39354 Minnesota Pollution Control Agency Post-Hearing Comment Period for Air Toxics Emissions Reporting Rule

Closed Mar 19, 2025 · Discussion · 2 Participants · 1 Topics · 2 Answers · 0 Replies · 0 Votes

2	1	2	0	0
PARTICIPANTS	TOPICS	ANSWERS	REPLIES	VOTES

SUMMARY OF TOPICS

SUBMIT A COMMENT

2 Answers · 0 Replies

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Janet Keyes · Citizen · (Postal Code: unknown) · Feb 27, 2025 4:51 pm

0 Votes

I have prepared and submitted the emissions reports for about ten D permit holders, a few Registration C permit holders, and two companies that were required to obtain the Low Emitting Facility permits. Many of these are or were collision repair facilities - small companies with fewer than 50 employees. They may use about 200 different paint products per year.

They do not do emissions testing, but use material balance for reporting.

We can handle the air toxics reporting. But the lack of de minimis for some products often found in paints will create an impossible situation for us. If it does not have to be included on a safety data sheet, we will have no way of determining if it is present. An example: a toner contains up to 0.8% of a chrome(III) complex black dye. We have included that in our calculations. But if another toner has 0.08% of that same dye, it will not be present on the SDS and we will not know it is present - but this proposal states we need to include it.

Page 47 of the SONAR states that it is reasonable to use the OSHA classifications of 0.1%/1% as the de minimis. The SONAR states that the MPCA would not expect facilities to test materials or contact the manufacturer if levels are below those cutoffs. But the SONAR does not explain why it is reasonable to have no de minimis for those the MPCA considers highly toxic.

--Janet Keyes, CIH, FAIHA
CHESS, Inc.

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Closed Mar 19, 2025 · Discussion · 2 Participants · 1 Topics · 2 Answers · 0 Replies · 0 Votes

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jkeyes@chess-safety.com

Andrew Morley · Citizen · (Postal Code: unknown) · Feb 28, 2025 3:14 pm

👍 0 Votes

Please find the attached file serving as comment from the Minnesota Chamber of Commerce.

RECEIVED
By: OAH on 2/28/2025
Andrew Morley Attachment

MINNESOTA CHAMBER OF COMMERCE
GROWING MINNESOTA

February 24, 2025

Administrative Law Judge Jessica Palmer-Denig
Minnesota Office of Administrative Hearings
600 N. Robert Street
St. Paul, Minnesota 55101
OAH Docket No. 71-9003-39354

Your Honor,

My name is Andrew Morley and I work as the Environmental Policy Director for the Minnesota Chamber of Commerce, a statewide organization representing more than 6,000 businesses and more than half a million employees. Thank you for the opportunity to comment today on the MPCA's proposed Air Toxics Emissions Reporting Rule (Rule).

The Chamber has engaged the Minnesota Pollution Control Agency (MPCA) regarding air toxics emissions reporting long before the enactment of Minn. Stat. 116.062, dating back to Chamber members voluntarily providing air toxics data in the mid-1990's. The following are recent examples:

- On August 6, 2020 (2020 letter), the Chamber sent a letter to MPCA providing feedback on potential collection of more air toxics data. The Chamber's feedback included suggestions on how MPCA could achieve its data collection goals while mitigating the burden of data collection on the regulated community;
- On September 21, 2023 (2023 letter), the Chamber's letter reiterated the same points as the previous letter and included further detail in the context of passage of Minn Stat. 116.062; and
- On January 15, 2025 (2025 letter), the Chamber submitted another letter, complete with a detailed timeline and addendum, of comments made to MPCA regarding air toxics emissions reporting following publication of the Rule's Statement of Need and Reasonableness (SONAR).

