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# Comparison of Personal, Indoor, and Outdoor Exposures to Hazardous Air Pollutants in Three Urban Communities

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Two-day average concentrations of 15 individual volatile organic compounds (VOCs) were measured concurrently in (a) ambient air in three urban neighborhoods, (b) air inside residences of participants, and (c) personal air near the breathing zone of 71 healthy, nonsmoking adults. The outdoor (O), indoor (I), and personal (P) samples were collected in the Minneapolis/St. Paul metropolitan area over three seasons (spring, summer, and fall) in 1999 using charcoal-based passive air samplers (3M model 3500 organic vapor monitors). A hierarchical, mixed-effects statistical model was used to estimate the mutually adjusted effects of monitor location, community, and season while accounting for within-subject and within-time-index (monitoring period) correlation. Outdoor VOC concentrations were relatively low compared to many other urban areas, and only minor seasonal differences were observed. A consistent pattern of  $P > I > O$  was observed across both communities and seasons for 13 of 15 individual VOCs (exceptions were carbon tetrachloride and chloroform). Results indicate that ambient VOC measurements at central monitoring sites can seriously underestimate actual exposures for urban residents, even when the outdoor measurements are taken in their own neighborhoods.

## Introduction

Volatile organic compounds (VOCs) are common constituents of urban air (1–4), and many, such as benzene, styrene, and toluene, are known or suspected to cause chronic adverse health effects in exposed populations (5). Many VOCs are designated as “hazardous air pollutants” under Title III, Section 112 of the 1990 Clean Air Act Amendments, and manufacturers are required to provide emissions data for numerous VOCs as part of the Toxics Release Inventory (TRI), which is mandated under Title III (Community-Right-to-

Know provisions) of the Superfund Amendments and Reauthorization Act (SARA).

Regulatory agencies typically maintain information about ambient, outdoor levels of VOCs (including emissions data, modeling results, and measured concentrations) for most major urban areas. There is, however, a scarcity of data on indoor VOC concentrations in nonoccupational environments (e.g., residences, offices, vehicles), where people tend to spend most of their time. Even less is known about VOC levels that people actually breathe as they move through a variety of indoor and outdoor microenvironments during their normal daily activities (6–8). The relatively few studies that have been conducted suggest that both indoor and personal exposures are typically higher than matched outdoor concentrations measured at central monitoring sites (9–11). Consequently, more and better data on real-world VOC exposures are needed to improve the quality of health risk assessments and to evaluate the efficacy of risk management decisions. This article reports data on concurrent outdoor, indoor residential, and personal measurements of 15 individual VOCs over three seasons in three urban neighborhoods.

## Study Design

The study was designed primarily to measure exposures to VOCs experienced by healthy, nonsmoking adults, and to compare results with concurrent measurements inside their residences and outside in their neighborhoods. A secondary objective was to measure  $PM_{2.5}$  exposures for a subset of the subjects, results of which have been published previously (12–15). As part of the process for selecting study communities, the Minnesota Pollution Control Agency (MPCA) compiled emission rates for eight VOCs from three source categories—industrial point (e.g., manufacturing facility), mobile (e.g., motor vehicles on an interstate), and area (e.g., sum for all dry cleaners in a particular community)—for the seven-county Minneapolis/St. Paul metropolitan area. A Gaussian plume air dispersion model (Industrial Source Complex 3 or ISCST3) was used to estimate maximum 24-hour concentrations for three individual compounds (benzene, toluene, and 1,3-butadiene), as well as for the sum of all eight compounds (the initial three plus carbon tetrachloride, chloroform, methyl chloride, styrene, and tetrachloroethylene). On the basis of those results, three urban neighborhoods (Phillips, East St. Paul, and Battle Creek) with different outdoor VOC concentration profiles (16) were selected for the exposure monitoring study.

Phillips (PHI) is an economically disadvantaged, predominantly minority, inner-city neighborhood in south central Minneapolis. It encompasses an area of approximately 2.8 km<sup>2</sup> with a population density of 2000–8000 per km<sup>2</sup>. Outdoor VOC concentrations in PHI were predicted to be relatively high because of contributions from multiple sources. East St. Paul (ESP) is a blue-collar, racially mixed neighborhood in St. Paul. It has an area of approximately 18.2 km<sup>2</sup> and a population density of 1000–4000 per km<sup>2</sup>. VOC concentrations were predicted to be relatively high, primarily as a result of emissions from a large nearby manufacturing plant. Battle Creek (BCK) is a predominantly white, affluent neighborhood on the eastern edge of St. Paul. It includes an area of 9.8 km<sup>2</sup> and has a population density of 500–2000 per km<sup>2</sup>. Predicted VOC concentrations were relatively low compared to those of the other two neighborhoods.

A centralized outdoor monitoring site (community site) was established by the MPCA in each neighborhood. Approximately 25 healthy, nonsmoking adults were recruited

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**TABLE 1. Summary of Valid, Matched, VOC Samples<sup>a</sup> by Community, Season, and Monitor Location**

	community	spring	summer	fall	all seasons
outdoor	Battle Creek	18	11	15	44
	East St. Paul	18	11	14	43
	Phillips	15	13	17	45
	all communities	51	35	46	132
indoor	Battle Creek	41	28	35	104
	East St. Paul	45	22	33	100
	Phillips	30	28	30	88
	all communities	116	78	98	292
personal	Battle Creek	39	29	34	102
	East St. Paul	43	20	32	95
	Phillips	29	29	33	91
	all communities	111	78	99	288

<sup>a</sup> Without duplicates.

from each neighborhood using house-to-house canvassing and direct solicitation. Time-activity diaries and questionnaires indicate that participants were exposed to little or no environmental tobacco smoke inside their residences. Participants tended to be female (77%), 18–65 years of age, and with some college education. Minorities in East St. Paul were under-represented. However, participants' household incomes spanned a relatively wide range, ages from 20 to 60 were well represented, and minorities accounted for nearly half of the Phillips participants. Future papers will explore the effects of sociodemographic characteristics on VOC exposures.

Matched 2-day samples were collected outdoors at the three community monitoring sites, indoors in participants' residences, and near participants' breathing zones using passive dosimeters. All outdoor community-site (O), indoor residential (I), and personal (P) samples were collected during three monitoring sessions in 1999: spring (April 26–June 20), summer (June 21–August 11), and fall (September 23–November 21). During the spring monitoring session, average daytime temperature was 16 °C (SD = 4.1), average daytime wind speed was 4.2 m/s (SD = 1.4), and average daytime mixing height was 1055 m (SD = 315). Corresponding values for the summer monitoring session were average temperature 23.7 °C (SD = 3.2), average wind speed 3.9 m/s (SD = 1.1), and average mixing height 1132 m (SD = 260), and, for fall the average temperature was 8.7 °C (SD = 4.1), average wind speed was 4.3 m/s (SD = 1.1), and average mixing height was 708 m (SD = 334). The number of matched VOC samples by community, season, and monitor location is provided in Table 1.

