

JV TASK 86 – IDENTIFYING THE SOURCE OF BENZENE IN INDOOR AIR USING DIFFERENT COMPOUND CLASSES FROM TO-15 DATA

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DIFFERENT COMPOUND CLASSES FROM TO-15 DATA**

ABSTRACT

Volatile organic compound (VOC) data that had already been collected using EPA method TO-15 at four different sites under regulatory scrutiny (a school, strip mall, apartment complex, and business/residential neighborhood) were evaluated to determine whether the source of indoor air benzene was outdoor air or vapor intrusion from contaminated soil. Both the use of tracer organics characteristic of different sources and principal component statistical analysis demonstrated that the source of indoor air at virtually all indoor sampling locations was a result of outdoor air, and not contaminated soil in and near the indoor air-sampling locations. These results show that proposed remediation activities to remove benzene-contaminated soil are highly unlikely to reduce indoor air benzene concentrations. A manuscript describing these results is presently being prepared for submission to a peer-reviewed journal.

TABLE OF CONTENTS

LIST OF FIGURES i

LIST OF TABLES i

EXECUTIVE SUMMARY ii

INTRODUCTION 1

EXPERIMENTAL APPROACH..... 2

RESULTS AND DISCUSSION..... 3

CONCLUSIONS..... 4

MANUSCRIPT.....Appendix A

LIST OF FIGURES

1 Classes of organics in urban air (from TO-15) 5

2 Single ratio plots (Freon 11/benzene) for indoor air, outdoor air, contaminated soil gas, and uncontaminated soil gas at each of the four sites 6

3 Representative double ratio plots for the four sample sites 7

4 Principal component analysis for the four sites 8

LIST OF TABLES

1 Principal Component Factors for the Plots Shown in Figure 4..... 9

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EXECUTIVE SUMMARY

The contribution of petroleum- and manufactured gas plant (MGP)-contaminated soils to indoor air benzene concentrations is often studied by soil gas measurements and modeling. Unfortunately, this approach tends to ignore the contribution of outdoor ambient air to indoor benzene concentrations. In addition, the conventional approach ignores several organic compounds that represent different sources that are measured by the EPA analytical method TO-15 for determining volatile organic compounds (VOCs) in ambient air. Such compound classes (e.g., chlorinated hydrocarbons, alkanes, oxygenated organics) can be fingerprinted for different potential sources of benzene in indoor air and, therefore, have good potential to be used to determine the relative contributions of outdoor air and soils contaminated with petroleum or MGP materials to indoor air benzene. In this study, we used existing TO-15 data for indoor air, outdoor air, and soil gas that were collected at four sites (a school, strip mall, apartment complex, and business/residential neighborhood) that were under regulatory scrutiny based on suspected indoor air benzene resulting from vapor intrusion from soil contaminated by former MGP activities. Two approaches were used to investigate the source of indoor air benzene, whether it was most likely a result of outdoor air or soil vapor intrusion. First, organic compounds commonly found in air known to be from different sources were used to generate ratio plots with benzene. The ratio of tracers for other sources of air pollutants to benzene demonstrated that contaminated soil gas vapor was not related to indoor air benzene nearly as strongly as outdoor air to indoor air benzene. In fact, the results show that soil gas organics in uncontaminated soils (especially shallow soils) are likely from outdoor air, similar to the results for indoor air. While this approach was based on knowledge of air chemistry (or “chemical common sense”), an entirely independent approach based on principal component analysis (PCA) also demonstrated that outdoor air was the likely source of indoor air benzene rather than vapor intrusion from soil gas. These two independent approaches to forensic source apportionment both agreed that outdoor air was responsible for indoor air benzene, and not contaminated soil. Therefore, it is highly unlikely that proposed remediation activities to remove contaminated soil will result in lower indoor air concentrations at the four sites studied.

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INTRODUCTION

Benzene is commonly found in indoor air at a few micrograms per cubic meter. However, the source of benzene is often unclear. In buildings where the influence of petroleum or other sources of hydrocarbons (such as manufactured gas plant [MGP] sites) is suspected, the majority of sampling efforts have focused on comparing indoor air concentrations of benzene to soil gas benzene concentrations. Sophisticated modeling is also applied to determine the potential impact of subsurface benzene on shallow soil gas and indoor air benzene.

These approaches tend to ignore both fundamental air chemistry and practical considerations related to source apportionment for indoor air benzene. These considerations include the following:

1. The rate of exchange of outdoor air with indoor air is normally much higher than the exchange of soil gas with indoor air.
2. Concentrations of benzene in indoor air are very often similar to those in outdoor air.
3. Soil breathes. The composition of soil gas collected just below or adjacent to the floor of a building often has a hydrocarbon distribution similar to ambient outdoor air. Thus benzene in soil gas samples may come from outdoor air.
4. Ambient air has several classes of organic compounds that are not related to petroleum or MGP materials. These compound classes can be used to investigate the source of benzene in indoor air.
5. Most studies use TO-15 (or similar) data, but only consider the benzene results. TO-15 can provide air concentrations of ca. 60 different organic compounds from several different compound classes that are indicative of different sources [1].

The essential problem with determining the source of benzene in indoor air is the fact that there are many different potential sources of benzene. Our approach is based on the nonbenzene organic chemical compositions of various sources of benzene in indoor air. In essence, potential sources of benzene have different compound class signatures: either the *presence* of certain organic compounds or the *absence* of certain compounds. For example, both petroleum products and MGP tars can emit large amounts of benzene and alkylbenzenes into air. However, MGP materials emit little or no amounts of alkanes (compared to aromatics emitted), while petroleum products emit much higher relative amounts of alkanes (compared to aromatics emitted). Thus, relatively high amounts of alkanes (compared to benzene) in an air sample indicate a petroleum source, while the relative absence of alkanes (compared to benzene) indicates an MGP source.

The chemical stew gets more complex for typical urban air. As shown in Figure 1, outdoor air typically contains hydrocarbons from petroleum fuels and vehicle exhaust, common

halogenated solvents and freons, as well as other compounds that are not related to petroleum or MGP materials. Indoor air is even more complex since it typically includes all the organic compounds found in outdoor air, as well as “personal use” organics related to smoking (e.g., nicotine), beauty products (e.g., acetone), and food (e.g., ethanol), as well as construction material emissions (e.g., formaldehyde).

While indoor air generally reflects outdoor air with the added personal use compounds just discussed, soil gas can range in composition from being essentially the same as outdoor air to being primarily influenced by soil (and groundwater sources) ranging from petroleum and MGP hydrocarbons to chlorinated solvents from a variety of sources such as dry cleaning stores. In essence, soil gas composition can range from being the same as outdoor air to being dominated by organics in contaminated soil or groundwater.

In this study, we collected TO-15 data from four different sites where indoor air benzene was suspected to come from soil contaminated by former MGP activities. Approximately 20 different organic compounds were detected in the majority of samples from each site. These concentration data were evaluated using both “chemical common sense” regarding different sources indicated by different compound classes and based on principal component analysis (PCA) of the same data sets to determine the statistical relationship of the various outdoor air, indoor air, and soil gas samples.

EXPERIMENTAL APPROACH

TO-15 data were obtained from four different sites where MGP hydrocarbons are suspected of being the source of benzene in indoor air. One site was a school in a residential area, the second was an apartment complex, the third was a mixed residential and commercial (small business) neighborhood, and the fourth was a strip mall. For the last two sites, samples were collected in a variety of different businesses representing a very broad range of activities including an auto body shop, post office, bakery, appliance dealer, beautician’s shop, bar/grill, pizzeria, as well as other activities. Each site included representative indoor air, outdoor air, and soil gas samples. The volatile organic compounds (VOCs) that were detected in the majority of samples from all four sites were compared using single ratio plots (test VOC concentration divided by benzene concentration vs. benzene concentration) and double ratio plots (first test VOC divided by benzene vs. second test VOC vs. benzene). Test compounds for the plots were selected based on different compound class sources, as shown in Figure 1. This approach essentially relies on an understanding of basic VOC chemistry and source profiles.

A second entirely different approach that is based solely on statistical analysis utilized PCA, a standard statistical technique that combines the various VOC concentrations with the goal of reducing the variance between all of the different air samples. PCA analysis does not “know” whether the sample is soil gas, indoor air, or outdoor air. Therefore, if the results of PCA analysis groups the soil gas and indoor air together, then indoor air is highly influenced by soil gas. Conversely, if the PCA analysis groups outdoor and indoor air together, then outdoor air is primarily responsible for the VOCs in indoor air. Data were analyzed using multivariate statistics in SAS[®] (SAS Institute, Cary, North Carolina). Analytes dominated by data below the reporting limit (nondetect) are removed from the data set prior to analysis. In addition, samples containing

nondetect values that exceeded the detected values are removed from the data set because the nondetect values contain no information about the analyte distribution in the air sample. Concentrations are transformed to rank values in SAS using mean values for ties. PCA is done on the correlation matrix of the ranked TO-15 data to determine whether the variability in the data set can be accounted for by a substantially smaller number of principal components. PCA results are evaluated graphically to determine whether PCA can adequately discriminate indoor, outdoor, and soil gas air samples.

RESULTS AND DISCUSSION

TO-15 data were obtained from four sites thought to be impacted by proximity to former MGP activities. At each site, parallel indoor, outdoor, and soil gas air samples were obtained, and the results for all organics reported by TO-15 were obtained. For the majority of organics, nondetects in most samples eliminated those compounds from the data set, resulting in ca. 15 to 20 organics being available for the source apportionment studies at each site.

