Solvent comparison for complex, heavily-loaded indoor samples

As the next step in method development we compared sonication in the two solvents for two complex, heavily-loaded filter samples of indoor air. One of these was collected from a San Francisco office where cigarette smoking occurred and was part of a study of breakthrough of semi-volatile PAH on XAD-4 (Breakthrough 3 Sample). Another very heavily-loaded filter was collected at the LBL Richmond Field Station from an environment polluted with cigarette smoke. The chromatograms for both of these samples had interferences which gave high backgrounds and some very broad peaks. Benzene-methanol extracts had better peak resolution, but may have had more interfering polar compounds than DCM extracts. In both cases quantitation using the internal standard was judged to be inaccurate because of the presence of interferences and an external standard was used to calculate concentrations. Such problems were not seen with Wisconsin indoor woodsmoke samples nor with NBS SRM-1649. Table V-5 presents the results obtained using calibration with the external standards A and B. DCM gave better overall recoveries for both samples. Sample cleanup using silica Sep-paks (Waters [Millipore] Corporation) may eliminate these problems.

Recovery of the internal standard for volatility losses

Tables V-3, V-4 and V-5 also contain results for recovery of fluoranthene-d_{10}. The range is 34 to 99 % for woodsmoke and NBS SRM-1649. For the complex, heavily-loaded samples.fluoranthene-d_{10} ranged from 32 to 250 %. For these samples, interferences from the sample matrix made quantitation of fluoranthene-d_{10} difficult. Overall, use of the benzene-methanol mixture as extraction solvent led to better recovery than use of dichloromethane; sonication gave better recovery than micro-Soxhlet extraction for both solvents. Sonication in the benzene-methanol mixture yielded about 70% of the added internal standard. This value is very close to that found for recovery of internal standards from dichloromethane extracts of XAD-4 resin used to sample vapor-phase PAH (Chapter IV). For particulate PAH, recovery of the semi-volatile fluoranthene-d_{10} was not necessarily related to recovery of the higher molecular weight PAH, since recovery of both types of compounds was solvent and method dependent.

Table V-5. Comparison of extraction solvents for complex indoor samples.

PAH	Breakthrough 3		Field Station	
	DCM	BzMeOH	DCM	BzMeOH
Results in pg/µl				
Phenanthrene	b	42.4	43.5	32.7
Anthracene	b	b	b	14.8
Fluoranthene	b	16.1	13	11.6
Pyrene	5.52	27.6	c	c
Benzo(a)anthracene	b	9.55	47.4	81.4
Chrysene	10.3	8.87	123	95.2
Benzo(e)pyrene	b	208	72.2	55.6
Benzo(b)fluoranthene	7.79	10.5	58.4	43.5
Benzo(k)fluoranthene	9.23	6.38	15.7	12
Benzo(a)pyrene	5.25	5.76	43.1	39.4
Benzo(ah)anthracene	31.0	16.7	b	b
Benzo(ghi)perylene	72.8	55.7	34.8	22.6
Indeno(cd)pyrene	50.9	26.1	47.5	49.1
Fluoranthene-d_{10} [d]	32 %	103 %	250 %	240 %

a.) DCM = dichloromethane; BzMeOH = benzene-methanol mixture (1:1, v:v); external standard calculation.
b.) Below quantitation limit of integration software.
c.) Present but not quantifiable due to interference.
d.) Estimated recovery as percent of added internal standard.

Extraction method selection

Our results and our experience in the laboratory indicated that sonication in either solvent gave better recovery for the semi-volatile PAH than micro-Soxhlet extraction, and it was not subject to the same opportunities for volatilization losses during extraction. Based on the results presented here, we chose to sonicate the field samples in the benzene-methanol mixture, to reproducibly extract and concentrate the whole range of PAH while using the less time-consuming and easier sonication technique.

Concentrations of PAH for standard reference material NBS SRM 1649

The National Institute of Standards and Technology (NIST) has certified concentrations of four PAH compounds in NBS SRM-1649, urban dust-organics. Concentration data are available for nine others from our list. NBS SRM-1649 was analyzed for PAH using sonication in benzene-methanol and the HPLC conditions described above. Table V-6 presents the averaged results for three 3 mg aliquots and compares them to the available data from NIST for 1 gram samples. Recovery of phenanthrene was considerably higher than obtained by NIST. This probably occurred because of reduced volatilization losses with benzene-methanol extraction compared to the dichloromethane extraction used by NIST. Excluding phenanthrene, our values averaged $105 \pm 27\%$ of the values determined by NIST, despite the much smaller sample size. The coefficient of variation, the standard deviation divided by the mean concentration, averaged 0.23 and varied from 0.02 for benzo(a)pyrene to 1.0 for dibenzo(a,c)anthracene. For three of the six samples the filter wrap released particles during the extraction. These particles were recovered as the extract was filtered. The PAH concentrations for these three samples were much lower (about 25%) than for the other aliquots, and the data were excluded from Table V-6. Particle inhomogeneity may have contributed to the large variations observed for some compounds. Such inhomogeneity is a greater problem for small rather than large sample size.

Blanks and Lower Limits of Detection

Table V-7 presents the results for the analyses of blanks. (Two blanks are omitted from the table: 039 was severely contaminated from unknown sources, and, inadvertently, 042 was never analyzed. None of the other blanks or samples showed evidence of contamination.) The average concentration, standard deviation and limit of detection are listed for each compound. The limit of detection was calculated as three times the standard deviation of the

Table V-6. Particulate PAH Concentrations on NBS SRM-1649 urban dust.

PAH	Average [a] µg/g	Std. Dev.	NBS	Std. Dev.	%NBS
Phenanthrene	7.93	2.59	4.5	0.3	176
Anthracene	0.53	0.14			
Fluoranthene	7.29	1.54	7.1	0.5 b	103
Pyrene	7.78	0.84	6.3	0.4	123
Benzo(a)anthracene	3.37	0.58	2.6	0.3 b	130
Chrysene	4.65	0.34	3.5	0.1	133
Benzo(e)pyrene	2.55	0.51	3.3	0.2	77
Benzo(b)fluoranthene	5.52	0.70	6.2	0.3	89
Perylene	c		0.80	0	
Benzo(k)fluoranthene	1.53	0.15	2.0	0.1	77
Dibenzo(ac)anthracene	0.40	0.40			
Benzo(a)pyrene	2.26	0.04	2.9	0.5 b	78
Dibenzo(ah)anthracene	0.63	0.28	0.41	0.1	154
Benzo(ghi)perylene	5.06	0.94	4.5	1.1 b	112
Indeno(cd)pyrene	2.55	0.32	3.3	0.5	77
Dibenzo(ae)pyrene	1.57	0.23			
Coronene	5.04	0.79			
Average recovery					105 +/- 27 [d]

a.) Three 3-mg samples sonicated in a benzene-methanol mixture (1:1, v:v).
b.) Certified value for extraction and analysis of 1.0 gram samples.
c.) Not resolved from benzo(b)fluoranthene.
d.) Recovery average excludes phenanthrene.

Table V-7. Concentrations of particulate PAH on blanks (ng/m^3).

PAH [a]	F017	F018	F023	F027	F033	Average	Std. Dev.	LD [b]
Phenanthrene	0.238	0.172	0.078	0.102	0.267	0.171	0.074	0.221
Anthracene	0.056	0.006	0.006	0.008	0.006	0.016	0.020	0.059
Fluoranthene	0.041	0.027	0.014	0.009	0.009	0.020	0.012	0.037
Pyrene	0.090	0.086	0.029	0.057	0.139	0.080	0.037	0.110
Benzo(a)anthracene	0.024	0.031	0.008	0.004	0.042	0.022	0.014	0.043
Chrysene	0.023	0.026	0.023	<.032	0.031	0.021	0.011	0.032
5-Methylchrysene	<.040	<.040	<.040	<.040	<.040	0.000	0.000	0.040
Retene	<.280	<.280	<.280	<.280	<.280	0.000	0.000	0.280
Benzo(e)pyrene	0.109	0.066	0.153	0.128	0.274	0.146	0.070	0.210
Benzo(a)pyrene	0.017	0.048	0.017	0.040	0.013	0.027	0.014	0.042
Benzo(k)fluoranthene	<0.005	0.002	0.005	<.005	0.002	0.002	0.002	0.005
Dibenzo(a,c)anthracene	0.022	0.012	0.028	0.006	0.013	0.016	0.008	0.023
Benzo(a)pyrene	<.018	<.018	<.018	<.018	<.018	0.000	0.000	0.018
Dibenzo(a,l)pyrene	<.018	<.018	<.018	<.018	<.018	0.000	0.000	0.018
Dibenzo(a,h)anthracene	0.036	0.011	0.019	0.014	0.109	0.038	0.037	0.110
Benzo(ghi)perylene	0.098	0.039	0.039	0.035	<.074	0.048	0.025	0.074
Indeno(c,d)pyrene	<.035	<.035	<.035	<.035	<.035	0.000	0.000	0.035
Dibenzo(a,e)pyrene	<.008	<.008	<.008	<.008	<.008	0.000	0.000	0.008
Coronene	nd	nd	<.006	<.006	<.006	0.000	0.000	0.006
Dibenzo(a,i)pyrene	0.027	0.028	0.027	0.027	0.028	0.027	0.000	0.001
Dibenzo(a,h)pyrene	0.010	0.009	0.010	0.012	0.010	0.010	0.001	0.003

a.) Concentrations calculated assuming an air volume 22.5 m^3.
b.) L D = limit of detection = 3 x standard deviation or 3 x signal/noise on light field samples.

concentration on blanks (Winefordner and Long, 1983). For some compounds the chromatograms showed no detectable level. The limit of detection was then estimated as three times the noise amplitude on chromatograms which contained the lowest observed concentrations of the compound.

PAH concentrations in blanks were calculated in ng/m^3 assuming a typical air volume of 22.5 m^3. Phenanthrene and pyrene and dibenzo(ah)anthracene had limits of detection of 0.22, 0.11 and 0.11 ng/m^3, respectively, due to observable PAH. Retene and benzo(e)pyrene had limits of detection of 0.28 and 0.21 ng/m^3, respectively, because they eluted on either side of benzo(e)pyrene-d_{12}, the internal standard for quantitation, and accurate measurement of peak height was obscured by the shoulders of the more intense internal standard peak. Chrysene and benzo(a)pyrene had more typical limits of detection of 0.032 and 0.018 ng/m^3, respectively.

Evaluation of the Method for Indoor and Outdoor Particles

Optical Attenuation

Attenuation (ATN) is a measure of filter blackness and is proportional to the amount of elemental or black carbon (Rosen et al., 1978) in the particles. For outdoor samples the attenuation is also proportional to amounts of selected particulate PAH (Gundel et al, 1982). We used a Kodak Reflectance Scale (a set of grey squares calibrated in optical density, designed for photography applications), to estimate attenuation, since attenuation is 100 times optical density when light scattering is ignored. Table V-8 contains estimates of the optical attenuation of particles on the filter samples, along with concentrations of six PAH and their sum. The six compounds are benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(ghi)perylene, indeno(cd)pyrene and coronene. Although the correlation is far from perfect (correlation coefficient = 0.68), attenuation and the sum of these PAH concentrations are proportional for this study of indoor and outdoor particles. For our purposes, the result indicates that batching samples for analysis using ATN values does indeed produce groups of samples with similar PAH concentrations.

Measurement of the filters included estimating ATN for areas of inhomogeneous loading, as indicated by darker centers or stripes on the filter. Most samples did have these features, but typically they were similar on replicates. The presence of a spot or clump of particles at

Lab Sample ID	Field Sample ID [a]	Atten	BbF	BkF	BaP	BghiP	IcdP	Cor	Sum
001	T-2N-O	19	0.22	0.06	0.14	0.16	0.21	<.01	0.78
002	T-2N-I (W,C,G)	37	0.19	0.06	0.20	0.11	0.35	<.01	0.90
003	T-2D-I (W,C,G)	86	2.03	0.77	5.14	7.71	4.18	3.12	22.96
004	T-2D-IR (W,C,G)	83	2.19	0.72	8.14	9.98	3.98	4.81	29.82
005	T-2D-O	21	0.22	0.10	0.23	0.22	0.31	<.01	1.08
006	T-1N-I (W)	21	0.05	0.02	0.04	0.32	0.07	0.00	0.50
007	T-1N-O	18	0.26	0.10	0.18	0.24	0.24	0.29	1.30
008	T-1N-OR	8	0.26	0.13	0.20	0.16	0.26	0.12	1.11
009	T-1D-I (W)	22	0.22	0.08	0.15	0.13	0.12	0.12	0.82
010	T-1D-IR (W)	23	0.23	0.07	0.11	0.25	0.13	<.01	0.79
011	T-1D-O	18	0.28	0.14	0.43	0.38	0.34	0.57	2.14
012	T-1D-OR	20	0.41	0.17	0.31	0.80	0.38	1.09	3.16
013	S-1D-I (N)	12	0.29	0.07	0.06	0.28	0.19	0.36	1.26
014	S-1D-IR (N)	13	<.04	0.02	0.03	0.08	0.13	0.09	0.35
015	S-1D-O	21	0.15	0.04	0.18	0.16	0.27	0.26	1.05
016	S-1D-OR	22	0.20	0.04	0.07	0.17	0.18	0.63	1.29
019	P-1D-I (C)	38	0.56	0.14	0.38	0.56	0.65	<.01	2.28
020	P-1D-IR (C)	28	0.60	0.15	2.99	0.33	0.36	<.006	4.43
021	P-1D-O	4	0.08	0.02	0.03	0.23	0.25	<.01	0.61
022	P-1D-OR	7	0.11	0.03	0.03	0.21	0.12	0.23	0.73
024	R-1D-I (N)	22	<.04	0.02	0.04	0.13	0.16	0.38	0.73
025	R-1D-IR (N)	22	0.06	0.01	0.03	0.18	0.12	0.27	0.68
026	R-1D-O	34	0.10	0.04	0.12	0.24	0.16	0.45	1.11
028	R-1N-I (N)	17	0.08	0.02	<.02	0.25	0.24	1.28	1.87
029	R-1N-O	17	0.26	0.06	0.07	0.44	0.22	0.64	1.70
030	R-2D-I (G)	16	0.08	0.03	0.03	0.14	0.14	0.23	0.65
031	R-2D-IR (G)	21	<.04	0.02	0.04	0.12	0.15	0.20	0.53
032	R-2D-O	18	0.14	0.05	0.08	0.26	0.27	0.38	1.18
034	R-2N-I (G)	4	<.04	<.005	<.02	<.074	<.035	<.006	<.18
035	R-2N-O	6	0.09	0.01	0.02	<.074	<.035	<.006	0.12
036	M-1D-O	51	0.10	0.04	0.09	0.28	0.20	0.29	1.01
037	M-1D-IR (C)	64	0.47	0.14	0.87	0.88	0.76	0.59	3.71
038	M-1D-I (C)	63	0.38	0.12	0.34	0.87	0.35	0.50	2.56
040	M-1N-I (C)	27	0.26	0.05	0.20	0.57	0.30	<.006	1.38
041	M-1N-O	21	0.10	0.02	0.04	0.55	0.25	<.006	0.97

a.) Sample ID: T= Truckee, S= Sacramento, P=Palo Alto, R=Rodeo, M=Milbrae, 1D= Day 1 (7AM-7PM), 2D=Day 2 (7AM-7PM), 1N=Night 1 (7PM-7AM), 2N=Night 2 (7PM-7AM), I=Indoor, O=Outdoor, R=Sample Replicate.Indoor sources present during the sampling (ws = wood stove, g = gas stove, s = environmental tobacco smoke, N= no combustion sources).

Table V-8. Filter blackness (attenuation) and concentrations of selected PAH (pg/m^3).

the center of the filter made division of the sample into equal halves more difficult, especially since the central clump was dislodged during cutting and recovery of loose particles was difficult. As much as possible the two halves contained mirror images of deposition patterns. Replicates 003 and 004, 011 and 012, 013 and 014, and 015 and 016 had dissimilar deposition patterns, i.e., unequal center spot deposition.

Uncertainty Analysis

Perturbation analysis was performed to estimate the contribution of uncertainty in each measurement parameter to the total relative uncertainty in computing the mass of the collected PAC. The approach is discussed in Chapter IV, and the results are presented in Table V-9 for calculation of the concentration of benzo(a)pyrene in sample 8 (T-1N-OR). Uncertainties in the peak heights of benzo(a)pyrene and the internal standard for quantitation, benzo(e)pyrene-d_{12}, dominate contributions to the relative uncertainty which totals 17.9%. Not included in the calculation are any considerations of sample inhomogeneity, sample matrix effects or sample complexity. These factors are discussed below along with other analysis issues.

Recovery of the internal standard for volatility losses

Table V-10 presents the recoveries of fluoranthene-d_{10} which was added to both samples and field blanks at the start of sonication in the benzene-methanol mixture. The blank extracts were concentrated by evaporation under dry N_2 while the samples were concentrated using rotary evaporation at 38°C. 81 $\pm$ 11% of the internal standard was recovered from the blanks, but 68 $\pm$ 18% was recovered from the indoor air extracts. (The larger uncertainty in sample extracts may be due to the presence of undeuterated fluoranthene which elutes close to fluoranthene-d_{10}, and the two compounds were not always completely resolved.) These values are not significantly different from each other or from the recovery of fluoranthene-d_{10} added to the XAD-4 extracts of semi-volatile compounds, as reported in Chapter IV of this report.

Table V-9. Perturbation analyses of variable uncertainties used to calculate the mass of particulate phase BaP.

Measurement Parameter	Units	Value	Abs.[a] Variable Uncert.	Rel.[b] Variable Uncert.	Abs.[c] Variable Perturb.	%[d] of Total Perturb.
C_{1647a}- concentration of BaP in NBS 1647a.	(µg/mL)	4.82	0.03	0.6	1.6E-6	0.1
Vs2- Volume of internal standard $BePD_{12}$ added by syringe to the sample extract.	(µL)	13	0.25	1.9	1.5E-5	1.2
Vp1- Volume of NBS 1647a added by pipette to the standard solution.	(mL)	1	0.002	0.2	1.6E-7	0.01
Vp3- Volume of internal standard $BePD_{12}$ added by pipette to the standard solution.	(mL)	4	0.01	0.3	2.5E-7	0.02
E- Area of the filter extracted	(cm^2)	7.13	0.07	1.0	3.8E-6	0.3
T- Total area of the filter.	(cm^2)	13.85	0.05	0.4	5.3E-7	0.04
PH1- Peak height of BaP for sample extract.	(iu)	1.1	0.05	4.5	8.4E-5	6.4
PH2- Peak height of BaP for standard solution.	(iu)	1.01	0.02	2.0	4.6E-4	35.2
PH3- Peak height of internal standard $BePD_{12}$ for sample extract.	(iu)	2.01	0.2	10.0	3.3E-4	25.5
PH4- Peak height of internal standard $BePD_{12}$ for standard solution.	(iu)	0.27	0.027	10.0	4.1E-4	31.2
Total absolute mass uncertainty.[e]	(mg)	0.036				
Unperturbed mass value.	(mg)	0.201				
Total relative mass uncertainty.	%	17.9				

a) Absolute variable uncertainty - estimated 95% confidence limits for data used to compute the mass of PAH in a sample extract.
b) Relative variable uncertainty - calculated as the absolute variable uncertainty divided by the variable value.
c) Absolute variable perturbation - computed as the square of the difference between the mass computed with and without variable perturbation.
d) Percentage of the total variable perturbation for each variable.
e) Total absolute mass uncertainty calculated as the square root of the sum of the individual variable perturbations.

Table V-10. Recovery of deuterated fluoranthene.

Sample	Added pg/ul	Absolute Recovery pg/ul	Relative Recovery %
Blanks			
F017	13.65	11.86	86
F018	12.99	11.30	87
F023	12.8	7.78	60
F027	10.71	8.04	75
F033	12.23	11.33	92
Average ± std dev			81 ± 11
Field Samples			
F001	11.54	4.04	35
F002	11.71	5.27	45
F004	5.99	5.55	92
F005	11.18	10.89	97
F006	11.61	5.16	44
F007	11.43	7.12	62
F008	11.76	9.36	79
F009	11.95	12.66	105
F010	8.06	8.79	109
F011	11.27	7.77	68
F012	11.38	6.17	54
F013	11.50	6.24	54
F014	11.61	8.64	74
F015	11.45	6.57	57
F016	11.73	6.34	54
F019	12.00	7.71	64
F020	11.78	7.95	67
F021	11.52	6.03	52
F022	11.52	6.00	52
F024	11.78	7.83	66
F025	11.59	10.00	86
F026	11.06	9.53	86
F028	11.27	6.72	59
F029	11.64	9.57	82
F030	11.23	7.39	65
F031	11.25	6.75	60
F032	11.47	5.52	48
F034	11.45	8.48	74
F035	11.66	9.61	82
F036	12.50	9.91	79
F037	8.99	7.66	85
F038	6.02	2.37	39
F040	11.25	8.21	72
F041	11.52	6.86	59
Average ± std dev			

Analysis Issues for Field Samples

Data reduction software

Because of the small sample size and consequent low levels of fluorescence, some of the peak areas fell below the software area reject threshold. The remedy was to smooth then multiply both standard and sample chromatograms by a scale factor (usually 20) before integration. Even so, integration of observed peaks by the Workstation software had to be carefully checked because the software was often unable to assign the desired baseline after the chromatograms had been smoothed and scaled. Some peaks had to be measured manually and then converted to fluorescence detector peak height units. Increasing the volume of extract per injection from 5 to 10 microliters would partially alleviate the problem..

Extreme care had to be taken to assign fluorescence program change times correctly. Since the small systematic drift had to be anticipated before each analysis, occasionally the wavelength change occurred as a peak eluted, instead of between peaks. The resulting chromatograms had to be checked carefully for correct assignment of integration baseline, and some peaks had to be remeasured manually because the software was unable to draw the correct baseline.

Determination of individual PAH

Semi-volatile PAH

Phenanthrene and anthracene. These compounds appeared above the limits of detection only in samples which contained woodsmoke or cigarette smoke. We cannot rule out the possibility of interferences from polar compounds in these complex samples.

Fluoranthene. This compound eluted just after the internal standard fluoranthene-d_{10}. The large coefficient of variation observed for this compound reflects the difficulty of accurate peak assignment when the deuterated compound was much higher in concentration than the undeuterated analogue.

Pyrene. No particular problems occurred with detection or quantitation of pyrene, although its concentration was below the limit of detection for more than a third of the field samples.

Benzo(a)anthracene. For many samples benzo(a)anthracene was not well separated from several other compounds (these were unassigned except for chrysene).

Chrysene. Complex samples (cigarette or wood smoke) frequently showed the presence of an interference, since the ratio of observed peak heights for the two fluorescence chromatograms did not agree with that determined for pure chrysene in standards.

5-methylchrysene and retene. These compounds were observed only in complex samples. Retene is a marker compound for woodsmoke, but its fluorescence sensitivity is very low for both fluorescence programs (and all other wavelengths we studied). This leads to substantial uncertainty in calculation of the relative contribution of 5-methylchrysene and retene in complex samples.

Particulate PAH

Benzo(e)pyrene. This compound elutes just after the internal standard for HPLC quantitation, benzo(e)pyrene-d_{12} and is not always well resolved from the deuterated compound. For some samples, especially complex indoor samples, an interference may be present.

Benzo(e)pyrene-d_{12}. The internal standard for HPLC quantitation sometimes gave unusually high response, indicating the presence of an unknown interference. For these samples the calculation of PAH concentrations using the relative response of this internal standard led to erroneously low values for all other PAH in the sample. For some replicate pairs the actual peak heights for many PAH are very close together, but the calculated concentrations are very different. This issue is discussed further below.

Benzo(b)fluoranthene. This compound coelutes with perylene, and calculated concentrations may be about 10% too high because of the presence of perylene.

Benzo(k)fluoranthene. The method is most sensitive for this compound so detection limits were very low--5 pg/m^3. Dibenzo(a,c)anthracene coelutes with it, but both compounds can be quantitated from the chromatograms at the two detector wavelength settings.

Dibenzo(a,c)anthracene. This compound coelutes with benzo(k)fluoranthene. Detectable levels of dibenzo(a,c)anthracene were typically seen only in complex indoor samples (woodsmoke or cigarette smoke).

Benzo(a)pyrene. Every field sample contained B(a)P. The analysis of measurement uncertainties predicted 18% uncertainty while the observed coefficient of variation (excluding complex samples) was 25%.

Dibenzo(a,l)pyrene. Only three field samples, all influenced by cigarette smoke, contained detectable levels of this PAH.

Dibenzo(a,h)anthracene. This compound was present at high concentrations in blanks, relative to most of the other PAH. Only six field samples had detectable levels, and all but one were from complex sources (wood smoke or cigarette smoke).

Benzo(g,h,i)perylene and indeno(1,2,3-c,d)pyrene. These PAH occurred in nearly every field sample. In about 20% of the samples their peak heights had to be measured manually because their areas fell below the area reject criterion of the software, even with scaling by a factor of 20.

Dibenzo(a,e)pyrene. Concentration results for this compound should be considered as upper limits because its HPLC peak was not typically well resolved from other unidentified peaks.

Coronene. The retention time and sensitivity for this PAH may change during the analytical day, due to column conditions.

Dibenzo(a,i)pyrene and Dibenzo(a,h)pyrene. The method is very sensitive for these compounds, with limits of detection of 1 and 3 pg/m3 respectively. However, only one complex sample had detectable amounts of either PAH.

Sample matrix and filter loading effects for field samples

Figures V-4 through V-7 show chromatograms for samples influenced by several types of sources. The upper and lower parts of each figure have the low and high wavelength traces, respectively. The samples were all members of replicate pairs, and they illustrate the important analysis issues that should be addressed in future studies of PAH in indoor air.

Fig.V-4 represents a lightly-loaded filter sample of outdoor particles taken in Sacramento (sample 16, S-1D-OR). With some exceptions the PAH concentrations agreed well for replicate pairs, even though these filters were very lightly loaded.

Fig.V-5 shows an indoor sample from Sacramento, sample 14, identified as S-1D-I in Chapter VI,taken indoors during the same time as Fig.V-4. The peak heights of benzo(e)pyrene-d_{12} did not agree for replicate pairs, suggesting that a co-eluting interference was present. Calculation of concentrations using the external standard method led to much better agreement between the replicates of this pair. Extraction and analysis of the remaining half of the filter could possibly resolve the problems with the internal standard.

Sample matrix and filter loading effects influenced the chromatograms shown in Figs.V-6 (cigarette smoke, sample 37, M-1D-I) and V-7 (all sources, sample 4, T-2D-IR). Two very broad peaks eluted before 15 min in the cigarette smoke sample, and they did not reproduce in retention time in repeat analysis of the same extract. In this example chrysene eluted on the downslope of one of these broad peaks; in some cigarette smoke extracts, fluoranthene-d_{10} and fluoranthene eluted on the top of a similar broad peak. The broad peaks may have been interferences from polar components of the extracts which did not separate well on the extremely non-polar column. Sample T-2D-IR, Fig.V-7, also showed the presence of interfering compounds where chrysene and benzo(a)pyrene were expected. In addition to these effects, the background fluorescence was high for both samples. This high background indicates the presence of highly absorbing material in these samples, and it may have caused absorption of fluorescence from PAH and reduction of the calculated PAH concentration. For both samples the response of BeP-d_{12} is higher than expected from standards and simple samples like that illustrated in Fig.V-4. For these samples a cleanup procedure before analysis should eliminate polar interfering compounds and lead to more accurate determination of PAH.