## Methods

All VOC concentrations (O, I, and P) were 2-day (approximately 48-hour) average values obtained with 3M model 3500 organic vapor monitors (3500 OVMs), which are charcoal-based passive air samplers. The suitability of these VOC badges for outdoor, indoor, and personal sampling has been demonstrated by Chung et al. (17, 18). These investigators have also described the determination of extraction efficiencies and the calculation of method detection limits. Valid analytical results were obtained for 15 VOCs (Table 2). The extraction solvent consisted of a 2:1 v/v mix of acetone and carbon disulfide, which provided a very low background for target analytes. All extracts were analyzed by GC/MS with a Hewlett-Packard 5890 series II Plus GC with an HP 5972 MS detector, HP 18593B autosampler, Vectra 486 computer with EnvironQuant ChemStation Software and NBS75K Spectra Library, using an RTX-1/60-m/0.25-mm i.d./1-mm film thickness capillary column. Analytical and internal standards were prepared, and VOC concentrations were calculated as described previously (18). Duplicate O, I, and P badges were collected periodically during the study (total  $n = 80$ ), and correlation coefficients were >0.95 for all individual VOCs except styrene (0.90), carbon tetrachloride (0.93), and chloroform (0.94).

Statistical analyses were performed using SAS (19) and S-plus (20). Concentrations less than the analytical detection limit were included in calculations. Nondetectable measurements (i.e., samples with no analytical response or those with values of  $\leq 0$  after blank subtraction) were assigned a value of one-half the analytical detection limit. As with most measurements of concentrations spanning multiple orders of magnitude, these values exhibit heterogeneity of variance across the range of concentrations; larger values tend to vary more than smaller ones. Without transformation, for estimation of mean relative concentrations the fit of regression models will be biased toward the behavior represented by these larger values. To stabilize the variance and thereby minimize this source of bias, estimated relative concentrations (ERCs: P/O, I/O) were calculated by computing the differences in log concentrations between P and O, and between I and O, for each combination of subject and time-index (the time marking the beginning of a monitoring period). Anti-logs of the estimated differences in the log scale arising from the regressions were taken and used to present the results in a ratio scale.

A central aim of this study was to estimate the effects of three factors, monitor location (personal, indoor, and outdoor), community, and season, on the concentrations of

**TABLE 2. Summary Statistics for Outdoor, Indoor, and Personal Locations, for Matched, VOC Sampling Periods**

VOC	outdoor (ug/m <sup>3</sup> )						indoor (ug/m <sup>3</sup> )						personal (ug/m <sup>3</sup> )					
	<i>n</i>	%det <sup>b</sup>	mean	median	Q10	Q90	<i>n</i>	%det <sup>b</sup>	mean	median	Q10	Q90	<i>n</i>	%det <sup>b</sup>	mean	median	Q10	Q90
benzene	132	100.0	1.6	1.3	0.6	3.3	292	99.7	5.8	1.9	0.8	15.3	288	100.0	7.6	3.2	1.4	18.3
carbon tetrachloride	132	99.2	0.6	0.6	0.5	0.9	292	99.7	0.6	0.5	0.4	0.9	288	99.7	0.6	0.6	0.4	0.9
chloroform	132	25.8	0.1	0.1	0.1	0.2	292	75.3	1.5	0.9	0.1	3.4	288	79.2	1.5	1.0	0.1	3.9
<i>p</i> -dichlorobenzene	132	58.3	0.1	0.1	0.1	0.2	292	72.6	1.2	0.2	0.1	1.5	288	83.3	3.2	0.4	0.1	5.1
ethyl benzene	132	98.5	0.7	0.5	0.2	1.4	292	99.0	3.9	1.4	0.5	8.9	288	100.0	5.6	2.2	0.9	11.8
<i>d</i> -limonene	121 <sup>a</sup>	86.8	0.3	0.2	0.1	0.6	262 <sup>a</sup>	99.6	16.1	9.0	2.2	30.7	258 <sup>a</sup>	100.0	23.4	11.9	4.1	52.6
methylene chloride	132	80.3	0.4	0.4	0.1	0.8	292	97.9	7.8	1.1	0.2	11.5	288	100.0	6.2	1.4	0.4	12.1
<i>a</i> -pinene	121 <sup>a</sup>	74.4	0.2	0.2	0.1	0.4	262 <sup>a</sup>	99.6	6.7	2.5	0.7	12.4	258 <sup>a</sup>	99.6	6.6	2.7	0.9	14.6
<i>b</i> -pinene	121 <sup>a</sup>	9.1	0.1	0.1	0.1	0.1	262 <sup>a</sup>	71.0	3.3	1.2	0.1	5.2	258 <sup>a</sup>	77.5	4.5	1.6	0.1	7.1
styrene	132	43.2	0.2	0.1	0.1	0.4	292	74.3	0.8	0.5	0.1	1.4	288	85.4	1.1	0.7	0.1	2.0
tetrachloroethylene	132	98.5	0.4	0.3	0.1	0.7	292	97.6	2.9	0.6	0.2	3.8	288	100.0	31.8	0.9	0.2	7.0
toluene	132	82.6	4.8	3.0	0.1	11.5	292	97.9	22.4	12.3	2.4	53.8	288	99.3	30.3	17.1	5.1	62.9
trichloroethylene	132	73.5	0.2	0.1	0.0	0.3	292	83.9	0.5	0.2	0.0	0.8	288	91.7	1.0	0.2	0.0	1.4
<i>o</i> -xylene	132	97.0	0.8	0.7	0.2	1.7	292	99.7	4.7	1.6	0.5	11.4	288	100.0	6.8	2.3	1.1	15.6
<i>m/p</i> -xylene	132	98.5	2.5	2.0	0.6	5.5	292	99.7	14.5	4.8	1.7	36.9	288	100.0	21.0	7.4	3.3	48.6

<sup>a</sup> Fewer valid samples were available because of calibration problems. <sup>b</sup> Percentage of samples with instrument readings above zero.

15 VOCs. Rather than present all 405 combinations ( $3 \times 3 \times 3 \times 15$ ) with inferential statements about each, key marginal distributions are examined ("marginal" here referring to the margins of this  $3 \times 3 \times 3 \times 15$  table). These include VOCs by each of the following: (a) monitor location, (b) monitor location and season, and (c) monitor location and community. In the statistical modeling of these factors for the outdoor concentrations, conditional on season and community, the outdoor measurements were treated as independent. Duplicate outdoor measurements for a subset of samples were processed by taking their geometric mean as a single measurement, and using inverse-variance reweighting to account for the greater precision that results for these cases. Accordingly, the mutually adjusted effects of community and season were estimated by a fixed-effects, analysis of variance (ANOVA)-type model, which was applied to each VOC.

