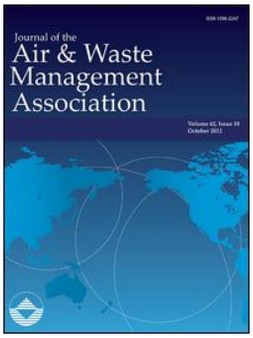

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Results of a Long-Term Study of Vapor Intrusion at Four Large Buildings at the NASA Ames Research Center

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ABSTRACT

Most of the published empirical data on indoor air concentrations resulting from vapor intrusion of contaminants from underlying groundwater are for residential structures. The National Aeronautics and Space Administration (NASA) Research Park site, located in Moffett Field, CA, and comprised of 213 acres, is being planned for redevelopment as a collaborative research and educational campus with associated facilities. Groundwater contaminated with hydrocarbon and halogenated hydrocarbon volatile organic compounds (VOCs) is the primary environmental medium of concern at the site. Over a 15-month period, approximately 1000 indoor, outdoor ambient, and outdoor ambient background samples were collected from four buildings designated as historical landmarks using Summa canisters and analyzed by the U.S. Environmental Protection Agency TO-15 selective ion mode. Both 24-hr and sequential 8-hr samples were collected. Comparison of daily sampling results relative to daily background results indicates that the measured trichloroethylene (TCE) concentrations were primarily due to the subsurface vapor intrusion pathway, although there is likely some contribution due to infiltration of TCE from the outdoor ambient background concentrations. Analysis of the *cis*-1,2-dichloroethylene concentrations relative to TCE concentrations with respect to indoor air concentrations and the background air support this hypothesis; however, this indicates that relative contributions of the vapor intrusion and infiltration pathways vary with each building. Indoor TCE concentrations were also compared with indoor benzene and background benzene concentrations. These data indicate significant correlation between background benzene concentrations and the concentration of benzene in the indoor air, indicating benzene was present in the indoor air primarily through infiltration of outdoor air into the indoor space. By comparison, measured TCE indoor air concentrations showed a significantly different relationship to background concentrations. Analysis of the results show that indoor air samples can be used to definitively define the source of the TCE present in the indoor air space of large industrial buildings.

IMPLICATIONS

Variability of indoor concentrations of VOCs via vapor intrusion from contaminated underlying groundwater is great enough that evaluation of buildings using current screening values based upon vapor intrusion modeling is unlikely to provide accurate assessment of large complex buildings. Direct measurements of indoor air concentrations along with background sampling and meteorological measurements provides a more reliable means of assessing vapor intrusion of VOCs into buildings with large footprints and complicated architecture and heating and ventilation systems.

INTRODUCTION

The National Aeronautics and Space Administration (NASA) Ames Research Center (ARC) and the former Naval Air Station (NAS) Moffett Field are located at the southern end of San Francisco bay, at the northern end of California's Silicon Valley. Portions of the ARC and the former NAS Moffett Field overlie a shallow regional groundwater plume contaminated with halogenated hydrocarbons and petroleum hydrocarbons from the Middlefield-Ellis-Whisman (MEW) and Moffett NAS (i.e., Moffett Federal Airfield [MFA]) superfund sites. The MEW site was the location of some of the original semiconductor manufacturing facilities in California's Silicon Valley. Concerns related to potential vapor intrusion from the regional groundwater plume lead NASA to conduct extensive indoor air investigations to elucidate the nature and extent of potential indoor air contamination.

Numerous measurements of indoor air volatile organic compound (VOC) concentrations using various analytical techniques have been published.[1–12] Some of these data are related to the presence of these VOCs in the indoor air via the vapor intrusion pathway from underlying groundwater.[1,11,12] Most of the vapor-intrusion-related data are for residential homes and small businesses. No data on vapor-intrusion-related indoor air VOC concentrations in large office and/or commercial buildings have been identified in the literature. In additional, although some data are available on the seasonal variability of indoor VOC concentrations, none of these data are related to the seasonal variability of VOCs in the indoor air of large commercial/office buildings.[2,6,8,9]

Because of the paucity of published data related to indoor air contamination in office and commercial buildings via vapor intrusion and the complicated building architecture, direct measurement of indoor air concentrations was selected as the most appropriate method of evaluation, rather than modeling the indoor air concentrations using the Johnson and Ettinger model,[13] which is based on groundwater or subslab soil gas concentrations. The lack of data on commercial buildings affected NASA's sampling plan with respect to the most appropriate time

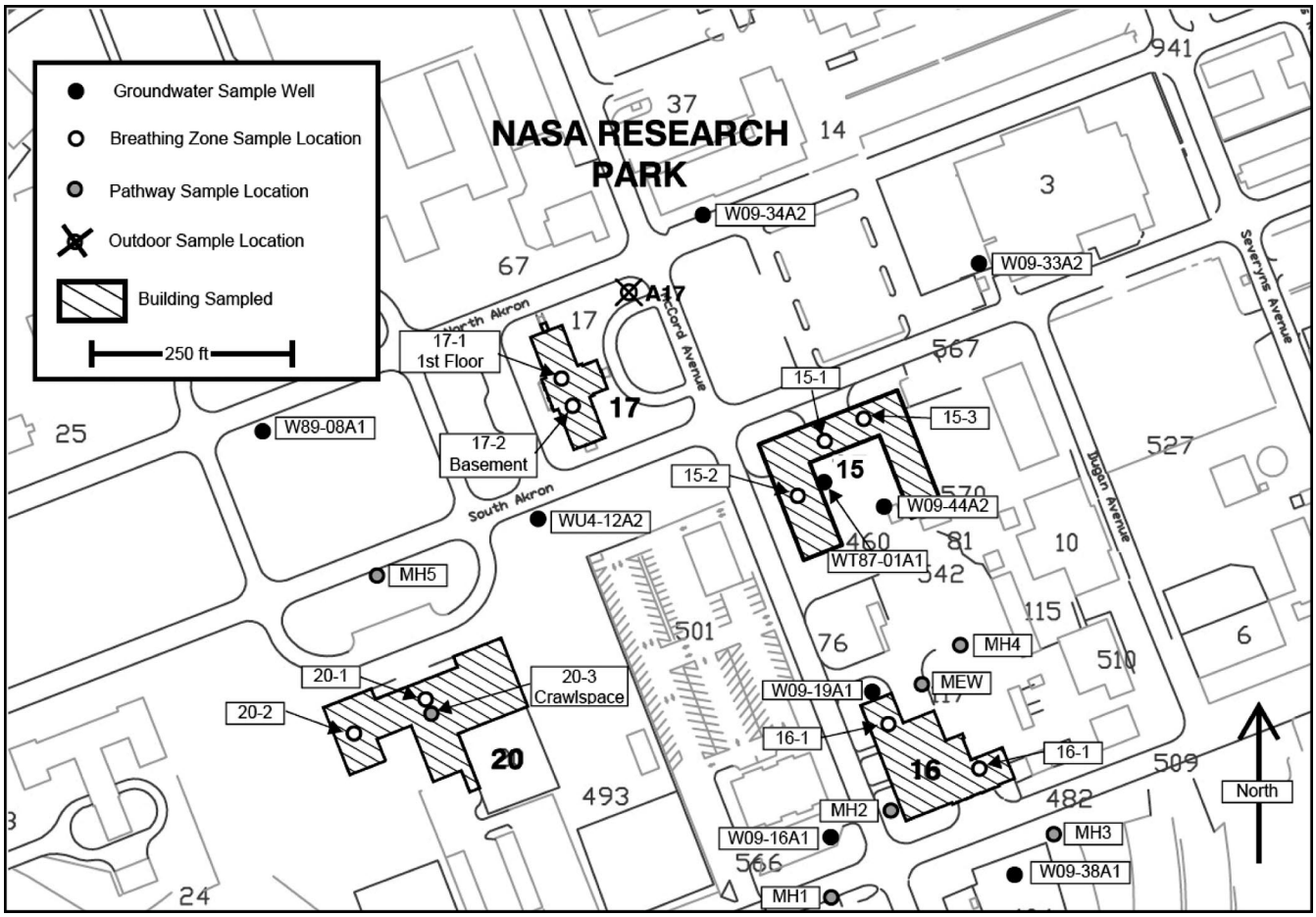

Figure 1. Building and sample locations.