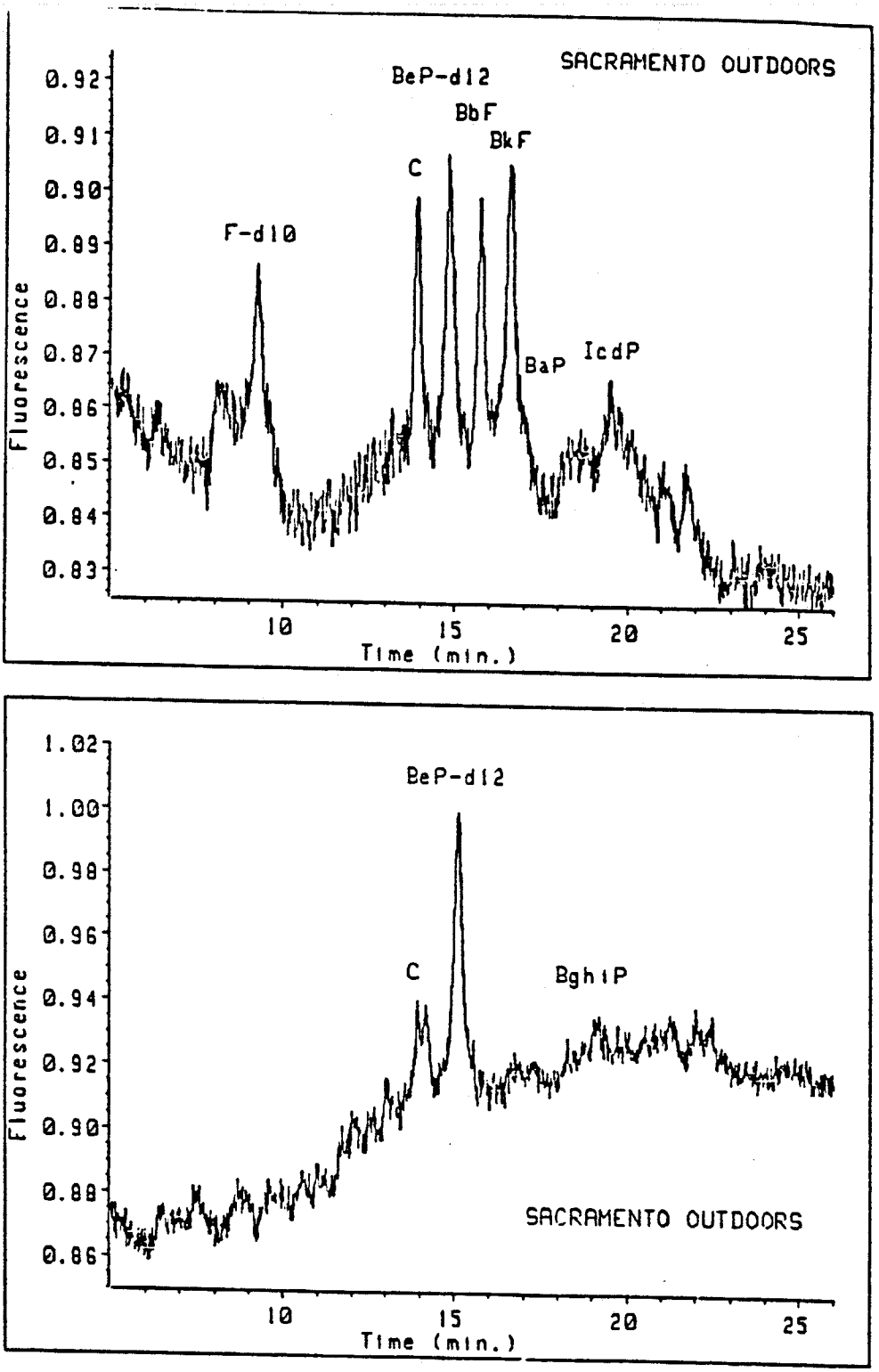


Figure V-4. Chromatograms of an extract of outdoor particles from Sacramento CA (filter sample 16). Top half: Low wavelength program. Lower half: High wavelength program. F-d10 = fluoranthene-d_{10}; C = chrysene; BeP-d12 = benzo(e)pyrene-d_{12}; BbF = benzo(b)fluoranthene; BkF = benzo(k)fluoranthene; IcdP = indeno(c,d)pyrene; BghiP = benzo(g,h,i)perylene; Cor = coronene.

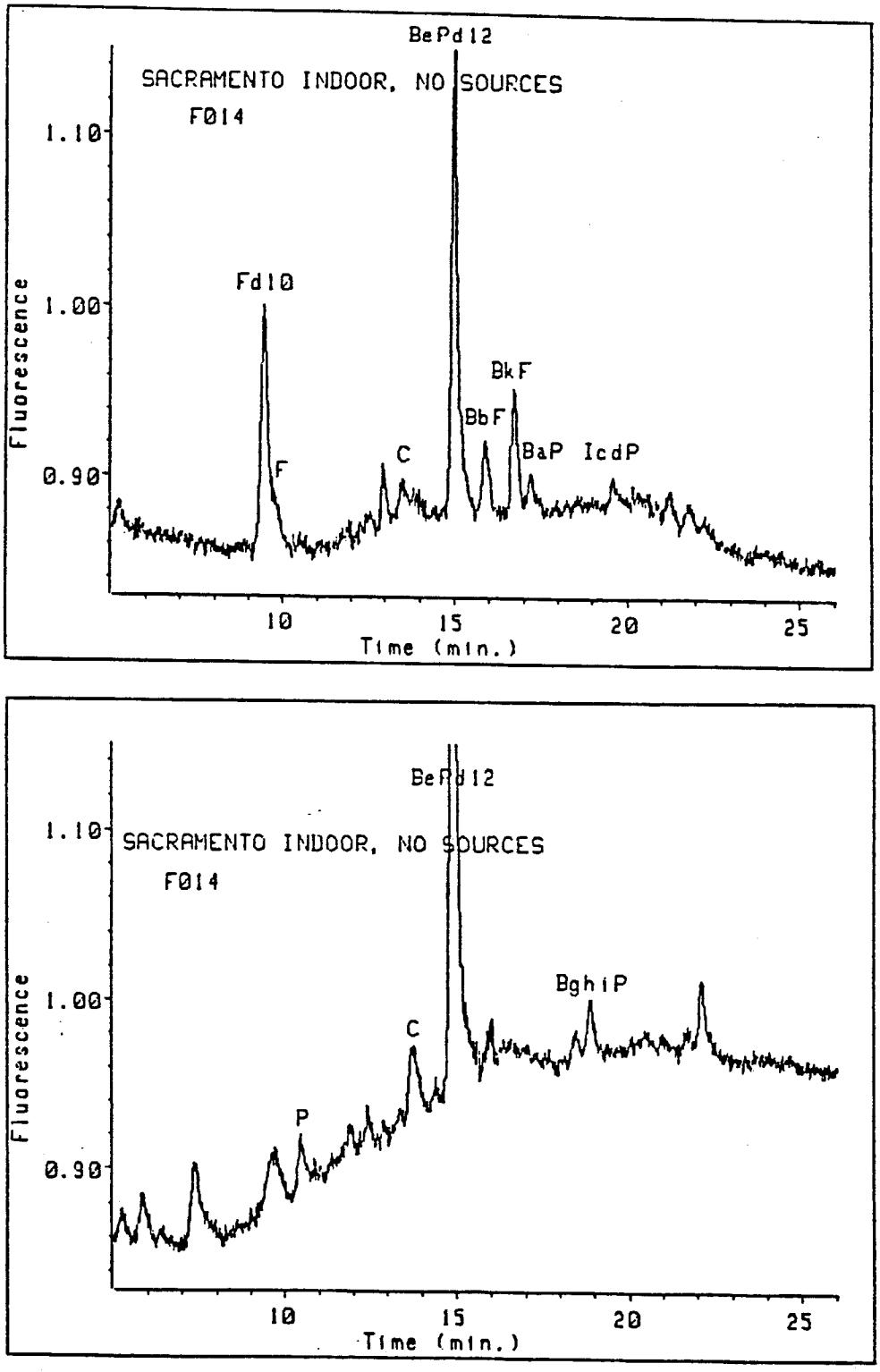


Figure V-5. Chromatograms of an extract of indoor particles from a commercial building in Sacramento CA (filter sample 14). Top half: Low wavelength program. Lower half: High wavelength program. Abbreviations are defined in the caption for Figure V-4.

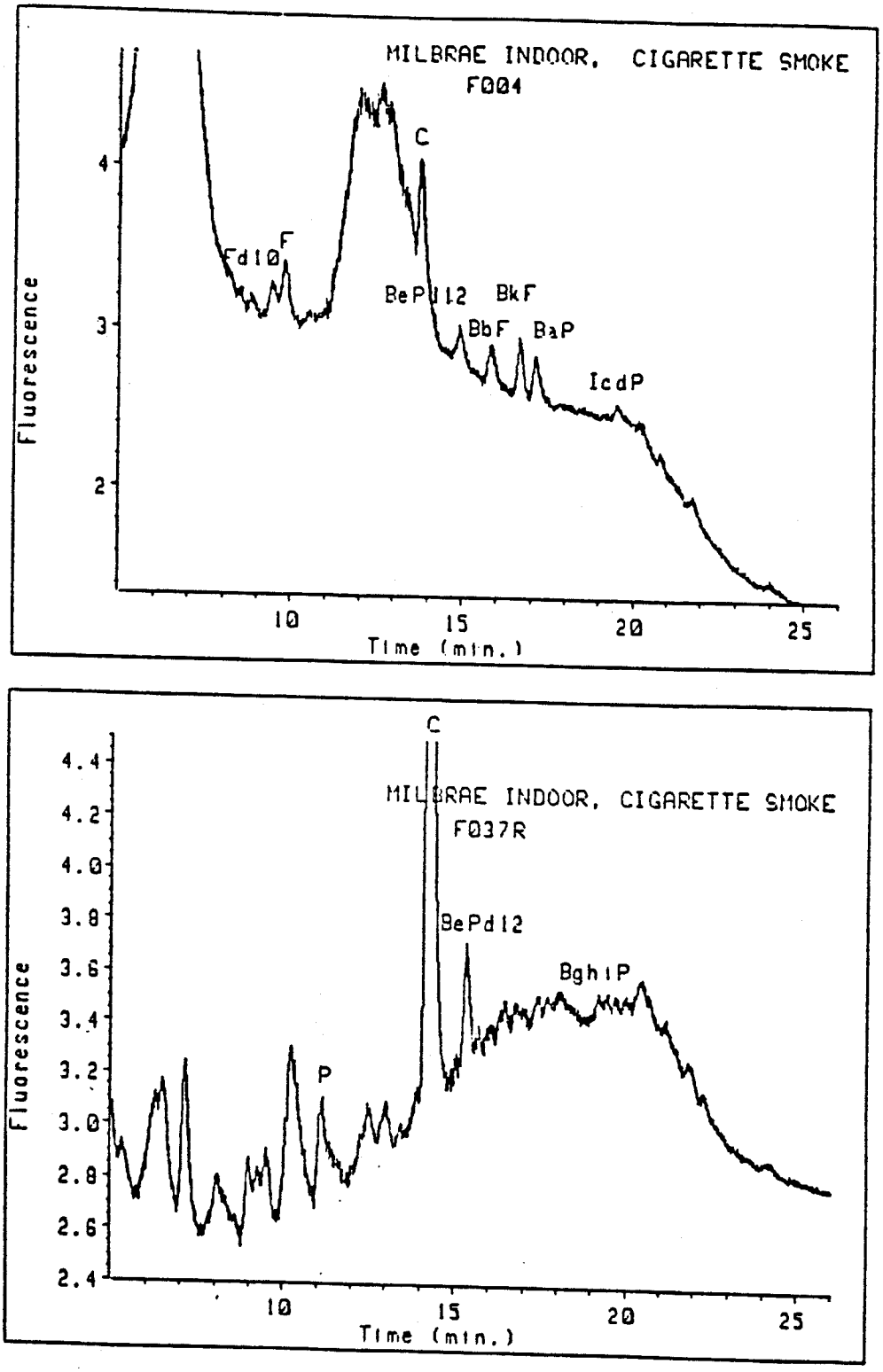


Figure V-6. Chromatograms of an extract of indoor particles from a residence where cigarette smoking occurred, in Milbrae CA (filter sample 37). Top half: Low wavelength program. Lower half: High wavelength program. Abbreviations are defined in the caption for Figure V-4.

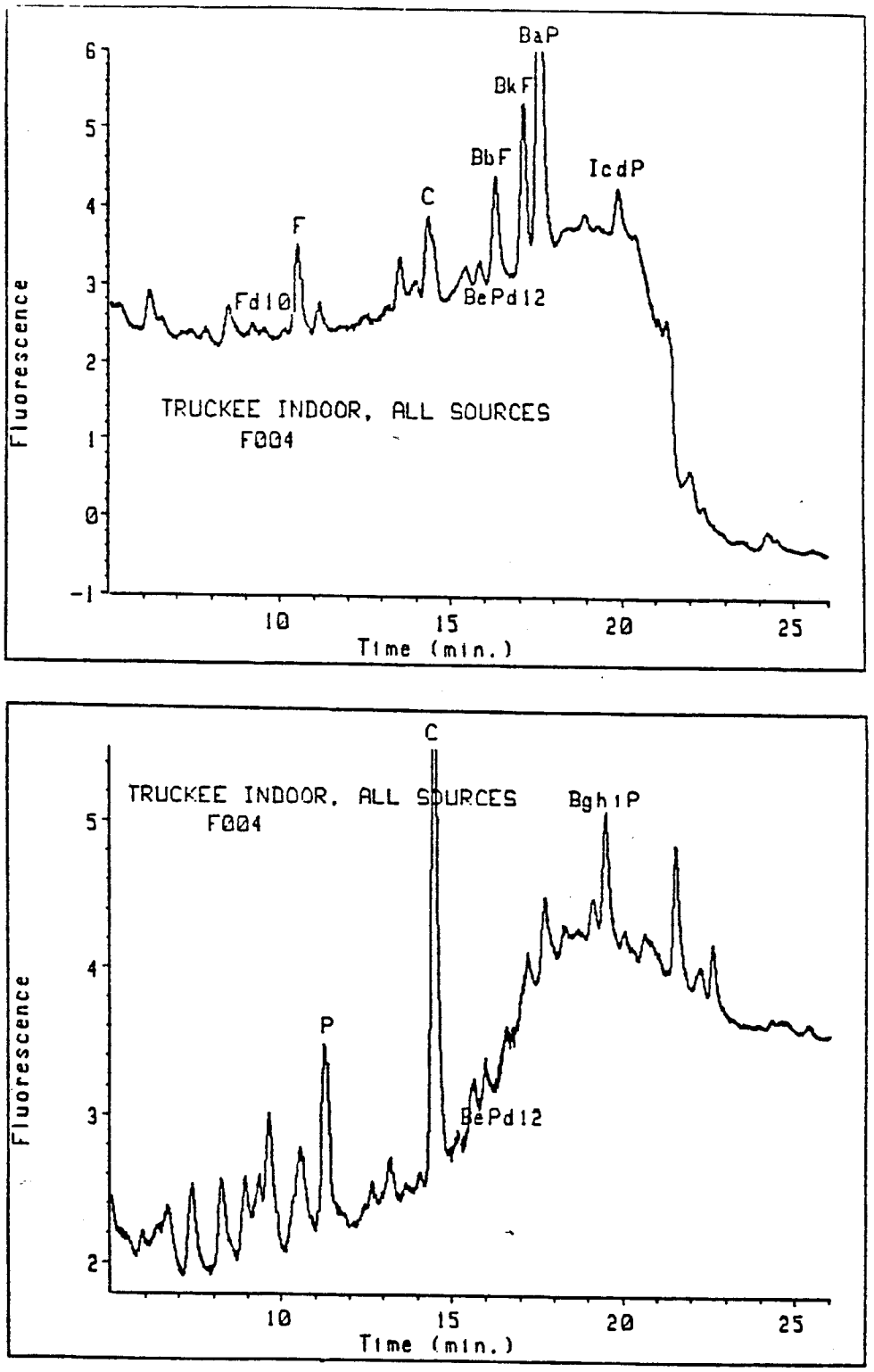


Figure V-7. Chromatograms of an extract of indoor particles from a residence in Truckee CA where cigarette smoke, wood smoke, and natural gas combustion particles were present (filter sample 4). Top half: Low wavelength program. Lower half: High wavelength program. Abbreviations are defined in the caption for Figure V-4.

Use of benzo(e)pyrene-d_{12} as an internal standard for quantitation

For some samples, especially heavily-loaded and complex samples (containing cigarette smoke), there was evidence of interferences which coeluted with benzo(e)pyrene-d_{12}. For comparison to the internal standard method we calculated the concentration of benzo(a)pyrene in all replicate pairs using the external standard method. In half of the samples (11) the two methods gave concentration results which differed by more than 30%. Using the internal standard method the concentrations in each pair differed from each other by more than 30% in 6 of the 11 pairs. Using the external standard method the concentrations in each pair differed by more than 30% in only 4 of the 11 pairs. Further evaluation of the internal standard method would require preparation of new extracts with benzo(e)pyrene-d_{12}.

Concentrations of all PAH were calculated for the replicate pair samples 3 and 4 (T-2D-I and T-2D-IR) using the external standard method. The average difference between pairs was 24 $\pm$22%, compared to 45 $\pm$32% using the internal standard method. Average benzo(a)pyrene concentration was 11.5 ng/m^3 for the external standard calculation, about twice as high as the internal standard method (6.6 ng/m^3). This result is consistent with the presence of a coeluting interference.

Two alternative solutions to the internal standard problem include elimination of the internal standard altogether and substitution of another deuterated compound for benzo(e)pyrene-d_{12}. The use of an internal standard for quantitation eliminates the need for accurate measurement of the extract volume. However, we measured the total extract volume in all samples at the time of preparation, and we found that the volume did not change with proper capping and low-temperature storage over a two month period. Use of no internal standard may be satisfactory, since HPLC instrument response does not require one for quantitation. Substitution of another deuterated PAH could also eliminate the problems with benzo(e)pyrene-d_{12}. One possibility is to use fluoranthene-d_{10} as the internal standard for quantitation and not use it to check for volatility losses.

D. SUMMARY

An extraction and analysis method has been developed which is suitable for determination of PAH in indoor air. The method used half of each filter sample of 22-25 m^3 air collected

in 12 hours, so that a second determination could be made if necessary. Remaining filter sections have been stored in a freezer. Twenty-one semi-volatile and particulate-phase PAH were determined, with levels of detection ranging from 0.28 ng/m^3 for retene to 0.001 ng/m^3 for dibenzo(a,h)pyrene. The detection limit for benzo(a)pyrene was 0.018 ng/m^3.

PAH were determined using reverse phase HPLC with gradient elution, flow programming and selective fluorescence detection. Two fluorescence programs were devised to determine closely-eluting and co-eluting pairs in two injections per sample.

Extraction techniques (sonication and micro-Soxhlet) and extraction solvents (dichloromethane and a benzene-methanol 1:1, v:v mixture) were compared for filter samples of indoor woodsmoke. Sonication and micro-Soxhlet extraction were found to be equivalent in recovery of PAH on average. Because sonication was less subject to evaporation losses, faster and less labor intensive than micro-Soxhlet extraction, sonication was chosen for extraction of field samples. The benzene-methanol mixture gave better recovery of the whole range of PAH, but dichloromethane had somewhat better recovery of the highest molecular weight particulate-phase PAH. Dichloromethane extracts had lower concentrations of semi-volatile PAH than benzene-methanol extracts. The benzene-methanol mixture was used to extract the field samples.

Recovery of PAH from NBS SRM 1649 (urban dust-organics) averaged 105 $\pm$ 27 % of reported values for sonication of 3 mg aliquots in the benzene-methanol mixture. Results for comparison of extraction methods and solvents were similar to those reported for extraction of indoor woodsmoke.

Recovery of fluoranthene-d_{10}, an internal standard for recovery of semi-volatile PAH, varied with extraction method and was not necessarily related to recovery of higher molecular weight particulate-phase PAH such as benzo(a)pyrene or coronene. Recovery was better for sonication than micro-Soxhlet extraction, and better for benzene-methanol than dichloromethane. 81 $\pm$ 11 % of fluoranthene-d_{10} added to blanks at the time of extraction was recovered; 68 $\pm$ 18 % was recovered from loaded field samples.

Complex indoor samples, those containing cigarette smoke or wood smoke, frequently showed evidence of interfering compounds. When interferences co-eluted with benzo(e)pyrene-d_{12}, the internal standard for quantitation, replicate analyses yielded large

coefficients of variation. When complex samples were excluded from calculation of the pooled standard of deviation of replicates, coefficients of variation averaged 34 %.

Based on perturbation analysis of measurement uncertainty, the largest contributors to the relative uncertainty for benzo(a)pyrene in simple samples (not containing cigarette smoke or woodsmoke) were peak height measurements in the sample and standard solution. About half of the measurement uncertainty was due to uncertainty in peak height measurement of the internal standard for quantitation, benzo(e)pyrene-d_{12}. This analysis does not take into account uncertainties due to interferences in complex samples.

Optical attenuation measurements of filter blackness indicated that amounts of black carbon were roughly proportional to the sum of the concentrations of benzo(b)fluoranthene, benzo(b)fluoranthene, benzo(a)pyrene, benzo(g,h,i)perylene, indeno(1,2,3-c,d)pyrene and coronene. ATN values were used to batch samples of similar blackness for analysis in groups with similar PAH concentrations.

E. RECOMMENDATIONS

The following are our recommendations for improving the analyses of particulate phase PAC.

1. Sample cleanup (on a Sep-Pak or similar silica column) is recommended for complex samples in order to eliminate interfering compounds.

2. For better recovery of high molecular weight particulate PAH, we recommend extraction in dichloromethane rather than a benzene-methanol mixture. Addition of 300 microliters of benzene to the extract before rotary evaporation should reduce evaporation losses of semi-volatile PAH. Preparation of dichloromethane extracts would also eliminate any problems introduced by interaction of methanol with silica Sep-Paks, as was observed in the development of an HPLC method for nitronapthalenes (Chapter VII).

3. We recommend investigation of the use of a different internal standard for quantitation rather than benzo(e)pyrene-d_{12} or recalibration of samples using the external standard method when the sensitivity of benzo(e)pyrene-d_{12} is more than 30 % different than expected from analysis of standards.

4. We recommend use of a 10 microliter injection loop or an automatic injector rather than a 5 microliter loop. This would decrease detection limits two-fold.

5. Installation of sub-ambient temperature control in the column compartment of the HPLC is recommended, to enhance temperature stability and allow better reproducibility of retention times.

6. Two fluorescence detectors in series would allow simultaneous HPLC analysis of an extract using both fluorescence programs. This would cut down on analysis and data reduction time and still allow detection of 22 compounds.

7. Before deployment in a large indoor air filed study the modified method should be validated on replicate pairs of indoor and outdoor samples.

8. For more rapid sample analysis and data reduction we recommend a single fluorescence program and determination of fewer compounds, for example only the particulate PAH which were found in detectable quantities in at least two thirds of the samples in this study, with some exceptions, and which can be detected with one set of fluorescence conditions. Such a list includes fluoranthene, pyrene (possibly), benzo(a)anthracene or chrysene, 5-methylchrysene (estimate), benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene, indeno(1,2,3-c,d)pyrene, coronene and four dibenzopyrenes (a,l; a,e; a,i and a,h). This list includes most of the particulate PAH carcinogens.

VI. FIELD MEASUREMENTS AND SAMPLER VALIDATION

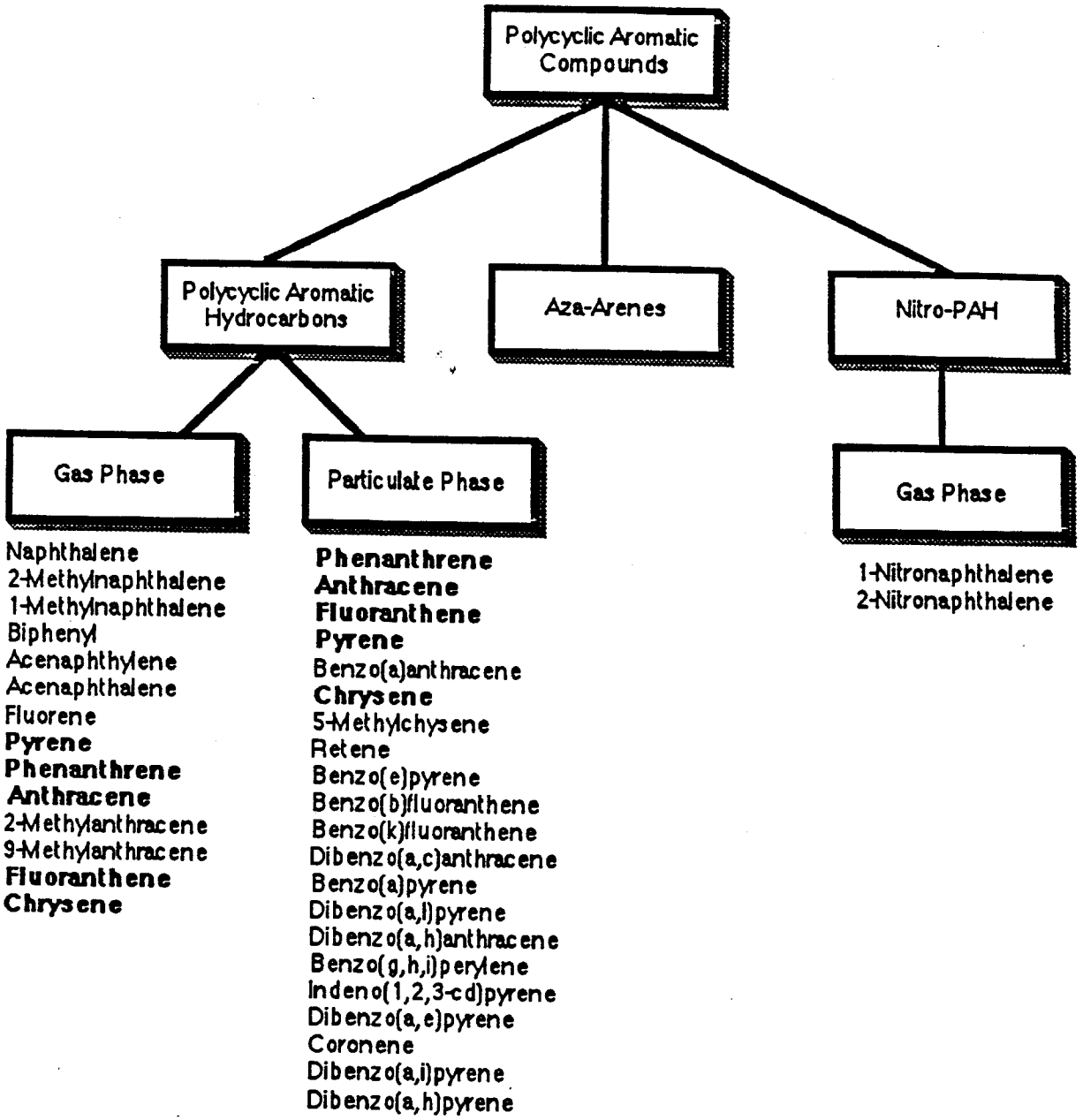
A. INTRODUCTION

We designed and conducted a pilot field study to validate the newly developed PAC sampler in occupied residences and commercial building settings. The primary purpose of this pilot field study was to validate the sampler collection efficiency, recovery, and measurement precision for gas and particulate phase PAC in actual indoor environments with a variety of indoor source configurations. A secondary purpose of this field study was to gather data regarding indoor and outdoor PAC concentrations in California for use in preparing preliminary estimates of the public health risk to these contaminants.

This pilot field study represents a very limited number of samples which provide important initial data toward meeting the study purposes. Many more samples will be required to develop a statistically acceptable estimate of the distribution of indoor PAC concentrations in California buildings.

The newly developed PAC sampler, described in detail in Chapter III, was designed to sample ~ 25 m^3 volume of air at a constant sampling rate of ~ 34 Lpm over a 12 hour period. The sample volume of 25 m^3 was selected to achieve the detection limits required for health risk assessments without significantly impacting the indoor PAC concentrations. The sampler pump is contained in an acoustically shielded fan cooled enclosure. The pump runs off of 115 VAC power and the operating time is recorded by a electro-mechanical timer.