The incorporation of monitor location effects calls for a more sophisticated approach than fixed-effects ANOVA. This study has a "hub-and-spoke" design, with four levels of potentially high correlation: (1) multiple subjects associated with each neighborhood-specific outdoor measurement, (2) multiple monitoring periods associated with each subject over time, (3) duplicate measurements taken from some subjects in some monitoring periods, and (4) duplicate measurements taken outdoors for some monitoring periods. To estimate the difference between, for example, the personal and outdoor levels of a VOC, standard *t*-statistics or fixed-effects ANOVAs do not account for this correlation and therefore could produce biased estimates as well as under-sized confidence intervals. To address this problem, for each VOC a hierarchical, mixed-effects statistical model (21, 22) was used to estimate the mutually adjusted effects of monitor location, community, and season while accounting for all four sources of correlation. Fixed effects were modeled for log P/O, log I/O, and for the additive effects of community and season on each of these log relative concentrations. Random effects were modeled for study subjects ( $n = 71$ ), for common O measurements at each sampling time-index, and for subject-time-index combinations with repeated measures. For the 12 O monitoring periods with duplicate measurements, the geometric mean of each duplicate was used with inverse variance reweighting to account for their higher precision. Exponentiation of these estimated effects yields P/O and I/O as relative concentrations, and the effects of community and season as multipliers of these relative concentrations.

## Results

A community- and time-index-matched sample refers to either an I or P sample for which there was at least one corresponding O measurement in the same community and over the same period of time. The number of valid, community- and time-index-matched, 2-day VOC samples is shown in Table 1 by monitor location (O, I, P), community (BCK, ESP, PHI), and season, spring (SPRG), summer (SUMR), fall (FALL)). There were 132 O samples, 292 I samples, and 288 P samples available for analysis. Sampling spanned a total of 110 days (55 2-day VOC monitoring periods), with 40 in SPRG, 30 in SUMR, and 40 in FALL. Comparable numbers of valid samples were collected for each community. The I and P samples represent data from 71 subjects, 25 in BCK (2–17 P samples per subject), 22 in ESP (5–18 P samples per subject), and 24 in PHI (2–15 P samples per subject).

A summary of measured concentrations for all 15 VOCs is provided in Table 2. Percentage of samples above the analytical detection limit tended to be highest for P samples (77.5–100%), intermediate for I samples (71–99.7%), and lowest for O samples (9.1–100%). The compound least often detected in O (9.1%), I (71%), and P (77.5%) air was *b*-pinene.

In contrast, benzene, carbon tetrachloride, ethyl benzene, tetrachloroethylene, *o*-xylene, and *m*/*p*-xylene were detected in more than 97% of all O, I, and P samples. Median and 90th percentile values for all compounds, except carbon tetrachloride, were highest in P samples, intermediate in I samples, and lowest in O samples.

A comparison of distributions of all VOCs by monitor location (O, I, P) is displayed in Figure 1. The VOCs are ordered by their median O concentrations. The same four compounds, chloroform, *p*-dichlorobenzene, styrene, and trichloroethylene, tended to be found in the lowest absolute concentrations for all sample types. Similarly, toluene, *m*/*p*-xylene, and benzene tended to be found in the highest absolute concentrations for all sample types. Both *a*-pinene and *d*-limonene were consistently found in relatively high concentrations for I and P samples.

Comparisons of distributions of all VOCs and monitor locations (P, I, O) are provided in Figure 2 by season and in Figure 3 by community. The VOCs are ordered as in Figure 1. The same general patterns (e.g.,  $P > I > O$ ) observed in the overall data (Figure 1) were also apparent within each season and within each community. In general, the same compounds as before were found in either relatively high or relatively low absolute concentrations across both seasons and communities.

The effects of community and season on outdoor concentrations alone are summarized in Table 3. The statistical model in this case comprises fixed effects only, and was fitted by maximum likelihood with software from SAS (19) and S-plus (20). The estimates in Table 3 are the anti-logs of the estimated fixed effects in the model, including 95% confidence intervals where appropriate (confidence intervals were not available for some VOCs with low detection rates).

The estimated outdoor VOC concentrations ( $\mu\text{g}/\text{m}^3$ ) in BCK in SPRG (referent values) are based on the fitted regression model. The effects of the other two communities (ESP, PHI) and the other two seasons (SUMR, FALL) are represented in terms of multiplicative factors (or "effect modifiers") on the estimated concentrations in BCK in SPRG. For example, averaged across all three seasons, the ESP outdoor site has twice the level of benzene as BCK. The model estimated concentration of benzene for ESP in FALL is  $2.0 \mu\text{g}/\text{m}^3$ , which is derived from  $0.7 \mu\text{g}/\text{m}^3$  (for BCK in SPRG)  $\times 2.0$  (effect modifier for ESP)  $\times 1.4$  (effect modifier for FALL).

The data indicate that estimated outdoor concentrations tended to be lower in BCK compared to ESP and PHI for most of the 15 VOCs (except carbon tetrachloride, *a*-pinene in PHI, *b*-pinene, and trichloroethylene in ESP). Estimated outdoor concentrations tended to be lower in SPRG compared to both SUMR and FALL for benzene, *p*-dichlorobenzene, ethyl benzene, styrene, *o*-xylene, and *m*/*p*-xylene. On the other hand, estimated outdoor concentrations in SPRG tended to be higher than both SUMR and FALL for carbon tetrachloride, *d*-limonene, methylene chloride, toluene, and trichloroethylene.