of year to collect indoor air samples from buildings overlying the contaminated groundwater at the NASA site. Therefore, it was decided that for an initial set of buildings, long-term air sampling would be conducted to identify the most appropriate time of year to collect the indoor air concentration variability as well as those environmental factors that might have the greatest effect on the indoor air concentration in the subject buildings.

Site History and Description

The U.S. military continuously operated the NASA MFA from its date of commission in April 1933 as the Sunnyvale NAS until it was transferred to NASA on July 1, 1994. The National Advisory Committee for Aeronautics (NACA) established Ames Aeronautical Laboratory in December 1939 on land adjacent to the Navy at Moffett Field. NASA ARC continues to be the largest federal tenant on the site. No heavy manufacturing or major aircraft maintenance was conducted; mostly unit- and intermediate-level maintenance occurred.

The NASA Research Park (NRP) is an 86-ha (213-acre) roughly triangular site, within the boundaries of the former Moffett NAS, located between the airfield, Highway 101, and the original ARC campus. Current uses in the NRP area include office space, retail and business services, airfield operations, vehicle maintenance, research facilities, and storage, some of which are used by the Army Reserve, Department of Defense Commissary and Exchange, Air Force, and Air National Guard. Most of the buildings on the NRP site are slated for demolition, but few buildings that were part of the original NAS MFA have been designated historical landmarks and will not be demolished. Four of these buildings (15, 16, 17, and 20) were evaluated for potential vapor intrusion of contaminants from the regional plume.

Contaminants detected in the groundwater below the NRP include the solvents trichloroethylene (TCE), perchloroethylene (PCE), 1,1,1-trichloroethane (1,1,1-TCA), methylene chloride (MC), and chloroform; breakdown products of these solvents including *cis*-1,2-dichloroethylene (c-1,2-DCE), *trans*-1,2-dichloroethylene (t-1,2-DCE), 1,1-dichloroethylene (1,1-DCE), 1,2-dichloroethane (1,2-DCA), and vinyl chloride (VC); 1,4-dioxane, which was a stabilizer[14] added to 1,1,1-TCA at a concentration of approximately 3.5%; and the BTEXs—benzene, toluene, ethyl benzene, and xylenes—which are primarily present in the groundwater because of leaks from underground petroleum storage tanks.

EXPERIMENTAL PROCEDURES

Building and Sample Location Descriptions

Samples were collected from four buildings during the course of the study. The locations of the buildings monitored during this study are shown in Figure 1. On Thursday, February 13, 2003, a site visit was conducted to select sample locations within buildings 15 and 17. A second

Table 1. Building description summary.

Building	Structure Level	Approximate Square Footage	Building HVAC System	Sample Locations	Occupancy	Notes
15	First	11,900	Steam, air conditioning	15-1: main wing, 15-2 and 15-3: east wing	24 hr, 7 days per week	Two HVAC zones
16	First	14,900	Steam	16-1: offices, 16-2: wood shop	Monday–Friday	Garage door open during warm months
17	First	3,900	Steam	17-1: first, 17-2: basement	Monday–Friday	Only first floor occupied
	Second	4,900				
	Basement	3,000				
20	First	9,000	Steam	20-1: main entrance, 20-2: west wing	Vacant	Building unoccupied crawlspace 3 ft high
	Second	9,000				
	Crawlspace	6,700				
	Basement	2,300				

site visit, as part of the second phase of sampling, was conducted on October 22, 2003 to inspect Buildings 16 and 20. The general approach to selecting sample locations was to find common areas in each building readily accessible after normal business hours. Care was taken to select locations not influenced by exits, elevator shafts, or mechanical equipment such as pipes or conduits that penetrate the foundation slab. NASA's purpose was to determine as closely as possible the actual exposure to occupants in the building. Thus, sample locations are in the breathing zone, rather than at ground level near pipes or conduits that may penetrate the slab.

Building and sample locations are shown in Figure 1, and relevant building details are summarized in Table 1. The main portion of Building 15 and the west wing contain office space (approximately two-thirds of the available floor area). Heating, ventilation, and air conditioning (HVAC) mechanical equipment and a garage occupy the eastern wing. Building 16 is a historic former locomotive repair facility. The building consists of offices, a wood shop, and a machine shop. Overhead doors in the machine and wood shops are usually left open during business hours during the warmer months. Building 17 is a historic two-story office building with a basement that was originally constructed in 1932–1933 to house the base administrative offices. There is a small crawlspace for mechanical equipment beneath the stairs on the east side of the building. The basement is approximately 6 ft deep; the remaining 2 ft are above ground level. Building 20 is the former Bachelors Officers Quarters (BOQ) and it is currently unoccupied. The foundation for the portion of the building not over the basement is supported on concrete piers approximately 3 ft above ground surface. Concrete blocks enclose the crawlspace thus formed by this part of the building, with occasional ventilation grills through the blocks around the perimeter.

Samples were collected from two outdoor locations: A17 and B258. Location A17 (Figure 1) was near Buildings 15 and 17 and is assumed to be representative of concentrations in air that may be impacted by the groundwater contaminants and regional air concentrations. Background air samples were collected near Building N258 (location B258) on the NASA ARC, which is located upwind from the sampled buildings, approximately 4700 ft northwest of Building 15. Building N258 is known not to overlie the regional groundwater plume and is therefore representative of regional air concentrations. The background samples therefore represent air concentrations to which people at NASA would be exposed in the absence of the underlying contaminated groundwater.

Building Chemical Use Survey

Before commencement of sampling and finalization of the sampling plan, a survey of chemical use in each building was conducted. This survey included use of various commercial and consumer products, equipment and appliances, fabrics and textiles, cleaning supplies, and personal hygiene products. In addition, information on recent building remodeling was obtained. The initial survey was conducted via a query of the Hazardous Materials Information System (HMIS) database. HMIS is a U.S. government database designed to track and locate all hazardous materials used at U.S. government facilities. A walkthrough of each building was also conducted before sampling to verify the results of the HMIS query. No chemicals or products containing the analytes present in the groundwater were identified in the database query or the building walkthrough.

Sampling Events and Frequency

Generally the sampling conducted during this study can be broken into three separate time periods: phase 1 (Buildings 15 and 17) from June 30, 2003 to September 26, 2003; phase 2 (Buildings 15, 16, 17, and 20) from December 1, 2003 to June 23, 2004; and phase 3 (Building 15) from September 7, 2004 to October 28, 2004.