The PAC sample cartridge includes a 47 mm diameter TIGF filter for collection of particulate phase PAC followed by a cartridge containing 2.5 grams of XAD-4 resin each in front and back sections for collection of vapor phase PAC. After sampling the filters and XAD-4 resin were extracted and analyzed as described in Chapters 4 and 5. GC-MS was used to analyze the gas phase extracts for 14 gas phase PAH ranging from naphthalene to chrysene. HPLC with fluorescence detection was used to analyze 21 additional particulate phase PAH compounds ranging from phenanthrene to dibenzo(a,h)pyrene as well as two gas phase nitro-PAH compounds, 1-nitronaphthalene and 2-nitronaphthalene. The individual compounds measured in this PAC pilot field study are depicted by type and phase in Figure VI-1.



Bold typed compounds were analyzed for in both gas and particulate phases.

Figure VI-1. Grouping of the different Polycyclic Aromatic Compounds analyzed in the pilot field study.

B. PILOT FIELD STUDY DESIGN

The following describes the site selection, field study plan, and measurement methods for the pilot field study.

Site Selection

Participant buildings for the pilot field study were selected on a voluntary, non-random basis to serve the primary purpose of the study which is to provide information on the precision and accuracy of the sampling and analytical method under a variety of real indoor environmental conditions. To accomplish this purpose we tested the method in three residences and two commercial buildings with and without three known indoor sources of PAC.

Table VI-1 is an outline of the set of residential and commercial field sites with and without the various known indoor sources of PAC. The selection of tobacco smoke, wood stoves, and gas ranges represents our current perception of the three most significant indoor sources of combustion generated PAC. Unvented space heaters and residential vented gas heating systems with leaks may also contribute to the indoor concentrations. We conducted five residential tests including one test with one of each of the three identified indoor combustion sources of PAC; tobacco smoke, wood stoves, and gas ranges as well as one site without any of these sources and one site with all three of these sources. Since it is important to expose the samplers to the suspected indoor sources of PAC as part of the validation program, we controlled the activity of the potential indoor sources in order to be assured of the exposure during the days of the tests. The control of the indoor sources was coordinated with the occupants of the study and a detailed log of the source usage was part of the field record generated for each sampling period.

Field Study Measurement Protocol

Residential Building Measurement Protocol. Table VI-2 describes the measurements we made for the residential building portion of the pilot field verification program. We simultaneously collected samples of the indoor and outdoor PAC in each of the residential tests over two consecutive 12-hour periods representing one daytime period followed by one nighttime period. The sampling periods were 7 AM to 7 PM and 7 PM to 7 AM.

Table VI-1. Selection of field sites with and without known indoor combustion related sources of PAC for the pilot field study.

# SITES	TYPE	BUILDING INDOOR PAC SOURCES Tobacco [a]	Heat [b]	Range [c]
1	Residential	NS	GFA	E
1	Residential	**S**	GFA	E
1	Residential	NS	**WS**	E
1	Residential	NS	GFA	**G**
1	Residential	**S**	**WS**	**G**
1	Commercial	NS	HWC	none
1	Commercial	**S**	HWC	none

a) **S** = tobacco smoking, NS = no tobacco smoking.
b) **WS**= woodstove, GFA = Gas Forced Air, HWC = hot water coil.
c) E = electric, **G** = gas. **BOLD** Type = known indoor combustion related source of PAC.

Table VI-2. Description of the measurements made for the residential building portion of the PAC pilot field study.

SITE ID	Measurement [b] Period	Air Exch[c] Rate	PAC Measurements [a] 1-Indoor & 1-Outdoor	1-Indoor Replicate	1-Outdoor Replicate
T-1	D	X	X	X	X
	N	X	X		X
T-2	D	X	X	X	
	N	X	X	X	
R-1	D	X	X	X	
	N	X	X		
R-2	D	X	X	X	
	N	X	X		
M-1	D	X	X	X	
	N	X	X		

(a) Measurements of both particulate and gas phase PAH.
(b) Measurement period was divided into two 12-hour collection periods; 1-day (D),7AM-7PM, 1-night (N),7PM-7PM.
(c) Local air exchange rate measurements were made using a sulfur hexafluoride tracer gas technique.

Arrangements were made with the occupants to operate the indoor PAC sources in a manner representative of typical residential use. We also measured the air exchange rate concurrently at the indoor PAC sampler location, using a tracer gas technique.

For the concurrent indoor and outdoor PAC measurements, we placed samplers at a single location in the residence and at a single outdoor location adjacent to the residence. The indoor samplers were placed in the center of the living/dining room area for both the daytime and nighttime measurements. Consideration was given to siting the nighttime sampler in the master bedroom since this would most likely provide a better estimate of the occupants' exposure during this measurement period. However we decided to keep the nighttime sampling site in the living/dining room for several reasons. First, the living/dining room area has been demonstrated in a survey of indoor room-to-room concentrations of respirable particles to provide a good measure of the average indoor concentration (Ju and Spengler, 1981). In that study the living room mean approximated the indoor mean within 5% in three of the four houses monitored in this study. Secondly, we felt that siting of the nighttime sampler in a bedroom might result in unacceptable noise levels to sleeping occupants. Finally, the reduction of the indoor concentration caused by the sampler and the resulting corrections would be expected to be larger for measurements made in a bedroom site which, with the door closed, has a small air volume and often a lower air exchange rate than the living area of the house.

An additional indoor sampler was simultaneously exposed during the daytime measurement period in each residence. An additional outdoor sampler was also simultaneously exposed at residence R-1 during both the daytime and nighttime measurement periods. These additional samplers were sited side-by-side with the indoor and outdoor samplers and were used to provide data on the overall precision of the sampling and analytical method. The flow rates of each sampler were measured with a rotameter. Rotameters were calibrated with a bubble meter as described in Chapter III. The flow rates were set for ~ 34 Lpm in order to collect ~ 25 m^3 of air over the 12 hour sampling period.

Air exchange measurements were made concurrently with the collection of the simultaneous indoor and outdoor PAC samples. We measured the building air exchange rate at one specific location adjacent to the paired indoor samplers using a tracer gas decay technique. The local age of air and local ventilation rate at the location of the indoor PAC sampler were computed from this measurement. The tracer gas technique is described briefly in Appendix C and in more detail in the noted references.

Commercial Building Field Study Table VI-3 describes the measurements for the commercial building portion of the field verification program. We made simultaneous measurements of the indoor and outdoor PAC concentrations at a single location in each of the two commercial office buildings over a single, 12-hour, occupied daytime period. The sampling period was 7 AM to 7 PM. No nighttime measurements were conducted in commercial buildings since such buildings are seldom occupied at night and their ventilation systems are typically shut down at night. The extent of diurnal variations were investigated in the residential part of the field study. With respect to indoor sources, one building was selected to be a building in which smoking is not permitted and the other a building with tobacco smoking. As in the residential portion of this field study air exchange rate measurements were made concurrently with the indoor and outdoor PAC measurements using a tracer gas measurement technique that yielded the actual local air exchange rate at the location of the PAC sampler location.

Table VI-3. Description of the measurements made for the commercial building portion of the PAC pilot field study.

			PAC Measurements (a)		
SITE ID	Measurement (b) Period	Air Exch(c) Rate	1-Indoor & 1-Outdoor	1-Indoor Replicate	1-Outdoor Replicate
S-1D	D	X	X	X	X
P-1D	D	X	X	X	X

(a) Measurements of both particulate and gas phase PAH.
(b) Measurement period was one 12-hour collection period.
(c) Local air exchange rate measurements were made using a sulfur hexafluoride tracer gas technique.

For the concurrent indoor and outdoor PAC measurements, samplers were placed at a single location in the building and at a single outdoor location adjacent to the building ventilation air inlet. Additional indoor and outdoor samplers were simultaneously exposed during the measurement period in each building. These duplicate samplers were sited side-by-side with the indoor and outdoor samplers and were used to provide additional data on

the precision of the sampling and analytical method. The sample flow rates of each sampler were measured with a calibrated rotameter. The sample flow rates were set for 34 Lpm in order to collect ~ 25 m^3 of air over the 12 hour sampling period.

Filter Performance Data

We measured the pressure drops across the filter and the associated weight gains to determine the maximum loading capacity of the filter at the maximum acceptable differential pressure drop for stable flow. The increase in the differential filter pressure drop was computed for each sample from differential pressure measurements taken before and after the sampling period. The differential pressures were measured using a water manometer. The total mass of collected particulate matter was computed from mass measurements of the filter before and after the sampling period. The mass measurements were made using an electronic microbalance at ambient laboratory humidity (e.g. ~ 50% relative humidity @ 21°C).

Additional Field Data

In addition to the PAC and air exchange rate measurements described above, the following data were assembled for each sample site.

- The type and usage of all identified indoor sources of PAC.
- The type of any local outdoor sources of PAC (e.g.highways, airports, power plants).
- The heating, air-conditioning, ventilating, and air cleaning characteristics of the building.
- The type of building, number of floors, and volume of air space.
- Number of occupants and smoking habits.
- The indoor and outdoor temperature and relative humidity and wind speed/direction during the measurement periods.

Pilot Field Study Measurement Summary

Table VI-4 summarizes the PAC data collected during the pilot field study in residential and commercial buildings, separately and together. A total number of 42 samples were collected and analyzed in the pilot field study representing 26 indoor samples and 7 replicate side-by-side samples. A total of 7 sample blanks were carried into field with the field samples and submitted for analysis.

Table VI-4. Summary of the number of samples collected during the PAC pilot field study in residential and commercial buildings.

	Residential	Commercial	Total
Total concurrent indoor/outdoor samples -	20	4	24
Total indoor replicate pairs -	5	2	7
Total outdoor replicate pairs -	2	2	4
Total field blanks -	5	2	7
Total PAC samples and blanks collected and analyzed -	32	10	42

The paired replicate samples were collected in order to compute the measurement precisions for each of the 37 species of PAC analyzed in this study. The precision determined from these data were compared to the estimated experimental uncertainties to identify the measurement parameters which contributed most to the imprecision. The 12 simultaneous indoor and outdoor samples along with the local ventilation rate data allowed for the computation of the indoor net emission rates for many of the PAC. These net emission rates may be used as a basis to estimate the indoor concentrations in buildings with different ventilation rates or source usage patterns. The net emission rates may be compared for each of the different sites along with the other data describing the house to identify and characterize indoor sources of gas phase and particulate phase PAC.

We recorded the local prevailing wind direction and airspeed three to four times during each measurement period at locations at and near to the building site. We measured the wind direction with a smoke tube and compass (corrected for true North) and measured the airspeed with a hot wire anemometer.

C. RESULTS AND DISCUSSION

Site Locations, Descriptions, Meteorology, and Air Exchange Rates

All of the test sites were buildings in California. The residential test sites were in the Lake Tahoe area for the two woodstove tests, in the Rodeo area for the test with a gas stove only and the test with no indoor combustion sources, and in the Milbrae area for the test with tobacco smoking only. The Truckee and Rodeo sites were residences which were occupied by a pair of researchers during the tests. The Milbrae residential site was occupied by the it's regular residents. The commercial building test sites were the Sacramento area for the non-smoking building and in the Palo Alto area for the smoking building. These buildings were normally occupied during the tests.

Figures VI-2 through VI-6 show the locations of the five field sites. These figures also show the major outdoor PAC sources in the vicinity of the site such as highways, airports, and major industry. The range of the prevailing wind direction over the sampling period is also noted on each map.

Table VI-5 summarizes pertinent building physical characteristics for each of the residential and commercial building field sites. The three residences in this pilot study were all single family detached residences. The Milbrae and Truckee sites were single story structures with fully ventilated crawlspaces, and the Rodeo site was a two story split level structure, half with a ventilated crawlspace and half with a concrete slab. The floor areas ranged from 90 m^2 to 150 m^2. All of the residences had forced air gas heating systems. For the Truckee tests where a wood stove was used for heat, the gas furnace was not used. In all cases, the gas furnace and water heater exhaust vents were inspected and found to be in good condition. Table VI-5 also summarizes the data collected regarding the usage of woodstoves (kg woodburned in 12 hours), tobacco smoking (cigarettes burned in 12 hours), and gas range (m^3 gas burned in 12 hours). The amount of tobacco smoking in commercial buildings represent the number of cigarettes smoked in the office suite where the sampler was located. The Palo Alto building, which permits tobacco smoking, had both cigarette and pipe smoking in the adjacent office suites.

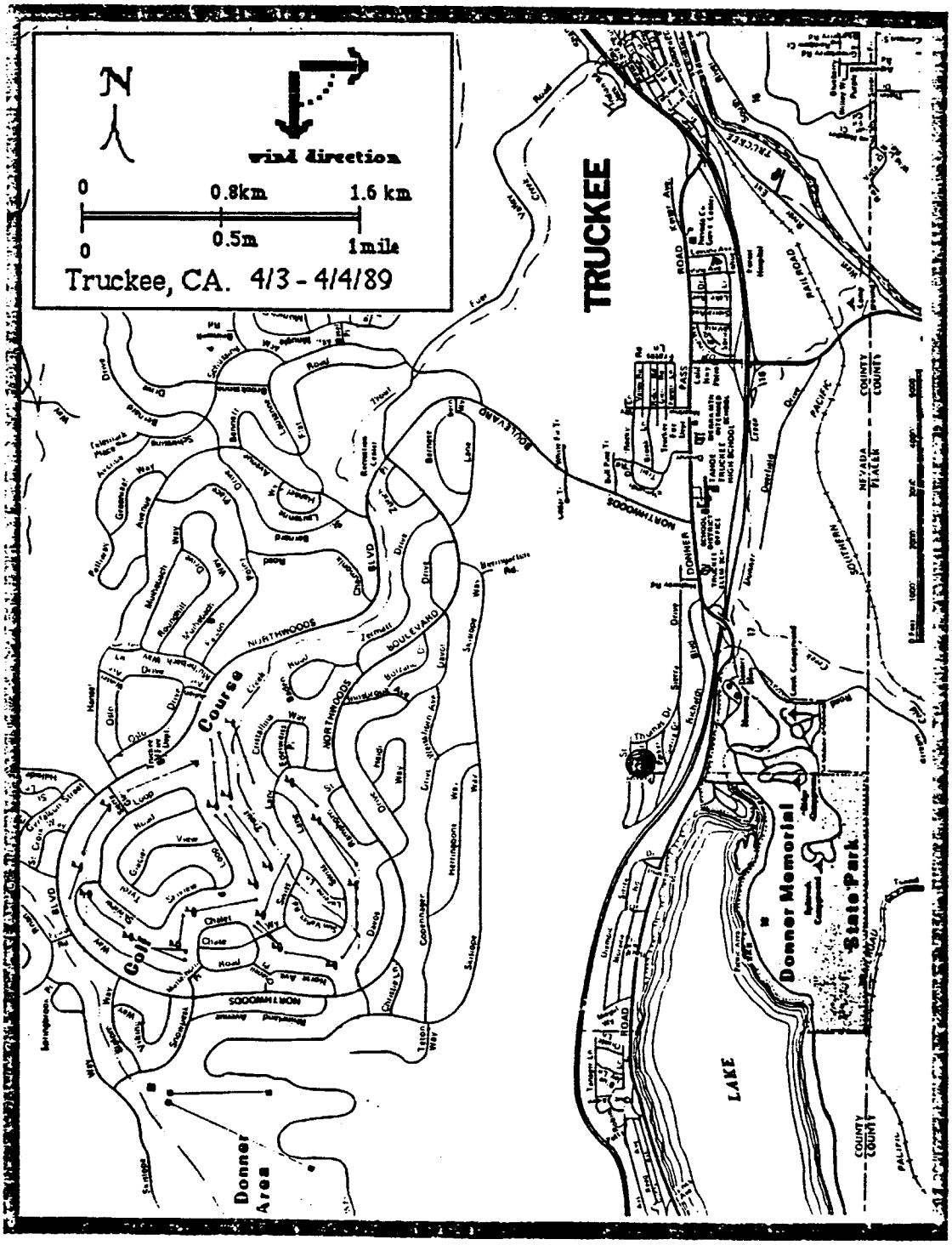


Figure VI-2. Location of the residential field sites T-1 and T-2 in Truckee, CA.

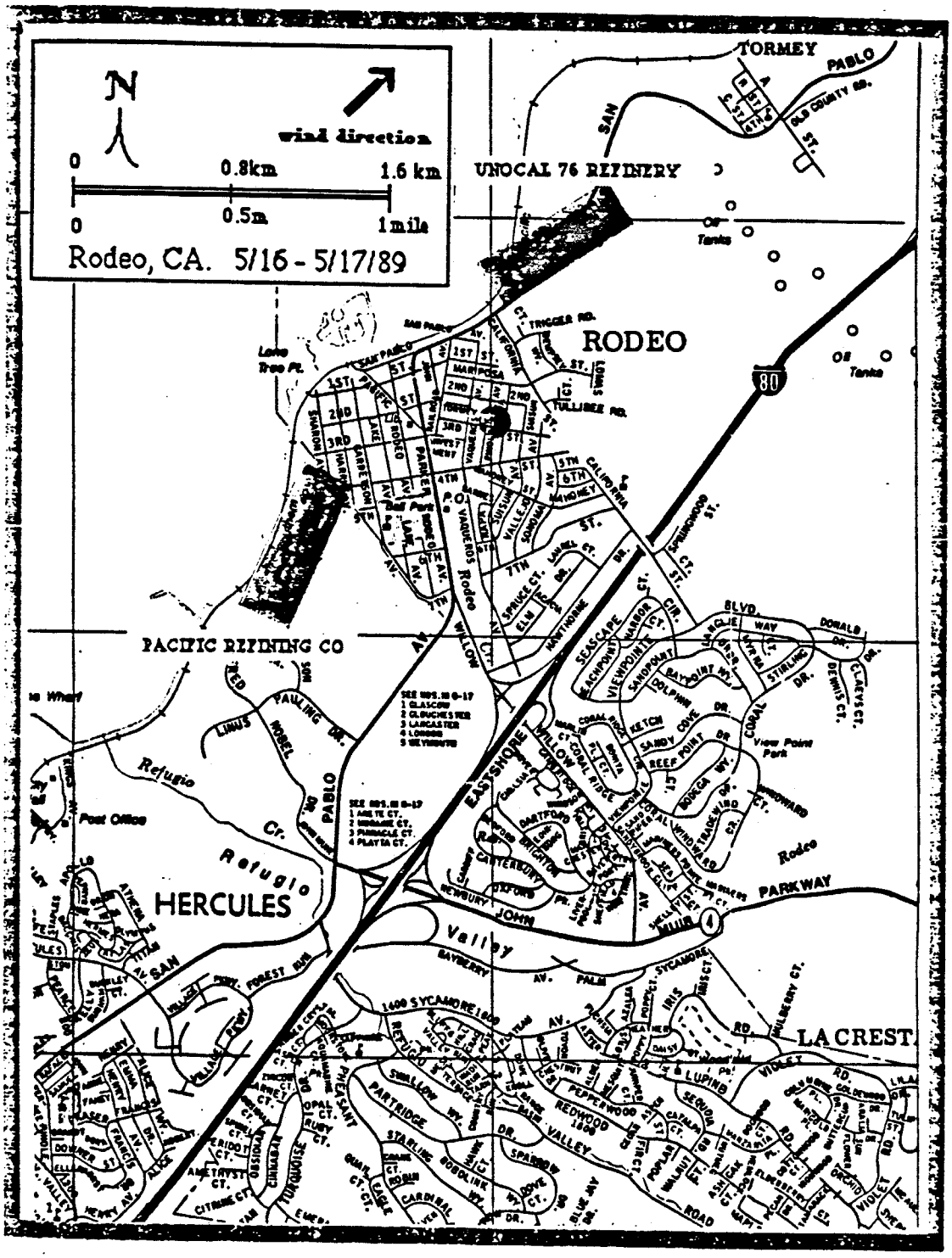


Figure VI-3. Location of the residential field sites R-1 and R-2 in Rodeo, CA.

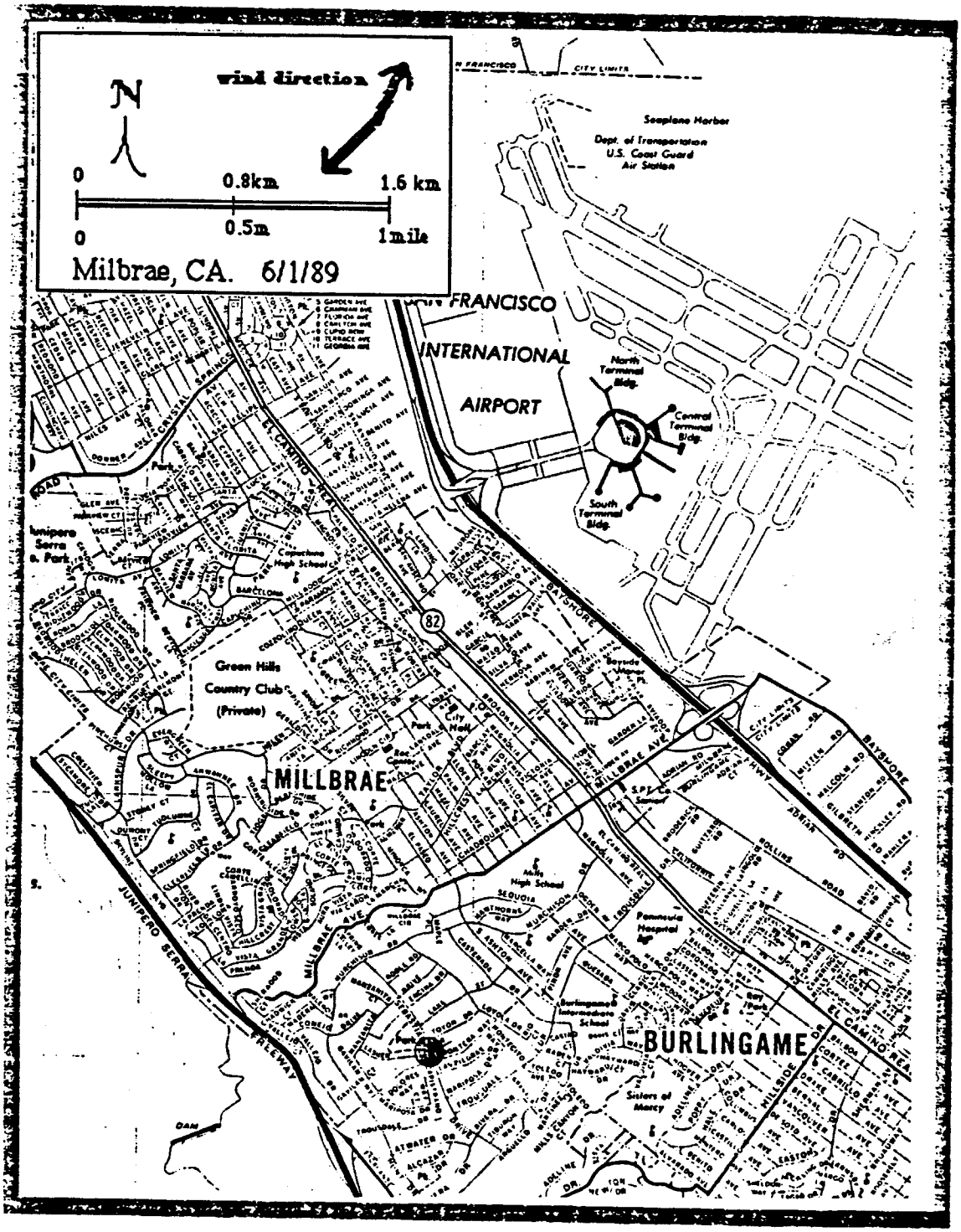


Figure VI-4. Location of the residential field site M-1 in Milbrae, CA

Figure VI-5. Location of the commercial field site S-1 in Sacramento, CA

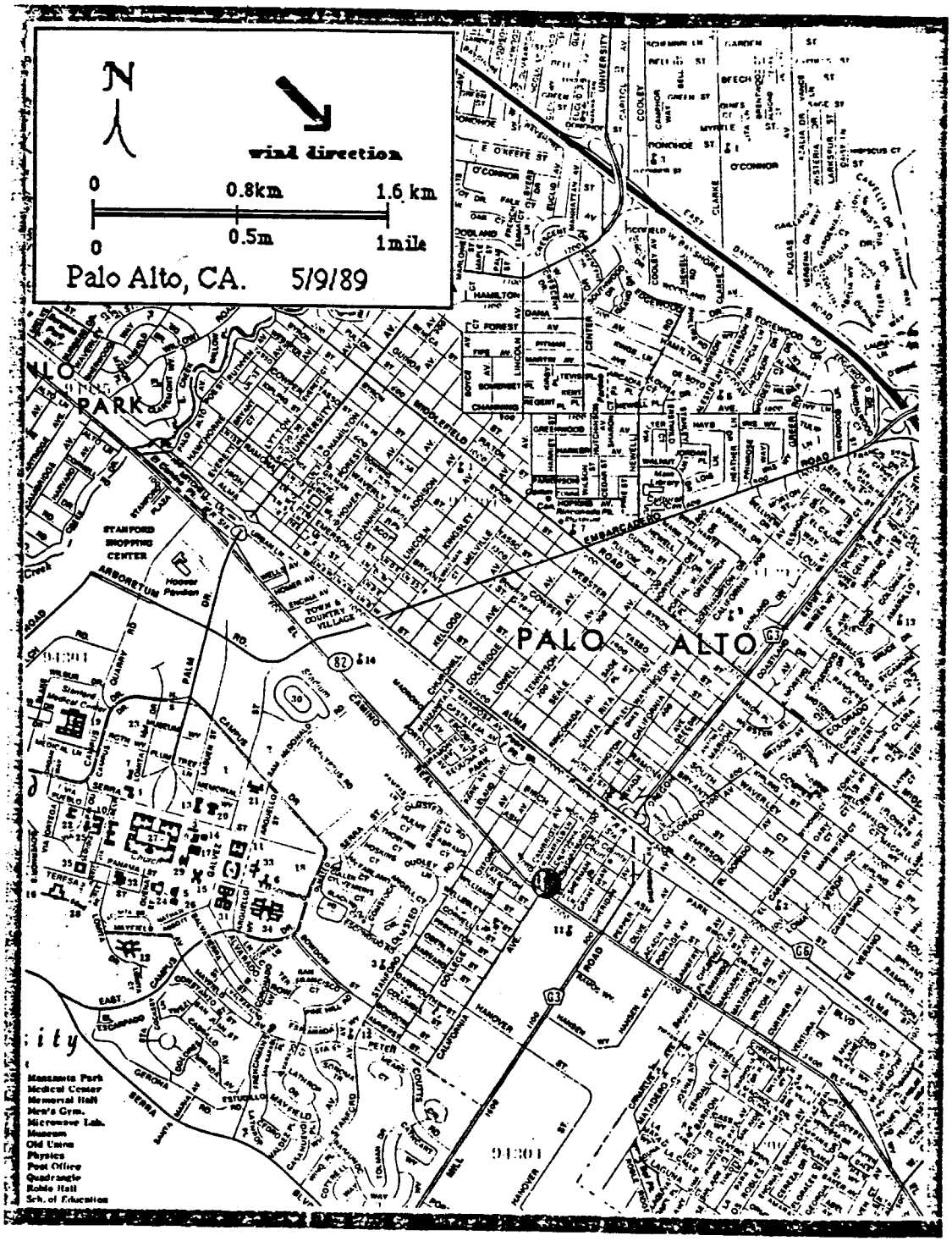


Figure VI-6. Location of the commercial field site P-1 in Palo Alto, CA

Table VI-5. Building characteristics and indoor PAC source data for each of the field sites in the pilot field study.