Examples of the compound classes which have the potential to differentiate various sources of air organics are shown in Figure 1. Generally speaking, urban air contains a mix of organics from all sources of human activity including petroleum products and their combustion residues, halogenated solvents and freon refrigerants and propellants, oxygenates from fuels, as well as some general oxygenated solvents. Indoor air typically contains the same organic mix as nearby outdoor air, with the addition of organics emitted by personal activities such as ethanol, isopropyl alcohol, and acetone. The presence (as well as absence) of different compound classes can be used to help determine the likelihood of different sources to benzene in an air sample. For example, if petroleum is the ultimate source of benzene in an air sample, the air sample should contain other major petroleum organics including some of the other volatile aromatic organics (e.g., alkyl benzenes) as well as petroleum alkanes such as isopentane. In contrast, if MGP products are responsible for benzene in an air sample, even though the distribution of benzene and other alkyl benzenes may look similar to a petroleum source, the *lack* of alkanes would indicate an MGP, and not a petroleum source. Halogenated organics such as freons are neither MGP nor petroleum hydrocarbons, but are ubiquitous in urban air. Therefore, the proportion of benzene to freons in indoor air should be similar to that in outdoor air, if outdoor air is the source of the indoor benzene. In contrast, if the indoor benzene is from soil gas (e.g., contaminated with petroleum or MGP products), then the relative proportion of benzene to freons should be much higher, since neither petroleum nor MGP contaminants should contribute freons to the air.

The use of single ratio plots is shown in Figure 2 with Freon 11 being used as the tracer compound. Freon 11 is ubiquitous in urban air. For the school, strip mall, and business/residential neighborhood, the single ratio plots clearly demonstrate that all indoor air, outdoor air, and uncontaminated soil gas cluster together and, therefore, have a common source of benzene (e.g., vehicle exhaust in outdoor air). All elevated soil gas concentrations are clearly differentiated with the single ratio plots. Thus the single ratio plots demonstrate that the most likely source of indoor air benzene is outdoor air, and not contaminated soil gas. For the apartment complex, there were only slightly elevated benzene concentrations in indoor air and soil gas. Therefore, the indoor air, outdoor air, and soil gas samples also cluster fairly closely in the single ratio plot (note the expanded scales for this site).

The use of double ratio plots is shown in Figure 3 by incorporating ratios of benzene with the Freon 11 (ubiquitous in urban air) and the gasoline (and vehicle exhaust) tracer, isopentane. Similar to the single ratio plots in Figure 2, the double ratio plots in Figure 3 show that indoor air, outdoor air, and uncontaminated soil gas all have a similar source (outdoor air), while the contaminated soil gas are substantially different. Therefore, the best explanation for indoor air benzene is again outdoor air, not contaminated soil gas vapor intrusion. As before, since there is no elevated soil gas benzene for the apartment complex site, all indoor air, outdoor air, and soil gas data cluster together, indicating a common source (outdoor air).

The approaches in Figures 2 and 3 rely on an in-depth knowledge of air chemistry and the source of various compound class sources of VOCs. In contrast, the PCA statistical analysis requires no chemical knowledge or “common sense” but, rather, relies on pure statistical analysis of the data. Since no information as to the type of air sample (whether indoor air, outdoor air, or soil gas) is used in the PCA, any resultant grouping of the results based on the type of air sample demonstrates a relationship between those particular air samples. As shown in Figure 4, virtually all soil gas samples group together apart from the indoor air and outdoor air samples, while the indoor and outdoor air samples overlap. Therefore PCA analysis demonstrates that there is a much stronger relationship between outdoor air and indoor air than there is between soil gas and indoor air.

CONCLUSIONS

The contribution of outdoor air to indoor air benzene is frequently ignored, even though indoor and outdoor benzene concentrations are often very similar, and even though buildings typically exchange their air with outdoor air at least one time per hour. Based on our studies to date, the use of organic compounds that are indicative of different sources of benzene should be useful for determining the relative contributions of outdoor air and soil gas to indoor air benzene.

Given the facts that 1) indoor and outdoor air benzene concentrations were very similar, 2) the single and double ratio plots with the tracer organics clearly show that contaminated soil gas is not related to indoor air, and 3) the PCA statistical analysis shows that soil gas is substantially different than indoor or outdoor air, but that indoor air and outdoor air are quite similar, we conclude that the major source of benzene in indoor air is outdoor air and can further conclude that any attempts to reduce indoor air benzene by reducing soil gas intrusion or by removing contaminated soil will be fruitless.

REFERENCES

[1] *Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, 2nd Edition*; Method TO-15, EPA/625R-96/010b, Jan 1999.

Halogenated (and freons): Some are ubiquitous, and some are from local sources. None is petroleum or MGP hydrocarbons.

BTEX and volatile PAHs come from MGP, petroleum, and solvents (paints, etc.).

Alkanes and cyclic alkanes are mostly from petroleum products and vehicle exhaust, but not MGP.

Some oxygenates (e.g., ethanol, acetone) are indicative of personal activities.

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Figure 1. Classes of organics in urban air (from TO-15).

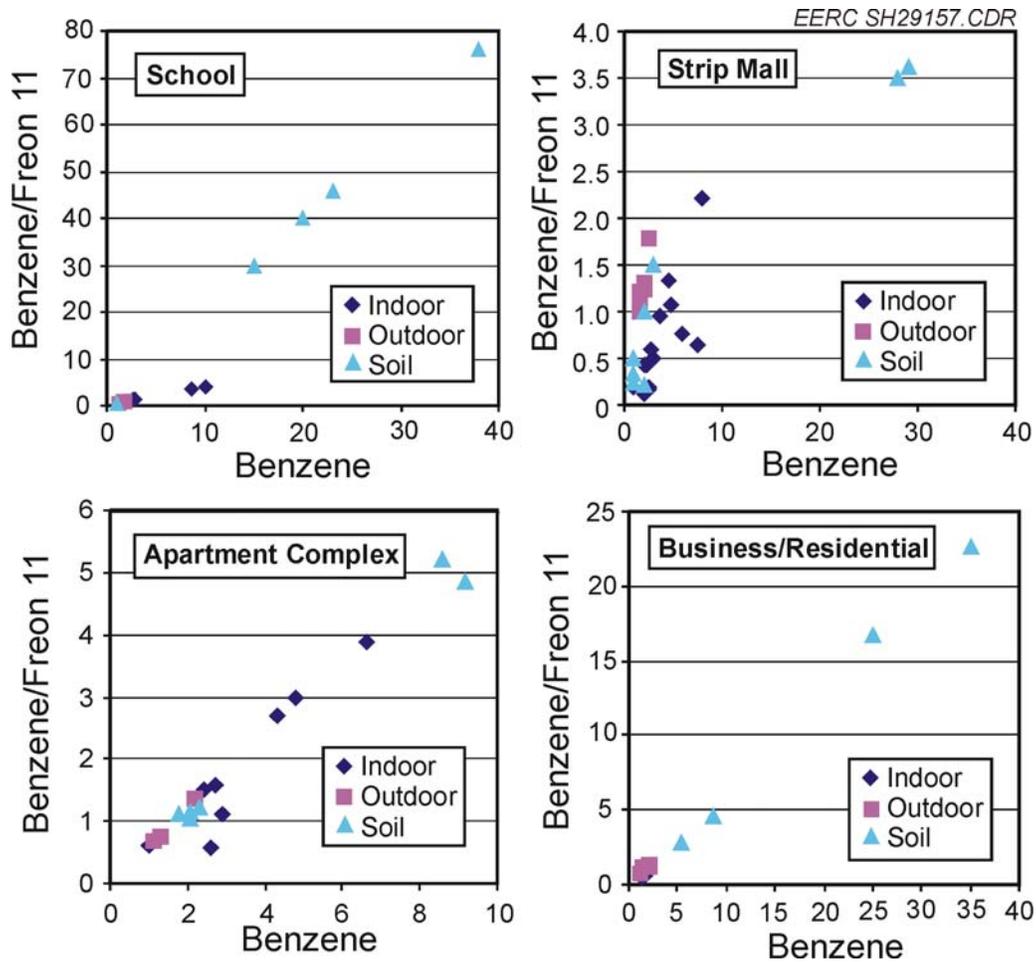


Figure 2. Single ratio plots (Freon 11/benzene) for indoor air, outdoor air, contaminated soil gas, and uncontaminated soil gas at each of the four sites.

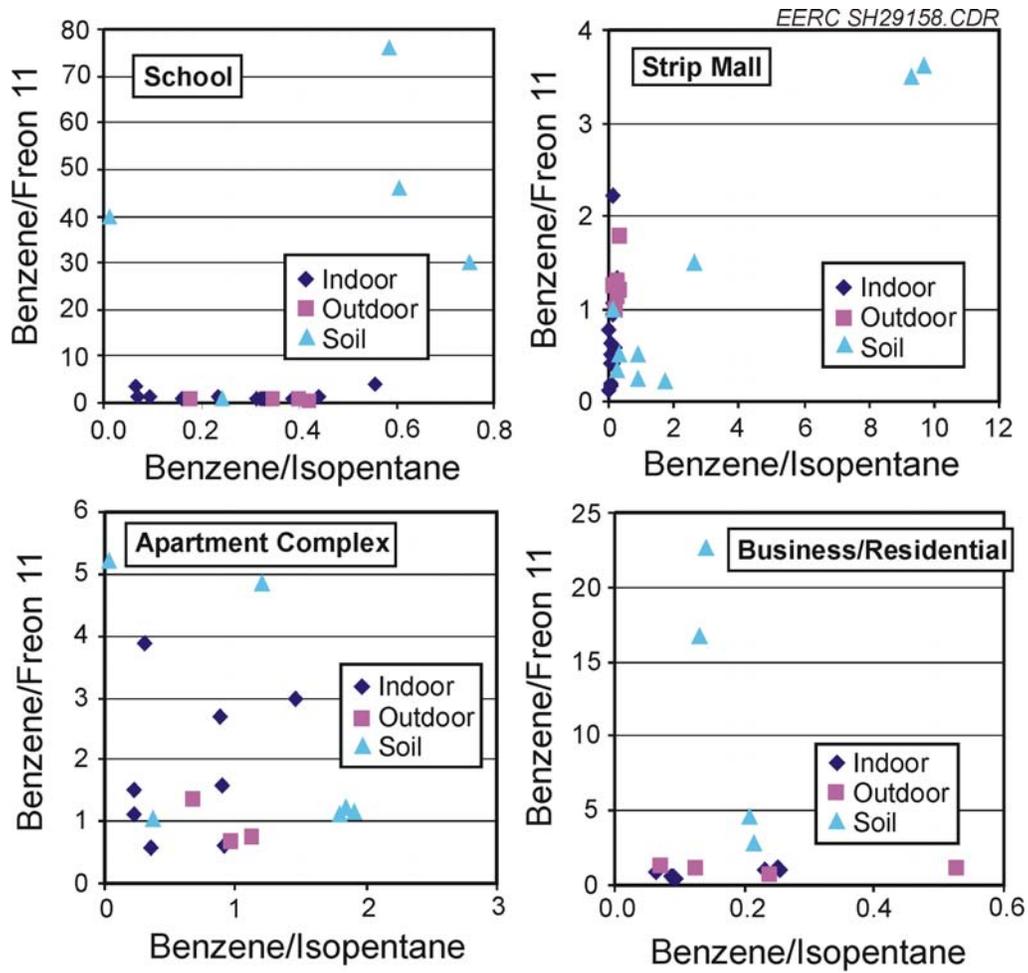


Figure 3. Representative double ratio plots for the four sample sites.