Breathing Zone Air Samples. A combination of 24- and 8-hr samples were collected in Buildings 15 and 17 and location A17. Only 24-hr or sequential 8-hr samples were collected from any given location on any given sampling day (i.e., 24- and 8-hr samples were not simultaneously collected from a given location at any given time). Only 24-hr samples were collected from Buildings 16 and 20 and the background location (B258).

The 24-hr sample collection typically began at approximately 8:00 a.m. and continued until approximately 8:00 a.m. the following day. The first sequential 8-hr sample was typically collected from 8:00 a.m. until 4:00

p.m., the second sequential 8-hr from 4:00 p.m. to 12:00 a.m., and the third sequential sample from 12:00 a.m. until 8:00 a.m.

Indoor and outdoor samples were collected daily during the workweek from Buildings 15 and 17 from June 30, 2003 until September 26, 2003. Sampling was discontinued after September 26, 2003 but recommenced on December 1, 2003. From December 1, 2003 until May 19, 2004, samples (either 24- or 8-hr) were collected 2 days per week from Buildings 15, 17, and location A17. During the month of June 2004, no samples were collected from Building 17, and only 24-hr samples, twice per week, were collected from Building 15 and location A17. For Buildings 15 and 17, each of the two locations within each building and the outdoor location were sampled with three consecutive 8-hr canisters, 1 day per week (except for June 2004). The day of the week was randomly varied over the course of the study.

Only 24-hr samples were collected from Buildings 16 and 20, 1 day per week (Monday–Friday), from two locations in each building, from December 1, 2004 to June 25, 2004. The day of the week was randomly selected, but sampling was conducted on the same day of the week as the Building 15 and/or Building 17 samples.

Background 24-hr samples (location B258) were collected 2 nonconsecutive days per week, randomly selected between Monday and Friday, during the July- to September-sampling period. From December 2003 through the end of June 2004, background samples were collected twice per week on every sampling day.

Groundwater Samples

Groundwater samples were collected in the shallow aquifer (A1 or A2) from wells in the vicinity of Buildings 15, 16, 17, and 20 during June 2003; December 2003; February 2004; March 2004; and June 2004. The locations of the wells are shown in Figure 1.

Sampling and Analysis Methods

Breathing Zone Air Samples. All breathing zone air samples were collected using individually certified 6-L Summa canisters using 24- or 8-hr flow controllers calibrated to collect 5 L of air over the sampling period: approximately 3.5 ml/min for the 24-hr samples and 10.4 ml/min for the 8-hr samples. Except as noted, all canisters were analyzed by the U.S. Environmental Protection Agency (EPA) Method TO-15A in selective ion mode (SIM). Severn Trent Laboratories of Los Angeles, CA (now Test America) and Air Toxics Limited of Folsom, CA, analyzed all samples. The list of chemicals analyzed in these samples is the same as the groundwater samples shown in Table 2, with the exception of xylenes (total). EPA Method TO-15 analyzed for *m*,*p*-xylenes and *o*-xylene.

Groundwater Samples. Samples were collected using downhole pumps or hand bailers. Three well volumes were purged and then, while purging continued, pH, temperature, and conductivity were monitored. Purging continued until the monitored parameters stabilized. Once the monitored parameters stabilized, a sample was collected and placed on ice for shipment to the analytical laboratory. EPA Method 624 was used to analyze the VOCs listed in Table 1.

Meteorological Data

Data from the MFA meteorological station (designated KNUQ, 73°23′59″ north 122°5′59″ west) were acquired for the sampling interval for each day of sampling from the Weather Underground website.[15] Available data included wind speed, barometric pressure, temperature, humidity, wind direction, visibility, and precipitation. Temperature and pressure data during the applicable sampling time interval from this weather station were used for conversions of concentration from parts per billion by volume (ppbv) to micrograms per cubic meter. The wind direction data available from the KNUQ only included the general wind direction (e.g., north-northwest). To evaluate the effect of wind direction on the sample results, wind direction in degrees was necessary. These data for each sampling day during the sampling month were downloaded from the Weather Underground website[16] for the KCMOUNT2 (73°23′21″ north 122°4′42″ west) weather station in Mountain View. KCMOUNT2 is located approximately 1.4 mi west of the KNUQ weather station. All wind roses and meteorological evaluations of ambient concentrations were generated using the daily KCMOUNT2 data.

Table 2. Summary of groundwater sampling results.

Analyte	CAS Number	Number of Samples	FOD (%)	Maximum	Mean	Median	Standard Deviation	Coefficient of Variation
1,1,1-TCA	71-55-6	21	43	10.0	3.622	2.30	2.91	0.803
1,1-Dichloroethane	75-34-3	26	85	45.0	16.0	12.5	13.9	0.867
1,1-Dichloroethene	75-35-4	26	85	39.0	13.6	12.0	10.5	0.777
1,4-Dioxane	123-91-1	26	65	23.0	12.6	11.0	6.36	0.503
cis-1,2-dichloroethene	156-59-2	31	97	3100	395	135	683.9	1.73
trans-1,2-dichloroethene	156-60-5	26	73	24.0	5.04	2.00	7.58	1.50
Tetrachloroethene	127-18-4	26	15	3.80	3.23	3.35	0.655	0.203
Trichloroethene	79-01-6	31	87	1900	485	140	583.5	1.204
VC	75-01-4	31	58	790	144	10.1	258	1.79
Benzene	71-43-2	30	27	2.00	1.11	0.790	0.646	0.582
Toluene	108-88-3	26	3.9	0.330	0.33	0.330	NA	NA
Xylenes (total)	1330-20-7	31	3.2	1.10	1.10	1.10	NA	NA

Notes: All results in μg/L. NA = not applicable.

Data Analysis

Analytes in samples where the reported laboratory analytical detection limit was more than 2 times the maximum detected concentration for any individual analyte were removed from the dataset and not evaluated. Replicate duplicate samples were within ±25% relative percent difference (RPD), and replicate split samples were within ±50% RPD of the primary samples for the analytes of interest.

All *P* values presented with the Mann–Whitney rank sum test, and regression analysis results are a function of the datasets analyzed. For the regression analysis, only those variables with *P* values less than 0.05 were considered significant.

RESULTS AND DISCUSSION

Sampling Summary

Groundwater Samples. Figure 1 shows the locations of the groundwater monitoring wells in the vicinity of the subject buildings. All of these wells are screened in the shallow (designated A1 or A2) aquifers beneath the site. Table 2 summarizes the results of the groundwater samples collected during the study period. A total of 31 samples were collected. A well was considered "associated" with a building if it was within approximately 375 ft of the building. Water level data were also collected from the wells during the study period. Analytical results for the groundwater samples are summarized in Table 2, and the analytical and groundwater level results are presented in Figure 2.

