.97	0.9	0.55	1.54	1.5	1.19	0.81	1.15
	Max	6.04	2.48	1.65	4.47	3.63	5.63	7.92	3.58	2.98	22.8	10.2
Toluene	Min	17.6	6.98	2.85	16.6	9.3	11.7	27.1	44.8	30.3	4.33	0.63
	Max	104	68.5	51.5	86.7	132	520	135	278	79.6	622	20.6
m,p-Xylene	Min	2.68	3.11	0.24	6.78	3.21	8.74	8.39	6.84	4.36	1.92	0.02
	Max	19.3	45.5	12.5	50.1	31.9	1760	53.7	102	28.4	28.6	12.5
o-Xylene	Min	1.04	1.14	0.17	2.49	0.95	2.39	3.37	2.58	1.8	0.78	0.01
	Max	6.78	9.74	3.55	14.9	10.9	62.1	21.3	38.3	11	10.1	3.49
Ethylbenzene	Min	1.12	1.04	0.19	3.1	1.09	2.25	3.99	3.45	1.33	0.73	0.01
	Max	7.85	13	6.83	18.4	10	107	29.7	45.5	12.4	8.5	2.96
Perchloroethylene	Min	1.27	0.45	0.16	0.49	0.42	0.22	1.27	0.52	1.24	0.24	0.32
	Max	4.89	2.16	8.49	6.35	4.83	21.1	7.41	43.8	11.6	83.4	5.17
Trichloroethene	Min	0.19	0.14	0.02	0.36	0.16	0.08	0.58	0.23	0.35	0.08	0.08
	Max	2.59	1.83	0.47	50.9	0.94	115	3.43	2.52	1.56	118	0.22
Carbon Tetrachloride	Min	0.41	0.8	0.02	0.74	0.77	0.35	0.7	0.68	0.63	0.38	0.02
	Max	1.2	2.5	0.85	1.49	1.84	7.53	2.02	2.39	1.37	1.02	1.25
Chloroform	Min	0.17	0.28	0.02	0.13	0.53	0.09	0.03	0.33	0.33	0.01	0.03
	Max	1.04	1.38	1.37	2.43	4.10	3.40	1.16	2.56	5.51	8.32	0.33
Styrene	Min	0.9	0.87	0.07	1.72	1.1	0.57	3.96	2.49	1.13	0.26	0.08
	Max	8.09	4.13	5.96	6.96	9.33	33.2	28.6	25.6	9.48	6.67	2.01
Methylene Chloride	Min	0.66	1	0.7	0.05	0.44	4.17	0.15	1.97	0.54	0.19	0.13
	Max	10.5	9.67	4.75	14.47	6.13	123	3.64	9.36	7.45	90.3	1.46
1,4-Dichlorobenzene	Min	0.71	0.59	0.06	0.61	0.56	0.05	0.99	1.34	0.77	0.16	0.12
	Max	8.52	25	3.13	1.91	17.2	44.2	40.1	50.3	1.82	171	7.51
MTBE	Min	0.76	1.69	0.02	1.53	1.54	0.58	1.09	0.7	1.19	0.75	0.03
	Max	8.48	7.18	1.56	26.63	10.4	46.5	32	10.3	13.8	9.94	8.49

Table 3: Precision and limits of detection

|	Precision	LOD (µg/m3)	% < LOD
1,3-Butadiene[a]	114%	0.17	11%
Methylene chloride	34%	2.55	24%
MTBE	38%	0.10	1%
Chloroform	39%	0.17	7%
Benzene	36%	0.20	0%
Carbon tetrachloride	44%	0.10	1%
Trichloroethene	51%	0.18	15%
2,2,4-Trimethylpentane	37%	0.17	0%
Toluene	42%	0.43	0%
Perchloroethylene	34%	0.22	0%
Ethylbenzene	42%	0.11	1%
m,p-Xylene	43%	0.30	1%
Styrene	40%	0.22	1%
o-Xylene	41%	0.19	1%
1,4-Dichlorobenzene	60%	0.43	7%
Formaldehyde	38%	1.29	0%
Acetaldehyde	24%	1.79	0%

[a] Winter data only reported for 2003-2004
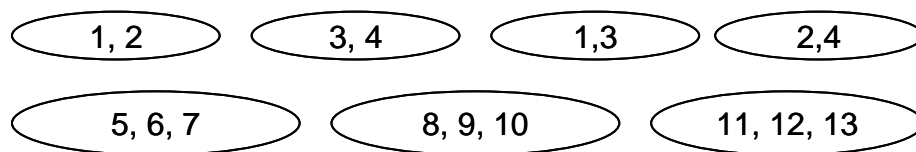
Figure 1: Example composite design scheme. Ovals represent a single sample. Numbers represent individual sites visited. Stores 1 to 4 were sampled twice, as indicated in the figure.

Literature Cited

(1)   Woolfenden, E.; McClenny, W. *Compendium method to-17: Determination of volatile organic compounds in ambient air using active sampling onto sorbent tubes*, U.S. Environmental Protection Agency, Report EPA/625/R-96/010b, 1997.