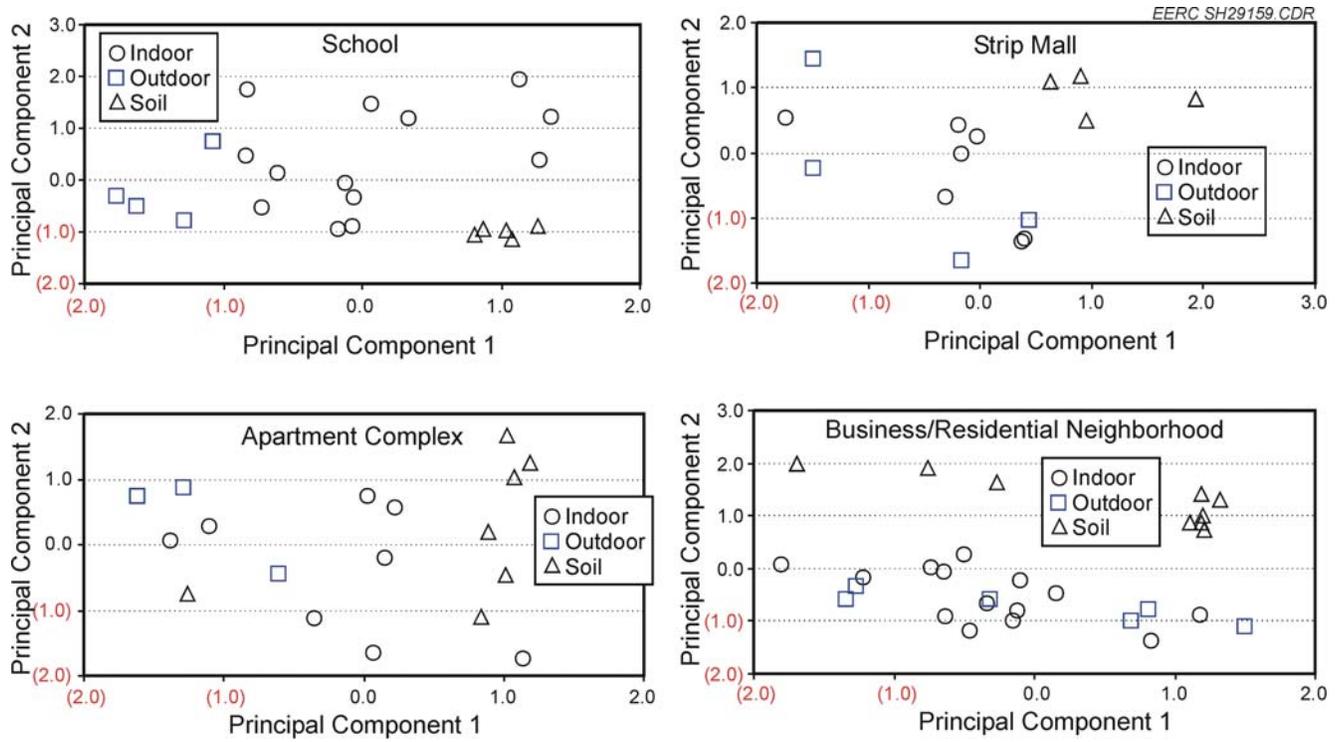


Figure 4. Principal component analysis for the four sites. The factors determining each principal component are given in Table 1.

Table 1. Principal Component Factors for the Plots Shown in Figure 4

Compound	School		Strip Mall		Residential/Business		Apartment Complex	
	Factor1	Factor2	Factor1	Factor2	Factor1	Factor2	Factor1	Factor2
<i>aromatics</i>								
benzene	0.71	-0.09	0.33	-0.45	0.59	0.49	0.49	0.79
toluene	0.48	-0.27	0.29	-0.15	0.16	0.76	0.89	0.20
o-xylene	0.94	-0.20	0.93	0.12	0.52	0.78	0.95	0.10
m/p-xylenes	0.92	-0.23	0.94	0.10	0.38	0.88	0.98	0.11
ethylbenzene	0.89	-0.24	0.92	0.10	0.51	0.78	0.92	-0.01
1,2,4-trimethylbenzene	0.93	-0.20	0.63	0.53	0.59	0.63	0.95	0.07
1,3,5-trimethylbenzene	0.85	-0.34	0.69	0.04	0.80	0.40		
4-Ethyltoluene	0.82	-0.20	na		0.81	0.41		
naphthalene			0.29	0.85				
<i>alkanes</i>								
isopentane	0.48	-0.09	-0.15	-0.73	0.19	0.95	0.20	0.92
hexane	0.56	-0.27			0.61	0.70		
2-methylpentane	na				0.41	0.74		
cyclohexane	0.64	-0.38			0.81	0.41		
heptane	0.63	-0.35			0.81	0.39		
2,3-Dimethylpentane	0.56	-0.55					0.08	0.06
2,2,4-Trimethylpentane					0.38	0.19	0.13	0.05
<i>halogenated</i>								
Freon11	-0.28	0.91	0.15	0.01	0.10	0.19	0.28	0.36
Freon12	-0.27	0.91	-0.13	-0.03	0.32	-0.04	0.25	-0.21
chloromethane	-0.11	0.86			-0.23	-0.37	-0.27	0.77
1,4-dichlorobenzene	0.25	0.27						
chloroform			-0.22	0.20				
tetrachloroethene			0.11	0.77	0.38	0.20	-0.35	0.24
<i>oxygenates</i>								
MEK			0.26	0.00				
MTBE			0.13	-0.53	0.86	0.24		
tetrahydrofuran			0.21	0.24	0.89	0.31		

APPENDIX A
MANUSCRIPT

**Benzene in soil gas, indoor, and outdoor air; source
identification based on tracer compounds and principal
component analysis**

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Benzene in soil gas, indoor, and outdoor air; source identification based on tracer compounds and principal component analysis

Abstract

Sources of indoor air benzene were evaluated using data from 66 air samples that had been collected at three sites with known soil and groundwater contamination from gasoline or former manufactured gas plant (MGP) activities. Aliphatic, aromatic, halogenated, and oxygenated volatile organic compounds (VOCs) reported by EPA method TO-15 in indoor air, outdoor air, and soil gas were evaluated as tracers for various sources of indoor air benzene. Volatile alkanes (e.g., isopentane) are useful tracers for petrogenic sources of benzene (such as gasoline), and the absence of alkanes indicates a pyrogenic source (e.g., MGP tars). Freon 11 was found to be a reliable tracer for the impact of outdoor air on indoor air benzene. Comparison of the benzene/tracer ratios from indoor air, outdoor air, and soil gas demonstrated that indoor air benzene was primarily contributed by outdoor air, and not by soil vapor intrusion. Cases of elevated indoor air benzene were found to be from gasoline storage or smoking. Principal components analysis (PCA) using the ranked TO-15 data also demonstrated that the VOC compositions of soil gas are distinct from those of indoor and outdoor air. Based on the use of organic tracers and on PCA statistical analysis, outdoor air was the principal source of indoor air benzene at these sites (once sources such as gasoline storage were removed), and soil vapor intrusion had no significant contribution.

Running Head: Indoor air benzene

Keywords: indoor air benzene, outdoor air, soil vapor intrusion, source identification

INTRODUCTION

The presence of benzene in indoor air is frequently attributed to intrusion from contaminated soil or groundwater, even though benzene concentrations in outdoor and indoor air are often very similar (Ilgen et al. 2001, Kingham et al. 2000, Sexton et al. 2004a, Sexton et al. 2004b, Chatzis et al. 2005, Lu et al. 2006, Edwards et al. 2001, Ohura et al. 2006). Considering the fact that residential and commercial buildings have traditionally been designed for approximately one exchange of indoor air with outdoor air every hour (ASHRAE 1981), it is ironic that the contribution of outdoor air to indoor air benzene is largely ignored in federal and state regulatory practices. The majority of modeling studies attempting to account for indoor air benzene also focus on soil vapor intrusion (Turczynowicz and Robinson 2001, Hers et al. 2002, Abreu and Johnson 2006, Fitzpatrick and Fitzgerald 2002, Freijer and Bloemen 2000, Hers et al. 2003), even though the input from groundwater to indoor air has been strongly disputed (McHugh et al. 2004), and others have concluded that indoor and outdoor air benzene are essentially at equilibrium in the absence of specific sources such as smoking or gasoline storage (Ilgen et al. 2001, Kingham et al. 2000). When either ground water or soil contamination is suspected from petroleum or manufactured gas plant (MGP) sources, site investigations normally only obtain samples of indoor air and soil gas and/or ground water benzene, and the contribution from outdoor air to indoor air benzene is ignored.