TCE and c-1,2-DCE had the greatest frequency of detection (FOD; 87 and 97%, respectively) and the highest detected concentrations (1900 and 3100 μg/L, respectively). VC was detected in just over half of the samples and had a maximum detected concentration of 854 μg/L. Variability in the maximum concentrations was small (Figure 2a). As described by Vogel[17] and Ferguson and Pietari,[18] c-1,2-DCE is one of the primary anaerobic biotic breakdown products of TCE in groundwater. It is not known to be used in any commercial product or have any other known end use in commerce. Consequently, the presence of c-1,2-DCE in groundwater is solely due to degradation of TCE, and the presence of c-1,2-DCE in indoor air is likely only due to the vapor intrusion pathway. Thus, c-1,2-DCE is a good tracer for the evaluation of the extent to which any of the observed concentrations of

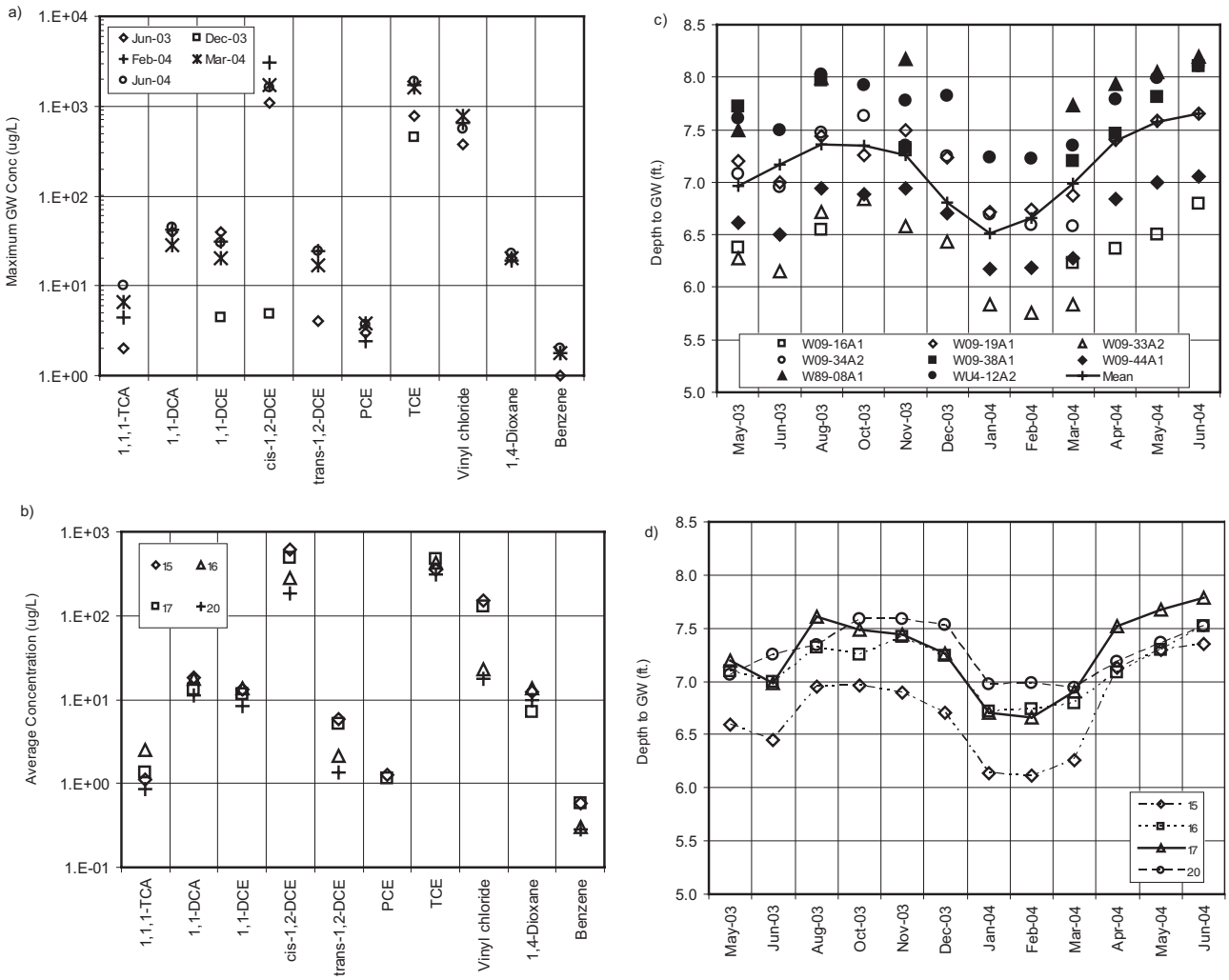

Figure 2. Groundwater analytical results and depth to groundwater levels: (a) maximum detected concentration by month (sample event), (b) average detected concentration by building, (c) monthly groundwater levels by month (sample event), and (d) average groundwater levels for each building by month (sample event).

the groundwater contaminants are present in the indoor air because of vapor intrusion. Another isomer, t-1,2-DCE, can also be formed from the degradation of TCE,[17,18] but the observed groundwater concentrations presented in Table 2 suggest that this is not an important pathway at this site.

Although the presence of the BTEX compounds in groundwater was expected because of their association with former underground storage tanks (USTs), BTEXs were not present at high concentrations or frequency in the wells in the vicinity of the subject buildings (Table 2). Benzene was detected at a maximum concentration of 2 μg/L and was only detected in 27% of the samples. Toluene and xylenes (total) were only detected in one sample, and ethyl benzene was not detected in any sample. On the basis of these groundwater results for the BTEXs, their presence in the indoor air of the subject buildings at significant concentrations because of vapor intrusion from the underlying groundwater was not expected.

Other chlorinated solvents and their associated breakdown products were also detected in the groundwater samples. Solvents include 1,1,1-TCA (as well as 1,4-dioxane, which was a stabilizer added to the commercial solvent) and tetrachloroethylene. Neither of these solvents was detected at elevated concentrations or at high frequencies in the samples collected. Degradation products of 1,1,1-TCA, such as 1,1-dichloroethane and 1,1-DCE, although detected in most of the samples, were ruled out as vapor intrusion tracers because of their lower concentration in the groundwater.

Groundwater elevations for each well are shown in Figure 2c, and average monthly depths during the sampling period in are shown in Figure 2d. Overall, the depth to groundwater was between 5.5 and 8 ft across all of the wells over the sampling period. During the study period, approximately 22 cm of rain fell from December 2003 through March 2004. From April 2004 through September 2004, only 0.3 cm of rainfall were measured. Recharge of the aquifer resulting from this rainfall is clearly reflected in the depth to groundwater data plotted in Figures 2, c and d. Depth to groundwater was generally shallowest for well W09-33A2 (northeast of Building 15; Figure 1) and deepest for well W89-008A1 (west of Building 17; Figure 1). Averaged depth to groundwater was shallowest around Building 15 (Figure 2d).

Air Samples. Over 750 24- and 8-hr primary and replicate (quality assurance) samples were collected from 16 indoor, outdoor, and pathway locations. Results of the quality control replicate samples were acceptable for intralab (replicate duplicate samples, ±25% RPD) and interlab (replicate split samples, ±50% RPD).