Site ID [a]	Building Type	Foundation Type	No of Floors	Floor Area/ Air Volume m^2/m^3	HVAC System	Wood-stove kg-burned		Tobacco [b] Smoke cigs burned		Gas Stove day m^3 burned		Number of occupants
						day	night	day	night	day	night	
T-1	Detached Single Family Residential	Ventilated Crawlspace	1	84/ 209	Forced Air Gas Heat	6.4	2.8	11	4	0.14	-	2
T-2	Detached Single Family Residential	Ventilated Crawlspace	1	84/ 209	Forced Air Gas Heat	10.6	7.0	-	-	-	-	2
R-1	Detached Single Family Residential	Ventilated Crawlspace/ Concrete Slab	2	110/ 254	Forced Air Gas Heat	-	-	-	-	-	-	2
R-2	Detached Single Family Residential	Ventilated Crawlspace/ Concrete Slab	2	110/ 254	Forced Air Gas Heat	-	-	-	-	0.19	-	2
M-1	Detached Single Family Residential	Ventilated Crawlspace	1	144/ 332	Forced Air Gas Heat	-	-	14	1	-	-	2
S-1	Commercial Office Space 1-floor zone	Concrete Slab	3	1280/ 6362 *	Constant Volume Diffuser	-	-	-	-	-	-	36
P-1	Commercial Office Space 6-floor zone	Concrete Slab	6	5165/ 16,656 **	Constant Volume Induction Supply	-	-	22	-	-	-	108

a) Site ID: T=Truckee, CA; S=Sacramento, CA; P=Palo Alto, CA; R=Rodeo, CA; M=Milbrae, CA; -1=Day 1 and/or Night 1; -2=Day 2 and/or Night 2.
b) Total number of cigarettes smoked in the residence or in the office suite that the PAC sampler is located.
* The first floor of this building had a separate ventilation system, and was considered separately to calculate the floor area and air volume of the test zone
**All six floors of this building share the same ventilation system and were added together to calculate the floor area and air volume of the test zone.

Figures VI-7 through VI-11 show the building floor plans with the location of the indoor and outdoor PAC samplers.

The wind speed, direction, indoor and outdoor dry bulb temperatures and relative humidities, and barometric pressure are tabulated in Table VI-6 for each of the 12-hour measurement periods.

Field Sample Times, Rates, and Volumes

Table VI-7 summarizes the Field Sample ID's and Lab Sample ID's for each sample along with the date, start and stop times, average air sampling rate, and total air volume sampled. A total of 42 field samples were collected starting April 4, 1989 and ending June 1, 1989. A sampling time of approximately twelve hours was used in each test. The air sampling rates were set between 28.9 and 34.2 Lpm yielding a total air sample volume of 20.9 m^3 - 24.6 m^3. The average air sampling rates presented in Table VI-7 reflect the computed average flow rate of air into the sampler at standard temperature and pressure (25°C and pressure 760 mmHg). The air flow rates were measured in the field every 2-3 hours with a calibrated rotameter as described in Chapter III and adjusted manually to re-establish the initial air sampling rate if required. The air sampling rates for each sampler were found to remain very stable throughout the 12 hour sampling period, with the maximum adjustment to the flow being less than 5%. The time weighted average flow rate was computed by averaging the intermittent air sampling rate measurements, assuming that any change in the air flow rate was linear with time.

Air Exchange Rates

The local air exchange rate measurements are tabulated in Table VI-6 along with the local meteorology data. These measurements represent the actual exchange rate of indoor and outdoor air at as measured next to the indoor PAC sampler. The local air exchange rates ranged from 0.14 air changes per hour (ach) to 0.47 ach in the residences with the nighttime measurements being slightly

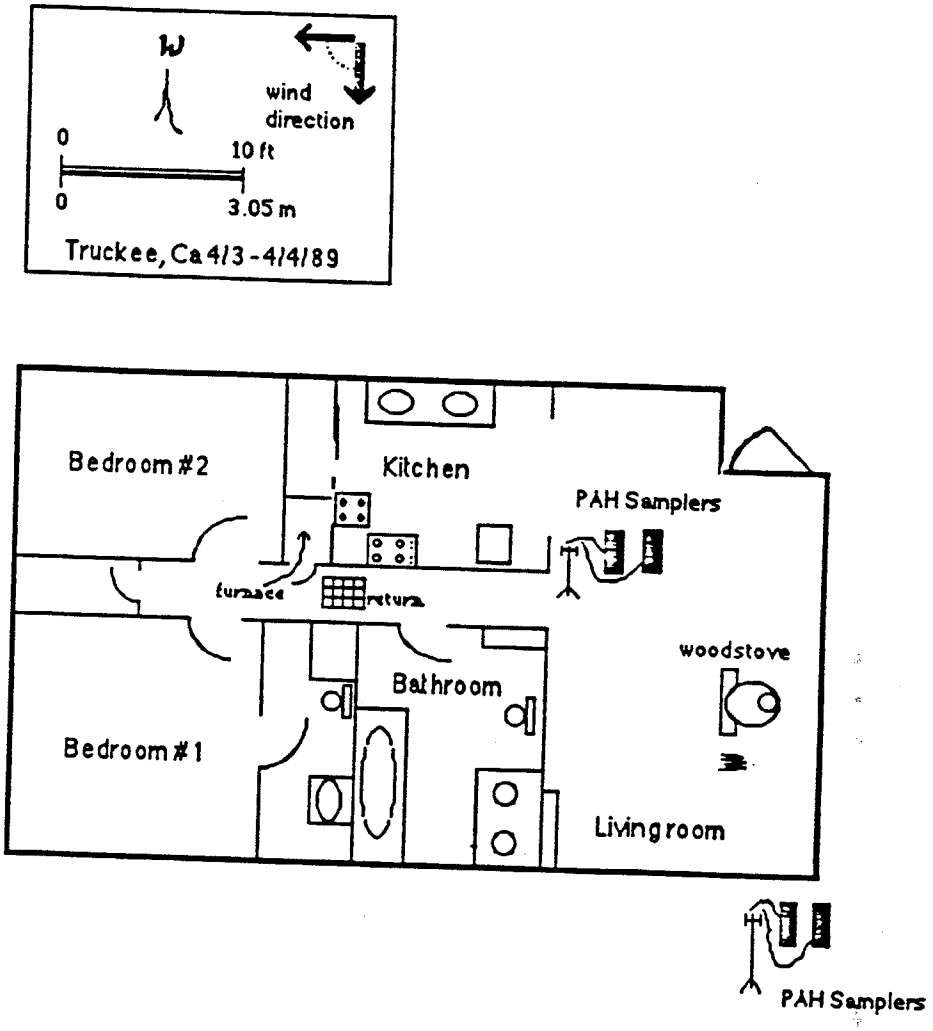


Figure VI- 7. Floor plan of the residential sites, T-1 and T-2, in Truckee, CA.

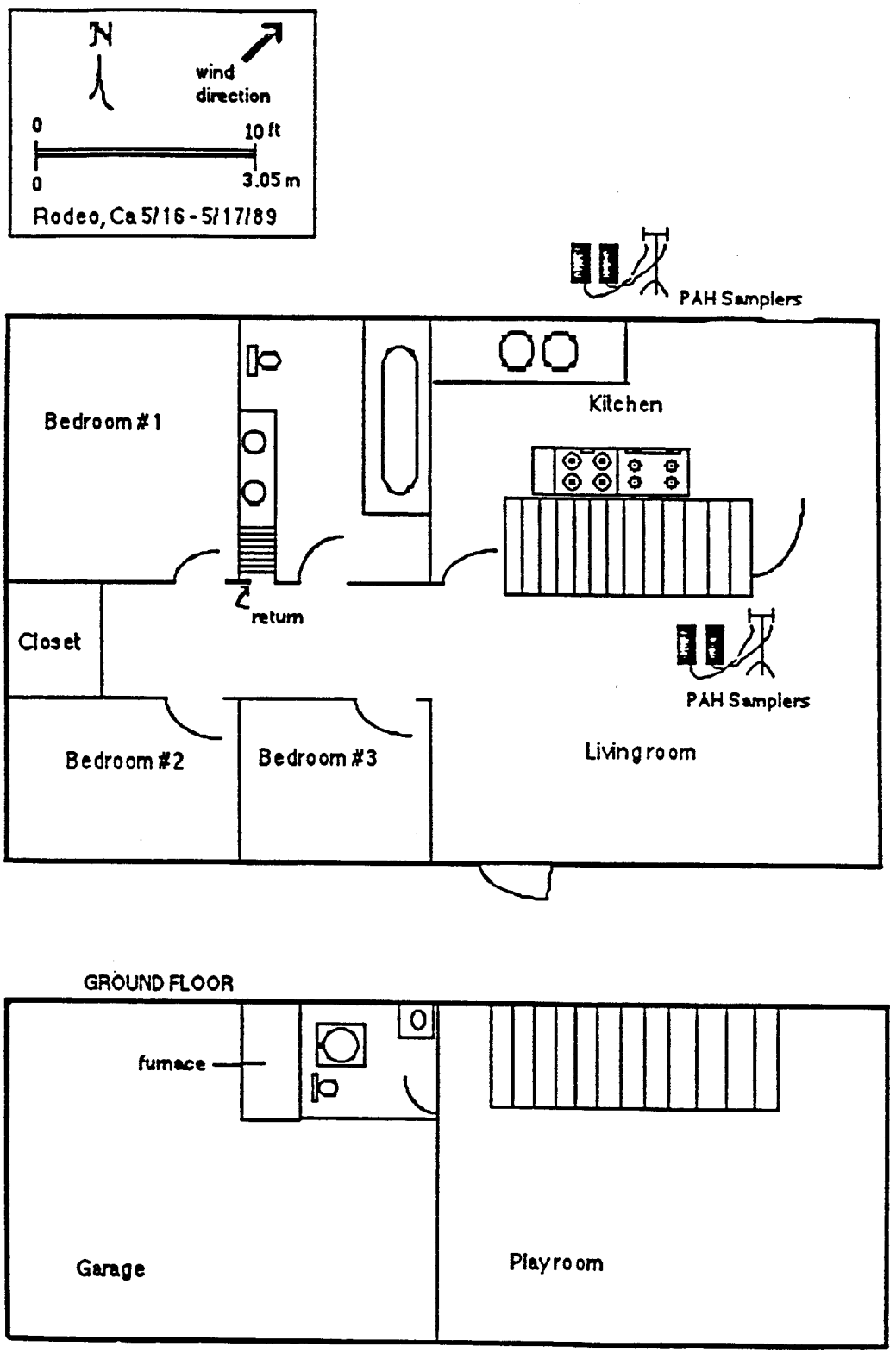


Figure VI-8. Floor plan of residential sampling site, R-1 and R-2, in Rodeo, CA.

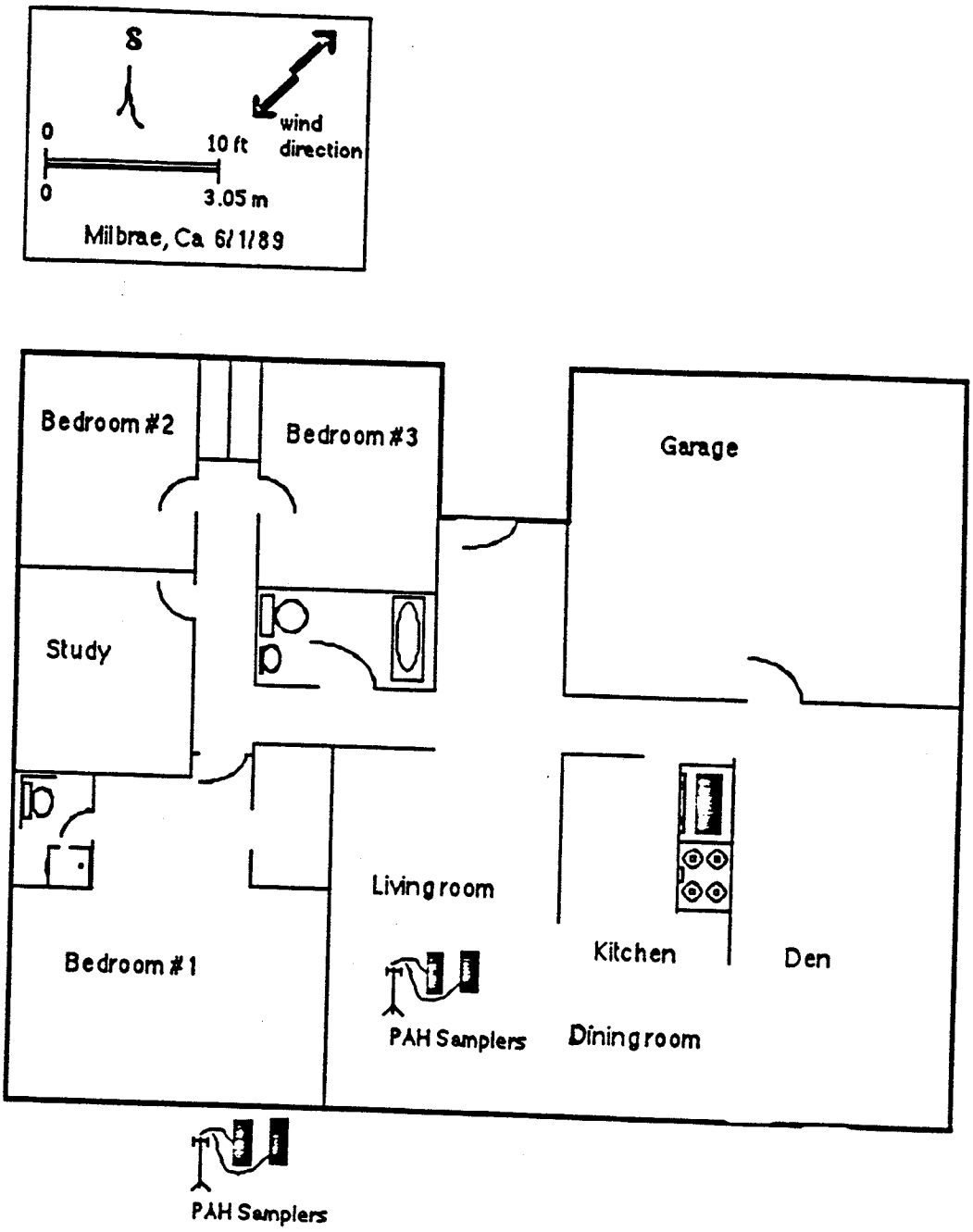


Figure VI-9. Floor plan of residential sampling site, M-1, in Milbrae, CA.

Table VI-6. Meteorology and indoor local air exchange rate for each of the field study in the PAC pilot field study.

Site ID [a]	Date	Site [b] Wind Speed	Site [b] Wind Direct-ion	Outdoor Air DB	Outdoor Air RH	Indoor Air DB	Indoor Air RH	Barometric Pressure	Air [c] Exchange Rate
		m/s		°C	%	°C	%	mm Hg	(1/hrs)
T-1D	4/3/89	1-3	NW	3-11	15-25	24-27	10-20	617-619	0.26
T-1N	4/3/89	1-2	W	-2-5	45-85	23-27	15-25	617-619	0.32
T-2D	4/4/89	1-3	N	-2-15	30-90	26-27	15-25	617-619	0.23
T-2N	4/4/89	1-2	N	0-15	35-95	21-29	20-30	617-619	0.31
R-1D	5/16/89	1-4	SW	12-24	50-80	23-30	50-68	758-760	0.14
R-1N	5/16/89	1-4	SW	12-22	50-80	20-29	50-85	758-760	0.30
R-2D	5/17/89	2-8	SW	12-18	65-80	23-26	45-68	760-762	0.34
R-2N	5/17/89	2-5	SW	10-15	65-85	23-26	45-58	760-762	0.38
M-1D	6/1/89	1-3	NE; SW	22-30	35-65	24-26	42-58	761-763	0.34
M-1N	6/1/89	1-4	SW	24-26	25-30	27-28	50-55	761-763	0.47
S-1D	4/13/89	2-7	S; SW	13-22	50-70	20-22	55-65	760-762	0.96
P-1D	5/9/89	3-5	NW	13-15	70-95	25-27	35-40-	756-758	0.80

a) Site I.D.; T=Truckee, CA; S=Sacramento, CA; P=Palo Alto, CA; R=Rodeo, CA; M=Milbrae, CA; -1D=Day (7AM-7PM) 1;-2D=Day (7AM-7PM) 2; -1N=Night (7PM-7AM) 2; -2N=Night 2 (7PM-7AM).
b) Prevailing local wind speeds and directions.
c) The local air exchange rate as measured using a tracer gas technique at an indoor location next to the indoor PAC sampler.

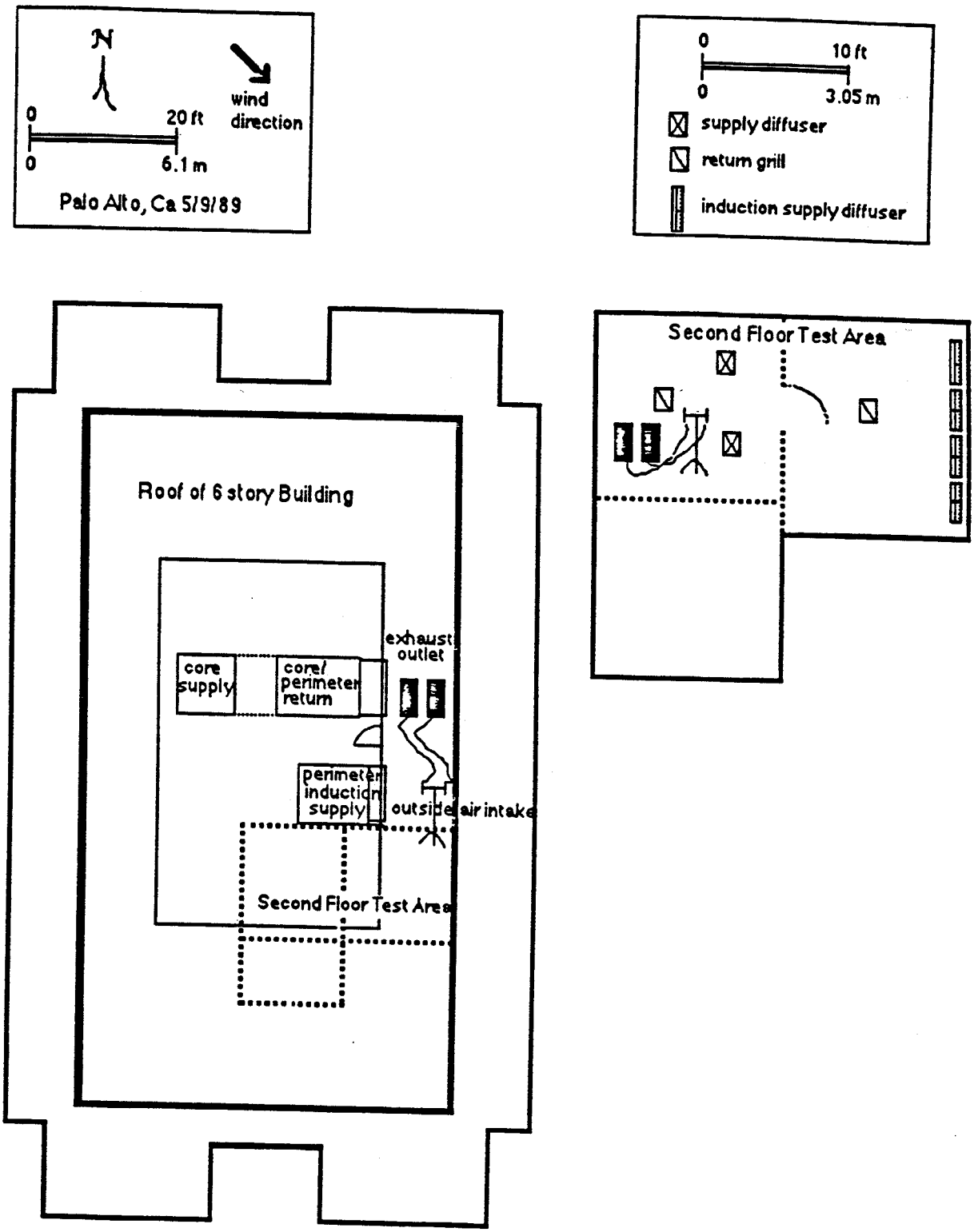


Figure VI-11. Floor plan of commercial sampling site, P-1, in Palo Alto, CA.

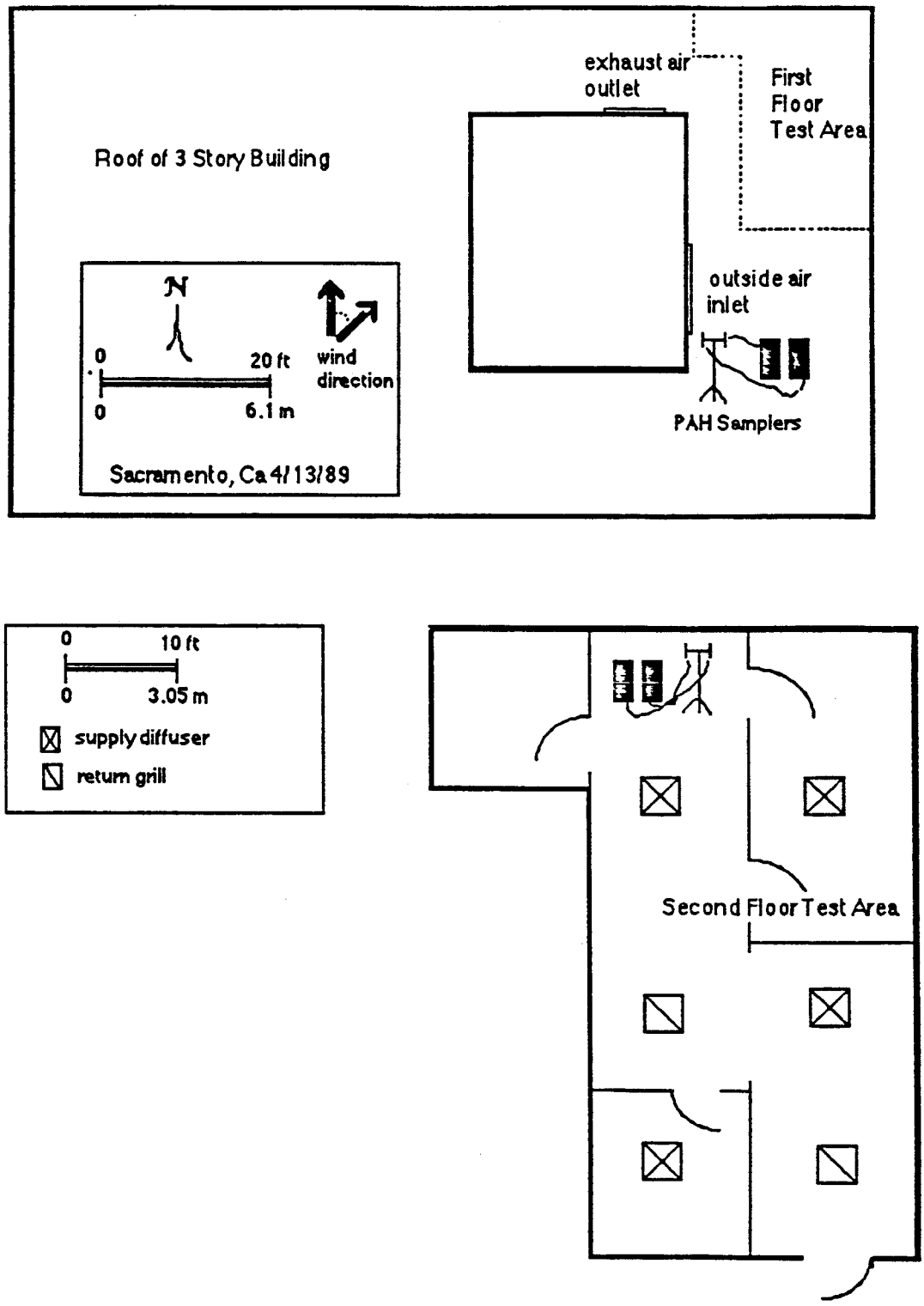


Figure VI-10. Floor plan of the commercial site, S-1, in Sacramento, CA.

Table VI-7. Sample field identification numbers, sample times, and sample air volumes for the 42 PAC samples collected during the PAC pilot field study.

Sample Location (Building Type)	Sample Date	Field [a] Sample ID	Lab Sample ID	Sample Time Start	Sample Time Stop	Sample Air Flow Rate Lpm	Sample [b] Volume m^3
Truckee (Residential)	4/3/89	T-1D-I	9	07:18	19:20	28.9	20.9
	4/3/89	T-1D-IR	10	07:20	19:21	28.9	20.9
	4/3/89	T-1D-O	11	07:14	19:10	30.2	21.7
	4/3/89	T-1D-OR	12	07:16	19:11	30.1	21.7
	4/3/89	T-1N-I	6	19:24	07:14	29.0	20.8
	4/3/89	T-1N-O	7	19:17	07:20	30.5	22.1
	4/3/89	T-1N-OR	8	19:17	07:19	30.5	22.1
Truckee (Residential)	4/4/89	T-2D-I	3	07:27	19:30	29.0	20.9
	4/4/89	T-2D-IR	4	07:27	19:29	29.0	20.9
	4/4/89	T-2D-O	5	07:22	19:24	30.1	21.7
	4/4/89	T-2N-I	2	19:32	07:32	29.0	20.8
	4/4/89	T-2N-O	1	19:26	07:26	30.2	21.8
Rodeo (Residential)	5/16/89	BLANK	27	-	-	-	-
	5/16/89	R-1D-I	24	06:58	19:00	32.9	23.7
	5/16/89	R-1D-IR	25	06:58	19:00	32.9	23.7
	5/16/89	R-1D-O	26	07:00	19:05	33.4	24.2
	5/16/89	R-1N-I	28	19:03	07:03	33.7	24.3
	5/16/89	R-1N-O	29	19:07	07:18	33.7	24.6

a) Field Sample Site ID: T=Truckee, CA; S=Sacramento, CA; P=Palo Alto, CA; R=Rodeo, CA; M=Milbrae, CA; -1D=Day 1;-2D=Day 2; -1N=Night 2; -2N=Night 2; I=Indoor Sample; IR=Indoor Sample Replicate; O=Outdoor Sample; OR=Outdoor Sample Replicate.
b)Sample air volume in standard cubic meters of air (@ 760 mm Hg ,25°C).

Table VI-7 continued. Sample field identification numbers, sample times, and sample air volumes for the 42 PAC samples collected during the PAC pilot field study.

Sample Location (Building Type)	Sample Date	Field [a] Sample ID	Lab Sample ID	Sample Time Start	Sample Time Stop	Sample Air Flow Rate Lpm	Sample [b] Volume m^3
	5/17/89	BLANK	33	-	-	-	-
	5/17/89	R-2D-I	30	07:07	19:05	32.0	23.6
Rodeo	5/17/89	R-2D-IR	31	07:07	19:05	33.0	23.6
(Residential)	5/17/89	R-2D-O	32	07:10	19:02	33.7	23.9
	5/17/89	R-2N-I	34	19:05	07:07	33.0	23.8
	5/17/89	R-2N-O	35	19:02	07:01	34.2	24.6
	6/1/89	BLANK	39	-	-	-	-
	6/1/89	BLANK	42	-	-	-	-
Milbrae	6/1/89	M-1D-I	38	07:07	19:08	33.0	24.4
(Residential)	6/1/89	M-1D-IR	37	07:07	19:08	33.0	24.4
	6/1/89	M-1D-O	36	07:02	19:10	33.0	24.7
	6/1/89	M-1N-I	40	19:26	07:07	34.0	23.8
	6/1/89	M-1N-O	41	19:32	07:04	32.8	22.7
	4/13/89	BLANK	17	-	-	-	-
	4/13/89	BLANK	18	-	-	-	-
Sacramento	4/13/89	S-1D-I	13	07:03	18:55	33.3	24.1
(Commercial)	4/13/89	S-1D-IR	14	07:05	18:55	33.3	24.1
	4/13/89	S-1D-O	15	06:58	19:00	33.3	24.1
	4/13/89	S-1D-OR	16	06:58	19:00	33.3	24.1
	5/9/89	BLANK	23	-	-	-	-
	5/9/89	P-1D-I	19	07:07	19:19	32.9	24.1
Palo Alto	5/9/89	P-1D-IR	20	07:07	19:19	33.4	24.1
(Commercial)	5/9/89	P-1D-O	21	07:10	19:03	33.9	23.8
	5/9/89	P-1D-OR	22	07:10	19:03	33.9	24.16

a) Field Sample Site ID: T=Truckee, CA; S=Sacramento, CA; P=Palo Alto, CA; R=Rodeo, CA; M=Milbrae, CA; -1D=Day 1;-2D=Day 2; -1N=Night 2; -2N=Night 2; -I=Indoor Sample; IR=Indoor Sample Replicate; O=Outdoor Sample; OR=Outdoor Sample Replicate.
b)Sample air volume in standard cubic meters of air (@ 760mm, Hg,25°C).

higher than the daytime measurements. This is consistent with the normally higher nighttime indoor-outdoor temperature differences. The local air exchange rates in the two commercial buildings were measured to be 0.80 ach and 0.96 ach. We estimate the measurement precision of the tracer gas measurements to be 0.05 ach at the 95% confidence level. These ventilation rates are typical of residential and commercial buildings.