Outdoor air benzene concentrations generally exceed regulatory action levels for indoor air. For example, the residential screening level for indoor air benzene in California is $0.084 \mu\text{g}/\text{m}^3$ (Eklund et al. 2007), a concentration that is ca. 25-fold lower than the mean outdoor air benzene concentration of ca. $2 \mu\text{g}/\text{m}^3$ measured at the 22 California monitoring stations reported by the U.S. Environmental Protection Agency (EPA) in 2006 (AQS Annual Summary 2006). Similar regulations exist in many states including Alaska, Colorado, Massachusetts, Oklahoma, and Oregon, which have residential screening levels for benzene ranging from 0.2 to $0.3 \mu\text{g}/\text{m}^3$ (Eklund et al. 2007), approximately 10-fold higher than ambient air concentrations of benzene reported by the EPA of ca. $2 \mu\text{g}/\text{m}^3$ in 2003 across the United States (USEPA 2003).

Similarly, the EPA's risk-based target indoor air concentration of $0.23 \mu\text{g}/\text{m}^3$ is much lower than ambient benzene concentrations across the nation (USEPA 2003). In essence, any indoor or outdoor air sample collected in any populated location throughout the United States will most likely exceed the concentrations at which regulatory concerns are raised.

The lack of ambient outdoor air benzene data at a site can lead to the erroneous conclusion that soil gas is the source of indoor air benzene, when the actual source is outdoor air and/or specific indoor sources such as smoking or gasoline vapors from an attached garage (Ilgen et al. 2001, McNabola et al. 2006, Ballesta et al. 2006). In such cases, steps taken to mitigate intrusion of soil gas are wasted, since any reduction in indoor air benzene is insignificant compared to the influence of outdoor air or specific indoor sources.

In many site investigations, only the benzene data from the commonly-used EPA TO-15 air method are considered, despite the fact that TO-15 reports data on more than 60 common organic air pollutants from a wide variety of sources, and includes aliphatic and aromatic hydrocarbons typical of petroleum products and vehicle exhaust, ubiquitous halogenated organics (e.g., Freons), and oxygenates such as ethanol, isopropanol, and acetone that are emitted by common domestic activities. Many of these pollutants have the potential for providing source apportionment information to help determine the source of benzene in indoor air. In the present study, we investigate the relationship between benzene and different classes (and different sources) of organic air pollutants at three sites where soil vapor was known to be impacted by gasoline contamination or by former MGP activities such as buried gas holders (Gas Research Institute 1996). Both a statistical approach (principal component analysis) and a more intuitive method based on urban air chemistry were used to investigate differentiate sources of indoor air benzene at these sites.

The goal of these investigations was to evaluate the ability of these approaches to determine the source of indoor air benzene using archived TO-15 data that had been collected at several sites. Our approach was also based on the assumption that we must use the data "in hand" for each site, with no ability to perform additional sampling or

increase the list of target compounds measured. These restrictions were placed on the study to best mimic the limitations in money, access, and legal considerations that generally surround sites that are under regulatory scrutiny.

METHODS

Air data from 15 sites thought to be impacted by soil and or ground water benzene (each with ca. 15 to 30 samples) were obtained from the responsible parties, and surveyed to find sites that met the minimum criteria of (1) having indoor, outdoor, and soil gas samples collected at the site during the same period of time and (2) sufficiently low detection limits that data were available for a range of aromatic, aliphatic, halogenated, and oxygen-containing organics typically measured by EPA method TO-15. Unfortunately, nearly all of the 15 sites did not include outdoor air samples, and several used substantially smaller samples of soil gas than indoor air, thus resulting in excessive "non-detects." Three sites met these criteria and were therefore chosen for this study.

Two independent approaches were used to determine if different classes of organic compounds detected in the TO-15 analyses could be used to differentiate the relative impacts of outdoor air and soil gas on indoor air benzene. First, the concentrations of organic compounds characteristic of likely sources were evaluated as forensic tracers for sources of indoor air benzene. Second, the concentration data were analyzed using multivariate statistics in SAS[®] (SAS Institute, Cary, NC). Principal components analysis (PCA) was done on the correlation matrix of the ranked TO-15 data to determine whether the variability in the data set could be accounted for by a substantially smaller number of principal components (PCs). A varimax rotation procedure was then used to minimize the variance of factor loadings on each of the PCs. Analytes dominated by data below the reporting limit (non-detect) were removed from the data set prior to analysis. Concentrations were transformed to rank values in SAS using mean values for ties. PCA results were evaluated graphically using scatter plots of the PCs which explained the largest percentage of variation in the data

(typically the first 3 PCs) to determine whether PCA can adequately discriminate indoor, outdoor and soil gas air samples. While the first approach is based on a knowledge of air chemistry combined with source compositions of common air pollutants, the PCA statistical approach involves no human bias and is blind to the source of the air sample (whether outdoor, indoor, or soil gas), and only tries to explain the variance in chemical composition between all samples.

RESULTS AND DISCUSSION

Sample sites and VOCs

The three sites used in this study were located in the states of New Jersey or New York in the north eastern United States. The first was a high school located in a large city with a population of over a million, and was located above a former MGP facility that ceased operation in 1925. The former MGP had produced gas by the carbureted water gas (CWG) process, which included the use of coal and light petroleum distillates (naphtha) (Gas Research Institute 1996). Air samples were collected throughout the building and at locations surrounding the building. The second site was a business/residential area in a city of ca. 25,000 population with sampling locations at a post office, an office building, a gasoline station (soil gas only), and auto body shop (soil gas only). The area was known to be impacted by gasoline-contaminated ground water and was the site of a former MGP facility which used the CWG process. The third site was at a strip mall that had a variety of businesses (including a bar/grill, play gym, beautician, bakery, pizzeria, and appliance dealer, all used as sampling locations) in a city with a population of ca. 10,000. This site was known to be located above a former coal gasification plant with a gas holder tank that had ceased operations in ca. 1915.

A total of 66 air samples were collected at these sites, and the number of indoor, outdoor, and soil gas samples and the range of VOC concentrations found are given in Table 1. Only 12 compounds were found at detectable levels at every site.

Other compounds that were commonly detected at an individual site were included in the PCA statistical analysis for that site.

Evaluation of tracer organic compounds

Urban air contains a mix of volatile organic compounds (VOCs) from a range of human activities including petroleum products (petrogenic hydrocarbons) and their combustion residues, halogenated solvents and Freon refrigerants and propellants, and oxygenates from fuels as well as some oxygenated solvents. Indoor air typically contains the same organic mix as nearby outdoor air, with the addition of organics emitted by personal activities. The presence (as well as absence) of different compound classes can be used to help determine the likelihood of different sources to benzene in an air sample. For example, if petroleum is the primary source of benzene in an air sample, the air sample should contain other major petrogenic organics including some of the other volatile aromatic organics (e.g., alkyl benzenes) as well as the volatile petroleum alkanes. In contrast, if coal-related MGP products (pyrogenic hydrocarbons) are responsible for benzene in an air sample, even though the distribution of benzene and other alkyl benzenes may look similar to a petroleum source, the *lack* of alkanes would indicate a coal-based MGP, and not a petroleum source. MGP sites that used petroleum can be contaminated with both petrogenic hydrocarbons (aromatics and alkanes) from the petroleum feedstock and/or with petrogenic hydrocarbons (primarily aromatics) from the MGP products. Halogenated organics such as Freons are neither MGP nor petroleum hydrocarbons, but are ubiquitous in urban air. Used primarily as propellants and refrigerants, they are not likely to be associated with groundwater contamination, in contrast to halogenated cleaning solvents such as perchloroethylene. Therefore, the proportion of benzene to Freons in indoor air should be similar to that in outdoor air, if outdoor air is the source of the indoor benzene. In contrast, if the indoor benzene is from soil gas (e.g., contaminated with petroleum or MGP products), then the relative proportion of benzene to Freons should be much higher, since neither petroleum nor MGP contaminants should contribute Freons to the air.

Caution must be used in evaluating any such tracer organics, because of the potential for spurious sources based on individual activities. For example, although ethanol, 2-propanol, and acetone were found in every sample, all three are specific to various human activities. Ethanol (e.g., from baking bread or alcohol consumption), peaked at $6300 \mu\text{g}/\text{m}^3$ in the bakery compared to only ca. 10 to $20 \mu\text{g}/\text{m}^3$ in all of the indoor air samples at the school (Table 1). Isopropanol (rubbing alcohol) peaked at $1500 \mu\text{g}/\text{m}^3$ in the school girl's locker room, while acetone (finger nail polish remover) peaked at $1500 \mu\text{g}/\text{m}^3$ in the beautician's shop.

Plots of the ratio of benzene concentrations to concentrations of different tracer compound classes (halogenated organics, alkanes, and alkyl benzenes) versus benzene concentrations were made for all compounds detected at each site. When multiple members of a compound class were detected (as listed in Table 1), their plots tended to be quite similar. For example, the ratio plots for the school using 1,4-dichlorobenzene, chloromethane, and Freon 12 are nearly identical to the plot shown in Figure 1 for Freon 11. Similarly, for other sites and compound classes, the ratio plots using the different alkanes listed in Table 1 for a particular site were generally quite similar to those shown for isopentane, and the plots for the alkyl benzenes were similar to those shown for toluene (Figure 1). Therefore, based on their presence at all sites, three VOCs; Freon 11, isopentane, and toluene, were used to represent the different compound classes for the ratio plots shown.

Case 1: High School

Figure 1 shows the benzene/tracer ratio plots for the air samples from the high school. Elevated benzene concentrations were found in 4 out of the 5 soil samples (from ca. 15 to $40 \mu\text{g}/\text{m}^3$), and two indoor air samples showed elevated benzene concentrations at ca. $10 \mu\text{g}/\text{m}^3$ compared to the remaining indoor air concentrations which all showed typical background ambient air concentrations between 1.3 to $2.8 \mu\text{g}/\text{m}^3$ (Figure 1 and Table 1).