Results of the indoor breathing zone samples from the subject buildings and the two outdoor locations are summarized in Table 3. TCE was detected in nearly 100% of indoor air breathing zone samples at an average concentration of 0.895 μg/m^3, in 95% of the outdoor ambient samples at an average concentration of 0.487 μg/m^3, and in 99% of the background samples at an average concentration of 0.614 μg/m^3. c-1,2-DCE was detected in 97% of the indoor breathing zone samples at an average concentration of 0.213 μg/m^3, whereas it was detected in 87.5% of the outdoor ambient samples at an average concentration of 0.05 μg/m^3 and in only 45% of the background samples at an average concentration of 0.04 μg/m^3. These results clearly demonstrate the elevated indoor air concentrations of these two contaminants, presumably as a result of the vapor intrusion pathway. Although the BTEX compounds were not detected at high frequency or at elevated concentrations in the groundwater, they were detected at high frequencies (99–100%) in indoor and outdoor air. Average indoor BTEX concentrations were essentially the same as the average outdoor concentrations. Mean indoor benzene concentrations across all indoor breathing zone locations was 0.85 μg/m^3 (SD 0.69 μg/m^3), and the mean of the all outdoor ambient samples was 1.16 μg/m^3 (SD 0.63 μg/m^3). Background benzene concentrations averaged 1.03 μg/m^3 and were detected in 99% of the samples. Benzene concentrations at residences in Japan[9] showed equivalent indoor and outdoor benzene concentrations, and the measured indoor concentration was attributed to outdoor benzene concentrations and some indoor sources (number of cigarettes and indoor pets) not applicable to the buildings studied at the NASA site. Data on regional outdoor benzene concentrations during the sampling period were not available, but the most recent data collected by the Bay Area Air Quality Management District (BAAQMD) in 2001[19] and 2002[20] at locations within approximately 15 mi of MFA showed average yearly benzene concentrations in the range of 3.2–8 μg/m^3. Fischer, et al.[21] have published data from 1995 for indoor and outdoor benzene concentrations related to traffic density in The Netherlands. In the high-traffic homes the indoor and outdoor benzene concentrations were nearly equal, whereas in the low-traffic homes the indoor benzene concentrations were approximately twice as high as the outdoor concentration. The measured benzene groundwater concentrations, the measured indoor and outdoor concentrations, the lack of identified benzene sources during the building chemical use review, a no smoking policy, and the published data indicate that the benzene concentrations measured in the indoor air at the NASA buildings is entirely from outdoor sources; most likely vehicular emissions.

On the basis of the summary results presented in Table 3 and their implications for discerning the relative importance of the vapor intrusion versus the infiltration pathways for TCE, further analysis of the data is focused on the following primary analytes: benzene (infiltration tracer), c-1,2-DCE (vapor intrusion tracer), and TCE.

With a few exceptions, daily indoor concentrations of TCE in Buildings 15 and 17 were generally greater than outdoor concentrations, and the concentrations in Building 15 were higher than those in Building 17 during all phases of the study. Comparison of the indoor TCE concentrations in Buildings 15 and 17 were statistically different from the outdoor concentrations measured at location B258 (Table 4). These TCE results are in contrast to the c-1,2-DCE and benzene concentrations. Except for the first few weeks of sampling at the beginning of phase 2, the indoor c-1,2-DCE concentrations in Building 17 were greater than those measured in Building 15; the opposite of TCE. There is also much less variability in the outdoor c-1,2-DCE concentrations than that observed for TCE.

Table 3. Summary of SUMMA canister sample results.

Analyte	CAS Number	Number of Samples[b]	FOD (%)	Maximum	Mean[a]	Median	Standard Deviation	Coefficient of Variation
Indoor ambient samples[c]								
1,1,1-TCA	71-55-6	513	99.6	0.248	0.212	0.212	0.258	1.04
1,1-Dichloroethane	75-34-3	513	73.5	0.0472	0.0382	0.0382	0.0304	0.725
1,1-Dichloroethene	75-35-4	513	69.0	0.0311	0.0247	0.0247	0.0326	1.08
1,4-Dioxane	123-91-1	513	0.585	0.281	0.224	0.224	0.016	0.684
cis-1,2-Dichloroethene	156-59-2	541	97.2	0.287	0.223	0.223	0.219	0.746
trans-1,2-Dichloroethene	156-60-5	513	36.6	0.0379	0.0194	0.0194	0.0490	1.17
Tetrachloroethene	127-18-4	541	99.1	0.510	0.323	0.323	0.867	1.69
Trichloroethene	79-01-6	541	99.8	1.69	0.895	0.895	2.33	1.38
VC	75-01-4	541	8.50	0.0210	0.0144	0.0144	0.089	2.26
Benzene	71-43-2	541	100	1.07	0.850	0.85	0.687	0.644
o-Xylene	95-47-6	513	99.8	0.572	0.402	0.40	0.487	0.850
m,p-Xylene	999-99-9	541	99.4	1.80	1.16	1.16	2.73	1.52
Ethyl benzene	100-41-4	513	99.8	0.470	0.343	0.343	0.359	0.763
Toluene	108-88-3	541	99.6	3.46	2.40	2.40	3.93	1.13
Outdoor ambient samples (location A17)								
1,1,1-TCA	71-55-6	113	100	0.856	0.185	0.178	0.0730	0.396
1,1-Dichloroethane	75-34-3	113	20.4	0.123	0.0485	0.0688	0.0197	0.405
1,1-Dichloroethene	75-35-4	113	10.6	0.091	0.0226	0.027	0.00794	0.352
1,4-Dioxane	123-91-1	113	1.77	0.563	0.287	0.1730	0.0390	0.136
cis-1,2-Dichloroethene	156-59-2	128	87.5	0.311	0.0499	0.0323	0.0463	0.929
trans-1,2-Dichloroethene	156-60-5	113	7.08	0.209	0.0353	0.0211	0.0315	0.895
Tetrachloroethene	127-18-4	128	95.3	2.35	0.246	0.145	0.288	1.17
Trichloroethene	79-01-6	128	95.3	6.41	0.487	0.208	0.875	1.80
VC	75-01-4	128	7.81	1.07	0.0348	0.179	0.129	3.70
Benzene	71-43-2	128	100	3.48	1.16	0.946	0.626	0.539
o-Xylene	95-47-6	113	100	2.50	0.611	0.471	0.394	0.644
m,p-Xylene	999-99-9	128	100	8.23	1.98	1.45	1.44	0.728
Ethyl benzene	100-41-4	113	100	1.83	0.503	0.381	0.333	0.662
Toluene	108-88-3	128	100	22.3	3.55	2.55	2.95	0.832
Outdoor background samples (Location B258)								
1,1,1-TCA	71-55-6	68	100	0.307	0.182	0.182	0.0382	0.21
1,1-Dichloroethane	75-34-3	68	17.6	0.318	0.0681	0.17	0.0667	0.369
1,1-Dichloroethene	75-35-4	68	1.47	0.0319	0.0214	0.0165	NA	NA
1,4-Dioxane	123-91-1	68	1.47	723	10.9	723	NA	NA
cis-1,2-Dichloroethene	156-59-2	84	45.2	0.112	0.041	0.0321	0.0249	0.658
trans-1,2-Dichloroethene	156-60-5	68	13.2	0.230	0.039	0.0144	0.0518	1.64
Tetrachloroethene	127-18-4	84	91.7	0.734	0.207	0.162	0.146	0.674
Trichloroethene	79-01-6	84	98.8	6.69	0.614	0.278	1.14	1.83
VC	75-01-4	84	11.9	2.66	0.127	0.732	0.771	0.788
Benzene	71-43-2	84	98.8	2.99	1.034	0.907	0.603	0.578
o-Xylene	95-47-6	68	100	2.08	0.404	0.250	0.392	0.972
m,p-Xylene	999-99-9	84	100	5.66	1.294	0.837	1.21	0.936
Ethyl benzene	100-41-4	68	100	1.12	0.327	0.218	0.279	0.853
Toluene	108-88-3	84	100	9.47	2.972	2.20	2.02	0.679

Notes: All results in $\mu g/m^3$ and calculated based on sample collection temperature and pressure; [a]Nondetect result values at laboratory reporting limit for calculation of mean; [b]Each set of three sequential 8-hr samples was averaged to give one 24-hr concentration and is counted as one sample in above summary; [c]Indoor ambient sample results are for locations 15-1, 15-2, 15-3, 16-1, 16-2, 17-1, 17-3, 20-1, 20-2. NA = insufficient number of detects to calculate.