The estimated relative concentrations (ERCs) for matched P/O, I/O, and P/I samples in BCK in SPRG (referent values), including 95% confidence intervals, are presented in Table 4, columns 3–5. Columns 6–9 show the estimated effects of the other two communities and seasons on the P/O ERCs in BCK in SPRG, while columns 10–13 show the estimated effects of the other two communities and seasons on the I/O ERCs in BCK in SPRG. The estimated community and seasonal effect modifiers represent the multiplicative effect, beyond that of the referent community (BCK) and season (SPRG), on either P/O or I/O. The data in Table 4 can also be used to derive approximate values for VOC-specific ERCs by community and season. For example, the P/O ERC for benzene in ESP during FALL is approximately 1.9, which is



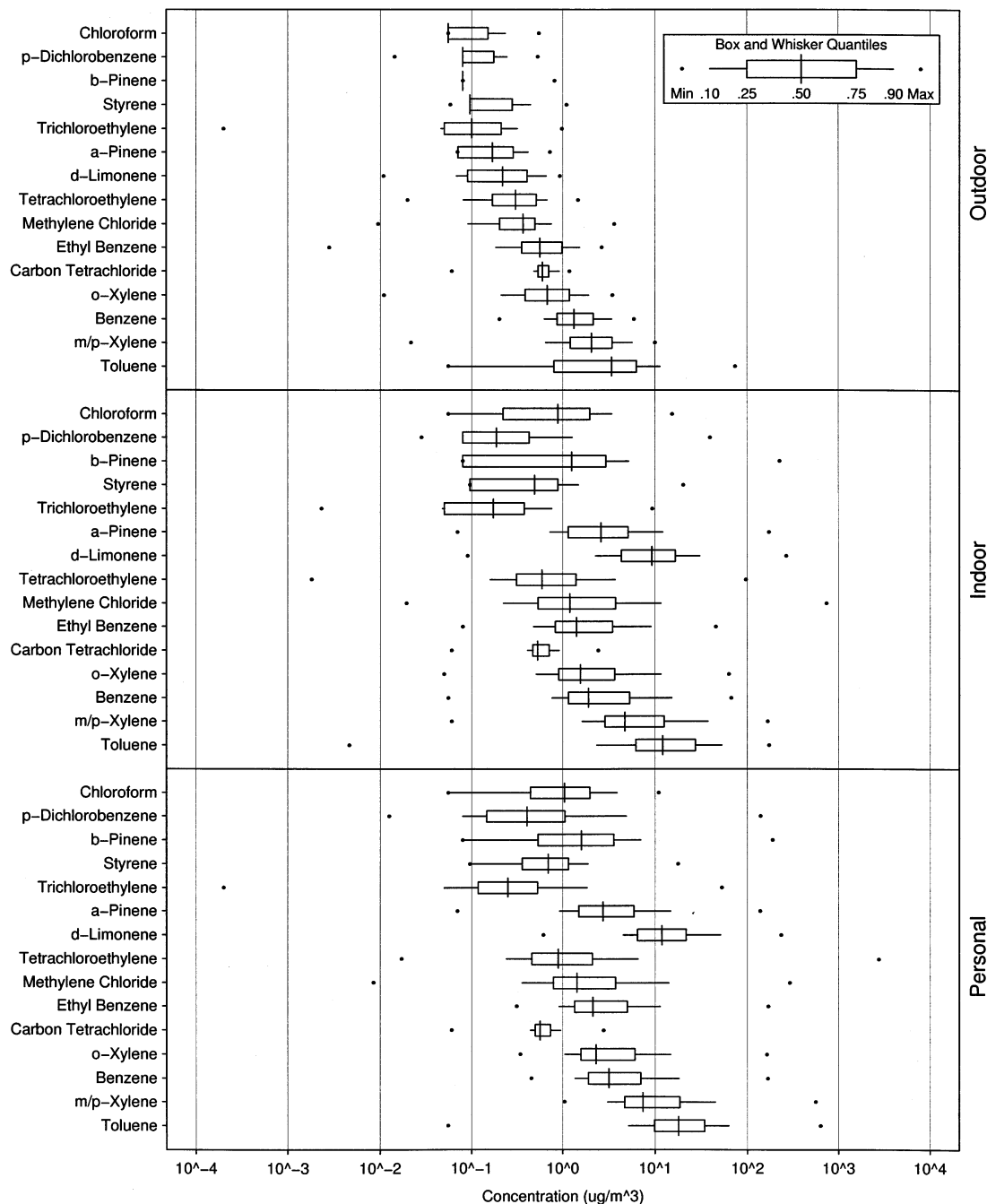


FIGURE 1. Distributions of all valid, matched VOC concentrations for outdoor, indoor, and personal samples

derived by multiplying 6.9 (P/O ERC for benzene in BCK in SPRG)  $\times$  0.3 (ESP effect modifier)  $\times$  0.9 (FALL effect modifier).

Consistent with previous analyses, concentrations of carbon tetrachloride are relatively constant for O, I, and P samples, and vary little across season and community (ERCs  $\approx$  1). There is substantial variability, however, in ERCs for the other VOCs. For example, the P/O ERCs in BCK in SPRG ranged from 3.0 (trichloroethylene) to 73.8 (*d*-limonene), I/O ERCs ranged from 1.6 (trichloroethylene) to 54.8 (*d*-limonene), and P/I ERCs ranged from 0.8 (chloroform) to 2.3 (*p*-dichlorobenzene). P/O ERCs were 3 or greater for 14 compounds, and I/O values were 3 or greater for 12 compounds. Eleven compounds had P/I ERCs  $>$  1, 3 compounds had P/I ERCs approximately equal to 1, and only chloroform (0.8) had a P/I ERC  $<$  1. For all measured VOCs in BCK in SPRG, except chloroform, mean P concentrations were  $\geq$  matched I concentrations, and, except for carbon

tetrachloride, mean I concentrations were  $>$  matched O concentrations.

The data indicate that for 11 of 15 VOCs, relative P/O concentrations tended to be lower in ESP and PHI as compared to BCK (effect modifiers  $<$  1.0), with carbon tetrachloride, chloroform, *b*-pinene, and trichloroethylene in ESP being the exceptions. For example, the P/O ERC for benzene in ESP or PHI was only 30% of the comparable value for BCK. The data also show that there is relatively little seasonal effect on P/O for most compounds, except for methylene chloride (twice as high in the summer and fall) and toluene (1.5 times higher in the summer and 2.0 times higher in the fall).

The situation is similar for I/O comparisons, with ERCs in ESP and PHI tending, on average, to be lower than those in BCK (effect modifiers  $<$  1.0), except for carbon tetrachloride, *p*-dichlorobenzene in PHI, and *b*-pinene, in ESP, and