As shown in Figure 1 (top left), the ratio of benzene to Freon 11 clearly differentiates the contaminated soils and the two elevated indoor air samples from all of

the remaining indoor air samples and outdoor air samples. Since the Freon 11 concentrations in all indoor and outdoor air samples at the school are essentially identical (Table 1), the similarity in the indoor and outdoor benzene to Freon 11 ratios show that (with the exception of the two elevated indoor air samples that had benzene concentrations about $10 \mu\text{g}/\text{m}^3$) outdoor air is the primary source of the indoor air benzene rather than soil gas.

The two indoor air samples with ca. $10 \mu\text{g}/\text{m}^3$ benzene were near a soil gas sampling location where the soil gas concentrations were ca. $20 \mu\text{g}/\text{m}^3$. However, gasoline was also found stored near the contaminated indoor air sampling locations, so both the gasoline and the soil gas appeared to be likely sources of the elevated benzene in the two indoor air samples. To determine the major source, the gasoline was removed and the air was re-sampled after six months. (Note that no remediation activity for the soil gas benzene was being performed, so no significant change in soil gas concentrations would be expected as confirmed by later soil gas analyses.) The second set of samples showed benzene concentrations reduced from ca. $10 \mu\text{g}/\text{m}^3$ to background levels (ca. $1.5 \mu\text{g}/\text{m}^3$), demonstrating that the gasoline, and not soil vapor intrusion was the source of elevated benzene in the two original indoor air samples (Figure 1).

As shown in expanded scale plot (upper right in Figure 1), the average indoor air benzene concentration from the first sampling event (excluding the two samples near the gasoline storage) was ca. 30% higher than the average outdoor air concentrations. Soil vapor intrusion as a source seems unlikely since the proximity of the indoor air samples to the four contaminated soil gas locations had no relationship to any elevated indoor air benzene concentrations. In addition, the gasoline storage may have been responsible for this small elevation in benzene concentrations throughout the school compared to outdoor air in the remaining indoor air samples. All of the indoor air samples collected after removal of the gasoline fell within the range of outdoor air benzene concentrations, thus demonstrating that the gasoline storage was the likely source of the ca. 30% elevation in indoor benzene levels in the initial sampling (Figure 1, upper right). Once the gasoline was removed, the results shown in Figure 1 make it

clear that outdoor air is the only significant source to indoor air benzene at this site, despite the presence of contaminated soil.

It is important to carefully observe the y-axis scale in order to evaluate the use of these ratios. Large differences in ratios between sources like the benzene/Freon 11 example for the school are needed to discriminate sources of indoor air benzene. For example, the average benzene/Freon 11 ratio for indoor and outdoor air was approximately 1, whereas the soil gas samples had ratios from 15 to 38. Small differences in ratios like those shown for the school plots for benzene/isopentane and benzene/toluene cannot be used to suggest significant differences in sources since their relative amounts can change by how they were introduced into the atmosphere (e.g., evaporated gasoline vs. vehicle exhaust), and their different transport and degradation properties.

The benzene ratio plots for the school with isopentane and toluene (Figure 1, bottom) do not show any significant deviations in the various indoor, outdoor, and soil gas samples, indicating some common petrogenic nature to their source. For the two elevated indoor air samples, this was consistent with further investigations of the site showing that gasoline was stored near those two indoor sampling locations. However, since the site was a former MGP site, we were initially confused that the ratio of benzene to isopentane was not substantially higher for the two contaminated soil gas samples (Figure 1, top), since coal tar or MGP gas condensate have no significant alkane content. Additional historical investigations showed that the affected area had been used to store petroleum naphtha (as an MGP feedstock), which is consistent with the fact that the contaminated soil gas shows benzene/isopentane ratios typical of petrogenic, not pyrogenic hydrocarbons.

Case 2: Business/residential neighborhood

Indoor and outdoor air samples in the business/residential neighborhood were collected at a post office and office building. Soil gas samples were not available at the post office, but were collected below the office building and at a nearby gasoline station and an auto body shop. The relatively small range in ratios of benzene to isopentane

(Figure 2, lower left--note the y-axis scales) indicate that benzene in all of the air samples came primarily from a petrogenic source (as was the case for the school discussed above). In addition, the soil gas samples all had alkyl benzene and alkane distributions that indicate gasoline as their source (Table 1), as confirmed by known gasoline contamination of groundwater in the area. All four soil gas samples showed elevated benzene concentrations, especially those collected at the auto body shop and the gasoline station, as might be expected.

As shown in Figure 2 (upper left), the benzene/Freon 11 ratios have a large range in values, and clearly show that the indoor air samples are completely dominated by outdoor air, and not detectably influenced by benzene-contaminated soil gas. When the scale of the plot is expanded (upper right of Figure 2) to observe the 4 outdoor and 7 indoor air samples that make up the cluster near the origins of the benzene/Freon 11 plot (upper left) the strong relationship between indoor and outdoor air benzene is easily observed. In addition, the benzene concentration in the seven indoor air samples ranged from 1.3 to 1.8 $\mu\text{g}/\text{m}^3$, directly reflecting the range of 1.1 to 2.0 $\mu\text{g}/\text{m}^3$ for the four outdoor air samples. A third set of evidence that soil gas vapor intrusion had no impact on indoor air benzene compared to outdoor air is the fact that the soil vapor collected at the office building was elevated (5.4 and 8.7 $\mu\text{g}/\text{m}^3$), but none of the three indoor air samples collected at that site had benzene concentrations elevated above the ambient outdoor air concentrations.

It is interesting to note the very high concentrations of toluene (260 to 270 $\mu\text{g}/\text{m}^3$) found in three of the four post office indoor air samples. In addition to being a common paint solvent, toluene is used frequently as an adhesive solvent and in such products as "liquid paper," uses that appear to account for the very high levels found. While this result is somewhat spurious (as discussed above for ethanol, acetone, and isopropanol), it has little effect on the plot in Figure 2 since the range of benzene/toluene ratios is so small.

Case 3: Strip mall

The final sampling site, a strip mall, provided a much more complex range of VOCs than the other two sites as a result of the variety of businesses present. As shown in Table 1, the strip mall showed the widest concentration ranges for several of the VOCs. It is hardly surprising (as noted above) that acetone (finger nail polish remover) was elevated up to $1500 \mu\text{g}/\text{m}^3$ at the beautician's, or that ethanol exceeds $1000 \mu\text{g}/\text{m}^3$ at several of the businesses involving alcohol consumption and baking bread. However, it is notable that Freon 12, which had nearly constant concentrations in indoor and outdoor air at the school and neighborhood sites (Table 1), varied greatly in the strip mall indoor air and in the soil gas. While it might not be surprising that the refrigerant Freon 12 is elevated to above $500 \mu\text{g}/\text{m}^3$ in the appliance dealer and the bakery, we were somewhat surprised to find Freon 12 concentrations as high as $820 \mu\text{g}/\text{m}^3$ in the children's play gym. Since Freon 12 is also used as a non-toxic propellant in products such as "silly string", we suspect that such aerosol play products were responsible for the high Freon 12 concentrations in the play gym.

In contrast to the previous two sites where Freon 11 concentrations were essentially $2 \mu\text{g}/\text{m}^3$ for all of the air samples, Freon 11 concentrations were more variable at the strip mall (Table 1), though not nearly so much as Freon 12. Despite the higher variability, the benzene/Freon 11 ratio still yields a clear distinction between the contaminated soil gas and the indoor air (Figure 3, upper left). The strip mall was also the first site where the range in benzene/isopentane ratios (Figure 3, lower left) was sufficiently large to demonstrate that the contaminated soil gas resulted from a pyrogenic and not a petrogenic source. This result was consistent with the fact that the contaminated soil gas samples were collected directly above an abandoned MGP gas holder, which would have held coal tar condensates ranging from benzene to 5- and 6-ring PAHs, but virtually no aliphatic hydrocarbons that are typical of petrogenic sources.

However, it is clear from the expanded scale plot of the benzene/Freon 11 plot (Figure 3, upper right) that there are six of the indoor air samples that have moderately elevated benzene concentrations (3.7 to $8 \mu\text{g}/\text{m}^3$), and that outdoor air is not the only

source of indoor air benzene at those locations. Since the mall was built over an abandoned MGP site, soil vapor intrusion was suspected, but only two out of nine soil gas samples had benzene concentrations higher than ambient air. The remaining seven soil gas samples had benzene concentrations lower than the indoor air samples, so would only have the potential to reduce (and not increase) the indoor air concentrations. The two indoor air samples collected above the two contaminated soil gas samples (which were collected above the known location of the abandoned MGP gas holder) had some of the lowest benzene concentrations (2.0 and $2.4 \mu\text{g}/\text{m}^3$, both within the range of outdoor air benzene concentrations) of all of the indoor air samples, clearly indicating that soil vapor intrusion was not a significant source of benzene to those indoor air samples. Therefore, soil vapor intrusion as the source of the elevated indoor air benzene is highly unlikely at this site.

Fortunately, the archived data had notes from the sampling team documenting smoking in the various businesses located in the strip mall site. Smoking was documented for five out of the six indoor air samples that fell in the 3.7 to $8.0 \mu\text{g}/\text{m}^3$ range, and certainly could have occurred at the sixth location. Given the fact that there was no elevated benzene in the indoor air collected directly above the highest soil gas contamination, it seems reasonable to conclude that the elevated indoor air benzene in the strip mall was from smoking, not from soil vapor intrusion.

Combined sites

Ideally, a single set of tracers could be used to differentiate sources of indoor air from all sites. As noted before, alkanes such as isopentane are useful for investigating potential petrogenic versus pyrogenic sources of benzene, but have little use for tracing the impact of outdoor air on indoor air. In contrast, Freon 11 was reasonably successful at each individual site to determine the contribution of outdoor air benzene to indoor air, and it was hoped that this tracer could be applied to the combined data from all of the sites. Figure 4 shows the benzene/Freon 11 ratio plot for the combined 66 air samples from the three sites. As was true for the individual sites, all samples with

elevated benzene are well-resolved by the benzene/Freon 11 ratio for the combined site data (Figure 4, left). The two soil samples that are not as clearly resolved in the y-axis direction by the benzene/Freon 11 ratio (benzene concentrations of ca. $28 \mu\text{g}/\text{m}^3$) are from the soil below the appliance dealer and had been contaminated by Freon 11, resulting in a lower benzene/Freon 11 ratio.