The difference in the indoor concentrations relative to the outdoor concentration at location B258 is statistically significant (Table 4). For benzene, there are no discernable differences between buildings and between indoor and outdoor concentrations (Table 4). These benzene results are consistent with indoor benzene concentrations resulting primarily (or solely) because of infiltration from outdoor air into the buildings.

Results for Buildings 16 and 20, relative to indoor and outdoor concentrations, for the three primary analytes are similar to those in Buildings 15 and 17.

Differences in the behavior of contaminants present in indoor air primarily because of vapor intrusion from the subsurface versus infiltration of outdoor air into a building are further illustrated in Figure 3. This figure is a plot of daily pairwise results (only measured concentrations at each location for the same sampling time are plotted) of the indoor and background (location B258) TCE and benzene results for Building 15, locations 15-1 and 15-2 (plots for the remaining buildings show similar results). The indoor TCE concentrations (Figure 3a) are all almost always greater than the outdoor concentration

Table 4. Results of statistical comparison of analyte concentrations at sample locations to concentrations at the background location (B258).

Location/Analyte	Test	Results (different/not different)	*P* Value	Number of Samples[a]
15-1				102;68
Benzene	M-W	Not different	0.742	
Trichloroethene	M-W	Different	<0.001	
cis-1,2-dichloroethene	M-W	Different	<0.001	
15-2				126;84
Benzene	M-W	Not different	0.541	
Trichloroethene	M-W	Different	<0.001	
cis-1,2-dichloroethene	M-W	Different	<0.001	
17-1				101;69
Benzene	M-W	Not different	0.239	
Trichloroethene	M-W	Different	0.001	
cis-1,2-dichloroethene	M-W	Different	<0.001	
17-2				105;68
Benzene	M-W	Not different	0.232	
Trichloroethene	M-W	Different	<0.001	
cis-1,2-dichloroethene	M-W	Different	<0.001	
16-1				25;43
Benzene	M-W	Not different	0.334	
Trichloroethene	M-W	Different	<0.001	
cis-1,2-dichloroethene	M-W	Different	<0.001	
16-2				23;43
Benzene	M-W	Not different	0.501	
Trichloroethene	M-W	Different	<0.001	
cis-1,2-dichloroethene	M-W	Different	<0.001	
20-1				24;43
Benzene	M-W	Not different	0.829	
Trichloroethene	M-W	Different	<0.001	
cis-1,2-dichloroethene	M-W	Different	<0.001	
20-2				25;43
Benzene	M-W	Not different	0.809	
Trichloroethene	M-W	Different	<0.001	
cis-1,2-dichloroethene	M-W	Different	<0.001	
A17				128;84
Benzene	M-W	Not different	0.055	
Trichloroethene	M-W	Not different	0.051	
cis-1,2-dichloroethene	*t* test	Different	0.007	

Notes: M-W = Mann–Whitney rank sum test; [a]Number of samples from location;number samples from B258.

(data point above the 1:1 concentration line). Contrast this behavior to that of the benzene data (Figure 3b). The pairwise indoor and background data all cluster around the 1:1 concentration line, which is expected if the source of the indoor contaminant is due to infiltration of the contaminant from the outdoor air. The distance of the plotted pairwise data point above the 1:1 concentration can be interpreted as a measure of the importance of the vapor intrusion pathway relative to infiltration of a contaminant from outside air. Using this interpretation of the data presented in Figure 3, the TCE present in the indoor air is primarily due to vapor intrusion.

Measured indoor air concentration was further investigated by developing multiple linear regression models that accounted for the measured meteorological conditions as reflected in the average daily outdoor air temperature, atmospheric pressure, wind speed, and wind direction. For all eight locations in the four buildings, temperature, wind speed, or both primarily affected the indoor air benzene concentrations. Benzene concentrations at location A17 were primarily a function of temperature and wind speed, whereas the concentrations at location B258 were primarily affected by atmospheric pressure and wind speed. These same four meteorological parameters had little or no effect on the measured TCE concentrations. At five locations (15-1, 15-2, 17-1, A17, and B258) none of the four meteorological parameters had a significant effect on the measured concentrations. At the remaining five locations (17-2, 16-1, 16-2, 20-1, 20-2) the primary meteorological parameters affecting the measured indoor TCE concentrations varied by location. Outdoor temperature and wind speed seemed to have the greatest impact on the greatest number of locations. For the infiltration pathway (benzene) and the vapor intrusion pathway (TCE), this can be because of building depressurization (wind speed), the stack effect because of heating (temperature), or the use of natural ventilation (temperature and wind speed). However, it would appear that over the range of meteorological conditions measured during the study period, infiltration of benzene from the outdoor air was more affected by the meteorological conditions than vapor intrusion of TCE from the subsurface.

One of the initial objectives of this study was to determine if there were any seasonal variations in the measured indoor concentrations. Monthly benzene,

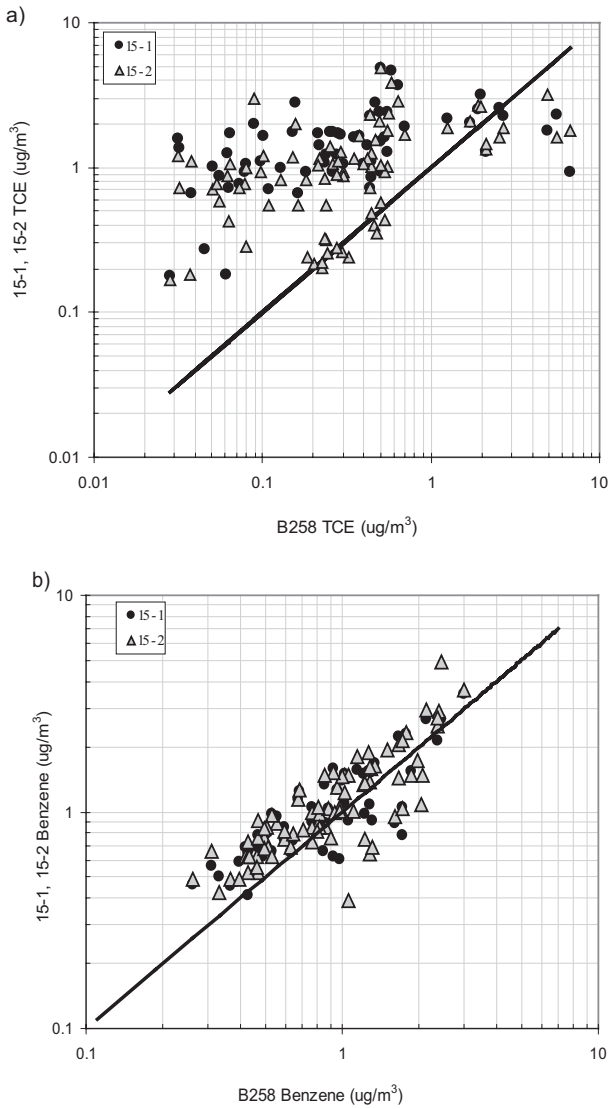

Figure 3. Pairwise daily result scatterplots of indoor air concentrations vs. background sample location concentrations: (a) Building 15 TCE, and (b) Building 15 benzene.