TSP Measurements

The net filter weight gains and the computed 12 hour average airborne particulate concentrations are reported in Table VI-8. Since the filters were used without a size-selective inlet, the computed concentrations represent total suspended particulate (TSP) concentrations. The outdoor concentrations ranged from 10 $\mu g/m^3$ - 64 $\mu g/m^3$ while the indoor concentrations ranged from 15 $\mu g/m^3$ - 281 $\mu g/m^3$. We noted that the deposition pattern of the collected particulate matter was not uniform across the filter. There was a dark center spot at the center of the filter opposite the inlet port of the filter cassette cover.

Filter Differential Pressure Measurements

The increase in the differential pressure drop across the TIGF filter cassette ranged from -1.2 mm Hg to 9.29 mm Hg as reported in Table VI-8. The maximum 9.29 mm Hg increase, occurred during the daytime measurements at the Truckee residential site with all three indoor combustion sources active, (T-2D-IR). This sample had a TSP concentration of 277 $\mu g/m^3$. This increase in the filter pressure drop represents a 33% increase over the initial 30 mm Hg filter pressure drop. As discussed in Chapter III, a 10 mm Hg increase in the filter pressure drop corresponds to an approximate 6.5% reduction in the air sampling flow rate. In this study, the sample flow rates were checked every 2-3 hours and if required the sample flow rate was manually corrected by adjusting the flow rate control valve.

PAC Concentrations

We determined the concentrations of 16 species of gas phase PAC and 21 particulate phase PAC measured in indoor and outdoor air during the PAC pilot field study. We collected and analyzed a total of 42 samples.

Table VI-8. Filter weight and differential pressure changes associated with the TIGF filter samples collected during the PAC sampler pilot field study.

Site [a] Description	Sample ID [b]	Filter Weight Gain	Differential Pressure Gain (final-initial)	Particulate Matter Concentration
		mg	mm Hg	$\mu g/m^3$
	T-1D-I	5.17	NA [c]	248
Truckee	T-1D-IR	5.45	NA	261
Residential	T-1D-O	0.45	NA	21
4/3/89	T-1D-OR	0.32	NA	15
ws	T-1N-I	3.01	1.01	145
	T-1N-O	0.21	-0.42	10
	T-1N-OR	0.38	-1.01	17
Truckee	T-2D-I	5.86	7.86	281
Residential	T-2D-IR	5.77	9.29	277
4/4/89	T-2D-O	0.57	1.01	26
ws,s,g	T-2N-I	2.47	3.38	119
	T-2N-O	0.35	-1.18	16
Rodeo	R-1D-I	1.80	3.85	76
Residential	R-1D-IR	1.50	3.37	63
5/16/89	R-1D-O	1.32	4.04	55
none	R-1N-I	0.63	-0.49	26
	R-1N-O	1.06	-0.49	43

a .) Test Site Description: Location (California) and building type, 5 residential and 2 commercial; Date of the testing; Indoor sources present during the sampling (**ws** = wood stove, **g** = gas stove, **s** = environmental tobacco smoke, = no indoor unvented combustion).
b.) Sample ID: T= Truckee, S= Sacramento, P=Palo Alto, R=Rodeo, M=Milbrae, 1D= Day 1 (7AM-7PM), 2D=Day 2 (7AM-7PM), 1N=Night 1 (7PM-7AM), 2N=Night 2 (7PM-7AM), I=Indoor, O=Outdoor, R=Sample Replicate.
c) Differential pressure measurements across the filters were not collected for these samples.(NA=not available)

Table VI-8 continued. Filter weight and differential pressure changes associated with the TIGF filter samples collected during the PAC sampler pilot field study.

Site [a] Description	Sample ID [b]	Filter Weight Gain	Differential Pressure Gain (final-initial)	Particulate Matter Concentration
		mg	mm Hg	$\mu g/m^3$
Rodeo	R-2D-I	1.53	-0.46	65
Residential	R-2D-IR	1.65	0.93	70
5/17/89	R-2D-O	0.71	0.00	30
g	R-2N-I	0.65	0.46	27
	R-2N-O	0.70	-0.46	28
Milbrae	M-1D-I	4.31	5.21	177
Residential	M-1D-IR	4.38	5.59	180
6/1/89	M-1D-O	0.98	2.70	40
s	M-1N-I	0.34	0.58	15
	M-1N-O	1.53	2.02	64
Sacramento	S-1D-I	0.70	1.85	29
Commercial	S-1D-IR	0.69	0.49	29
4/13/89	S-1D-O	0.67	0.68	28
none	S-1D-OR	0.81	1.36	34
Palo Alto	P-1D-I	3.43	3.85	143
Commercial	P-1D-IR	3.69	4.71	153
5/9/89	P-1D-O	0.62	0.67	26
s	P-1D-OR	0.51	1.15	21

a .) Test Site Description: Location (California) and building type, 5 residential and 2 commercial; Date of the testing; Indoor sources present during the sampling (**ws** = wood stove, **g** = gas stove, **s** = environmental tobacco smoke, **none** = no indoor unvented combustion).
b.) Sample ID: T= Truckee, S= Sacramento, P=Palo Alto, R=Rodeo, M=Milbrae, 1D= Day 1 (7AM-7PM), 2D=Day 2 (7AM-7PM), 1N=Night 1 (7PM-7AM), 2N=Night 2 (7PM-7AM), I=Indoor, O=Outdoor, R=Sample Replicate.
c) Differential pressure measurements across the filters were not collected for these samples.(NA=not available)

For each XAD-4 sample, we quantitated a total of 14 gas phase PAH ranging in volatility from naphthalene to chrysene . Table VI-9 summarizes the gas phase PAH measurements. The concentrations for the two species of gas phase nitro-PAH analyzed for in this study are presented in Chapter VII. For each TIGF sample, we quantitated a total of 21 particulate phase PAH ranging in volatility from phenanthrene to dibenzo(a,h)pyrene. Table VI-10 summarizes the particulate phase PAH measurements.

The PAC concentration data in these tables are organized chronologically first for the five residential tests followed by the two commercial building tests. Information regarding the sample date, time, and indoor PAC sources are presented in the first column on this table. These data are further organized with day followed by night, indoor in **bold** type, and replicate samples paired.

PAC Experimental Precision Analysis

The overall measurement precision of the method was computed from the data generated from the eleven indoor and outdoor paired replicate samples. The pooled variance was computed for each contaminant according to standard analysis of variance techniques (Ku, et al, 1969). From the pooled variance analyses, 95% confidence intervals in ng/m^3 were constructed for each compound. The 95% confidence intervals were computed by multiplying the pooled standard deviation by the value of the Student's t distribution for n degrees of freedom where the degrees of freedom equal the number of replicate pairs analyzed. The relative precisions were also computed by dividing the 95% confidence intervals by the mean values for each pool of paired replicates. If the concentrations for a particular PAC species was below the method detection limit for one or both of the samples in a replicate pair, the data for this pair were excluded from the measurement precision analysis. We note that the construction of 95% confidence limits using a Student's t distribution assumes a normal distribution.

The results of these computations are summarized in Table VI-11 for the gas phase PAH and Table VI-12 for the particulate phase PAH and TSP. A total of 11 replicate pairs were collected and analyzed representing 7 indoor samples and 4 outdoor samples. The pooled variances were computed first for the combination of indoor and outdoor samples and then separately for the indoor samples and the outdoor samples. The precision computations were conducted for each compound for which there were three or more sample replicate pairs with data above detection limits.

Table VI-9. Concurrent 12-hour time weighted average indoor and outdoor gas phase PAH concentrations collected during the pilot field study.

Test Site [a] Description	Sample [b] ID	GAS PHASE PAH CONCENTRATIONS (ng/m^3) [c] NAPH	2NAPH	1NAPH	BiPHE	ACNPY	ACNPE	FLRN	PHEN	ANTH	2ANTH	9ANTH	FLUOR	PYREN	CHRYS
Truckee	**T-1D-I**	**1691**	**1144**	**591**	**471**	**64.5**	**21.9**	**44.3**	**38.1**	**19.6**	**1.2**	**<0.1**	**4.3**	**4.9**	**0.3**
	T-1D-IR	**1720**	**1058**	**542**	**560**	**60.1**	**26.8**	**39.4**	**37.3**	**27.0**	**1.1**	**0.2**	**4.3**	**4.8**	**0.4**
Residential	T-ID-O	303	165	74	73	19.1	4.8	7.7	17.2	2.0	0.5	<0.1	3.0	2.9	0.2
	T-ID-OR	310	168	75	55	19.4	4.7	7.8	18.0	2.0	0.5	<0.1	3.0	2.9	0.1
4/3/89	**T-1N-I**	**1830**	**991**	**507**	**421**	**54.2**	**35.5**	**41.0**	**34.2**	**18.5**	**0.9**	**<0.1**	**4.0**	**4.8**	**0.4**
ws	T-1N-O	120	58	29	71	7.8	9.1	11.0	20.5	2.0	0.3	<0.1	2.8	2.3	0.1
	T-1N-OR	118	54	27	68	7.2	8.3	10.0	18.4	1.7	0.2	<0.1	2.4	2.0	<0.1
Truckee	**T-2D-I**	**2856**	**861**	**522**	**581**	**406**	**46.5**	**65.1**	**67.2**	**52.8**	**2.4**	**0.4**	**19.9**	**29.8**	**2.1**
	T-2D-IR	**2892**	**893**	**537**	**562**	**405**	**41.0**	**61.1**	**68.8**	**38.8**	**2.2**	**0.8**	**19.3**	**29.0**	**2.1**
Residential	T-2D-O	297	143	67	112	9.6	29.4	31.3	51.0	6.1	0.4	<0.1	4.9	3.2	0.2
4/4/89	**T-2N-I**	**2029**	**834**	**463**	**395**	**151**	**28.6**	**37.9**	**81.5**	**8.9**	**1.5**	**<0.1**	**5.5**	**6.9**	**0.6**
ws, s, g	T-2N-O	232	120	57	94	7.9	24.0	28.2	51.7	5.8	0.7	0.2	5.2	3.4	0.3
Rodeo	**R-1D-I**	**1304**	**939**	**470**	**433**	**17.6**	**17.6**	**46.5**	**66.1**	**4.8**	**0.9**	**<0.1**	**4.0**	**3.1**	**<0.1**
	R-1D-IR	**1281**	**911**	**456**	**313**	**15.4**	**16.6**	**43.3**	**151**	**14.4**	**0.9**	**<0.1**	**4.1**	**3.1**	**0.2**
Residential	R-1D-O	469	216	98	378	6.4	6.2	11.0	21.6	0.6	0.1	<0.1	4.1	2.7	0.2
5/16/89	**R-1N-I**	**1268**	**919**	**464**	**263**	**14.2**	**14.4**	**39.6**	**51.0**	**2.6**	**0.5**	**<0.1**	**3.0**	**2.2**	**<0.1**
none	R-1N-O	367	158	68	135	4.1	2.7	4.6	9.6	0.1	<0.1	<0.1	1.6	1.3	<0.1

a .) Test Site Description: Location (California) and building type, 5 residential and 2 commercial; Date of the testing; Indoor sources present during the sampling (ws = wood stove, g = gas stove, s = environmental tobacco smoke, none = no indoor unvented combustion)
b.) Sample ID: T= Truckee, S= Sacramento, P=Palo Alto, R=Rodeo, M=Milbrae, 1D= Day 1 (7AM-7PM), 2D=Day 2 (7AM-7PM), 1N=Night 1 (7PM-7AM), 2N=Night 2 (7PM-7AM), I=Indoor, O=Outdoor, R=Sample Replicate.
c.) Gas phase polycyclic aromatic hydrocarbons: NAPH=Naphthalene, 2NAPH=2-Methylnaphthalene, 1NAPH=1-methylnaphthalene, BiPHE=Biphenyl, ACNPY=Acenaphthylene, ACNPE=Acenaphthalene, FLRN=Fluorene, PHEN=Phenanthrene, ANTH=Anthracene, 2ANTH=2-Methylanthracene, 9ANTH=9-Methylanthracene, FLUOR=Fluoranthene, CHRYS=Chrysene. **Bold** = Indoor; paired data = replicate samples.

Table VI-9 continued. Concurrent 12-hour time weighted average indoor and outdoor gas phase PAH concentrations collected during the pilot field study.

Test Site [a] Description	Sample [b] ID	GAS PHASE PAH CONCENTRATIONS (ng/m^3) [c] NAPH	2NAPH	1NAPH	BiPHE	ACNPY	ACNPE	FLRN	PHEN	ANTH	2ANTH	9ANTH	FLUOR	PYREN	CHRYS
	R-2D-I	**1135**	**846**	**423**	**350**	**14.9**	**12.3**	**38.5**	**35.1**	**2.4**	**0.6**	**<0.1**	**2.5**	**2.0**	**0.3**
Rodeo	**R-2D-IR**	**1164**	**836**	**416**	**492**	**15.2**	**11.5**	**38.7**	**39.2**	**2.7**	**0.6**	**<0.1**	**2.6**	**2.0**	**0.2**
Residential	R-2D-O	283	124	54	94	4.6	2.6	4.4	6.0	0.3	<0.1	<0.1	1.5	1.3	<0.1
5/17/89	**R-2N-I**	**1061**	**846**	**426**	**332**	**13.1**	**12.7**	**38.8**	**38.1**	**2.0**	**5.7**	**<0.1**	**2.7**	**1.9**	**0.1**
g	R-2N-O	No	Data												
	M-1D-I	**3463**	**530**	**308**	**532**	**28.9**	**13.4**	**27.7**	**68.0**	**7.4**	**2.1**	**0.1**	**3.7**	**3.0**	**0.8**
Milbrae	**M-1D-IR**	**3130**	**538**	**315**	**461**	**29.3**	**12.6**	**28.9**	**137**	**16.0**	**2.3**	**0.1**	**4.2**	**3.2**	**1.0**
Residential	M-1D-O	741	258	128	639	7.4	5.2	14.3	17.9	0.5	0.2	<0.1	4.1	2.5	0.3
6/1/89	**M-1N-I**	**1692**	**390**	**217**	**425**	**19.9**	**11.9**	**22.2**	**51.2**	**4.6**	**1.8**	**0.1**	**3.5**	**2.9**	**0.6**
s	M-1N-O	727	276	122	206	9.1	6.1	7.8	9.8	0.4	0.1	<0.1	1.4	0.9	<0.1
Sacramento	**S-1D-I**	**527**	**322**	**146**	**496**	**7.5**	**11.5**	**24.9**	**44.4**	**1.2**	**0.3**	**0.1**	**6.3**	**3.5**	**0.2**
Commercial	**S-1D-IR**	**494**	**300**	**137**	**401**	**5.9**	**10.6**	**22.5**	**42.1**	**1.2**	**0.2**	**<0.1**	**6.2**	**3.3**	**0.1**
4/13/89	S-1D-O	343	214	93	348	5.4	3.9	7.0	32.1	0.5	<0.1	<0.1	21.6	10.8	0.6
none	S-1D-OR	336	207	90	437	5.7	3.7	7.3	30.3	0.5	<0.1	<0.1	19.3	9.9	0.5
Palo Alto	**P-1D-I**	**929**	**610**	**361**	**312**	**38.0**	**16.2**	**31.0**	**29.2**	**32.5**	**5.1**	**0.5**	**6.7**	**5.3**	**1.8**
Commercial	**P-1D-IR**	**922**	**617**	**368**	**300**	**39.7**	**17.0**	**30.7**	**27.2**	**35.1**	**5.6**	**1.0**	**7.3**	**5.7**	**1.9**
5/9/89	P-1D-O	257	137	60	72	7.3	1.4	3.6	5.1	0.5	0.1	<0.1	1.3	1.3	0.1
s	P-1D-OR	246	126	55	51	6.7	1.2	3.1	5.4	0.5	<0.1	<0.1	1.3	1.4	<0.1

a .) Test Site Description: Location (California) and building type, 5 residential and 2 commercial; Date of the testing; Indoor sources present during the sampling (ws = wood stove, g = gas stove, s = environmental tobacco smoke, none = no indoor unvented combustion)
b.) Sample ID: T= Truckee, S= Sacramento, P=Palo Alto, R=Rodeo, M=Milbrae, 1D= Day 1 (7AM-7PM), 2D=Day 2 (7AM-7PM), 1N=Night 1 (7PM-7AM), 2N=Night 2 (7PM-7AM), I=Indoor, O=Outdoor, R=Sample Replicate.
c.) Gas phase polycyclic aromatic hydrocarbons: NAPH=Naphthalene, 2NAPH=2-Methylnaphthalene, 1NAPH=1-methylnaphthalene, BiPHE=Biphenyl, ACNPY=Acenaphthylene, ACNPE=Acenaphthalene, FLRN=Fluorene, PHEN=Phenanthrene, ANTH=Anthracene, 2ANTH=2-Methylanthracene, 9ANTH=9-Methylanthracene, FLUOR=Fluoranthene, CHRYS=Chrysene. **Bold** = Indoor; paired data = replicate samples.

Table VI-10. Concurrent 12-hour time weighted average indoor and outdoor particulate phase PAH concentrations collected during the pilot field study.

Test Site [a] Description	Sample [b] ID	PARTICULATE PHASE PAH CONCENTRATIONS (ng/m^3) [c]										
		Phen	Anth	Fluor	Pyren	BaA	Chrys	5-MC	Ret	BeP	BbF	BkF
Truckee	**T-1D-I**	**0.26**	**0.75**	**0.13**	**11.68**	**0.19**	**2.39**	**0.51**	**17.40**	**1.89**	**0.22**	**0.076**
	T-1D-IR	**<.22**	**<.06**	**0.13**	**16.94**	**0.21**	**3.65**	**0.73**	**28.30**	**2.32**	**0.23**	**0.073**
Residential	T-1D-O	<.22	0.13	0.05	0.19	0.28	0.22	<.04	<.28	0.56	0.28	0.135
	T-1D-OR	<.22	<.06	0.07	<.11	0.14	0.30	<.04	<.28	<.21	0.41	0.165
4/3/89	**T-1N-I**	**<.22**	**0.11**	**<.04**	**31.22**	**<.04**	**2.48**	**0.19**	**0.86**	**1.45**	**0.05**	**0.019**
ws	T-1N-O	<.22	<.06	0.09	<.11	0.13	0.22	<.04	<.28	<.21	0.26	0.104
	T-1N-OR	<.22	<.06	0.35	0.50	0.07	0.20	0.14	<.28	0.31	0.26	0.125
Truckee	**T-2D-I**	**0.39**	**<.06**	**0.98**	**2.96**	**0.54**	**3.57**	**0.20**	**<.28**	**2.18**	**2.03**	**0.767**
	T-2D-IR	**1.37**	**0.57**	**2.92**	**6.67**	**0.67**	**6.23**	**0.38**	**<.28**	**2.73**	**2.19**	**0.719**
Residential	T-2D-O	<.22	<.06	0.18	<.11	0.16	0.14	<.04	<.28	0.60	0.22	0.101
4/4/89	**T-2N-I**	**<.22**	**1.13**	**0.06**	**0.80**	**0.05**	**0.17**	**0.41**	**nr**	**0.37**	**0.19**	**0.063**
ws, s, g	T-2N-O	<.22	<.06	<.04	0.13	<.04	0.56	<.04	<.28	<.21	0.22	0.058
Rodeo	**R-1D-I**	**<.22**	**<.06**	**<.04**	**<.11**	**<.04**	**<.03**	**<.04**	**<.28**	**<.21**	**<.04**	**0.015**
	R-1D-IR	**<.22**	**<.06**	**0.04**	**<.11**	**<.04**	**<.03**	**<.04**	**<.28**	**<.21**	**0.06**	**0.013**
Residential	R-1D-O	<.22	<.06	0.06	<.11	0.07	0.07	<.04	<.28	<.21	0.10	0.039
5/16/89	**R-1N-I**	**0.35**	**0.11**	**<.04**	**0.14**	**<.04**	**0.08**	**<.04**	**<.28**	**0.03**	**0.08**	**0.019**
none	R-1N-O	<.22	<.06	0.17	<.11	0.09	0.15	<.04	<.28	<.21	0.27	0.061

a .) Test Site Description: Location (California) and building type, 5 residential and 2 commercial; Date of the testing; Indoor sources present during the sampling (**ws** = wood stove, **g** = gas stove, **s** = environmental tobacco smoke, **none** = no indoor unvented combustion).
b.) Sample ID: T= Truckee, S= Sacramento, P=Palo Alto, R=Rodeo, M=Milbrae, 1D= Day 1 (7AM-7PM), 2D=Day 2 (7AM-7PM), 1N=Night 1 (7PM-7AM), 2N=Night 2 (7PM-7AM), I=Indoor, O=Outdoor, R=Sample Replicate.
c.) Particulate phase polycyclic aromatic hydrocarbons: Phen=Phenanthrene, Anth=Anthracene, Fluor=Fluoranthrene, Pyren=Pyrene, BaA=Benzo(a)anthracene, Chrys=Chrysene, 5-MC=5-Methylchyrsene, Ret=Retene, BeP=Benzo(e)pyrene, BbF=Benzo(B)fluoranthene, BkF=Benzo(B)fluoranthene. **Bold = Indoor**; nr=not resolvable.

Table VI-10 continued. Concurrent 12-hour time weighted average indoor and outdoor particulate phase PAH concentrations collected during the pilot field study.

Test Site [a] Description	Sample [b] ID	PARTICULATE PHASE PAH CONCENTRATIONS (ng/m^3) [c]										
		Phen	Anth	Fluor	Pyren	BaA	Chrys	5-MC	Ret	BeP	BbF	BkF
	R-2D-I	**<.22**	**<.06**	**0.06**	**<.11**	**<.04**	**<.03**	**<.04**	**<.28**	**<.21**	**0.08**	**0.027**
Rodeo	R-2D-IR	<.22	<.06	0.04	<.11	<.04	0.03	<.04	<.28	<.21	<.04	0.021
Residential	R-2D-O	<.22	<.06	0.07	<.11	0.05	0.08	<.04	<.28	<.21	0.14	0.054
5/17/89	**R-2N-I**	**<.22**	**<.06**	**<.04**	**0.20**	**0.19**	**0.76**	**<.04**	**<.28**	**<.21**	**<.04**	**<.005**
g	R-2N-O	<.22	<.06	<.04	<.11	<.04	0.14	<.04	<.28	<.21	0.09	0.011
	M-1D-I	**<.22**	**0.20**	**nr**	**1.76**	**<.04**	**0.62**	**<.04**	**<.28**	**1.26**	**0.38**	**0.120**
Milbrae	**M-1D-IR**	**0.29**	**0.23**	**0.86**	**1.51**	**0.23**	**6.55**	**0.47**	**<.28**	**0.60**	**0.47**	**0.144**
Residential	M-1D-O	<.22	0.07	0.12	<.11	0.06	0.04	<.04	<.28	0.19	0.01	0.0418
6/1/89	**M-1N-I**	**<.22**	**<.06**	**0.07**	**0.19**	**<.04**	**0.30**	**<.04**	**<.28**	**0.58**	**0.26**	**0.052**
s	M-1N-O	<.22	<.06	0.05	<.11	<.04	0.11	<.04	<.28	0.16	0.10	0.021
Sacramento	**S-1D-I**	**<.22**	**<.06**	**0.07**	**<.11**	**<.04**	**0.11**	**<.04**	**<.28**	**<.21**	**0.29**	**0.071**
Commercial	**S-1D-IR**	**<.22**	**<.06**	**0.06**	**<.11**	**<.04**	**<.03**	**<.04**	**<.28**	**<.21**	**<.04**	**0.017**
4/13/89	S-1D-O	<.22	<.06	0.06	0.21	0.05	0.46	<.04	<.28	<.21	0.15	0.041
none	S-1D-OR	<.22	<.06	0.09	<.11	<.04	0.09	<.04	<.28	<.21	0.20	0.037
Palo Alto	**P-1D-I**	**<.22**	**0.11**	**<.04**	**0.58**	**0.42**	**1.99**	**<.04**	**<.28**	**0.50**	**0.56**	**0.142**
Commercial	**P-1D-IR**	**<.22**	**0.11**	**0.42**	**1.07**	**0.61**	**9.10**	**<.04**	**<.28**	**0.29**	**0.60**	**0.154**
5/9/89	P-1D-O	<.22	<.060	<.04	<.11	<.04	0.06	<.04	<.28	<.21	0.08	0.017
s	P-1D-OR	<.22	<.060	<.04	<.11	<.04	0.13	<.04	<.28	<.21	0.11	0.026

a .) Test Site Description: Location (California) and building type, 5 residential and 2 commercial; Date of the testing; Indoor sources present during the sampling (**ws** = wood stove, **g** = gas stove, **s** = environmental tobacco smoke, **none** = no indoor unvented combustion).
b.) Sample ID: T= Truckee, S= Sacramento, P=Palo Alto, R=Rodeo, M=Milbrae, 1D= Day 1 (7AM-7PM), 2D=Day 2 (7AM-7PM), 1N=Night 1 (7PM-7AM), 2N=Night 2 (7PM-7AM), I=Indoor, O=Outdoor, R=Sample Replicate.
c.) Particulate phase polycyclic aromatic hydrocarbons: Phen=Phenanthrene, Anth=Anthracene, Fluor=Fluoranthrene, Pyren=Pyrene, BaA=Benzo(a)anthracene, Chrys=Chrysene, 5-MC=5-Methylchyrsene, Ret=Retene, BeP=Benzo(e)pyrene, BbF=Benzo(B)fluoranthene, BkF=Benzo(B)fluoranthene. **Bold** = Indoor; nr=not resolvable.

Table VI-10 continued. Concurrent 12-hour time weighted average indoor and outdoor particulate phase PAH concentrations collected during the pilot field study.