The right side of Figure 4 shows expanded x- and y-axis scales so that the relationship of indoor, outdoor, and several of the uncontaminated soil gas samples can be observed. Except for the five indoor air samples from the strip mall that were impacted by smoking, all of the indoor air samples and uncontaminated soil gas samples cluster with the outdoor air samples, clearly demonstrating the importance outdoor air contributions to indoor air benzene as well as other VOCs found in ambient air. Note also that the similarity in benzene/Freon 11 ratios between outdoor air, indoor air, and several of the soil gas samples show that outdoor and/or indoor air is the likely source of VOCs in some soil gas samples, as previously reported by McHugh et al 2006.

PCA statistical analysis

As discussed above, several VOCs can be contributed by individual human activities and can result in extremely variable concentrations from one indoor air sample to another. Most notable in the data used from this study were the widely varying ethanol, acetone, and isopropanol concentrations. This spurious behavior makes these compounds unsuited to trace benzene sources using the ratio plots presented above. In order to mitigate such behavior for PCA, ranked data (rather than concentrations) were used. PCA was done for each site using data sets with and without ethanol, acetone, and isopropanol to determine which approach best reduced the variance. In addition to the VOCs that were found at all sites (Table 1), any additional VOCs that were measured at individual sites were included in the PCA.

For the business/residential site, the amount of variance explained by each principal component was essentially the same with or without including the ethanol, acetone, and isopropanol data. However, for the strip mall and school, including the ethanol, acetone, and isopropanol data resulted in ca. 5% less variance explained (based

on three principal components). Therefore, subsequent discussions about PCA results do not include the ethanol, acetone, and isopropanol data.

Figure 5 shows the first two principal components for the three sites. Plots of the first two principal components show that the soil gas samples remain distinct from the outdoor and indoor air samples and, generally speaking, the indoor and outdoor air samples overlap significantly, especially for the strip mall and business/residential sites. Plots of the first and third principal components (not shown) show similar behavior. Since the goal of PCA is to reduce the variation in the data sets, and since PCA is "blind" to the sample source (there is no distinction of indoor, outdoor, and soil gas samples in the PCA data input), the fact that the soil gas samples cluster away from indoor air samples, and the fact that outdoor and indoor air samples tend to cluster together yield the same conclusion as drawn from the ratio plots in Figures 1 to 4. That is, when individual sources of benzene (gasoline storage and smoking) are removed, outdoor air is the principal contributor of benzene to indoor air at these three sites, despite the elevated levels of soil gas benzene.

PCA of the combined data from the three sites was limited to the list of compounds detected at all sites given in Table 1. For the combined data sets (Figure 6), the distinction between soil gas and indoor and outdoor air samples is not as clear as for PCA of the individual site data shown in Figure 5, however, the trends for soil gas samples to cluster away from indoor and outdoor air are still clear. Interestingly, the organic compound classes that dominate each factor for the combined data set are the same as proposed above as tracers for the ratio plots. As shown in Table 2, alkyl benzenes dominate the first principal component, Freon 11 and 12 dominate the second, and isopentane dominates the third.

CONCLUSIONS

Federal and many state action levels for indoor air benzene are unrealistically low, since they are set at or lower than typical outdoor urban air concentrations. The contribution of outdoor air to indoor air benzene is frequently ignored, despite the fact

that outdoor air is the primary source of indoor air, and that indoor air and outdoor air benzene concentrations are often the same. While seeking data sets for this study, we found it general policy not only to ignore outdoor air contributions to indoor air, but that the vast majority of sampling studies failed to even collect outdoor air samples. Even though each of the sites that we present here were under regulatory scrutiny and clearly had benzene contamination in the soil, the data analysis presented here demonstrates that soil gas vapor intrusion was not a significant source of indoor air benzene at any of the sampling locations, and that (in most cases) outdoor air benzene was the most important source of indoor air benzene. When elevated benzene concentrations (compared to outdoor air concentrations) did occur, gasoline storage and tobacco smoking were the sources. As such, any efforts made to reduce indoor air benzene by attempts to reduce soil benzene concentrations near buildings are highly unlikely to have any effect on indoor air benzene at these sites. These results clearly demonstrate that the collection of outdoor air samples and consideration of the contribution of outdoor air to indoor air benzene should be an integral part of any regulatory response to indoor air benzene.

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Figure Legends

Figure 1: Benzene/tracer ratios versus benzene air concentrations at the school. The plot on the upper right expands the axes so that the cluster of samples near the origin can be observed. Indoor and outdoor air samples designated "resampled" were collected six months after the stored gasoline was removed from the building.

Figure 2: Benzene/tracer ratios versus benzene air concentrations in the business/residential neighborhood. The plot on the upper right expands the axes so that the cluster of data points near the origin can be observed.

Figure 3: Benzene/tracer ratios versus benzene air concentrations at the strip mall. The plot on the upper right expands the axes so that the cluster of data points near the origin can be observed.

Figure 4: Benzene/Freon 11 ratios for the combined data from the school, business/residential neighborhood, and the strip mall. The plot on the right side expands the axes so that the cluster of data points near the origin can be observed.

Figure 5: Principal component 1 versus 2 plots for the three individual sites.

Figure 6: Principal component plots for the combined data from the school, business/residential neighborhood, and the strip mall.

Tables

Table 1: VOCs detected at all sites ($\mu\text{g}/\text{m}^3$).

Table 2: Principal component factors for the combined data from all sites.