c-1,2-DCE, and TCE results for Buildings 15 and 17 were evaluated. Concentration data by month and season for Buildings 16 and 20 were not evaluated because of the insufficient number of samples. All three primary analytes at all locations display variation in the monthly concentration data. Box plots for the TCE and benzene results for location 15-1 are provided in Figure 4. Generally, concentrations of the benzene and TCE were highest (in some cases by an order of magnitude) during December, January, and February and lowest during June, July, and August. The months when the highest concentrations were measured typically correspond to the months with the shallowest depth to groundwater (Figure 2) and the lowest average monthly outdoor air temperature. Conversely, the monthly concentrations were lowest when the depth to groundwater and the average monthly outdoor air temperature were greatest. Attempts were made to fit the air concentration, average monthly air temperature, and groundwater level data to multiple linear regression models, but because of the limited number of months when groundwater level data were available, the power of these models was insufficient to establish significant relationships between these three parameters.

Review of Figure 4 reveals that the monthly benzene data showed very similar patterns for the indoor concentrations and the two outdoor locations. As already discussed, the measured indoor benzene concentrations are primarily, if not exclusively, due to infiltration of outdoor air; thus, the similarity of the indoor and outdoor monthly profiles is not surprising. Overall, the monthly TCE data show greater variability than the corresponding benzene data, with median concentrations tending to be higher during the winter months. The higher winter concentrations and the pattern of the median concentrations are similar to the total VOC results reported by Schlink et al.[6] for residences in three German cities between 1994 and 1998.

As previously mentioned, a walkthrough of the buildings and review of authorized solvent and toxic substances was conducted before sampling. No uses for TCE or PCE were authorized. All of the buildings sampled were utilized for general or research office space and computer facilities. There were no manufacturing or maintenance facilities in any of the buildings. Review of commercial products reveals only limited uses of solvents such as TCE (e.g., gun cleaners). Samples were collected 5 days per week for many weeks at most of the indoor locations discussed. If unauthorized products containing any of the subject halogenated solvents (TCE and PCE) were used, it would be expected that spikes in the measured concentrations would have been detected. As an example, 1,4-dichlorobenze concentrations were measured (but not reported herein) in samples during the early portions of the study. Over a 2-week period, elevated concentrations of 1,4-dichlorobenzene were observed in samples collected from location 17-1. Further investigation revealed that a graduate student who had just accepted a position had temporarily stored clothes in an office adjacent to the sample location. The clothing had been stored with mothballs, the primary ingredient of which is 1,4-dichlorobenzene. As soon as the clothing was removed, the measured concentration of 1,4-dichlorobenzene reverted to levels measured before the beginning storage period. Further evidence of the lack of indoor TCE sources can be seen in Figure 5. Most building occupants in Building 15 worked from approximately 8:00 a.m. to 5:00 p.m. If TCE was present in the indoor air because of indoor sources (via vapor intrusion), the concentrations measured from 8:00 a.m. to 4:00 p.m. would be elevated relative to the 4:00 p.m. to 12:00 a.m. samples. This is not the case. Additional evidence is found in the c-1,2-DCE results. c-1,2-DCE can only be present in the indoor air because of vapor intrusion because it is a breakdown product of TCE in groundwater and is not used or present in solvents. Comparison of the TCE and c-1,2-DCE results for locations 15-1 and 15-2 show similar diurnal trends. If TCE was present in the indoor air because of indoor sources, the diurnal patterns for the sequential 8-hr Summa canister samples would be different.

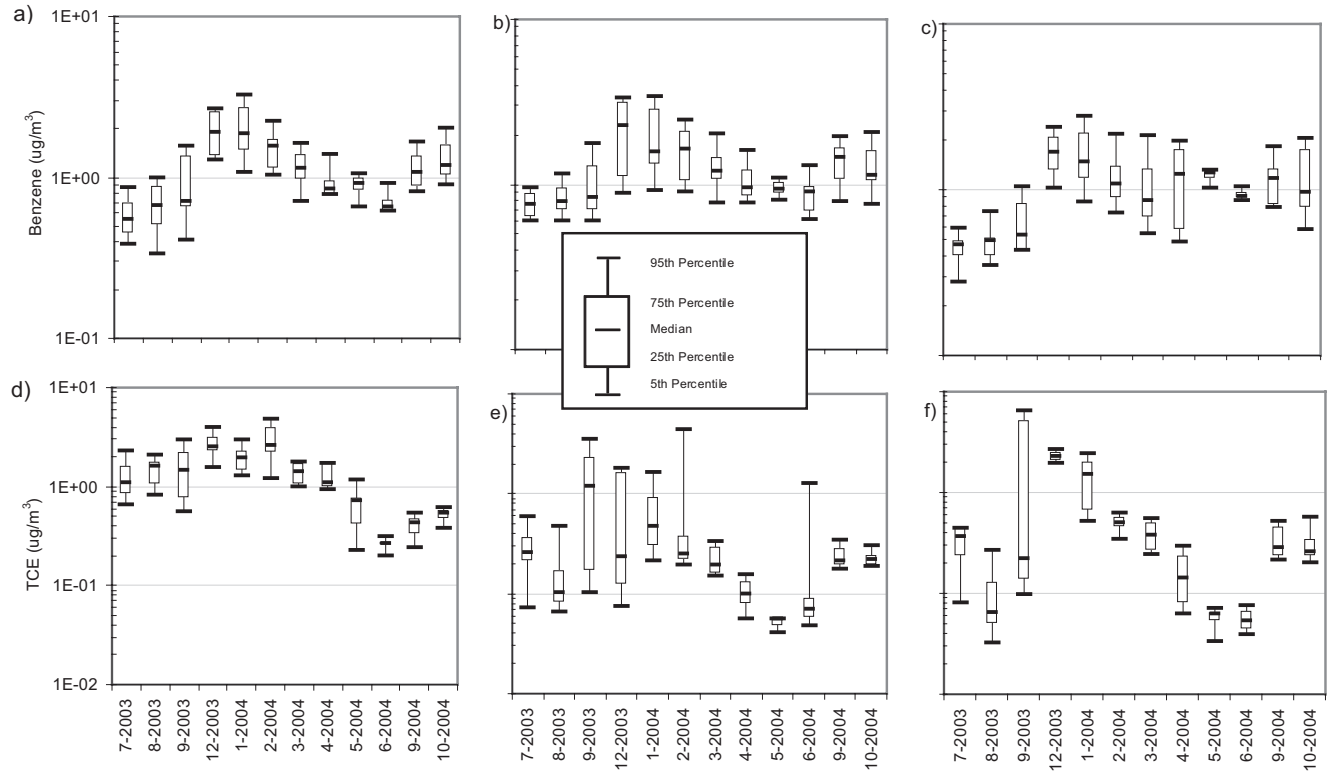

Figure 4. Box plots of monthly data by analyte and location: (a) 15-1 benzene, (b) A17 benzene, (c) B258 benzene, (d) 15-1 TCE, (e) A17 TCE, and (f) B258 TCE.