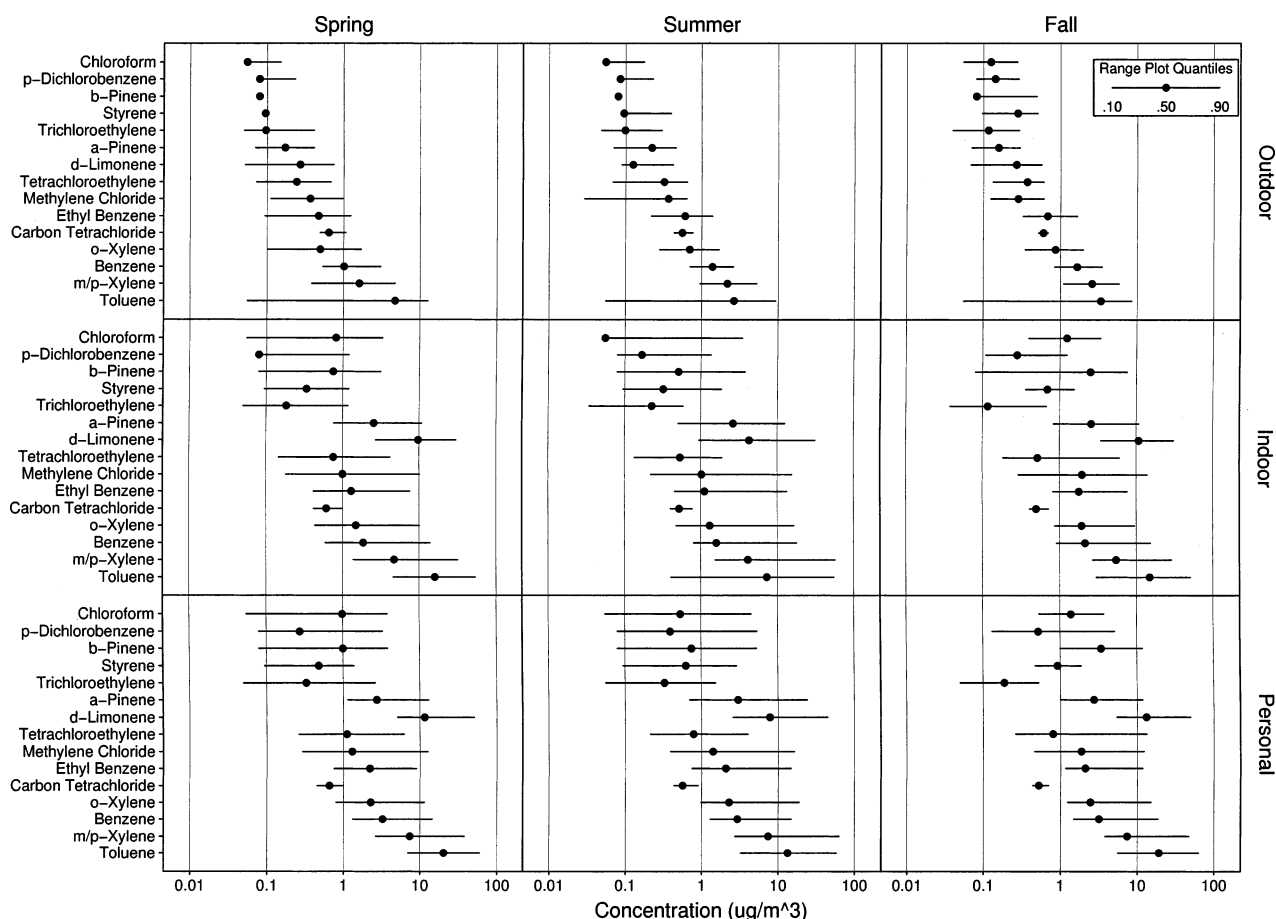


FIGURE 2. Distributions of all valid, matched VOC concentrations by monitor location and season

trichloroethylene in ESP. The I/O ERCs for benzene in ESP and PHI, for example, are only 30% that of BCK. The I/O ERCs were similar across seasons for most VOCs (effect modifiers  $\approx 1.0$ ), except for chloroform in summer (0.6 compared to spring), methylene chloride (twice as high in summer and fall compared to spring), *b*-pinene in fall (2.7 times higher than spring), and toluene in the fall (1.9 times higher than spring). Both P/O and I/O ERCs for BCK generally exceed one, several of these by a factor of 10. The P/O and I/O ERCs for ESP and PHI are generally lower, but still exceed one in all but a few cases.

## Discussion

For 14 of the 15 VOCs measured in this study, 2-day average concentrations were highest for personal samples, intermediate for indoor residential samples, and lowest for outdoor community air samples. Carbon tetrachloride was the exception ( $P \approx I \approx O$ ) because airborne concentrations appeared to be relatively uniform indoors and out. This finding is consistent with the fact that carbon tetrachloride is banned and no longer produced so that measured ambient levels represent global background values. It also indicates that carbon tetrachloride is equilibrated in the indoor environment within the time scale of our measurements. The  $P > I > O$  pattern, which is consistent with previous studies (9–11), persisted across all three urban neighborhoods and for all three seasons.

While accommodating the three-way interaction of monitor location, season, and community for each of these 15 VOCs would produce different estimates, this was not our aim. We believe it is important and relevant to estimate the overall effects in each of these three categories, for example, the overall effect of East St. Paul, across all three seasons.

Comparing all 15 VOCs in this way alone creates a great deal of information by itself, and keeps the focus on overall effects. The addition of all three-way interactions would create many more tables of output, while not contributing substantially to our understanding of these overall effects.

Outdoor VOC concentrations were relatively low compared to those in other metropolitan areas, primarily because the Minneapolis-St. Paul metro area is (a) predominantly downwind of rural areas in the U. S. and Canada that tend to have low VOC emissions, (b) well ventilated by consistent winds, and (c) not situated in a valley that could trap pollutants. Although outdoor concentrations were similar in the three neighborhoods, levels in BCK tended to be marginally lower than those in ESP and PHI (in agreement with model predictions). No important seasonal differences were identified. The 2-day sampling time allowed for enough material to be collected so that the percentage of samples above the analytical detection limit was reasonably good for most compounds (all exceeded 70% detection except the O samples of *b*-pinene (9%), chloroform (26%), styrene (43%), and *p*-dichlorobenzene (58%)).

Indoor residential VOC concentrations are a function of both outdoor sources (such as automotive exhaust and smokestack emissions) and indoor sources (as for example environmental tobacco smoke, consumer products, and cooking emissions). In addition, indoor concentrations can also be influenced by factors such as ventilation rates, chemical reactions, and sorption to surfaces. Of the 15 VOCs measured in this study, one (carbon tetrachloride) originates exclusively outdoors, five (chloroform, *p*-dichlorobenzene, *d*-limonene, and *a*- and *b*-pinene) are almost solely from indoor sources, and nine (benzene, ethyl benzene, methylene chloride, styrene, toluene, trichloroethylene, tetrachloro-