Unfortunately, MPCA disregarded nearly all input from the Chamber in the four and a half years since MPCA first engaged on the concept of annual air toxics emissions reporting. While Minn Stat. 116.062 was enacted in May of 2023, many of the suggestions included in the 2020 letter are still applicable. Constructive input from the largest trade association in the state, with a diverse mix of businesses of all sizes, appears to barely register as a factor in the MPCA's decision-making for implementation of a statute that can significantly burden our state's economy.

Therefore, I want to briefly detail some of the consistent comments made throughout the years that were not at all incorporated in the agency's draft rule.

MPCA Rule is a broad, sector-wide policy

Non-point source emissions (distributed, local-scale sources not typically regulated individually) have proven to contribute to individual air pollution exposure more than large, regulated facilities as a group. The 2020 letter includes a peer-reviewed study from an MPCA scientist on this exact topic. The 2023 letter reiterated those same points. Finally, the addendum to the 2025 letter noted that the SONAR acknowledges the impact of non-point sources such as transportation emissions and wood smoke as leading causes of negative health impacts.

Rule includes nearly 900 materials
Despite the MPCA's contention that "… the proposed requirements in the MPCA's air toxics emissions reporting rule do not make Minnesota's air emissions inventory reporting requirements significantly more or less stringent than air programs in neighboring states and the EPA"[1], Minnesota's Rule does just the opposite. Tables 6 and 7 of the SONAR make it clear that Minnesota includes the most burdensome requirements, on balance, than the Neighboring States' and EPA Region 5 States' Rules.

The Chamber is on record suggesting a narrowly tailored list of air toxics since its first engagement and has remained consistent. The 2020 letter suggests starting with a limited set of sources and compounds with the most health risk, and the 2023 letter further supports that assertion. The 2025 letter notes that there is no evidence that MPCA screened existing data to find materials and sources that most adversely impact human health.

Convening stakeholder group for feedback
Outside stakeholders in the business community have offered for years to create a group to offer advice on rulemaking. Practitioners and engineers are tasked to comply with these reporting requirements and could provide valuable insight on what is feasible for compliance. This offer was never taken up by the agency.

In short, MPCA's proposed rule does not address comments submitted prior to or during the rulemaking process. The SONAR does not support the broad applicability of the rule to sources or the number of included pollutants. MPCA did not leverage decades of existing air toxics data they already collect to explain why the details of the rule are appropriate or will create net benefits for Minnesotans.

We therefore ask that the Air Toxics Emissions Reporting Rule take into account the significant input provided multiple times but never heeded from more than 6,300 businesses across the state.

Thank you for holding an administrative hearing on the Air Toxics Emissions Reporting Rule. The Minnesota Chamber of Commerce, comprised of Minnesota's leading emissions practitioners, has sought to help the agency draft a workable rule, especially in the wake of enacting the broad 116.062. We appreciate this opportunity to comment.

Sincerely,

Andrew Morley
Director, Environmental Policy
Minnesota Chamber of Commerce
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763-221-7523

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[1] https://www.pca.state.mn.us/sites/default/files/aq-rule2-02h.pdf page 70

MINNESOTA CHAMBER OF COMMERCE
GROWING MINNESOTA

January 15, 2025

Administrative Law Judge Jessica Palmer-Denig
Minnesota Office of Administrative Hearings
600 N. Robert Street
St. Paul, Minnesota 55101
OAH Docket No. 71-9003-39354

Comments submitted electronically through OAH's website
https://minnesotaoah.granicusideas.com/discussions/39354-minnesota-pollution-control-agency-dual-notice-of-intent-to-adopt-rules

Your Honor:

On behalf of the Minnesota Chamber of Commerce (Chamber), a statewide organization representing 6,300 businesses and more than half a million employees throughout Minnesota, we appreciate the opportunity to comment in response to the Minnesota Pollution Control Agency's (MPCA or "Agency") dual notice of intent to adopt rules related to air toxics emissions reporting in Minnesota Rules (Minn. R.) chapters 7002, 7005, 7007, and 7019, and to repeal the emergency affirmative defense provisions in Minn. R. 7007.1850.