8-hr Air Samples. Sequential 8-hr samples were collected to evaluate diurnal variability in indoor air concentrations. Results of the 8-hr sampling in Buildings 15 and 17 and outdoor location A17 during phase 1 of the study are shown in Figure 5 for TCE, c-1,2-DCE, and benzene for Building 15. Only data in which samples were successfully collected from all three canisters in the sequence are presented; for example, if the second of the three canister samples was not analyzed because the canister went to ambient pressure at the end of the sample period, data from the other two canisters in the sequence (the first and third canisters) are not included.

For the two analytes present in the indoor air primarily or exclusively because of vapor intrusions, TCE, and c-1,2-DCE, the general trend was that the median concentration in the first canisters (8:00 a.m. to 4:00 p.m.) were less than the median concentration in the second canister (4:00 p.m. to 12:00 a.m.), which was less than the median concentration in the third canister (12:00 a.m. to 8:00 a.m.). These results can be explained by consideration of building ventilation (HVAC, steam heat, or natural ventilation), atmospheric stability, and occupancy. During the time when the first canister was collected, the buildings occupied during the course of normal working hours and ventilation would have been at or near their maximum for comfort purposes. This would result in the greatest perturbation of the indoor atmosphere, resulting in the lowest concentrations. The results for TCE and c-1,2-DCE at location A17 also show the same trend; indicating that the more unstable daytime atmosphere also resulted in the lowest measured concentrations. During the second and third collection period in the sequence, the buildings would have been mostly unoccupied or lightly occupied, necessitating lower ventilation for comfort purposes. This would then result in the higher observed indoor concentrations. The outdoor concentrations at location A17 are also slightly higher during the second and third collection periods because of less perturbation of the atmosphere during these time periods.

Contrast these results with those observed for benzene. For benzene, the measured median concentrations in the first and third canisters were higher than the second canister. Benzene is present in the indoor air as a result of infiltration from the outdoor air. If it is assumed that the benzene in the outdoor air is a result of emissions from mobile sources (i.e., motor vehicles), then the observed indoor and outdoor benzene concentrations can be explained by consideration of vehicle traffic patterns. The first canister sample would have captured air concentrations during the morning and evening rush hour, the second sample would have captured air during the evening rush hour, and the third sample would have captured air resulting from the morning rush hour. Because the atmosphere would be more stable during the morning rush hour, it would be expected that the benzene concentration during the morning rush hour would be higher than the evening rush hour, when the atmosphere is well mixed because of heating of the Earth's surface throughout the day. The measured benzene concentrations are consistent with this hypothesis. In a study of benzene concentrations in indoor and outdoor air in low- and high-floor apartments in high-rise apartment buildings in Korea, Jo et al.[4] also observed elevated benzene levels during the nighttime monitoring period. Although smoking appeared to be a significant contributor

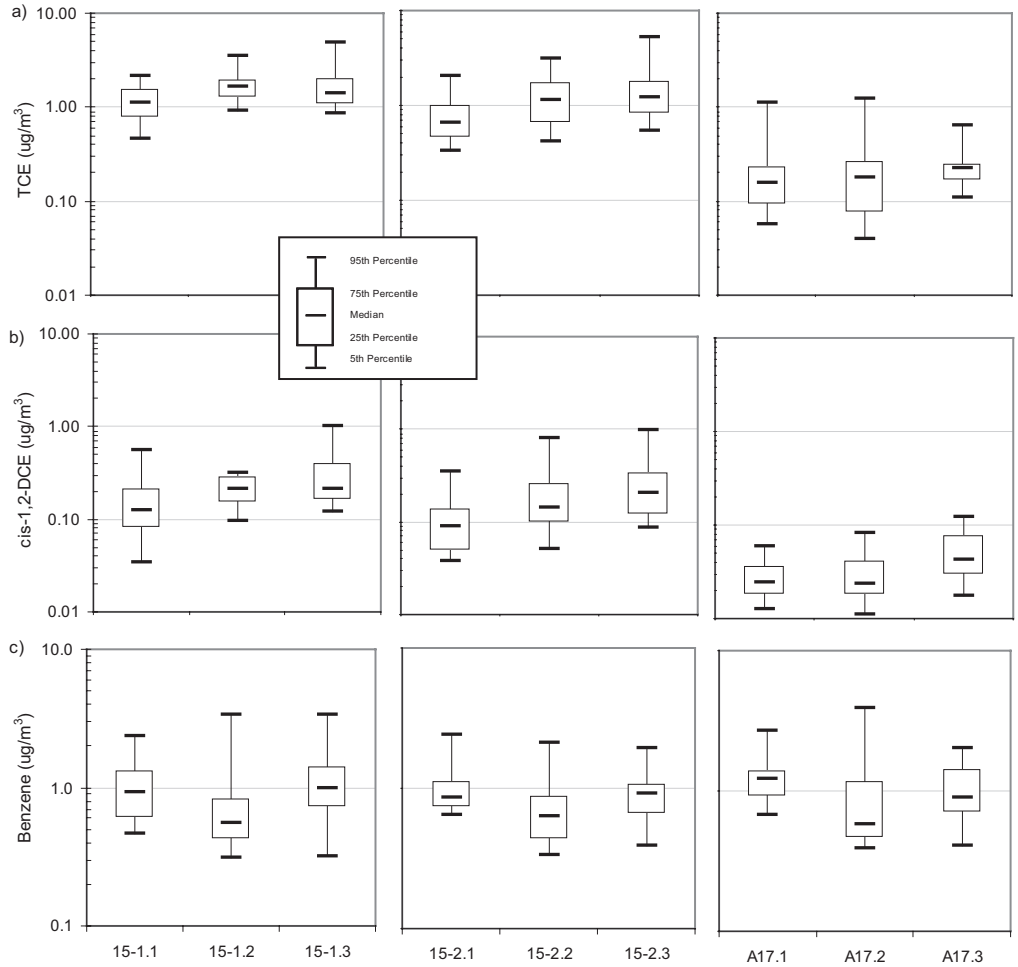

Figure 5. Box and whisker plots for sequential 8-hr samples: (a) TCE, (b) c-1,2-DCE, and (c) benzene.

to the observed indoor benzene concentrations, the authors concluded that there was a contribution from heavier vehicular traffic during the nighttime monitoring events.

CONCLUSIONS

Monthly seasonal variability analysis showed that the indoor air concentration in the four subject buildings was highest in the winter and lowest during the summer months. The empirical evidence presented shows that the measured indoor air concentration was related to the outdoor air temperature and the depth to groundwater. Although there appears to be diurnal variation in the concentrations of the primary analytes, as measured by the sequence of three 8-hr samples, the overall differences during the day are small and do not change the overall conclusions drawn from the 24-hr canister samples. Day-to-day variation over 1 month of sampling generally only varied by a small amount, typically a factor of approximately 2.

In two of the buildings sampled, Buildings 15 and 20, the results from both locations were similar throughout the sampling period, whereas the results for both locations in Buildings 16 and 17 were different between the sample locations. This was expected for the locations in Building 17, because one sample was collected from the first floor and the other from the basement, but it was an unexpected result for the two locations in Building 16.

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