Figure 1

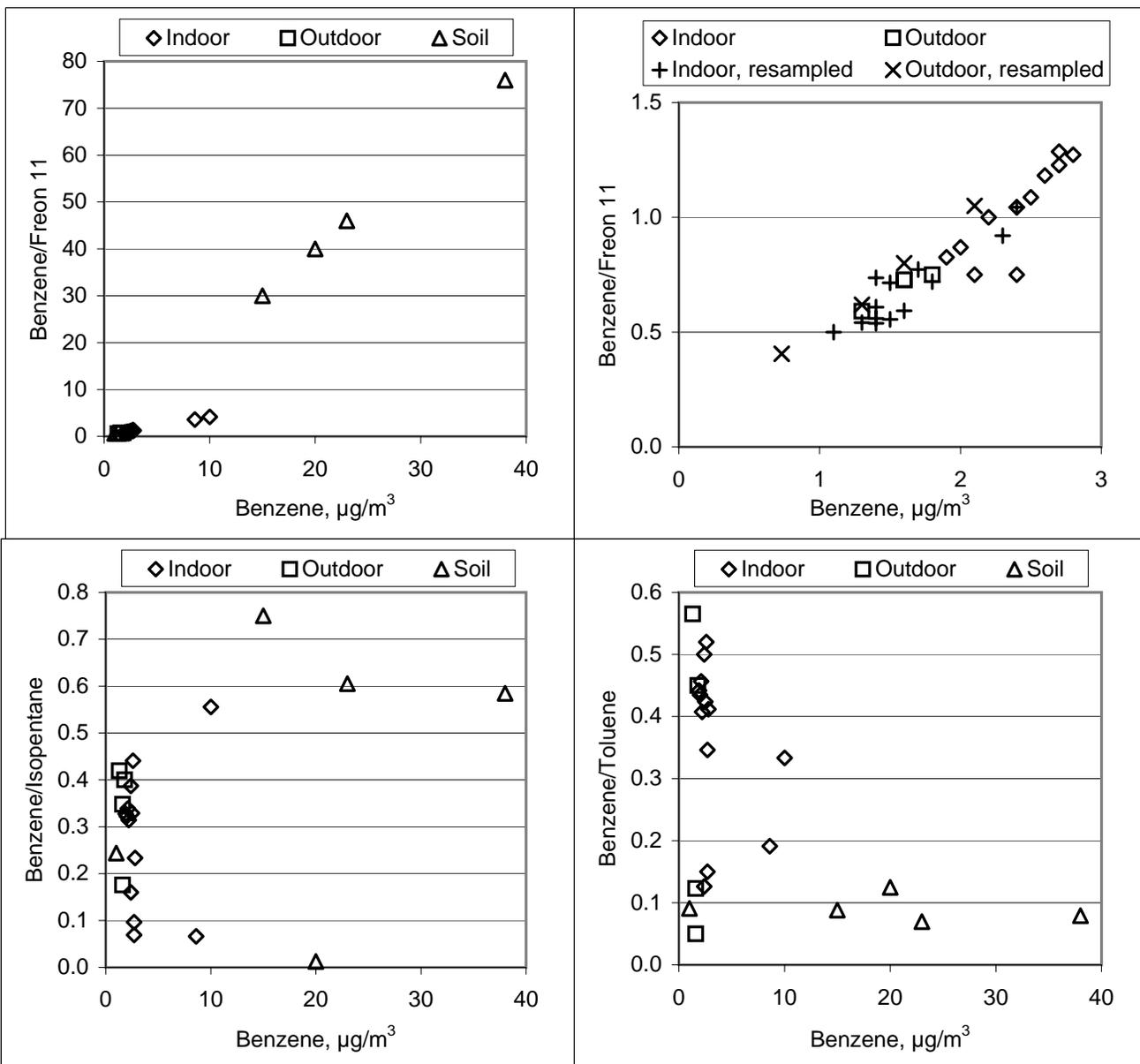


Figure 2

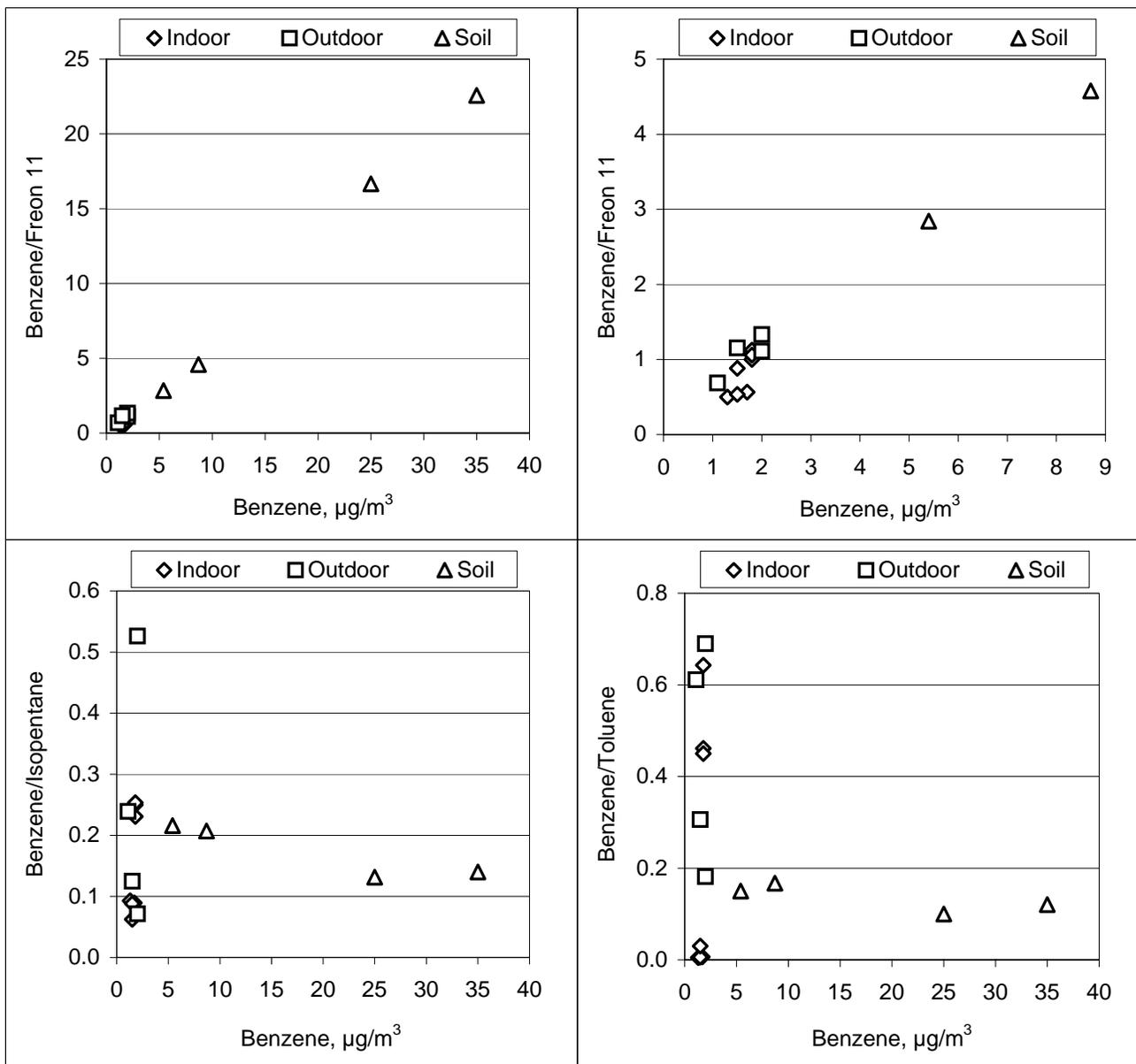


Figure 3

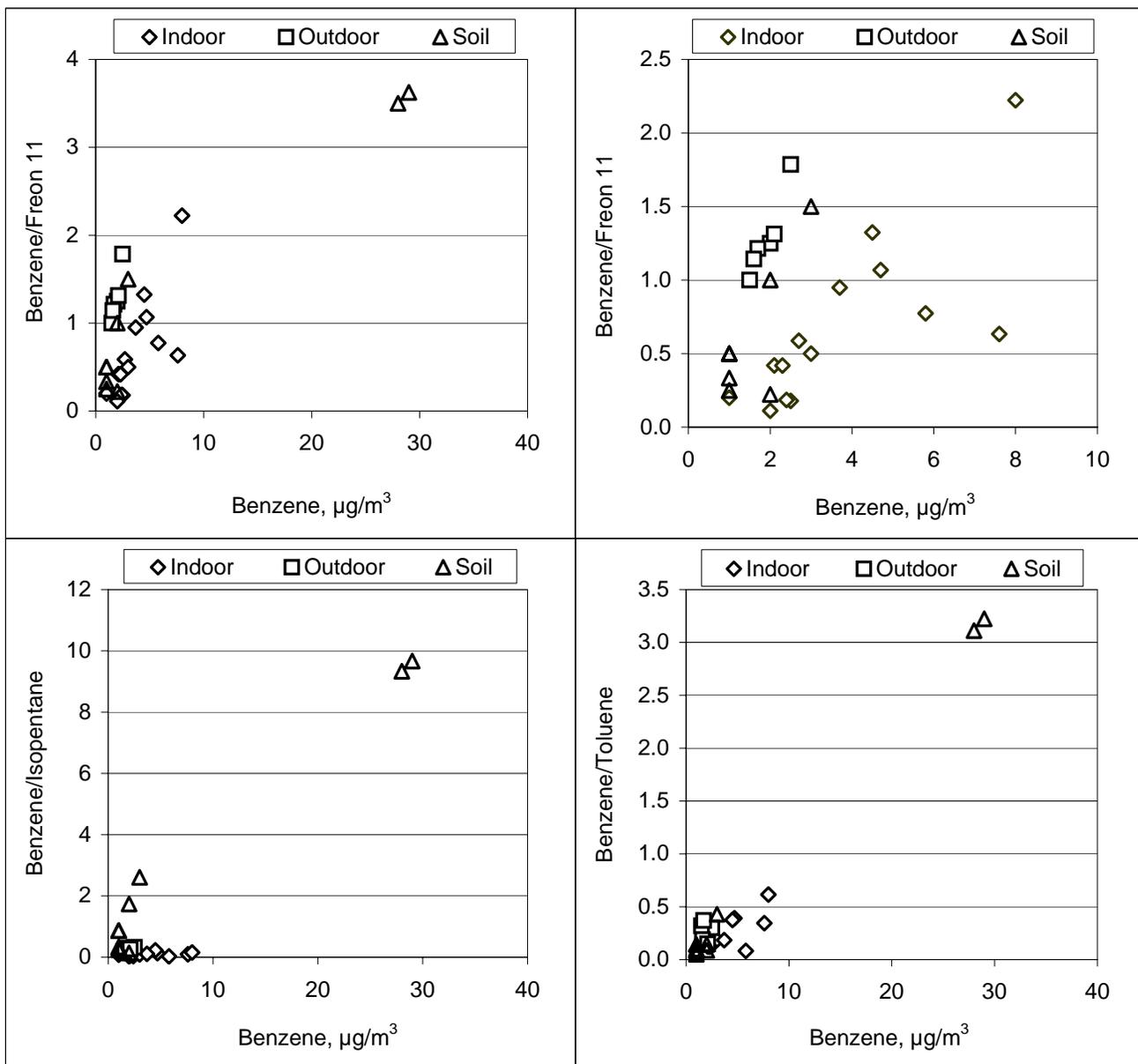


Figure 4

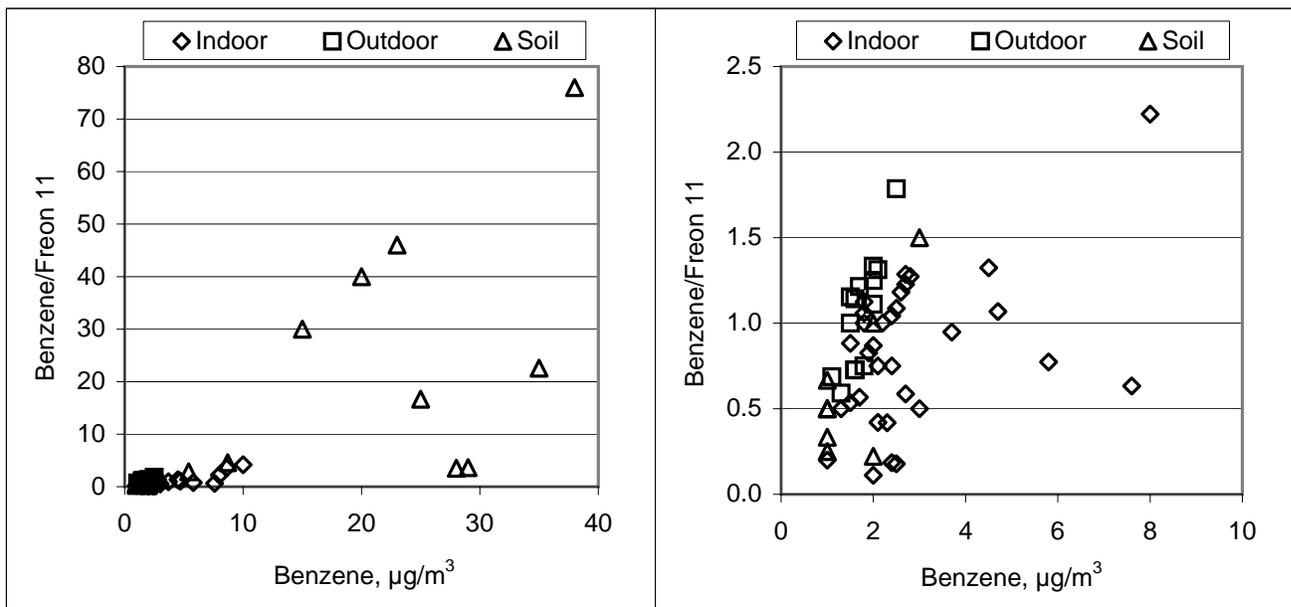


Figure 5

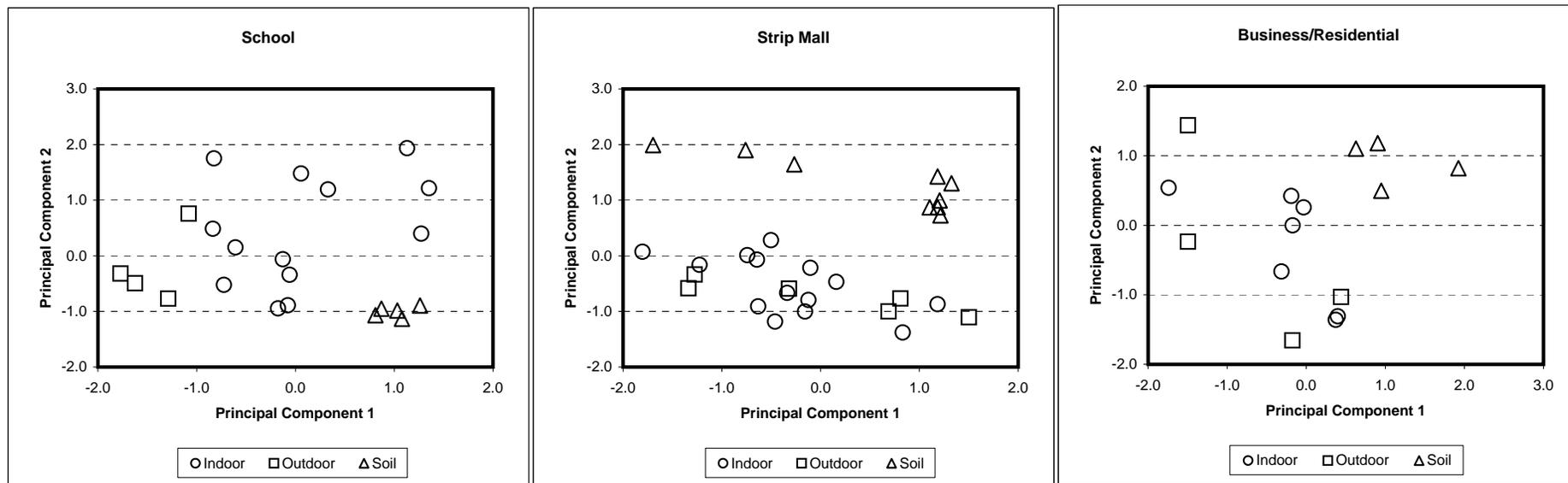


Figure 6

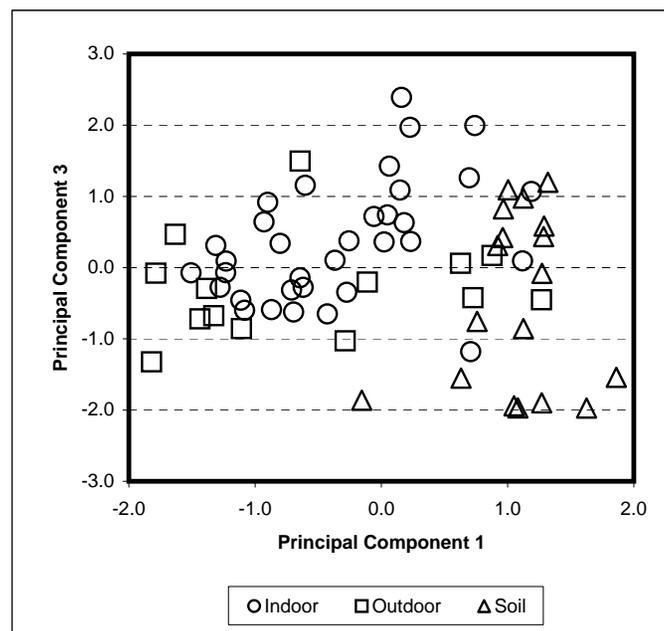
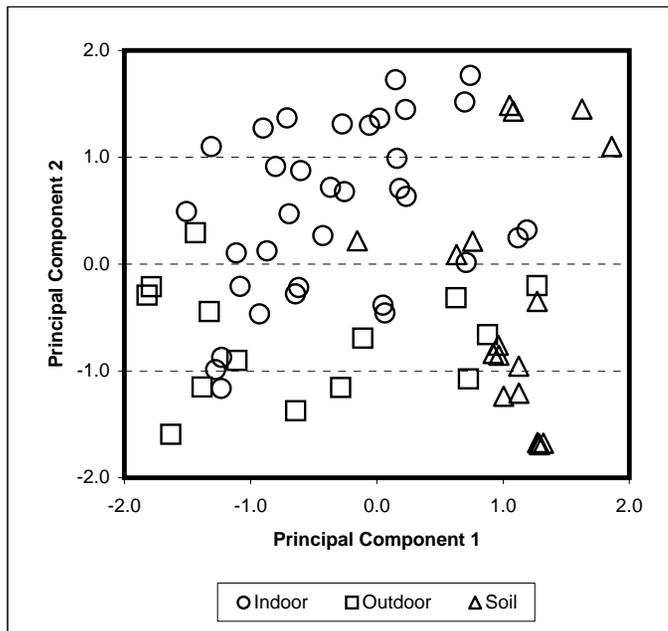


Table 1: VOCs detected at all sites ($\mu\text{g}/\text{m}^3$)

	School			Strip Mall			Business/Residential		
	min	max	median	min	max	median	min	max	median
indoor air		n=13			n=14			n=7	
benzene	1.9	10.0	2.5	1.0	8.0	2.9	1.3	1.8	1.7
toluene	4.3	45.0	5.9	9.5	71.0	13.0	2.8	270.0	50.0
o-xylene	0.8	13.0	1.4	0.4	5.4	2.0	0.7	2.3	1.5
m,--xylene	2.5	38.0	4.1	2.0	17.0	5.1	1.4	6.6	3.5
ethylbenzene	0.8	13.0	1.2	0.4	6.1	1.7	0.3	2.5	1.2
1,2,4-trimethylbenzene	1.2	22.0	2.3	0.5	6.3	3.2	1.1	2.6	1.6
isopentane	5.8	130.0	7.6	12.0	210.0	33.0	7.1	24.0	14.0
ethanol	9.4	25.0	14.0	370.0	6300.0	865.0	15.0	54.0	44.0
2-propanol	6.1	1500.0	38.0	5.0	120.0	20.5	2.2	11.0	7.3
acetone	6.5	68.0	12.0	17.0	1500.0	62.5	5.5	27.0	21.0
Freon 12	3.9	5.9	4.3	7.2	820.0	104.5	3.0	14.0	4.3
Freon 11	2.1	3.2	2.3	3.4	18.0	5.3	1.6	3.0	1.8
outdoor air		n=4			n=6			n=4	
benzene	1.3	1.8	1.6	1.5	2.5	1.9	1.1	2.0	1.8
toluene	2.3	32.0	8.5	4.6	14.0	8.4	1.8	11.0	3.9
o-xylene	0.4	0.4	0.4	1.6	7.6	3.4	0.3	1.6	0.7
m,--xylene	1.0	2.1	1.6	3.4	16.0	7.4	0.9	3.8	2.1
ethylbenzene	0.4	0.4	0.4	1.0	5.5	2.4	0.3	1.8	0.6