Test Site [a] Description	Sample [b] ID	PARTICULATE PHASE PAH CONCENTRATIONS (ng/m^3) [c]									
		dBacA	BaP	dBalP	dBahA	BghiP	IcdP	dBaeP	Cor	dBaiP	dBahP
	T-1D-I	**0.05**	**0.15**	**<.02**	**<.11**	**0.13**	**0.12**	**0.056**	**0.121**	**<.001**	**<.003**
Truckee	**T-1D-IR**	**0.09**	**0.11**	**<.02**	**<.11**	**0.25**	**0.13**	**0.088**	**<.006**	**<.001**	**<.003**
Residential	T-1D-O	<.02	0.43	<.02	<.11	0.38	0.34	<.008	0.570	<.001	<.003
	T-1D-OR	<.02	0.31	0.03	<.11	0.80	0.38	0.150	1.092	<.001	<.003
4/3/89	**T-1N-I**	**<.02**	**0.05**	**<.02**	**0.22**	**0.32**	**0.07**	**0.089**	**<.006**	**<.001**	**<.003**
ws	T-1N-O	<.02	0.18	<.02	<.11	0.24	0.24	0.017	0.286	<.001	<.003
	T-1N-OR	<.02	0.20	<.02	<.11	0.16	0.26	<.008	0.116	<.001	<.003
	T-2D-I	**0.24**	**5.1**	**0.08**	**2.21**	**7.7**	**4.18**	**0.298**	**3.12**	**<.001**	**<.003**
Truckee	**T-2D-IR**	**1.48**	**8.1**	**0.16**	**2.94**	**10.0**	**3.98**	**<.008**	**4.81**	**.167**	**.114**
Residential	T-2D-O	<.02	0.23	<.02	<.11	0.22	0.31	<.008	<.006	<.001	<.003
4/4/89	**T-2N-I**	**<.02**	**0.20**	**<.02**	**<.11**	**0.11**	**0.35**	**0.037**	**<.006.**	**<.001**	**<.003**
ws, s, g	T-2N-O	0.09	0.14	<.02	<.11	0.16	0.21	0.066	<.006	<.001	<.003
	R-1D-I	**<.02**	**0.04**	**<.02**	**<.11**	**0.13**	**0.16**	**<.008**	**0.380**	**<.001**	**<.003**
Rodeo	**R-1D-IR**	**<.02**	**0.03**	**<.02**	**<.11**	**0.18**	**0.12**	**<.008**	**0.270**	**<.001**	**<.003**
Residential	R-1D-O	<.02	0.12	<.02	<.11	0.24	0.16	<.008	0.452	<.001	<.003
5/16/89	**R-1N-I**	**<.02**	**<.02**	**<.02**	**<.11**	**0.25**	**0.24**	**0.046**	**1.280**	**<.001**	**<.003**
none	R-1N-O	<.02	0.07	<.02	<.11	0.44	0.22	<.008	0.641	<.001	<.003

a .) Test Site Description: Location (California) and building type, 5 residential and 2 commercial; Date of the testing; Indoor sources present during the sampling (ws = wood stove, g = gas stove, s = environmental tobacco smoke, none = no indoor unvented combustion).
b.) Sample ID: T= Truckee, S= Sacramento, P=Palo Alto, R=Rodeo, M=Milbrae, 1D= Day 1 (7AM-7PM), 2D=Day 2 (7AM-7PM), 1N=Night 1 (7PM-7AM), 2N=Night 2 (7PM-7AM), I=Indoor, O=Outdoor, R=Sample Replicate.
c.) Particulate phase polycyclic aromatic hydrocarbons: dBacA=Dibenz(a,c)anthracene, BaP=Benzo(a)pyrene, dBalP=Dibenzo(a,l)pyrene, dBahA=Dibenzo(a,h)anthracene, BghiP=Benzo(g,h,i)perylene, IcdP=Indeno(1,2,3-cd)pyrene, dBaeP=Dibenzo(a,e)pyrene, Cor=Coronene, dBaiP=Dibenzo(a,i,)pyrene, dBahP=Dibenzo(a,h)pyrene. **Bold** = Indoor; nr = not resolvable.

Table VI-10 continued. Concurrent 12-hour time weighted average indoor and outdoor particulate phase PAH concentrations collected during the pilot field study.

Test Site [a] Description	Sample [b] ID	PARTICULATE PHASE PAH CONCENTRATIONS (ng/m^3) [c]									
		dBacA	BaP	dBalP	dBahA	BghiP	IcdP	dBaeP	Cor	dBaiP	dBahP
	R-2D-I	**<.02**	**0.03**	**<.02**	**<.11**	**0.14**	**0.14**	**<.008**	**0.231**	**<.001**	**<.003**
Rodeo	**R-2D-IR**	**<.02**	**0.04**	**<.02**	**<.11**	**0.12**	**0.15**	**0.032**	**0.199**	**<.001**	**<.003**
Residential	R-2D-O	<.02	0.08	<.02	0.12	0.26	0.27	<.008	0.381	<.001	<.003
5/17/89	**R-2N-I**	**<.02**	**<.02**	**<.02**	**<.11**	**<.07**	**<.04**	**<.008**	**<.006**	**<.001**	**<.003**
g	R-2N-O	<.02	0.02	<.02	<.11	<.07	<.04	<.008	<.006	<.001	<.003
	M-1D-I	**0.12**	**0.34**	**<.02**	**0.29**	**0.87**	**0.35**	**0.137**	**0.500**	**<.001**	**<.003**
Milbrae	**M-1D-IR**	**0.13**	**0.87**	**<.02**	**<.11**	**0.88**	**0.76**	**0.039**	**0.587**	**<.001**	**<.003**
Residential	M-1D-O	<.02	0.09	<.02	<.11	0.28	0.20	0.043	0.288	<.001	<.003
6/1/89	**M-1N-I**	**0.06**	**0.20**	**0.15**	**0.29**	**0.57**	**0.30**	**0.164**	**<.006**	**<.001**	**<.003**
s	M-1N-O	<.02	0.04	<.02	<.11	0.55	0.25	<.008	<.006	<.001	<.003
Sacramento	**S-1D-I**	**<.02**	**0.06**	**<.02**	**<.11**	**0.28**	**0.19**	**0.038**	**0.355**	**<.001**	**<.003**
Commercial	**S-1D-IR**	**<.02**	**0.03**	**<.02**	**<.11**	**0.08**	**0.13**	**<.008**	**0.094**	**<.001**	**<.003**
4/13/89	S-1D-O	<.02	0.18	<.02	<.11	0.16	0.27	<.008	0.260	<.001	<.003
none	S-1D-OR	<.02	0.07	<.02	<.11	0.17	0.18	<.008	0.633	<.001	<.003
Palo Alto	**P-1D-I**	**0.09**	**0.38**	**0.31**	**<.11**	**0.56**	**0.65**	**<.008**	**<.006**	**<.001**	**<.003**
Commercial	**P-1D-IR**	**0.13**	**2.99**	**0.12**	**<.11**	**0.33**	**0.36**	**0.223**	**<.006**	**<.001**	**<.003**
5/9/89	P-1D-O	<.02	0.03	<.02	<.11	0.23	0.25	<.008	<.006	<.001	<.003
s	P-1D-OR	<.02	0.03	<.02	<.11	0.21	0.12	<.008	0.228	<.001	<.003

a .) Test Site Description: Location (California) and building type, 5 residential and 2 commercial; Date of the testing; Indoor sources present during the sampling (**ws** = wood stove, **g** = gas stove, **s** = environmental tobacco smoke, **none** = no indoor unvented combustion).
b.) Sample ID: T= Truckee, S= Sacramento, P=Palo Alto, R=Rodeo, M=Milbrae, 1D= Day 1 (7AM-7PM), 2D=Day 2 (7AM-7PM), 1N=Night 1 (7PM-7AM), 2N=Night 2 (7PM-7AM), I=Indoor, O=Outdoor, R=Sample Replicate.
c.) Particulate phase polycyclic aromatic hydrocarbons: dBacA=Dibenz(a,c)anthracene, BaP=Benzo(a)pyrene, dBalP=Dibenzo(a,l)pyrene, dBahA=Dibenzo(a,h)anthracene, BghiP=Benzo(g,h,i)perylene, IcdP=Indeno(1,2,3-cd)pyrene, dBaeP=Dibenzo(a,e)pyrene, Cor=Coronene, dBaiP=Dibenzo(a,i,)pyrene, dBahP=Dibenzo(a,h)pyrene. **Bold** = Indoor; nr = not resolvable.

Table VI-11. Precision of gas phase PAH measurements as determined from comparison of side-by-side paired samples collected indoors and outdoors during the pilot field study.

COMPOUND	INDOOR + OUTDOOR				INDOOR				OUTDOOR			
	n	Mean [a] (ng/m3)	Abs. [b] Prec. (ng/m3)	Rel. [c] Prec. (%)	n	Mean [a] (ng/m3)	Abs. [b] Prec. (ng/m3)	Rel. [c] Prec. (%)	n	Mean [a] (ng/m3)	Abs. [b] Prec. (ng/m3)	Rel. [c] Prec. (%)
Naphthalene	11	1161	160	14	7	1679	215	13	4	254	15	6
2-Methylnaphthalene	11	524	47	9	7	743	63	9	4	141	14	10
1-Methylnaphthalene	11	277	26	9	7	399	35	9	4	63	6.2	10
Biphenyl	11	338	120	36	7	447	151	34	4	147	92	62
Acenaphthylene	11	56	2.7	5	7	82	3.6	4	4	10	0.9	9
Acenaphthene	11	14	3.6	25	7	20	4.8	24	4	4.6	0.9	20
Fluorene	11	27	3.6	13	7	39	4.8	12	4	7.2	1.2	16
Phenanthrene	11	45	51	113	7	61	69	114	4	18	2.9	16
Anthracene	11	12	10	80	7	18	13	71	4	1.2	0.2	19
2-Methylanthracene	9	1.5	0.3	22	7	1.8	0.4	21	<3			
9-Methylanthracene	3	0.5	0.8	160	3	0.5	0.8	160	<3			
Fluoranthene	11	6.8	1.2	17	7	6.8	0.6	9	4	6.9	2.2	33
Pyrene	11	6.2	0.6	10	7	7.3	0.6	8	4	4.2	0.9	22
Chrysene	8	0.8	0.2	22	6	0.9	0.2	21	<3			

a) Mean concentration for n pairs of duplicate samples. Analyses for groups with n≥3 pairs of data with concentrations above detection limits.
b) Absolute precision reported as the 95% confidence interval as computed from the pooled variance of n pairs of samples.
c) Relative precision computed as the absolute precision divided by the mean concentration for n pairs of duplicate samples.

Table VI-12. Precision of particulate phase PAH measurements as determined from comparison of side-by-side paired samples collected indoors and outdoors during the pilot field study.

COMPOUND	INDOOR + OUTDOOR				INDOOR				OUTDOOR			
	n	Mean [a] (ng/m^3)	Abs. [b] Prec. (ng/m^3)	Rel. [c] Prec. (%)	n	Mean [a] (ng/m)^3	Abs. [b] Prec. (ng/m)^3	Rel. [c] Prec. (%)	n	Mean [a] (ng/m)^3	Abs. [b] Prec. (ng/m)^3	Rel. [c] Prec. (%)
TSP	11.0	101.1	11.8	11.7	7.0	146.6	14.0	9.5	4	21.5	11.9	55.2
Phenanthrene	<3				<3				<3			
Anthracene	<3				<3				<3			
Fluoranthene	7	0.4	1.2	340	4	0.5	1.9	347	3	0.1	0.3	283
Pyrene	4	5.4	6.3	118	4	5.4	6.3	118	<3			
Benzo(a)anthracene	5	0.3	0.2	68	3	0.4	0.3	69	<3			
Chrysene	8	2.2	5.6	251	4	4.3	7.6	178	4	0.2	0.4	181
5-Methylchrysene	<3				<3				<3			
Retene	<3				<3				<3			
Benzo(e)pyrene	4	1.5	1.0	66	4	1.5	1.0	66	<3			
Benzo(b)fluoranthene	8	0.5	0.1	25	4	0.8	0.2	21	4	0.2	0.1	62
Benzo(k)fluoranthene	11	0.1	0.04	30	7	0.2	0.05	29	4	0.1	0.04	46
Dibenzo(a,c)anthracene	4	0.3	1.2	421	4	0.3	1.2	421	<3			
Benzo(a)pyrene	11	0.9	1.9	210	7	1.3	2.5	193	4	0.2	0.2	89
Dibenzo(a,l)pyrene	<3				<3				<3			
Dibenzo(a,h)anthracene	<3				<3				<3			
Benzo(g,h,i)perylene	11	1.1	1.1	100	7	1.5	1.4	94	4	0.3	0.4	144
Indeno(1,2,3-cd)pyrene	11	0.6	0.3	43	7	0.8	0.3	42	4	0.3	0.2	62
Dibenzo(a,e)pyrene	<3				<3				<3			
Coronene	8	0.8	1.1	126	5	1.1	1.4	132	3	0.5	0.9	175
Dibenzo(a,i)pyrene	<3				<3				<3			
Dibenzo(a,h)pyrene	<3				<3				<3			

a) Mean concentration for n pairs of duplicate samples..Analyses for groups with n≥3 pairs of data with concentrations above detection limits.
b) Absolute precision reported as the 95% confidence interval as computed from the pooled variance of n pairs of samples.
c) Relative precision computed as the absolute precision divided by the mean concentration for n pairs of duplicate samples.

Gas Phase PAH Measurement Precision. The relative precision of the gas phase PAH for the combination of indoor and outdoor samples ranged from 5% for acenapthylene to 160% for 9-methylanthracene. The high relative imprecision percentage for 9-methylanthracene was a result of both the low mean value of the air measurements (i.e. close to the analytical detection limit) and the low number of replicate pairs (i.e only 3). If we eliminate consideration of the analyses for 9-methylanthracene and chrysene which had pooled mean values less than 1 ng/m^3 the pooled relative precision for the remaining 12 gas phase PAH compounds ranged from 5% to 25% except for biphenyl, phenanthrene, and anthracene which had relative precision percentages of 36%, 113% and 80% respectively.

If we separate the precision analyses into indoor and outdoor groups of replicate pairs and re-examine the relative precisions, we can compare the indoor and outdoor results to see if the measurement precisions are similar indoors and outdoors. In Table VI-11, it is apparent that the high relative imprecisions for phenanthrene and anthracene in the combined indoor and outdoor precision analyses were a result of the high relative imprecisions of the indoor samples and not of the outdoor samples. The indoor relative precisions for phenanthrene and anthracene were 114% and 71%, respectively, while for the outdoor samples, the relative precisions were 16% and 19%, respectively. As discussed in Chapter IV, there appeared to be some interferent present in the indoor samples which compromised the precision of the analytical analyses of these two compounds.

Particulate Phase PAH Measurement Precision.

The relative precisions of the particulate phase PAH measurements, which are presented in Table VI-12, were dominated by the very large differences between the replicate samples from indoor environments with cigarette smoke or wood smoke particles. When the indoor and outdoor replicates are considered together, the pooled variance analyses result in relative precisions at the 95% confidence level ranging from 25%-30% for benzo(b)fluoranthene and benzo(k)fluoranthene, to 210% for benzo(a)pyrene, and to over 400% for dibenzo(a,c)anthracene. As discussed in Chapter V, the pilot field samples had two recurrent analytical difficulties: interfering compounds and high fluorescent background.

When interfering compounds co-eluted with the internal standard used for quantitation, benzo(e)pyrene-d_{12}, concentration values for all PAH were compromised. The amount of the interference appeared to be different for each member of the replicate pair. This occurred for the sample of particles collected from the Truckee site, T-2, when all three indoor sources, tobacco smoke, wood stove, and gas range were present simultaneously.

For samples collected outdoors, relative precisions were similar and absolute precisions were substantially lower than those found for indoor samples The average relative precision for the eight outdoor paired PAH was 130% with an average absolute precision of 0.3 ng/m^3, while the average relative precision for the twelve indoor paired PAH was 140% with an average absolute precision of 2.0 ng/m^3. The large values of relative precision at the 95% confidence level underscore the need for further method development work as discussed in Chapter V.

Measurement Uncertainty Analysis

The uncertainties of each of the individual measurements involved in a mutifactor computation may be assessed using uncertainty perturbation theory to compute the theoretical measurement precision from the sum the estimated uncertainties introduced by each of the input variables used in the computation. Such an analysis is useful for two purposes:

1.) to compare the estimated measurement uncertainty to experimentally determined precision. If there is a large disagreement between the two numbers then there may be a flaw either in the model used to produce the computation or in the estimated uncertainties for each of the measurements.

2.) to examine the impacts of each measurement variable upon the precision of the method to determine where further optimization of the measurement method may be made.

The precision of the sampling and analytical method as determined from the pooled variance analyses of the paired replicate samples is influenced by uncertainties in the measurements of the volume of air sampled and the mass of PAC measured in the sample. The uncertainty associated with the air volume measurement was estimated in Chapter III to

be just 2%. The uncertainty in the measurement of the mass of gas phase PAH has been estimated to be 20.5% in Chapter IV. The uncertainty in the measurement of the mass of particulate phase PAH has been estimated in Chapter V to be 17.9% for a single compound (i.e.benzo(a)pyrene) well resolved and without internal standard interferences. These estimates for the volume and mass measurement uncertainties may be combined as the square root of the sum of the squares of the individual uncertainties to yield the total uncertainty in the concentration computations. The total relative uncertainty for the gas phase concentration measurements was computed in this manner to be 20.6% and 18.0% for particulate phase PAH. It is obvious from these results that the dominant uncertainty for either gas or particulate phase contaminant concentration measurements is the computation of the mass of contaminant and not the volume of the air sampled.

These relative uncertainties computed for the PAH concentration measurements may be compared to the actual measured relative precisions as determined from the variance analysis of the replicate paired samples.

For the gas phase contaminants there is reasonable agreement between the estimated measurement uncertainties and the observed measurement precisions with the exceptions of biphenyl in the outdoor samples and phenanthrene, anthracene, and 9-methylanthracene in the indoor samples.

For the particulate phase contaminants there is considerable discrepancy between the estimated measurement uncertainties and the observed measurement precisions for both the indoor and outdoor sample replicates. As discussed in Chapter V there were compounds present in the samples which interfered with the internal standards used to quantitate the mass of PAH.

PAC Concentrations Group Comparisons

We compared the differences between indoor and outdoor concentrations collected simultaneously at each of the field sites; in residences during 12-hour day and 12-hour night time sampling periods, and in commercial buildings during 12-hour day time sampling periods. The median differences between the mean indoor and mean outdoor concentrations were evaluated using a nonparametric sign test for each of the 35 species of PAH. A total of 12 simultaneous indoor/outdoor comparisons were made; 5 residential building daytime, 5 residential building nighttime, and 2 commercial building daytime

comparisons. We also compared day and night indoor and day and night outdoor PAH concentrations to determine if there were significant differences between day and night time concentrations. A total of 9 consecutive daytime/nighttime comparisons were made; 5 residential indoor and 4 outdoor. Comparisons were made only for those PAH for which there were five or more pairs of data with concentrations above detection limits. Day/night comparisons for outdoor samples were not performed since there were less than five pairs of these data.

Gas Phase PAH Comparisons.

Table VI-13 presents the comparison of simultaneous indoor and outdoor gas phase PAH measurements. The combined day and night indoor concentrations were significantly higher (i.e. at the 95% confidence level) than the outdoor concentrations for each of the 14 gas phase PAH compared except for 9-methylanthracene, fluoranthene, and chrysene. We then compared day and night indoor measurements. The daytime concentrations were significantly higher than the nighttime concentrations for only four of the gas phase PAH: biphenyl, acenaphthalene, anthracene, and pyrene.

Particulate Phase PAH Comparisons.

Table VI-14 presents the comparison of simultaneous indoor and outdoor particulate phase PAH measurements. The combined day and night indoor concentrations were significantly higher than the outdoor concentrations for five of the particulate phase PAH: anthracene, pyrene, benzo(e)pyrene, dibenzo(a,e)pyrene, and coronene. We then compared day and night indoor measurements. Of the seven particulate phase PAH with five sets of data above detection limits, the daytime concentrations were significantly higher than the nighttime concentrations for only benzo(a)pyrene.

Comparison to Other California Measurements of PAH Concentrations

Figures VI-12 and VI-13 present a comparison of the concentrations of gas phase and particulate phase PAH made in this study (Offermann et. al. 1990) with another California study (Atkinson et. al. 1988) which only measured PAH in outdoor air. These figures

Table VI-13. Comparison of indoor/outdoor and day/night differences in gas phase PAH concentrations collected during the pilot field study.

Compound [a]	INDOOR vs OUTDOOR					DAY vs NIGHT- INDOOR				
	n	In [a] Mean ng/m^3	Out [a] Mean ng/m^3	Sign [b] In-Out	p [c] Value	n	Day [a] Mean ng/m^3	Night [a] Mean ng/m^3	Sign [b] Day - Night	p [c] Value
Naphthalene	11	1702	437	+	0.0005	5	2090	1576	+	0.1875
2-Methylnaphthalene	11	762	214	+	0.0005	<5	864	796		
1-Methylnaphthalene	11	407	105	+	0.0005	5	463	415	+	0.1875
Biphenyl	11	425	223	+	0.0059	5	473	367	+	0.0312
Acenaphthylene	11	74.3	11.0	+	0.0005	5	106	50.4	+	0.0312
Acenaphthene	11	20.9	10.1	+	0.0005	5	22.3	20.6	+	0.5000
Fluorene	11	38.1	14.4	+	0.0005	5	44.4	35.9	+	0.1875
Phenanthrene	11	51.5	24.1	+	0.0005	5	54.9	51.2	+	0.5000
Anthracene	11	14.1	4.9	+	0.0005	5	17.4	7.3	+	0.0312
2-Methylanthracene	11	1.6	0.7	+	0.0059	5	1.4	2.1	+	0.1875
9-Methylanthracene	<5	0.1	0.1			<5	0.2	0.1		
Fluoranthene	11	5.8	5.2	+	0.1133	5	6.9	3.7	+	0.1875
Pyrene	11	6.2	3.4	+	0.0059	5	8.6	3.7	+	0.0312
Chrysene	11	0.6	0.3	+	0.0547	<5	0.7	0.4		

a) Mean concentration for n samples collected in the PAC pilot field study. Analyses for groups with n≥5 pairs of data with concentrations above detection limits.
b) Sign of median difference in compared concentrations as computed from a nonparametric sign test.
c) The probability that the median difference in compared concentrations is zero.
Bold type indicates compounds with significant median differences as evaluated at ≥ 95% confidence level .

Table VI-14. Comparison of indoor/outdoor and indoor day/night differences in particulate phase PAH concentrations collected during the pilot field study.

Compound [a]	INDOOR vs OUTDOOR					DAY vs NIGHT- INDOOR				
	n	In [a] Mean ng/m^3	Out [a] Mean ng/m^3	Sign [b] In-Out	p[c] Value	n	Day [a] Mean ng/m^3	Night [a] Mean ng/m^3	Sign [b] Day - Night	p[c] Value
Phenanthrene	<5					<5				
Anthracene	**6**	**0.23**	**0.07**	**+**	**0.0156**	<5				
Fluoranthene	9	0.14	0.08	+	0.5	<5				
Pyrene	**10**	**4.15**	**0.13**	**+**	**0.0107**	5	3.324	6.51	-	0.5
Benzo(a)anthracene	11	0.14	0.09	+	0.2744	<5				
Chysene	12	1.04	0.19	-	0.3872	5	1.328	0.758	-	0.5
5-Methylchrysene	<5					<5				
Retene	<5					<5				
Benzo(e)pyrene	**8**	**0.76**	**0.27**	**+**	**0.0352**	<5				
Benzo(b)fluoranthene	12	0.35	0.16	-	0.3872	5	0.55	0.124	+	0.1875
Benzo(k)fluoranthene	11	0.11	0.06	-	0.5	5	0.201	0.0316	+	0.1875
Dibenzo(a,c)anthracene	6	0.06	0.03	+	0.1094	<5				
Benzo(a)pyrene	11	0.55	0.13	-	0.5	**5**	**1.14**	**0.097**	**+**	**0.0312**
Dibenzo(a,l)pyrene	<5					<5				
Dibenzo(a,h)anthracene	5	0.32	0.11	+	0.1875	<5				
Benzo(g,h,i)perylene	11	0.93	0.27	+	0.5	5	1.796	0.264	+	0.5
Indeno(1,2,3-cd)pyrene	10	0.57	0.23	+	0.377	<5				
Dibenzo(a,e)pyrene	**8**	**0.07**	**0.02**	**+**	**0.0352**	<5				
Coronene	**9**	**0.50**	**0.24**	**+**	**0.002**	5	0.8708	0.2608	+	0.1875
Dibenzo(a,i)pyrene	<5					<5				
Dibenzo(a,h)pyrene	<5					<5				

a) Mean concentration for n samples collected in the PAC pilot field study. Analyses for groups with n≥5 pairs of data with concentrations above detection limits.
b) Sign of median difference in compared concentrations as computed from a nonparametric sign test.
c) The probability that the median difference in compared concentrations is zero.
Bold type indicates compounds with significant median differences as evaluated at ≥ 95% confidence level.

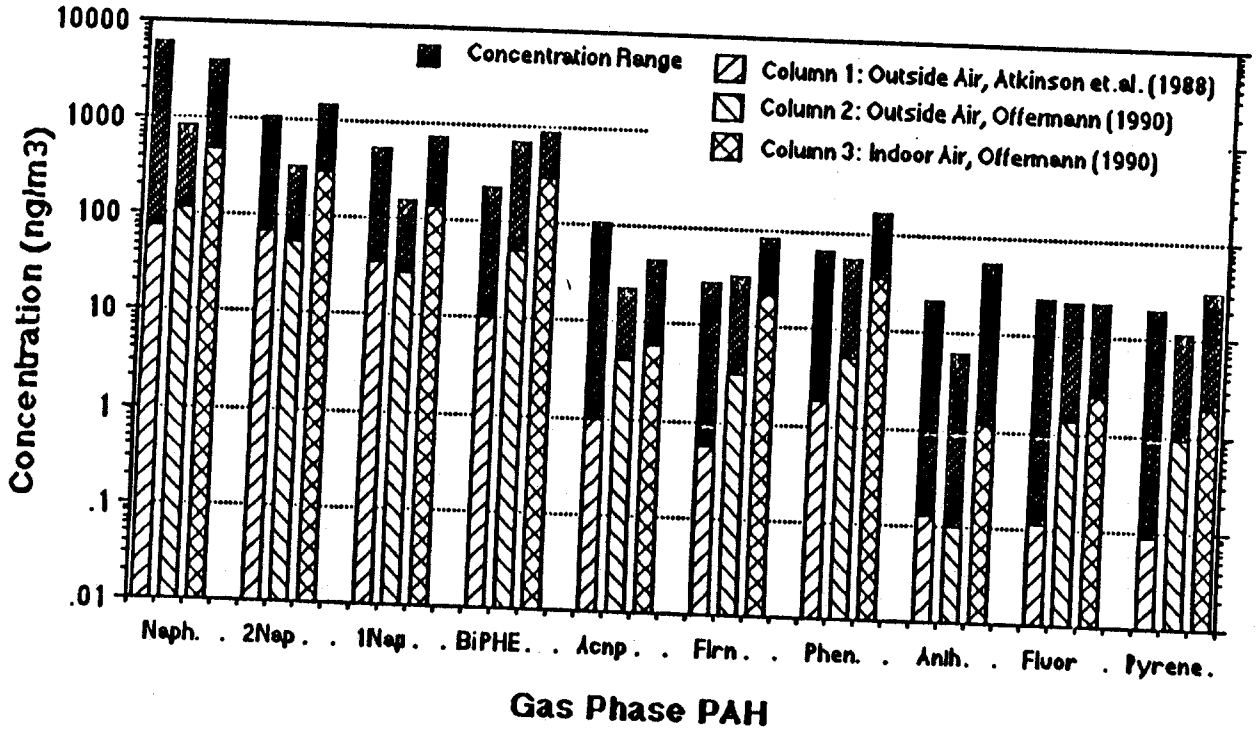


Figure VI-12 Comparison of gas phase PAH measurements made indoors and outoors in California.