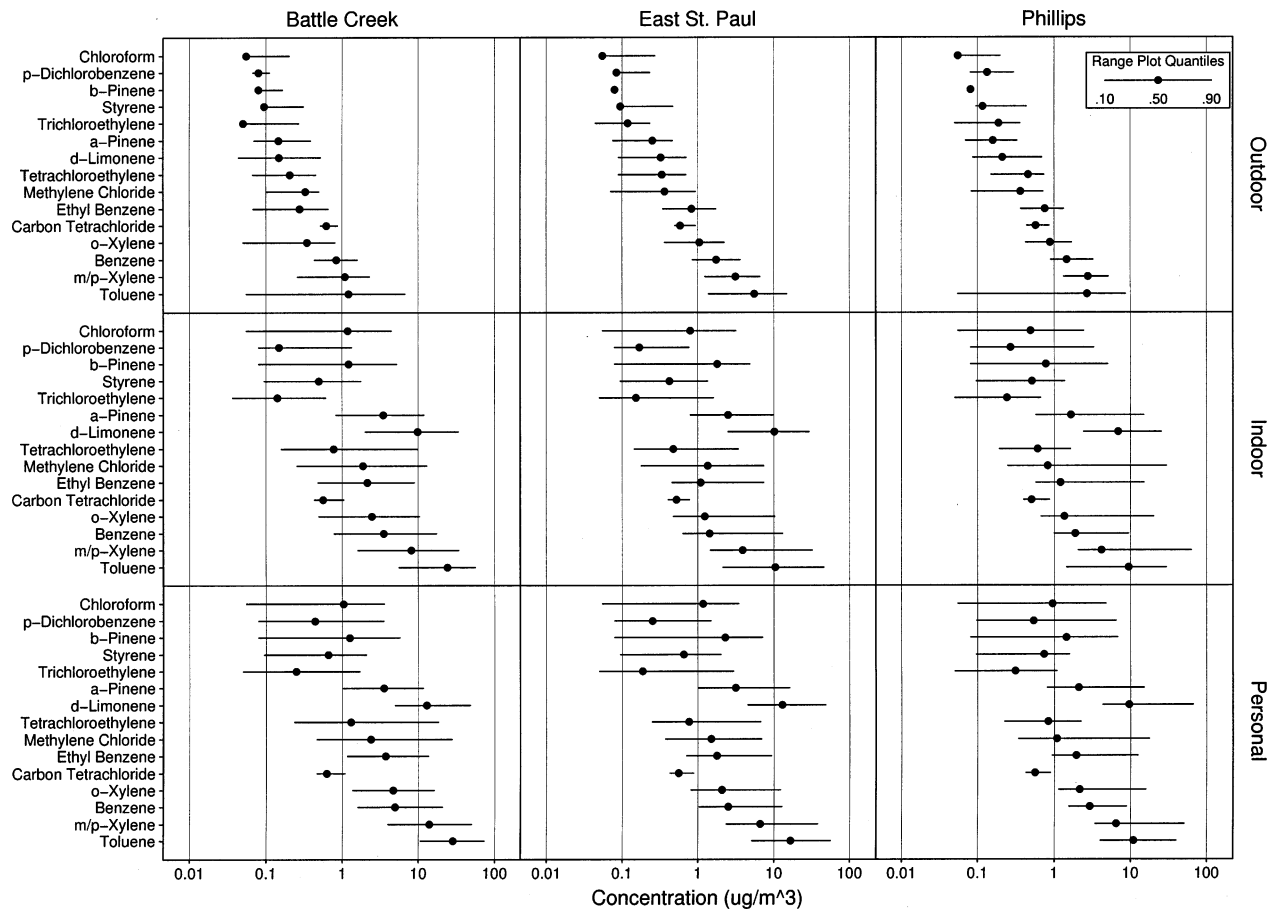


FIGURE 3. Distributions of all valid, matched VOC concentrations by monitor location and community

TABLE 3. Modeling Results for Comparison of Outdoor VOC Concentrations by Community and Season

voc	n	est. (ug/m <sup>3</sup> ) for BCK in SPRG	community and season effect modifiers (relative to BCK in SPRG)			
			ESP	PHI	SUMR	FALL
benzene	132	0.7 (0.6, 0.9)	2.0 (1.6, 2.6)	1.9 (1.5, 2.4)	1.1 (0.9, 1.4)	1.4 (1.1, 1.7)
carbon tetrachloride	132	0.7 (0.6, 0.8)	1.0 (0.9, 1.1)	0.9 (0.8, 1.0)	0.9 (0.8, 1.0)	0.9 (0.8, 1.0)
chloroform	132	0.1 (NA <sup>b</sup> , NA)	1.1 (NA, NA)	1.2 (NA, NA)	1.0 (NA, NA)	1.7 (NA, NA)
p-dichlorobenzene	132	0.1 (NA, NA)	1.3 (NA, NA)	1.7 (NA, NA)	1.1 (NA, NA)	1.5 (NA, NA)
ethyl benzene	132	0.2 (0.1, 0.2)	3.6 (2.5, 5.0)	3.1 (2.2, 4.4)	1.2 (0.9, 1.7)	1.7 (1.2, 2.4)
d-limonene	121 <sup>a</sup>	0.2 (0.1, 0.2)	1.7 (1.1, 2.5)	1.3 (0.9, 2.0)	0.7 (0.5, 1.1)	0.9 (0.6, 1.3)
methylene chloride	132	0.3 (0.2, 0.5)	1.2 (0.8, 1.7)	1.1 (0.8, 1.7)	0.6 (0.4, 0.9)	0.8 (0.5, 1.1)
a-pinene	121 <sup>a</sup>	0.1 (0.1, 0.2)	1.4 (1.1, 1.9)	1.0 (0.8, 1.4)	1.2 (0.9, 1.7)	0.9 (0.7, 1.2)
b-pinene	121 <sup>a</sup>	0.1 (NA, NA)	0.9 (NA, NA)	1.0 (NA, NA)	1.0 (NA, NA)	1.4 (NA, NA)
styrene	132	0.1 (NA, NA)	1.3 (NA, NA)	1.2 (NA, NA)	1.4 (NA, NA)	2.1 (NA, NA)
tetrachloroethylene	132	0.2 (0.1, 0.2)	1.5 (1.1, 2.1)	2.0 (1.4, 2.8)	1.0 (0.7, 1.4)	1.3 (0.9, 1.8)
toluene	132	1.0 (0.5, 1.8)	7.2 (3.6, 14.4)	2.4 (1.2, 4.8)	0.5 (0.2, 0.9)	0.6 (0.3, 1.2)
trichloroethylene	132	0.1 (0.1, 0.1)	1.0 (0.7, 1.6)	1.6 (1.0, 2.4)	0.8 (0.5, 1.3)	0.8 (0.6, 1.3)
o-xylene	132	0.2 (0.2, 0.3)	3.4 (2.5, 4.6)	2.9 (2.1, 4.0)	1.4 (1.0, 1.9)	1.7 (1.3, 2.3)
m-/p-xylene	132	0.6 (0.5, 0.8)	3.6 (2.6, 5.0)	3.1 (2.3, 4.3)	1.3 (0.9, 1.9)	1.6 (1.2, 2.2)