1,2,4-trimethylbenzene	0.4	0.8	0.4	1.6	11.0	5.9	0.4	1.0	0.6
isopentane	3.1	9.1	4.6	5.6	14.0	7.8	3.8	28.0	8.3
ethanol	6.4	10.0	8.5	25.0	66.0	30.5	2.8	4.8	3.4
2-propanol	1.0	3.3	2.5	14.0	28.0	22.0	1.0	36.0	2.1
acetone	6.0	13.0	8.1	31.0	160.0	56.0	4.3	11.0	7.8
Freon 12	3.8	4.4	4.2	3.7	9.6	4.1	2.5	3.1	2.8
Freon 11	2.2	2.4	2.2	1.4	1.6	1.5	1.3	1.8	1.6
soil gas		n=5			n=9			n=4	
benzene	1.0	38.0	20.0	1.0	29.0	2.0	5.4	35.0	16.9
toluene	11.0	480.0	170.0	7.0	23.0	10.0	36.0	290.0	151.0
o-xylene	3.4	230.0	110.0	1.6	13.0	6.0	8.0	38.0	23.0
m,--xylene	9.9	630.0	320.0	3.0	24.0	11.0	31.0	120.0	74.0
ethylbenzene	2.6	180.0	75.0	1.0	7.0	5.0	8.2	38.0	21.5
1,2,4-trimethylbenzene	7.4	280.0	190.0	5.0	24.0	11.0	8.7	22.0	16.0
isopentane	4.1	1600.0	38.0	1.2	14.0	3.0	25.0	250.0	116.0
ethanol	1.0	53.0	24.0	21.0	330.0	53.0	16.0	47.0	16.0
2-propanol	1.0	95.0	20.0	4.0	60.0	14.0	210.0	540.0	310.0
acetone	1.0	250.0	41.0	27.0	320.0	140.0	41.0	170.0	103.0
Freon 12	0.5	3.0	0.5	3.0	100.0	15.0	3.0	3.9	3.4
Freon 11	0.5	1.5	0.5	2.0	9.0	3.0	1.5	1.9	1.7

Table 2: Principal component factors for the combined data from all sites.

Compound	Factor 1	Factor 2	Factor 3
Benzene	0.40	0.03	0.32
Toluene	0.49	0.08	0.38
o-Xylene	0.96	-0.03	0.16
m,p-Xylenes	0.94	-0.03	0.19
Ethylbenzene	0.93	0.00	0.25
1.2.4-Trimethylbenzene	0.91	-0.06	-0.13
Isopentane	0.16	0.01	0.92
Freon12	0.00	0.96	-0.03
Freon11	-0.07	0.96	0.05

Cumulative			
% variance ^a	54	75	87

^aThe fraction of variance accounted for by each factor.