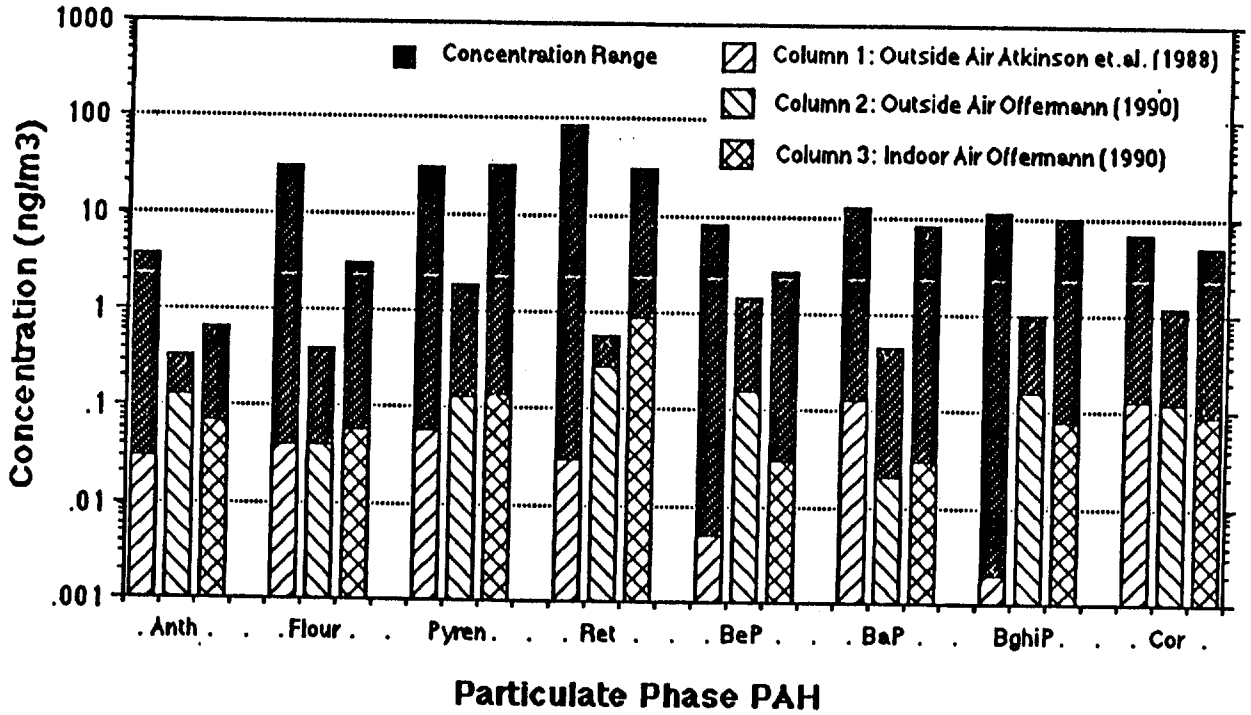


Figure VI-13 Comparison of particulate phase PAH measurements made indoors and outoors in California.

compare the reported concentration ranges. Atkinson used Tenax to collect naphthalene, PUF to collect additional gas phase PAH, and glass fiber filters to collect particulate phase PAH in outdoor air from seven California locations. The ranges of Atkinson's outdoor measurements compares to the range of our outdoor measurements for most compounds except naphthalene which was measured by Atkinson to be 75 ng/m^3 - 6100 ng/m^3 and was measured in our study to be 118 ng/m^3 to 741 ng/m^3. Since the number of measurements are relatively small for both studies, and the samples were collected at different locations and seasons, the difference in the measured ranges are probably the result of actual differences in the outdoor concentrations which vary significantly depending upon local source emission activities and meteorology rather than differences in the sensitivity of the measurement methods.

PAH Indoor Net Emission Rates.

Table VI-15 presents our computations of the indoor net emission rates for gas phase PAH. The lack of adequate precision of the particulate phase PAH concentration data precludes the quantitative computation of net indoor emission rates for most of these compounds. Based upon the current uncertainty in the particulate phase PAH analyses we estimate the minimum measurable net emission rate to be 5 ng/m^3-hr. The net emission rates computed from these data were all less than 5 ng/m^3-hr except for pyrene 9.6 ng/m^3-hr and retene 5.3 ng/m^3-hr. These net emission rates were for the test of the Truckee residential site R-1 with a wood stove operating.

The indoor net emission rate describes the combined net rate of indoor source emissions and indoor removal. While indoor/outdoor concentration ratios or differences may be computed to indicate the sign of an indoor net emission rate (i.e. positive or negative) use of the air exchange rate data collected concurrently with the concentration measurements allows computation of both the sign and the magnitude of the indoor net emission rate. The net emission rate is computed as the product of the difference between simultaneous indoor and outdoor concentrations and the building air exchange rate. The indoor net emission rates are useful for estimating the indoor concentrations in other buildings which may have the same indoor net emission rate but different air exchange rates or different outdoor concentrations. An indoor net emission rate of 1 ng/m^3-hr for a particular contaminant corresponds to an indoor concentration which is 1 ng/m^3 higher than the outdoor concentration for a building with an air exchange rate of 1 ach. For a building with a lower air exchange rate of 0.33 ach and the same net indoor emission rate, the indoor

Table VI-15. Indoor net emission rates for gas phase PAH as measured in the pilot field study.

Test Site [a] Description	Sample ID	INDOOR NET EMISSION RATES (ng/m^3- hr) [c]													
		NAPH	2NAPH	1NAPH	BiPHE	ACNPY	ACNPE	FLRN	PHEN	ANTH	2ANTH	9ANTH	FLUOR	PYREN	CHRYS
Truckee Residential s	T-1D	322	215	113	104	9.9	4.5	7.8	4.6	4.9	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
	T-IN	530	290	148	109	15	8.3	9.5	4.6	5.2	< 0.5	< 0.5	< 0.5	0.8	< 0.5
Truckee Residential ws,s,g	T-2D	670	191	120	120	103	3.7	8.3	4.4	10	0.5	< 0.5	3.8	6.8	0.5
	T-IN	575	229	130	96	46	1.5	3.1	9.5	1.0	< 0.5	< 0.5	< 0.5	1.1	< 0.5
Rodeo Residential None	R-1D	115	99	51	-0.7	1.4	1.5	4.7	12	1.3	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
	R-IN	270	228	119	38	3.0	3.5	11	12	0.7	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
Rodeo Residential g	R-2D	295	244	124	111	3.6	3.2	12	11	0.8	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
	R-2N	NO	DATA												
Milbrae Residential s	M-1D	869	94	62	-48	7.4	2.7	4.8	29	3.8	0.7	< 0.5	< 0.5	< 0.5	< 0.5
	M-1N	454	54	45	103	5.1	2.7	6.8	20	2.0	0.8	< 0.5	1.0	0.9	< 0.5
Sacramento Commercial none	S-1D	164	97	48	54	1.1	7.0	16	12	0.7	< 0.2	< 0.2	-13.6	-6.7	-0.4
Palo Alto Commercial s	P-1D	539	386	246	196	26	12	22	18	27	4.2	0.5	4.6	3.3	1.4

a .) Test Site Description: Location (California) and building type, 5 residential and 2 commercial; Date of the testing; Indoor sources present during the sampling (ws = wood stove, g = gas stove, s = environmental tobacco smoke, none = no indoor unvented combustion).
b.) Sample ID: T= Truckee, S= Sacramento, P=Palo Alto, R=Rodeo, M=Milbrae, 1D= Day 1 (7AM-7PM), 2D=Day 2 (7AM-7PM), 1N=Night 1 (7PM-7AM), 2N=Night 2 (7PM-7AM).
c.) Indoor net emission rates calculated as the product of the difference of simultaneous indoor and outdoor 12-hour time averaged concentrations and the local indoor air exchange rate. Particulate phase polycyclic aromatic hydrocarbons: NAPH=Naphthalene, 2NAPH=2-Methylnaphthalene, 1NAPH=1-methylnaphthalene, BiPHE=Biphenyl, ACNPY=Acenaphthylene, ACNPE=Acenaphthalene, FLRN=Fluorene, PHEN=Phenanthrene, ANTH=Anthracene, 2ANTH=2-Methylanthracene, 9ANTH=9-Methylanthracene, FLUOR=Fluoranthene, CHRYS=Chrysene.

concentration will be 3 ng/m^3 higher than the outdoor concentration. A contaminant with a negative indoor net emission rate describes a compound which has an indoor removal rate which is greater than the indoor source emission rate. For a contaminant with no significant indoor source or removal mechanisms the indoor net emission rate will be zero, and the indoor and outdoor concentrations will be the same.

With a few exceptions, the gas phase PAH all had positive indoor net emission rates. These ranged from less than 1 ng/m^3-hr for the less volatile compounds (i.e. phenanthrene to chrysene) to 115 - 869 ng/m^3-hr for naphthalene. The minimum measurable net emission rate for the less volatile compounds was estimated to be 0.5 ng/m^3-hr for residential sites and 0.2 ng/m^3-hr for commercial sites. The lower limit for the commercial buildings reflect the higher outside air ventilation rates in the commercial buildings; 0.8-1.0 ach in commercial buildings as compared to 0.14-0.47 ach in residences.

In general the indoor net emission rates for the gas phase PAH are greater for those indoor environments with the most indoor unvented combustion activity (i.e. tobacco smoking and wood stoves) and for the more volatile PAH.

We note that the unusually high daytime negative net emission rate of -48 ng/m^3-hr for biphenyl observed in the residence with tobacco smoking, M-1, may reflect the abrupt drop in the unusually high outdoor concentration. During the daytime the outdoor concentration of biphenyl was 639 ng/m^3. This outdoor concentration dropped to 206 ng/m^3 during the nighttime measurement period. It is possible that emissions of PAC from the air traffic at nearby San Francisco airport impacted this site and the major shift in the wind direction between the day and night measurement periods may have caused this large drop in the outdoor concentration. During the daytime measurement period the wind was blowing out of the north east from the airport toward the M-1 residence while during the nighttime measurement period the wind changed directions and blew from the south west; a 180° switch in direction. With this pattern of outdoor concentrations, high during the day and low during the night, and no significant indoor sources, the indoor concentrations will change along with the outdoor concentrations, but the change in the indoor concentrations will lag the change in the outdoor concentrations. The degree of lag depends upon the building air exchange rate. The lower the air exchange rate the longer time it takes for changes in the outdoor concentration to impact the indoor concentration. It takes three air changes to re-establish indoor concentrations within 95% of their equilibrium value after a change is introduced. Thus for the M-1 residence where the outdoor concentrations

changed from high during the day to low during the night, the indoor concentrations will be lower than outdoors during the day and higher than outdoors during the night. This scenario yields a negative net emission rate for the daytime measurement period and positive net emission rate for the nighttime measurement period which agrees with the results presented here.

The set of indoor net emission rates for the residence without any indoor unvented combustion sources, R-1, contains five compounds with significant positive rates; naphthalene (115 ng/m^3-hr, day; 270 ng/m^3-hr, night), 2-methylnaphthalene (99 ng/m^3-hr day; 228 ng/m^3-hr night) 1-methylnaphthalene (51, ng/m^3-hr day; 119 ng/m^3-hr night), fluorene (4.7 ng/m^3-hr, day; 10.5 ng/m^3-hr night), and phenanthrene (12 ng/m^3-hr, day; 12 ng/m^3-hr night). There may be some other indoor sources of these gas phase compounds that are not associated with indoor combustion sources. We have not positively identified any materials in this residence which may be emitting these compounds however we note that there are numerous petroleum based products used in paints, finishes and other materials which are commonly used in residences and which may emit these compounds. We also note that buildings may have "memories" of exposure to previous sources of contaminants as a result of adsorption and desorption of the contaminants to indoor surfaces.

It is also interesting to note that in this residence without any indoor unvented combustion sources that the net emission rates for naphthalene, 2-methylnaphthalene, 1-methylnaphthalene, and fluorene are nearly double during the nighttime measurement period as compared to the daytime. The indoor and outdoor concentrations remained about the same through these tests. However, the air exchange rate doubled from 0.14 ach to 0.30 ach. The fact that the indoor concentrations for these compounds remained the same despite the increased ventilation rate suggests that the emission rates of these compounds increased with the increasing ventilation rate. This is a characteristic of diffusion dominated transport of gas from building materials.

Comparison of Residential Gas Phase PAH Net Emission Rates

The net emission rates for each of the gas phase PAH measured may be compared on a site-by-site basis along with information regarding the presence and activity of potential indoor sources to obtain indications of the type and amount of PAH emitted by each of the indoor sources. In this pilot field study we tested one residence without any unvented indoor

combustion sources (all residences had vented gas forced air heaters) and we tested one residence each with one of each of the following indoor combustion sources of PAH; gas range, tobacco smoke, and wood stove. By comparing the net emissions computed for each of the residences with an indoor source to the residence without any indoor unvented combustion sources we may obtain indications of the type and amount of PAH emitted by each of the sources.

For those compounds where there were significantly higher net emission rates (e.g. > 100%) in the residence with an indoor combustion source than in the residence without an indoor combustion source we calculated the percentage difference. The percentage difference was calculated from the average of the day and night net emission rates where there were both periods of measurement. In this manner we hoped to gain indications of the most significant PAH emitted from each of the three different indoor combustion sources. We note for the gas phase PAH that there are indoor sources which may not be directly combustion related, and thus there may be significant differences in the indoor source emission rates from residence to residence apart from the activity of the combustion sources. This comparison assumes that the emissions from the non-combustion related sources are the same in the residence with the indoor combustion source as the residence without and indoor combustion source and that any differences in the net emission rates are the result of the presence and activity of the indoor combustion source.

Tobacco Smoking. Compared to the residence without any indoor unvented combustion sources, R-1, the residence with only tobacco smoking, M-1, had significantly higher indoor net emission rates of the following gas phase PAH; naphthalene (243%) and phenanthrene (97%). For this residence the net emission rate of naphthalene was measured to be 869 ng/m^3-hr during the day when 14 cigarettes were smoked indoors and 454 ng/m^3-hr during the night when 1 cigarette was smoked indoors. The net emission rates of phenanthrene in this residence, M-1, were 29 ng/m^3-hr (day) and 20 ng/m^3-hr (night).

Wood Stoves. Compared to the residence without indoor unvented combustion sources, R-1, the residence with a wood stove, T-1, had significantly higher indoor net emission rates of the following gas phase PAH; naphthalene (121%), biphenyl (465%), acenaphthylene (454%), and acenaphthalene (156%). The indoor net emission rates of naphthalene in the residence with a wood stove were 322 ng/m^3-hr (day) and 530 ng/m^3-hr (night). These values are elevated over the residence without indoor unvented combustion sources but less than those for the residence with tobacco smoking.

Gas Stoves. Compared to the residence without indoor unvented combustion sources, R-1, the residence with a gas stove, R-2, had significantly higher indoor net emission rates of the following gas phase PAH; biphenyl (490%). This residence with a gas stove, R-2, was the same residence as the residence without indoor unvented combustion sources, R-1, only a gas stove was temporarily installed in the kitchen. The test with the gas stove followed the test without a gas stove.

Comparison of Commercial Building PAH Net Emission Rates

We compared the indoor net emission rates of each of the measured species of PAH in the two commercial buildings which we studied. We compared the net emission rates measured in one commercial office building with no tobacco smoking, S-1, to one commercial office building, P-1, with significant tobacco smoking (i.e. 21 cigarettes/12hours) in the office suite where the PAC sampler was located.

Compared to the building without tobacco smoking, S-1, the building with tobacco smoking, P-1, had significantly higher indoor net emission rates of the following gas phase PAH; naphthalene (228%), 1-methylnaphthalene (412%), 2-methylnaphthalene (300%),and biphenyl (264%),and acenapthalene (2180%).

We also note that in the Sacramento office building, S-1, there was a significant negative net emission rates for two of the less volatile gas phase PAH; fluoranthene at -13.6 ng/m^3-hr and pyrene at -6.7 ng/m^3-hr.

D. SUMMARY AND CONCLUSIONS

The newly developed indoor PAC sampler was evaluated in a pilot PAC field study conducted in three residences and two commercial buildings. The sampler was designed to collect a 25 m^3 air sample over a 12-hour sampling period. Particulate phase PAH were collected on 47 mm TIGF filters followed by a sorbent cartridge packed with two sections, 2.5 grams each, of XAD-4 resin for collection of gas phase PAH. A GC-MS was used to analyze the gas phase extracts for 14 gas phase PAH ranging from naphthalene to chrysene. An HPLC with fluorescence detection was used to analyze 21 particulate phase PAH compounds ranging from phenanthrene to dibenzo(a,h)pyrene. A total of 42 field

samples were collected and analyzed. The PAC sample pumps performed quietly and reliably throughout the PAC pilot field study.

The precision of the sampler was evaluated by computing the pooled variance of paired replicate samples collected indoors and outdoors. The relative precision of the gas phase PAH concentrations for the combination of indoor and outdoor samples ranged from 4.8% for acenapthylene to 160% for 9-methylanthracene. The high relative imprecision for 9-methylanthracene was a result of both the low mean value of the air measurements (i.e. close to the analytical detection limit) and the low number of replicate pairs available for this analysis (i.e only 3). For the gas phase contaminants there was reasonable agreement between our estimated measurement uncertainty, 20.6% and our observed measurement precision except for biphenyl in the outdoor samples and except for phenanthrene, anthracene, and 9-methylanthracene in the indoor samples. With minor development work the method for measuring the gas phase PAH will be ready for deployment in a large indoor field study.

The measurement precision of the particulate phase PAH for the combination of indoor and outdoor samples ranged from 25%-30% for benzo(b)fluoranthene and benzo(k)fluoranthene, to 210% for benzo(a)pyrene, to over 400% for dibenzo(a,c)anthracene. These large relative imprecisions appear to be the result of two recurrent analytical difficulties: interfering compounds and high fluorescent background. In particular there were problems with compounds which co-eluted and interfered with the internal standards used to quantitate the mass of PAH. The large values of relative precision at the 95% confidence level underscore the need for further method development as described in Chapter V. The method for measuring particulate phase PAH will require some further development work to improve the measurement precision before it is ready for deployment in a large indoor field study.

The indoor concentrations of most of the gas phase PAH were generally higher indoors than outdoors which is consistent with the presence of the known indoor sources in this study. In the one residence without any indoor combustion sources, there were many gas phase PAH with significantly higher indoor concentrations suggesting the presence of indoor sources which are not directly combustion related.

The indoor concentrations of particulate phase PAH were not as different from the outdoor concentrations as those for the gas phase PAH. The concentrations of five of the twenty

one particulate phase PAH were significantly higher indoors than outdoors; anthracene, pyrene, benzo(e)pyrene, dibenzo(e)pyrene, and coronene. We note that these concentration differences are associated with those sites with active indoor combustion sources.

Our comparison of the indoor net emission rates for residences with and without specific indoor combustion sources of PAC suggests that the following PAC may be associated with the following sources:

Tobacco smoke - Gas phase: naphthalene and phenanthrene

Wood stove - Gas phase: naphthalene, biphenyl, acenaphthylene, and acenaphthalene.
- Particulate phase: pyrene and retene.

Gas range - Gas phase: biphenyl

In summary the the indoor PAC sampler and analytical methods are ready for deployment in a larger field study for most of the gas phase PAH but not for the particulate phase PAH or gas phase nitro-PAH contaminants measured in this study. The particulate phase PAH and gas phase nitro-PAH analytical methods will require some further development before deployment in a large indoor filed study. Since the concentrations of the particulate phase PAH and gas phase nitro-PAH were similar in indoor air and since we believe that the existing evidence indicates that the particulate phase PAH are more potent carcinogens than the gas phase nitro-PAH, we recommend that further development of the analytical method for the particulate phase PAH be given a higher priority than that for the gas phase nitro-PAH. The recommended particulate phase PAH development work, which is described in Chapter 5, includes examination of sample clean up procedures and use of an external standard.

VII. AN ANALYTICAL METHOD FOR GAS-PHASE, NITRO POLYCYCLIC AROMATIC HYDROCARBONS IN INDOOR AIR

A. INTRODUCTION

Several basic analytical methods have been developed for nitro derivatives of polycyclic aromatic hydrocarbons (NPAH). These methods have primarily been used to quantify NPAH in samples of ambient outdoor air and diesel exhaust particles (e.g., Atkinson et al., 1988; MacCrehan et al., 1988; Arey et al., 1989). In general, the methods have not been validated for analysis of samples collected in indoor environments. In fact, there is only a single report of measurements of NPAH in indoor air (Wilson and Chuang, 1987).

Because of the complexity of urban air samples, analytical schemes for NPAH often incorporate a preliminary fractionation step to isolate these compounds from the other components of the samples. Fractionation by semipreparative high-performance liquid chromatography (HPLC) has been successfully used (e.g., Atkinson et al., 1988). Others have used open bed columns for fractionation (e.g. MacCrehan et al., 1988).

The most powerful analytical technique for the identification and measurement of NPAH is capillary gas chromatography-mass spectrometry (GC-MS). The high chromatographic resolution and selectivity of this technique make it particularly well suited to the analysis of complex environmental samples. Both electron-impact and chemical-ionization GC-MS instruments have been used with chemical ionization providing the greatest sensitivity (Wilson and Chuang, 1987; Atkinson et al., 1988; Arey et al., 1989). However, even chemical-ionization GC-MS may not be sufficiently sensitive for the analysis of indoor air samples because concentrations of NPAH are expected to be low (several nanograms per cubic meter and often less) and the volumes of air that can be sampled in residences are restricted (25 m^3 in this study). Another disadvantage of chemical-ionization GC-MS is the generally high cost and limited availability of the instrumentation.

High-performance liquid chromatography with fluorescence detection has been demonstrated to have high sensitivity and selectivity for the analysis of polycyclic aromatic hydrocarbons (PAH). Since the NPAH become fluorescent when they are reduced to the corresponding aromatic amines, reduction of NPAH makes the analysis of these

compounds by HPLC with fluorescence detection feasible (MacCrehan and May, 1984; Tejada et al., 1986; MacCrehan et al., 1988). This technique provides sensitivity down to low picogram levels and is a less expensive alternative to chemical-ionization GC-MS.

Several methods for the on-line reduction of NPAH to amino-PAH have been reported. One approach used a reduction column, placed between the analytical column and the detector. The reduction column was packed with a mixture of zinc powder and silica (MacCrehan and May, 1984; MacCrehan et al., 1988). In another method, a truly catalytic reduction column, packed with alumina that was coated with platinum and rhodium, was similarly used (Tejada et al., 1986). Because of its simplicity, the method employing the zinc reducer column was selected for development as a method for analysis of selected NPAH in indoor air.

The primary goal of this portion of the study was to develop and validate a method that would be suitable for use in a proposed, large-scale survey of polycyclic aromatic compounds in residential indoor air. It was decided to focus on the analysis of vapor-phase, semi-volatile compounds because these generally would be expected to be present at higher concentrations than particulate-phase compounds. The design objectives were to: (1) provide adequate sensitivity for NPAH in 25 m^3 samples of air collected in indoor environments having a variety of potential sources of these compounds; (2) provide sufficient precision to be able to distinguish concentration differences among environments and sources; (3) incorporate an internal standard to correct for recovery losses of the analytes; and (4) keep the method as simple as possible. The method which was developed was used to quantify 1- and 2-nitronaphthalene in extracts of sorbent samples (Chapter IV) that had been composited to represent indoor and outdoor locations at five collection sites.

B. METHODS

Preparation of Composite Samples

Due to time constraints, it was necessary to reduce the number of samples to be analyzed. Following the analysis of the vapor-phase PAH described in Chapter IV, 28 of the extracts of the front sections of the sorbent samplers were composited into 12 samples representing indoor and outdoor locations at each of the five collection sites (Table VII-1). The

Table VII-1 Consitutuents of composite samples.

COMPOSITE ID	SITE [a]	INDOOR [b] SOURCE	SAMPLE ID	AIR VOLUME SAMPLE (m^3)	AIR VOLUME COMPOSITE (m^3)
TIA	Truckee Indoor	ws	T-1D-IR T-1N-I	15.1 15.0	30.1
TIB	Truckee Indoor	ws,s,g	T-2D-I T-2D-IR T-2N-I	15.0 15.0 15.0	45.0
TO	Truckee Outdoor		T-ID-O T-1N-O T-2D-O T-2N-O	15.0 14.9 15.2 15.0	60.1
RIA	Rodeo Indoor	none	R-1D-I R-1N-I	15.0 15.2	30.2
RIB	Rodeo Indoor	g	R-2D-I R-2N-I	15.0 15.0	30.0
RO	Rodeo Outdoor		R-1D-O R-1N-O	15.1 15.0	30.1
MA	Milbrae[c]	s	M-1D-IR M-1D-O	14.8 14.8	29.6
MB	Milbrae[c]	s	M-1D-I M-1N-I M-1N-O	15.0 15.1 15.1	45.2
SI	Sacramento Indoor	none	S-1D-I S-1D-IR	15.2 15.0	30.2
SO	Sacramento Outdoor		S-1D-O S-1D-OR	15.0 15.0	30.0
PI	Palo Alto Indoor	s	P-1D-I P-1D-IR	15.1 15.0	30.1
PO	Palo Alto Outdoor		P-1D-O P-1D-OR	15.0 15.0	30.0

a. Palo Alto and Sacramento are commercial sites, all others are residential
b. ws = wood stove, s = cigarette smoke, g = gas range.
c. Mixture of indoor and outdoor samples.

predominant known indoor sources of PAH and NPAH at these sites were cigarette smoke, wood stoves and gas ranges. To prepare the composite samples, the total volume in each of the original extracts was measured with a syringe, and an extract volume equivalent to approximately 15 m^3 of air was added to the appropriate sample. The total air volume represented by each composite sample was 30-60 m^3. Indoor and outdoor samples from the Milbrae residential site were accidentally mixed, precluding any comparisons of indoor/outdoor concentration differences for this site. Two composite field blank samples were additionally prepared. Each of these consisted of the combined extracts of the front sections of two blank sorbent samplers.

Sample Cleanup

Arey et al. (1989) collected high-volume outdoor air samples for PAH and NPAH analyses on polyurethane foam (PUF) plugs. The PUF plugs were Soxhlet extracted with dichloromethane (DCM). The DCM extracts were concentrated and then fractionated by HPLC using a semipreparative silica column and a mobile phase program employing n-hexane, DCM and acetonitrile. In this way, separate fractions were obtained for PAH and NPAH analyses. Using the separation of PAH and NPAH that was achieved with this method (Atkinson et al., 1988) as a guide, a simple sample cleanup procedure was developed which employed solid-phase extraction with Sep-Pak silica cartridges (Part No. 51900, Millipore Corp., Milford, MA).

Sep-Pak cartridges were cleaned prior to use by elution with 10 mL of n-hexane followed by 10 mL of DCM. Remaining solvent was forced from the cartridges, and the cartridges were allowed to air dry over a period of several days. All solvents used in this study were high purity, distilled in glass, grade (B&J Brand, Baxter Healthcare Corp., Muskegon, MI).

The composite sample extracts, which were in benzene, were reduced in volume to approximately 150 μL by blowdown with an inert gas if required. A concentrated extract was slowly transferred to the top of the silica packing of a clean cartridge with a syringe. A stream of inert gas was next introduced into the inlet of the cartridge to dry the extract. Enough n-hexane to completely wet the silica packing (approximately 1.5 mL) was added to the cartridge, then an additional 2 mL of n-hexane was added and collected at a steady drip rate in a graduated conical tube. One milliliter of a mixture of n-hexane and DCM (1:1

by volume) was next added, and an additional 1 mL of solvent was collected in the same tube. This fraction was expected to contain the PAH and other nonpolar, hexane-extractable components of the sample. Using another graduated conical tube, 3 mL of the n-hexane/DCM solvent mixture were added to the cartridge and collected. This fraction was expected to contain the NPAH.

The n-hexane/DCM fractions were concentrated and solvent exchanged to ethanol by rotary evaporation. The extracts were transferred to conical tipped 1-mL vials and further concentrated to about 100 µL with a stream of inert gas.

HPLC Analysis of Sample Extracts

The NPAH, 1-nitronaphthalene (1-NN) and 2-nitronaphthalene (2-NN), in the fractionated sample extracts were quantified using HPLC with on-line reduction to the corresponding amines followed by fluorescence detection after the methods of MacCrehan and May (1984) and MacCrehan et al. (1988). A small volume of a solution of 9-nitroanthracene (9-NA) was added to each extract immediately prior to analysis with a microliter syringe. This compound served as an internal standard for quantitation.

The NPAH used as calibration standards and as the internal standard were obtained commercially (Aldrich Chemical Co., Milwaukee, WI). Stock solutions of single or mixed standards were made by weighing the pure compounds on an electronic microbalance and dissolving them in methanol in volumetric flasks. Calibration and internal standards were prepared daily by diluting aliquots of these stock solutions with methanol in volumetric flasks.

Analyses were performed using a liquid chromatograph (HP 1090M with DR5 solvent delivery system, Hewlett Packard Co., Palo Alto, CA) equipped with a programmable fluorescence detector (HP 1046A, Hewlett Packard Co.) and a chromatography data system (HP 799994A, Hewlett Packard Co.). Samples were injected by completely filling a 5-µL sample loop of a syringe-loading injector. Chromatographic separations were achieved with a reversed-phase octadecylsilane (C-18) modified silica column (VYDAC 201TP5215, Separations Group, Hesperia, CA) of 2.1 mm I.D. x 15 cm dimensions and packed with 5-µm particles. The analytical column was protected with a C-18 guard column cartridge (VYDAC 201TP, Separations Group). A reduction column connected to

the outlet of the analytical column was used for the on-line reduction of the NPAH nitro group to the amine (MacCrehan et al., 1988). This column consisted of a stainless steel tube, 2.1 mm I.D. x 10 cm, packed with a mixture of 7-µm zinc dust (Alfa Products, Morton Thiokol, Inc., Danvers, MA) and cleaned silica packing removed from Sep-Pak cartridges (1:1 by weight).