<sup>a</sup> Fewer valid samples were available because of calibration problems. <sup>b</sup> NA = not available due to low outdoor detection rates.

ethylene, o-xylene, and m-/p-xylene) are emitted by both indoor and outdoor sources. Previous studies suggest that levels of many VOCs are typically higher inside residences

than matched outdoor concentrations (9–11). In this study, for instance, in BCK in SPRG d-limonene, which is primarily from indoor sources such as room deodorizers, furniture

**TABLE 4. Comparison of Estimated Relative Concentrations (ERCs) for VOCs (P/O, I/O, P/I) Based on a Mixed-Effects Model Fitted for Each VOC**

VOC	n	community and season ERC effect modifiers (relative to BCK in SPRG)										
		ERC for BCK in SPRG			P/O				I/O			
		P/O	I/O	P/I	ESP	PHI	SUMR	FALL	ESP	PHI	SUMR	FALL
benzene	636	6.9 (4.8, 10.0)	4.4 (3.1, 6.4)	1.6 (1.3, 1.9)	0.3 (0.2, 0.4)	0.3 (0.2, 0.5)	1.0 (0.8, 1.2)	0.9 (0.7, 1.1)	0.3 (0.2, 0.4)	0.3 (0.2, 0.6)	0.9 (0.7, 1.2)	1.0 (0.8, 1.2)
carbon tetrachloride	636	1.0 (0.9, 1.1)	1.0 (0.9, 1.1)	1.0 (1.0, 1.1)	0.9 (0.8, 1.0)	1.0 (0.9, 1.1)	1.1 (1.0, 1.3)	0.9 (0.8, 1.0)	0.9 (0.8, 1.0)	1.0 (0.9, 1.1)	1.1 (1.0, 1.2)	0.9 (0.8, 1.0)
chloroform	636	9.5 (5.9, 15.2)	11.6 (7.2, 18.5)	0.8 (0.6, 1.1)	1.0 (0.6, 1.9)	1.1 (0.6, 2.0)	0.7 (0.4, 1.1)	1.3 (0.9, 1.9)	0.8 (0.4, 1.5)	0.6 (0.3, 1.0)	0.6 (0.4, 0.9)	1.2 (0.8, 1.8)
p-dichlorobenzene	636	5.6 (3.3, 9.4)	2.4 (1.4, 4.1)	2.3 (1.7, 3.1)	0.5 (0.2, 1.0)	0.8 (0.4, 1.7)	1.0 (0.7, 1.5)	1.1 (0.8, 1.6)	0.6 (0.3, 1.2)	1.0 (0.5, 1.9)	1.2 (0.8, 1.8)	1.2 (0.8, 1.7)
ethylbenzene	636	18.8 (12.1, 29.1)	12.1 (7.8, 18.7)	1.6 (1.3, 1.9)	0.2 (0.1, 0.3)	0.2 (0.1, 0.3)	0.9 (0.6, 1.2)	0.7 (0.5, 1.0)	0.2 (0.1, 0.3)	0.2 (0.1, 0.4)	0.8 (0.6, 1.2)	0.8 (0.6, 1.1)
d-limonene	570 <sup>a</sup>	73.8 (45.0, 121.0)	54.8 (33.5, 89.8)	1.3 (1.1, 1.6)	0.6 (0.3, 1.2)	0.8 (0.4, 1.5)	1.0 (0.6, 1.7)	1.2 (0.8, 2.0)	0.6 (0.3, 1.2)	0.7 (0.4, 1.2)	0.9 (0.5, 1.5)	1.3 (0.8, 2.0)
methylene chloride	636	5.8 (3.1, 10.8)	4.4 (2.4, 8.2)	1.3 (1.1, 1.6)	0.5 (0.2, 1.3)	0.4 (0.2, 1.0)	2.0 (1.2, 3.1)	2.0 (1.3, 3.0)	0.5 (0.2, 1.2)	0.5 (0.2, 1.0)	2.0 (1.3, 3.2)	2.3 (1.5, 3.5)
a-pinene	570 <sup>a</sup>	20.5 (12.9, 32.5)	20.2 (12.8, 32.1)	1.0 (0.9, 1.2)	0.7 (0.4, 1.3)	0.7 (0.4, 1.3)	0.9 (0.6, 1.4)	1.3 (0.9, 1.8)	0.6 (0.3, 1.2)	0.6 (0.3, 1.1)	0.9 (0.6, 1.3)	1.3 (0.9, 1.9)
b-pinene	570 <sup>a</sup>	6.5 (4.0, 10.5)	6.4 (4.0, 10.4)	1.0 (0.7, 1.4)	1.8 (1.0, 3.4)	1.0 (0.5, 1.9)	0.8 (0.5, 1.4)	3.0 (2.0, 4.5)	1.2 (0.7, 2.3)	0.6 (0.3, 1.2)	0.9 (0.5, 1.4)	2.7 (1.8, 4.1)
styrene	636	4.3 (2.9, 6.2)	3.2 (2.2, 4.6)	1.3 (1.1, 1.7)	0.9 (0.6, 1.5)	0.8 (0.5, 1.3)	1.1 (0.8, 1.5)	1.1 (0.8, 1.4)	0.8 (0.5, 1.2)	0.8 (0.5, 1.4)	1.0 (0.7, 1.3)	1.1 (0.9, 1.5)
tetrachloroethylene	636	9.4 (5.5, 16.3)	5.5 (3.2, 9.4)	1.7 (1.4, 2.2)	0.4 (0.2, 0.8)	0.3 (0.1, 0.6)	0.7 (0.5, 1.1)	0.7 (0.5, 1.1)	0.4 (0.2, 0.9)	0.3 (0.2, 0.7)	0.7 (0.5, 1.0)	0.8 (0.5, 1.1)
toluene	636	27.1 (13.1, 56.4)	20.8 (10.0, 43.2)	1.3 (1.0, 1.6)	0.1 (0.0, 0.2)	0.1 (0.1, 0.3)	1.5 (0.7, 3.4)	2.0 (1.0, 4.2)	0.1 (0.0, 0.2)	0.1 (0.1, 0.4)	1.0 (0.4, 2.1)	1.9 (0.9, 3.9)
trichloroethylene	636	3.0 (1.8, 5.2)	1.6 (0.9, 2.8)	1.9 (1.4, 2.5)	1.0 (0.5, 1.9)	0.6 (0.3, 1.3)	1.1 (0.6, 1.9)	0.8 (0.5, 1.3)	1.1 (0.6, 2.2)	0.9 (0.4, 1.7)	1.1 (0.6, 1.9)	1.0 (0.6, 1.6)
o-xylene	636	18.0 (11.7, 27.8)	11.0 (7.2, 17.0)	1.6 (1.4, 2.0)	0.2 (0.1, 0.3)	0.2 (0.1, 0.4)	0.8 (0.6, 1.1)	0.7 (0.5, 1.0)	0.2 (0.1, 0.3)	0.2 (0.1, 0.4)	0.7 (0.5, 1.0)	0.8 (0.6, 1.1)
m-p-xylene	636	19.2 (12.5, 29.7)	12.4 (8.1, 19.2)	1.5 (1.3, 1.9)	0.2 (0.1, 0.3)	0.2 (0.1, 0.3)	0.8 (0.6, 1.1)	0.8 (0.6, 1.0)	0.2 (0.1, 0.3)	0.2 (0.1, 0.3)	0.7 (0.5, 1.0)	0.8 (0.6, 1.1)

<sup>a</sup> Fewer valid samples were available because of calibration problems.