The two solvent mixtures used for the analysis were: (A) 50% methanol, 50% water; and (B) 95% methanol, 5% water. Both mixtures were buffered with ammonium acetate (0.01 M). The solvent flowrate was 0.3 mL min^{-1}. The solvent program was a combination of solvents A and B resulting in an initial methanol composition of 61.2% held for 6 min, ramped linearly to 93.6% methanol over 8 min, held for 3 min, ramped linearly back to the starting condition over 3 min, and held for a 3-min equilibrium period before starting the next injection cycle. For these conditions, typical elution times were 6.8 min for 1-NN, 8.1 min for 2-NN and 14.3 min for 9-NA.

Fluorescence spectra of the aromatic amines produced by the catalytic reduction of the corresponding NPAH have been published by Tejada et al. (1986). The spectra of the compounds of interest were confirmed by stopped-flow fluorescence scans of reduced standard NPAH. Based on the spectra of 1- and 2-aminonaphthalenes, the detector was programmed for an initial excitation wavelength of 243 nm and an initial emission wavelength of 429 nm. At 12 min, prior to the elution of 9-aminoanthracene, these were changed to an excitation wavelength of 263 nm and an emission wavelength of 505 nm.

Data Reduction and Analysis

Chromatographic peaks were detected and peak-height responses were determined using the HPLC data system. Peak heights rather than peak areas were selected because heights are less affected by compounds which may not be completely resolved from the analytes of interest.

The compounds were quantified based upon comparisons of their peak height responses to the peak height response of the internal standard for quantitation which was added to the extracts at the time of analysis. On each day of analysis, three new calibration standards were prepared, each containing the same concentration of 9-NA and different concentrations of 1- and 2-NN. Multipoint calibrations were performed using these

standards. Relative response factors for the analytes in these standard mixtures were determined using Equation IV-2, Chapter IV. The masses of 1- and 2-NN in the sample extracts were then calculated using Equation IV-3. These calculated masses were corrected for estimated recovery losses to the XAD-4 resin used to collect the samples and to the Sep-Pak cartridges used for sample cleanup. The recoveries of both 1- and 2-NN from the XAD-4 resin were assumed to be approximately equal to the average recovery of the surrogate compound, naphthalene-d_8, for indoor and outdoor samples of 70.8% (See Table IV-4, Chapter IV). Finally, the sample masses were divided by the air volumes represented by the composite samples (Table VII-1) to obtain concentrations in nanograms of analyte per cubic meter of air.

C. RESULTS

Method Development

MacCrehan and May (1984), who reported on the use of a zinc reduction column for the analysis of NPAH by HPLC with fluorescence detection, found that residual oxygen in the mobile phase rapidly consumed the small amount of zinc in the reducer column. This resulted in decreased conversion of the NPAH from the nitro to the amino forms. These researchers first used a zinc oxygen scrubber column to remove oxygen from the mobile phase (MacCrehan and May, 1984). For later work, they switched to a platinum scrubber column which catalyzes the reduction of dissolved oxygen by methanol added to the mobile phase (MacCrehan et al., 1988). The use of this oxygen scrubber significantly increased the useful life of the reducer column.

During the first phase of method development for this study, a similar platinum oxygen scrubber column was installed on the HPLC system. With this column in place, it was not possible to obtain a low, stable baseline, and its use was discontinued. Instead, simple continuous purging of the solvent reservoirs with high-purity helium was used to deoxygenate the mobile phase. This was apparently sufficient, since during periods when only standards were being analyzed, there was no significant loss of analytical sensitivity.

Another discovery during the early phase of method development was that the chromatographic resolution of standards prepared in benzene was poor. This was

overcome by switching to an alcohol as the solvent for both standards and the sample extracts. Ethanol, rather than methanol, was selected as a convenient solvent since its boiling point (78.5^{o}C) is higher than that of n-hexane (69°C) which was used for the extraction of the Sep-Pak cartridges and which also interfered with the HPLC analysis.

Even after switching to ethanol as a solvent, chromatographic resolution was significantly below that which is routinely obtained for PAH when only the analytical column is used. As a result of this relatively poor resolution, complete baseline separation of 1- and 2-NN could not be achieved. Another consequence of this degradation was that the use of perdeuterated 1-nitronaphthalene as an internal standard was not possible because it could not be separated from 1-NN. It was concluded that this band broadening was due to the use of the zinc reducer column. MacCrehan et al. (1988) reported similar band broadening when a reducer column was used.

Preliminary experiments indicated that the fractionation scheme described in the Methods section would result in nearly complete elution of 1- and 2-NN into the n-hexane/DCM fraction. Replicate samples using three different matrices were then prepared to systematically evaluate this recovery. The first matrix was simply 1- and 2-NN standards in ethanol. Two Sep-Pak cartridge blanks were prepared, analyzed and found not to contain 1- or 2-NN. Next, approximately 50 ng of each of the two compounds was spiked onto three replicate cartridges. These were extracted as described, and the n-hexane/DCM fractions were analyzed using 9-NA as an internal standard for quantitation. One of the three n-hexane fractions was also analyzed. As shown in Table VII-2, 1- and 2-NN were not present in the n-hexane fraction, and the recoveries of 1- and 2-NN in the n-hexane/DCM fraction averaged 84 and 89%, respectively with coefficients of variation (standard deviation/mean) of about 15%.

A large portion of the observed loss was due to the solvent reduction and glassware transfer steps. A separate experiment was performed to isolate this loss. Three replicate 3-mL mixtures of n-hexane/DCM (1:1 by volume) were spiked with 1- and 2-NN. These were reduced in volume and transferred to 1-mL vials with the same procedures used to treat the n-hexane/DCM extracts of the Sep-Pak cartridges. Recoveries of 1- and 2-NN averaged 88 and 92%, respectively, demonstrating that losses to the Sep-Pak cartridges in the above experiment were probably negligible.

Five replicate composite samples of both indoor and outdoor XAD-4 extracts were prepared to evaluate the recoveries of 1- and 2-NN for fractionation and cleanup of realistic sample matrices. Each replicate indoor and outdoor sample represented an aggregate of approximately 15 or 23 m^3, respectively, of air sampled at all sites. The recoverable masses of 1- and 2-NN, present as sample constituents, were quantified for two of the five replicate samples of each matrix. The remaining three replicate samples were spiked with approximately 50 ng each of 1- and 2-NN and fractionated as described above. The recoveries that were obtained are shown in Table VII-2. For the indoor sample matrix, the recovery of 1-NN in the n-hexane/DCM fraction averaged 67% with a large uncertainty while an interfering compound(s) prevented the analysis of 2-NN. For the outdoor sample matrix, the recoveries of 1- and 2-NN averaged 56 and 64%, respectively. Recoveries for one of the outdoor replicate samples were very low and were excluded as outliers. Analysis of a single n-hexane fraction for each matrix indicated that much of the unaccounted masses of 1- and 2-NN eluted early into this fraction. Apparently, the components of these sample matrices had a significant effect on the retention and fractionation of the analytes. Additional experimentation to reduce the volumes of solvent used for elution of the Sep-Pak cartridges might have improved the recoveries. However, since there were no more XAD-4 sample extracts available for this purpose, it was decided to use the existing method without further modification.

The original intention was to add an internal standard to the sample extracts prior to the fractionation step. This approach would ideally compensate for any losses of the analytes during fractionation on an individual sample basis. However, the analytes and this internal standard for recovery must behave identically for such an approach to be valid. This was investigated in an experiment which measured the recovery of 9-NA added to Sep-Pak cartridges. Three replicate cartridges, each containing 260 ng of 9-NA were prepared. These cartridges were extracted as before, and the n-hexane/DCM fractions were analyzed using 1-NN as an internal standard for quantitation. As shown in Table VII-2, the average recovery was only 24%, and the variability was high. The 9-NA was not found in the n-hexane fraction, nor could it be recovered by subsequent elution of one of the cartridges with DCM. This disappearance of 9-NA was, therefore, attributed to reactive losses during the fractionation step.

Another more stable NPAH, which could be resolved from the analytes and which would be expected to present in the samples at low concentrations, was not readily available.

Table VII -2. Recoveries of analytes in extract fractions of Sep Paks by matrix type.

Compound[b]	Extract Fraction	BLANK n	BLANK Mean (%)	BLANK STD (%)	BLANK CV[a] (%)	INDOOR n	INDOOR Mean (%)	INDOOR STD (%)	INDOOR CV (%)	OUTDOOR n	OUTDOOR Mean (%)
1-Nitronap	Hexane	1	0.0			1	15.3			1	27.7
	Hexane/DCM	3	84.2	12.4	14.8	3	67.4	16.7	24.8	2	55.8
	Total		84.2				82.7				83.5
2-Nitronap	Hexane	1	0.0				INT[c]			1	21.0
	Hexane/DCM	3	88.7	13.5	15.2		INT[c]			2	64.4
	Total		88.7								85.4
9-Nitroant	Hexane	1	0.0								
	Hexane/DCM	3	23.9	15.4	64.2						
	Total		23.9								

a. CV = Coefficient of variation (Standard deviation/Mean) in percent.
b. Compounds: 1-Nitronap=1-Nitronaphthalene, 2-Nitronap=2-Nitronaphthalene, 9-Nitroant=9-Nitroanthracene
c. INT = Interfering compound(s), no data.

Consequently, it was decided to use 9-NA solely as an internal standard for quantitation by adding it to the fractionated sample extracts just prior to analysis. This meant that it would not be possible to compensate for fractionation losses of 1- and 2-NN on an individual sample basis. Instead, the recoveries of 1- and 2-NN for the three different matrices described above were averaged and were used as the best estimates of recovery for the fractionation step. These averages are presented in Table VII-3.

Table VII-3. Recoveries of analytes in hexane/DCM fraction of Sep Paks averaged for three matrices (i.e.indoor, outdoor, and blank samples).

Compound	n	RECOVERY Mean (%)	RECOVERY STD (%)	CV[a] (%)
1-Nitronaphthalene	3	69.1	11.7	16.9
2-Nitronaphthalene	2	76.5		

a. CV = Coefficient of variation (Standard deviation/Mean) in percent

The compounds were identified on the basis of their chromatographic retention times. For the conditions of this analysis, these retention times were quite stable. However, they differed slightly between standards and samples as shown in Table VII-4. The retention times of 1-NN were identical for these two matrices, but 2-NN and 9-NA eluted earlier in the samples than in the standards.

Table VII-4. Retention times of analytes in standard mixtures and sample extracts.

	RETENTION TIMES [a]			
	STANDARDS		SAMPLES	
Compound	Mean (min.)	+/-95% CI[b] (min.)	Mean (min.)	+/-95% CI (min.)
1-Nitronaphthalene	6.77	0.13	6.80	0.12
2-Nitronaphthalene	8.12	0.28	7.84	0.35
9-Nitroanthracene	14.29	0.23	14.04	0.17

a. n = 17 for standards, n = 8 for samples.
b. CI = Confidence interval

Masses of 1- and 2-NN were calculated using peak-height responses and 9-NA as an internal standard for quantitation. Calibrations were performed daily with three freshly prepared standards, each containing different concentrations of 1- and 2-NN. Peak-height responses were linear with concentration. The precision of the relative response factors calculated from these calibration standards is one of the major factors which determines the precision of the analysis of samples. Typical response-factor precisions are presented in Table VII-5. When performed on a single day, multiple injections of a single standard or a multipoint calibration using three standards produced nearly identical response factors with coefficients of variation of 5% or less. Interday variations were greater. Response factors for calibrations performed over a period of four days had coefficients of variation up to 12%. This increased variation was probably due to changes in the relative efficiency of conversion of the nitro group to the amine for the three NPAH.

The limits of quantitation (LOQ) for measurement of 1- and 2-NN were estimated from the variation in the magnitude of the instrumental noise and the sensitivity of the analysis. The conventional definition of the LOQ as ten times the standard deviation of the blank or,

Table VII-5. Relative response factors (RF) for analytes calculated from peak-height responses in standard mixtures.

Compound	n	RELATIVE RF Mean	STD	CV [a] (%)
Single standard [b]				
1-Nitronaphthalene	3	2.8	0.10	3.8
2-Nitronaphthalene	3	2.6	0.10	3.0
9-Nitroanthracene		1.0		
Multipoint calibration[b]				
1-Nitronaphthalene	3	2.9	0.00	1.6
2-Nitronaphthalene	3	2.8	0.10	5.2
9-Nitroanthracene		1.0		
Multiple calibrations[c]				
1-Nitronaphthalene	4	2.5	0.20	9.9
2-Nitronaphthalene	4	2.5	0.30	11.8
9-Nitroanthracene		1.0		

a. CV = coefficient of variation (standard deviation/mean) in percent.
b. Analysis on a single day.
c. Analysis on different days.

in this case, the noise was used (Keith et al., 1983). This value was 0.01-0.02 arbitrary height units, and the analytical sensitivity was about 200 picograms per height unit. These result in a LOQ of approximately 3 pg m^{-3} assuming an injection volume of 5 µL, a final extract volume of 100 µL, and an air volume of 25 m^3.

Analysis of Sample Extracts

Significant problems were encountered in the analysis of the composite sample extracts, particularly the extracts representing the indoor locations. In some of these, interfering compound(s) were present which coeluted with 1-NN and/or 2-NN making analysis impossible . Another problem was significant loss of sensitivity for the 9-NA internal standard added to the indoor composites obtained from the Rodeo site (RIA, RIB). It was

assumed that this loss was confined to 9-NA and was due to the reaction of 9-NA with some component of the samples. External standard analysis was used as an alternate procedure to estimate the masses of 1- and 2-NN in these two samples.

Analysis of the sample extracts also resulted in the rapid degradation of the reducer column. After only a few extracts had been analyzed, the sensitivity for all analytes decreased substantially, and the reducer column had to be repacked with a fresh mixture of zinc powder. The guard column cartridge was also replaced frequently in an attempt to prevent a large tailing peak from shifting retention time and coeluting with 1- and 2-NN.

The sample masses of 1- and 2-NN were corrected for the estimated average losses during the fractionation procedure (Table VII-3) and for an estimated average recovery of 70.8% from the XAD-4 resin used to collect the samples. There was no blank correction since neither 1-NN nor 2-NN were detected in the two composite field blank samples. These corrected masses were divided by the air volumes represented by the samples (Table VII-1). The calculated airborne concentrations of 1- and 2-NN at the sample sites are presented in Table VII-6.

There is considerable uncertainty associated with the concentrations largely due to the use of the average recovery factors in the calculations. The aggregate uncertainty due to these two factors alone is probably as much as +/-50% as measured by a 95% confidence interval. The interference problems encountered for some samples and the apparent reactivity of the 9-NA internal standard contributed further uncertainty to the results.

Nevertheless, several trends are apparent in the concentration data. In all of the samples that could be fully analyzed, the concentration of 1-NN was higher than the concentration of 2-NN. Also, at the sites with both indoor and outdoor data, the indoor concentrations were always higher. The difference between indoor and outdoor concentrations was particularly significant at the Truckee site which had the highest indoor concentrations and the lowest outdoor concentrations along with the Palo Alto site.

Table VII-6 Concentrations of analytes in composite samples.

COMPOSITE ID	LOCATION	CONCENTRATION [a] 1-NN (ng/m^3)	2-NN (ng/m^3)
TIA	Indoor	0.73	INT [b]
TIB	Indoor	2.72	1.56
TO	Outdoor	0.05	0.03
RIA	Indoor	0.53 [c]	INT
RIB	Indoor	0.48 [c]	0.34 [c]
RO	Outdoor	0.25	0.14
MA	Mixed	INT	INT
MB	Mixed	1.51	0.68
SI	Indoor	0.31	0.19
SO	Outdoor	0.15	0.10
PI	Indoor	INT	INT
PO	Outdoor	0.05	0.04

a. Corrected for estimated recoveries from XAD-4 and Sep Pak
b. INT = Interfering compound(s), no data.
c. Calculated using external standard analysis.

D. DISCUSSION

Evaluation of the Method

Because this HPLC method employs fluorescence detection, it has very high sensitivity for NPAH when they are reduced to the amino forms. This high sensitivity makes the method potentially well suited for use in indoor environments where concentrations of NPAH are expected to be low and where sample volumes, which must be collected without significantly perturbing concentrations, are restricted. Methods which employ GC-MS techniques are generally less sensitive and, therefore, require larger sample volumes.

In their survey of ambient concentrations of PAH and NPAH, Atkinson et al. (1988) collected high-volume samples to obtain sufficient masses of the analytes for analysis. The vapor-phase NPAH were collected from ~470 m^3 of air using PUF plugs. For analysis, the extracts of these samples were composited to yield samples representing several thousand cubic meters of air. The composite extracts were fractionated using semipreparative HPLC and analyzed for 1-NN, 2-NN and 3-nitrobiphenyl by electron-

impact GC-MS with selected-ion detection. Concentrations as low as a few picograms per cubic meter were quantified. Wilson and Chuang (1987) collected ~100 m^3 samples of indoor air on XAD-4 resin. The sample extracts were directly analyzed for four NPAH (1- and 2-NN were not analyzed) by negative chemical-ionization GC-MS. Concentrations as low as 8 pg m^{-3} were quantified.

Because of its greater sensitivity, it is clear that negative chemical-ionization GC-MS is the superior GC-MS technique for the analysis of NPAH in indoor air. Although negative chemical-ionization GC-MS is less sensitive than the HPLC method presented here, it does have the advantages of greater chromatographic resolution and greater specificity, in that molecular weights are obtained. The major disadvantage of negative chemical-ionization GC-MS, other than its lower sensitivity, is the generally high cost and limited availability of the required instrumentation.

More development of the HPLC method presented here is required before it can be reliably employed in any large-scale survey of indoor air quality. The major problems with the method in its current state of development are: (1) inadequate resolution of chromatographic peaks; (2) lack of an appropriate, non-reactive, internal standard; and (3) insufficient cleanup of sample extracts.

The chromatographic resolution of the HPLC system was significantly degraded by the reduction column which was attached to the outlet of the analytical column. As a result, other components of the sample extracts often coeluted with 1- and 2-NN and interfered with the analysis. It might be possible to improve resolution to sufficiently reduce this problem by: (1) decreasing the length of the reducer column; (2) changing the ratio of zinc to silica packing material; (3) substituting an alternate packing material, such as C-18 modified silica; (4) modifying the method of packing the column; or (5) employing a combination of modifications. In making these modifications, it would be important to at least maintain the capacity of the reduction column since, in its current form, it was quickly depleted when sample extracts were analyzed.

Alternately, a different type of reduction column could be used in an attempt to improve chromatographic resolution. For example, Tejada et al. (1986) presented an alternate scheme for the reduction of the NPAH nitro group to the amino form. They employed a

short reducer column containing 5-μm alumina coated with platinum and rhodium which functioned as a true catalyst with an an indefinite lifetime.

Improved chromatographic resolution might also eliminate the problems that were encountered with the internal standard. The 9-NA that was used is too reactive and can be present as a component of the sample extracts. Because of its reactivity, 9-NA could not be sufficiently recovered from the Sep-Pak cartridges. As a result, it was not possible to individually correct the masses of NPAH for losses during the fractionation step. Perdeuterated 1-nitronaphthalene would be an ideal internal standard. It is not present in air and would be expected to behave identically to 1- and 2-NN. With improved chromatographic performance, it might be possible to separate this compound from the 1-NN peak, making its use feasible. If so, the perdeuterated compound could even be added to the sorbent sampler prior to sample collection and, thereby, provide a reliable means of correcting for all potential losses.

The sample cleanup procedure also proved to be inadequate, particularly for the preparation of the indoor sample extracts. Cigarette smoking occurred at four of the five sampling sites. Consequently, many of the XAD-4 sample extracts were brown in color, smelled like cigarettes, and probably had high loadings of organic compounds. The n-hexane/DCM fractions of these extracts contained components which frequently interfered with the analysis of 1- and 2-NN. These were presumed to be more polar compounds because of their poor chromatographic peak shapes.

It might be possible to refine the present fractionation procedure to eliminate more polar components and enhance the recovery of 1- and 2-NN. However, it is unlikely that dramatic improvements could be achieved because the Sep-Pak cartridges are very short with limited resolving power. Semipreparative HPLC techniques, such as used by Atkinson et al. (1988), could be used for fractionation, but this approach would greatly increase the complexity of the analysis. Another approach is to use a dual-column, multidimensional HPLC system. Tejada et al. (1986) used such a system in conjunction with their catalytic reducer column for the analysis of NPAH. By this method, the NPAH were separated on the first column, reduced to amino-PAH by the reducer column, and, then, directed to a second column for further separation. This method is intermediate in complexity between semipreparative HPLC and fractionation with Sep-Pak cartridges.

Indoor and Outdoor Concentrations of NPAH

There are no existing data for indoor air with which to compare the concentrations of 1- and 2-NN measured in this study. There are, however, recent data for outdoor air from seven sites in the State of California (Atkinson et al., 1988). These seven sites were selected to represent a broad spectrum of contaminant concentrations. The ranges of concentrations of 1- and 2-NN measured at these sites are compared to the ranges measured in the present study in Table VII-7. When a Southern California site, heavily impacted by motor vehicles, is removed from the data set of the previous study, there is reasonably good agreement between the outdoor concentration ranges for the two studies. Indoor concentrations were notably higher than outdoor concentrations in the present study, with the highest concentrations measured at the site with both cigarette smoke and a wood stove as sources. These high indoor concentrations approached, but were less than the highest concentrations measured at the Southern California outdoor site.

Table VII-7. Comparison of concentration ranges of NPAH between this study and previous study of outdoor air in California.

LOCATION/STUDY	CONCENTRATION RANGE 1-NN (ng/m^3)	2-NN (ng/m^3)
Outdoor air, 7 sites Atkinson et al., 1988	0.02-5.70	<0.02-3.10
Outdoor air, 6 sites [a] Atkinson et al., 1988	0.02-0.81	<0.02-0.61
Outdoor air, 4 sites This study	0.05-0.25	0.03-0.14
Indoor air, 4 sites This study	0.31-2.72	0.19-1.56

a. Motor vehicle impact site omitted.

E. RECOMMENDATIONS

This study demonstrated that an analytical method based on HPLC analysis of fractionated extracts with post-column reduction and fluorescence detection can be used for the analysis of NPAH in indoor air. However, significant problems were encountered due to the complex nature of the samples. Consequently, the method requires further development before it can be reliably used in any large-scale survey of indoor air quality. If the difficulties, which were discussed in detail above, can not be resolved, it will be necessary to explore alternate methods. One possibility would be to use negative chemical-ionization GC-MS, although this method would probably necessitate the compositing of samples to obtain sufficient analyte masses. The method which is finally selected must be specifically validated for use in indoor air because indoor samples are generally more difficult to analyze the outdoor samples. Finally, an interlaboratory comparison, preferably using different techniques, should be conducted to assess the accuracy of the selected method.

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IX. APPENDICES

Appendix A

Lower Limits of Detection (LLD) for Specific PAH Using Selected Methods of Analyses and Detection .

Compound	Picograms Injected			
	HPLC/Fluorescence		GC/FID	GC/MS/SIM
	a	b	c	d
Naphthalene	30	130	-	-
Phenanthrene	130	-	-	-
Anthracene	120	-	-	-
Fluoranthene	40	-	-	-
Benz(a)anthracene	35	0.6	-	-
Chrysene	70	2.3	50	-
Pyrene	75	-	-	-
Benzo(a)pyrene	2.5	-	100	60
Benzo(e)pyrene	45	5.1	-	-
Dibenz(a,h)anthracene	4	-	-	60
Perylene	-	0.6	-	-
Cyclopenta(c,d)pyrene	-	-	-	-
Benzo(b)fluoranthene	3	-	-	30
Benzo(j)fluoranthene	-	-	-	-
Benzo(k)fluoranthene	0.3	-	-	-
Benzochrysene	-	-	-	-
Dibenzo(a,i)pyrene	-	-	-	300
Benzo(g,h,i)perylene	9	-	-	-
Coronene	-	-	200	-
Indeno(1,2,3-cd)pyrene	8	-	-	-

a.) Ogen and Slavin, 1979;
Excitation wavelength = 305 nm; Emission wavelength = 430 nm.
b.) Das and Thomas, 1978;
benz(a)anthracene; Excitation wavelength = 280 nm; Emission wavelength = 389 nm
benzo(e)pyrene; Excitation wavelength = 280 nm; Emission wavelength = 389 nm
c.) Grimmer et al., 1982.
d.) Lawrence and Das, 1986.

Appendix B

Lower Limits of Detection (LLD) for Specific Nitro-PAH Using Selected Methods of Analyses and Detection.

Compound	Picograms Injected		
	HPLC/Fluorescence [a]	GC Thermionic Detection	GC/MS/SIM
9-Nitroanthracene	34	110 [b]	-
1-Nitronaphthalene	4	-	-
2-Nitronaphthalene	14	-	-
2-Nitrofluorene	14 [c]	-	-
2,7-Dinitrofluorene	-	-	-
1-Nitropyrene	10	-	-
2-Nitropyrene	-	-	-
2-Nitrofluoranthene	-	-	-
3-Nitrofluoranthene	-	-	-
8-Nitrofluoranthene	-	-	-
1,3-Dinitropyrene	-	-	-
1,6-Dinitropyrene	10	-	-
1,8-Dinitropyrene	50	-	-
LLD non-compound specific.		36 [d] 50 [e]	

a.) Tejada et.al., 1986.
b.) White et.al., 1984.
c.) MacCrehan at.al., 1988.
d.) Kopczynski, 1987.
e.) D'Agostino et.al., 1983.

Appendix C

Description of Tracer Gas Measurement Method.

Measurements of the building air exchange rate in the residences and commercial buildings were conducted using a tracer gas decay technique. This technique which is described by Offermann (1988), provide the means of non-invasively measuring the actual delivery rate of outside air to specific points in the building. This measurement is called the local ventilation rate and differs from the building nominal or average ventilation rate depending on the flow pattern of outside air to that local zone. We used sulfur hexafluoride, which is a colorless, odorless, non-reactive, harmless tracer gas. A portable gas chromatograph equipped with a sensitive electron capture detector was used to measure tracer concentrations in the range of 10^{-12} to 10^{-9}. The instrument was calibrated before and after each test period using bottled certified standard calibration gases.

The nominal ventilation rate or air exchange rate is defined as the rate at which outside air is delivered to the building divided by the volume of the indoor air space. The nominal ventilation rate is the most frequently cited building ventilation parameter and is commonly used in terms of air changes per hour (ach). The nominal ventilation rate may be computed directly from measurements of the volumetric flow rate of outside air entering the building divided by the volume of the indoor air space.

In buildings where all of the outside air enters through the outside air inlet of the ventilation system, the outside airflow rate is measured using routine air velocity scans across the face of the air inlets. Other potentially significant sources of ventilation, such as duct leakage and infiltration, are not detected with this technique. Using either tracer gas decay or constant injection techniques, the nominal ventilation rate may be computed from the exponential rate constant in the latter part of the test or the inverse of the average age of air in the exhaust airstream. The nominal ventilation rate, N, may also be computed from the steady-state indoor tracer concentration, Css, at the end of a constant injection test.

While the nominal ventilation rate provides information regarding the total amount of outside air entering the building, it provides no information regarding the distribution of outside air within the building. Tracer gas techniques have been employed to measure local

ventilation rates, which reflect the actual delivery rates of outside air to specific indoor locations.

These techniques follow from concepts developed in chemical reactor engineering as applied to building ventilation systems using age distribution theory (Sandberg 1983). Local ventilation rates as reported from a tracer gas decay test are calculated as the reciprocals of the local ages of air :

$$n_i = \frac{C_i(0)}{\int C_i(t)\,dt} = \frac{1}{A_i}$$

where:

n_i = the local ventilation rate at location i (h^{-1}).

$C_i(t)$ = the tracer gas concentration at location i at time t.

$C_i(0)$ = the perfectly mixed initial concentration.

A_i = the local age of air at location i (h).

For a constant tracer injection test, this same equation may be used provided the concentrations are transformed by subtracting the measured concentration data from the final steady-state indoor concentration.

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