**TABLE 5. Comparison of Benchmarks for Acceptable Lifetime Cancer Risk and Measured Personal, Indoor, and Outdoor VOC Concentrations (in  $\mu\text{g}/\text{m}^3$ )**

volatile organic chemical (CAS no.)	concentration for benchmark cancer risk <sup>a</sup>	personal		indoor		outdoor	
		median	90th percentile	median	90th percentile	median	90th percentile
benzene (71-43-2)	1.3 <sup>b</sup>	3.2	18.3	1.9	15.3	1.3	3.3
carbon tetrachloride (56-23-5)	0.7 <sup>c</sup>	0.6	0.9	0.5	0.9	0.6	0.9
chloroform (67-66-3)	0.4 <sup>c</sup>	1.0	3.9	0.9	3.4	0.1	0.2
p-dichlorobenzene (106-46-7)	0.9 <sup>d</sup>	0.4	5.1	0.2	1.5	0.1	0.2
methylene chloride (75-09-2)	20 <sup>b</sup>	1.4	12.1	1.1	11.5	0.4	0.8
trichloroethylene (79-01-6)	5 <sup>d</sup>	0.2	1.4	0.2	0.8	0.1	0.3

<sup>a</sup> Estimated lifetime excess cancer risk (95th percentile upper-bound) of  $1 \times 10^{-5}$  (1 in 100 000) for an individual exposed to this concentration for a 70-year lifetime. <sup>b</sup> Minnesota Health Risk Value (HRV). <sup>c</sup> U. S. Environmental Protection Agency IRIS (Integrated Risk Information System) Value. <sup>d</sup> California Environmental Protection Agency Value.

polishes, and household cleaners, had an I/O ERC of 54.8 (95% CI: 33.5, 89.8). The VOC that was most often found in the highest absolute concentrations in O, I, and P samples was toluene, which has many outdoor and indoor sources. It had an I/O ERC of 20.8 (95% CI: 10.0, 43.2) in BCK in SPRG.

Personal exposures (P samples in this study) are a function of VOC concentrations in the various microenvironments through which people move during their normal daily activities, and the time they spend in those microenvironments. Past research indicates that P concentrations tend to be higher than matched I residential concentrations (as well as outdoor levels) for many VOCs (9–11). This is because most people spend more than 90% of their time indoors (home, work, school, restaurants, inside vehicles) where VOC concentrations are often relatively high. For the majority of

people, highest personal VOC exposures are likely to occur away from home (for example, filling the car at a self-service station, working in a poorly ventilated office, sitting next to an active smoker at dinner, commuting in heavy traffic, visiting a dry cleaner). Some people, however, live in homes with significant indoor VOC sources (for example, VOC-intensive hobbies, occupants who smoke, VOC contamination from an attached garage, high-VOC-emission products, furnishings, or materials), which can be a major determinant of their personal exposure. The P/I ERCs were predominantly greater than 1 across all communities and seasons in this study, with most P concentrations exceeding matched I concentrations by 30% or more.

To put measured values in the context of related health effects, observed P, I, and O concentrations are compared in Table 5 to acceptable risk limits for the six VOCs in this



study that are designated human carcinogens (5, 23, 24). The established risk threshold in Minnesota (24) is the airborne concentration ( $\mu\text{g}/\text{m}^3$ ), which, if breathed over a 70-year lifetime, is estimated (using a 95th percentile upper-bound estimate) to increase an exposed individual's lifetime cancer risk by  $1 \times 10^{-5}$  (1 in 100 000). All median and 90th percentile concentrations in P, I, and O samples were below the acceptable risk level for methylene chloride and trichloroethylene. All measured concentrations of carbon tetrachloride, which were relatively constant across O, I, and P samples, were at or near the risk threshold value ( $0.7 \mu\text{g}/\text{m}^3$ ). For chloroform and *p*-dichlorobenzene, median and 90th percentile concentrations in outdoor air were below acceptable risk limits. However, in I and P samples, 90th percentile values for *p*-dichlorobenzene and both median and 90th percentile values for chloroform exceeded the applicable reference levels. For benzene, the median and 90th percentile concentrations exceeded the acceptable risk value in O, I, and P samples.

Further research is needed to better understand the significance of these results for health risk assessments and related risk management decisions. It is especially important to gain insight into how outdoor concentrations affect indoor levels in buildings and vehicles, and how outdoor and indoor levels in important microenvironments affect personal exposures. It is also crucial to learn more about indoor sources and to better understand the nature and magnitude of indoor emissions. Subsequent analyses of this data set will investigate inter-individual and intra-individual variability in VOC exposures over time, and examine cross-sectional and longitudinal correlations between outdoor and personal measurements.

In summary, it is common for regulatory agencies to rely on ambient air measurements at central monitoring sites as a proxy for human exposures to hazardous air pollutants in urban areas (25, 26). Often this approach is used as part of a screening risk assessment, which aims to make conservative estimates of potential health risks (e.g., use assumptions that tend to over-estimate risk with an appropriate margin of safety or uncertainty). But the data presented here suggest that outdoor measurements at central neighborhood sites can substantially under-estimate actual exposures (and associated health risks) for local residents.

The evidence, which is consistent with previous studies, suggests that people typically encountered substantially higher VOC concentrations during their normal daily activities compared to ambient VOC levels recorded at central monitoring sites. It is worth noting that observed differences between indoor and outdoor concentrations may be less in urban areas with higher ambient VOC levels (lower I/O ERCs even if indoor residential VOC levels are similar because outdoor values may be higher). Results suggest that other indoor (e.g., inside vehicles, inside at work) and outdoor (e.g., walking on a busy street) microenvironments beyond those measured in this study are also important determinants of real-world VOC exposures.

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