Proposed Air Toxics Emissions Reporting Rules

MPCA cites its "specific statutory authority to adopt these rules under Minn. Stat. § 116.062, Minnesota Session Law – 2023, H. F. No. 2310, chapter 60, article 8, section 2 as follows: Sec. 2. Air Toxics Emissions Reporting. (b) The commissioner must require owners and operators of a facility issued an air quality permit by the agency, except a facility issued an Option B registration permit under Minnesota Rules, part 7007.1120, to annually report the facility's air toxics emissions to the agency, including a facility not required as a condition of its air quality permit to keep records of air toxics emissions."

In general, MPCA's Statement of Need and Reasonableness (SONAR) includes speculative rationale that does not support its specific rule proposals. The following list is not all inclusive:

- Figure 1 in the SONAR includes MNRISKS data for all sources. To justify increased reporting for a subset of sources, MPCA should present total MNRISKS data and then data for only the sources to be covered by the rulemaking. That demonstration may illustrate that the covered sources are important for risk reduction. However, MPCA data released in various reports in the past have shown the opposite; namely, that regulated facilities are a small part of the overall air toxics emissions inventory and related risks.
- MPCA claims that sources have no incentive to report accurately in the current voluntary system. Yet the Agency fails to demonstrate or explain how 30+ years of voluntary reporting and detailed analysis show current data are inaccurate or otherwise incomplete in a way that impacts MPCA's related policy and regulatory work.

- MPCA points to possible year-to-year variability in emissions as a reason for increasing the frequency of reporting from every-three-years to annually. Again, MPCA provides no data that shows air toxics emissions and concentrations fluctuate significantly that justifies its insinuation that more frequent data collection is necessary to close important gaps in knowledge.

MPCA says it will use the data from the rule to feed modeling and risk assessments at MPCA and US EPA. Further, it says "the MPCA does not wish to burden facilities but considers the benefits of air toxics emissions data from reporting to far outweigh the burden of annual reporting." These modeling and risk analysis activities are already happening, and it is misleading to use them as justification for new reporting with specific context.

Page 15 of MPCA's SONAR states that MPCA began collecting air toxics data from facilities in 2011. That is incorrect. MPCA has been collecting air toxics emissions data from facilities since at least the mid-1990s and was part of a US EPA Region 5 collaborative effort related to emissions and databases from at least the 1990s through the early 2000s. It is important that the record accurately reflect the duration of data collection efforts because having data for such a long period of time is important information against which to judge MPCA assertions and insinuations regarding the need for additional data collection.

The Chamber understands the Legislature has required MPCA to conduct rulemaking to make annual air toxics reporting mandatory. The points above, however, are examples of MPCA's failure to present a case for how the rules it has proposed will provide any real value for public health or air pollution understanding. If there is no real value, MPCA should approach the rulemaking effort with a targeted and flexible approach. Its proposed rule is not targeted and pulls in an expansive list of materials with minimal off-ramps. The end result will require a significant effort from regulated facilities for negligible benefit in the real world.

We attached a copy of the Chamber's September 21, 2023, comment letter on this planned rulemaking and the Chamber's August 6, 2020 letter requesting information on at the outset of potential changes to air toxics reporting. The Chamber and its members have been talking to MPCA about air toxics reporting and the possibility for increased reporting frequency since at least 2020. Chamber members offered to meet with MPCA staff to work on potential policy or rules that met the agency's data needs without broad new mandates. Despite the offers, MPCA never convened a stakeholder group of regulated parties. The proposed rule takes a maximalist approach with broad requirements, few off-ramps, and a very long list of reportable materials without any specific support for that approach. A more targeted approach would achieve any related public policy or health outcomes without the significant reporting burden on regulated facilities. A refined approach should be pursued instead of the rule as proposed.

In addition to our comments above, we note the following:

- MPCA references U.S. Environmental Protection Agency (EPA) Air Emissions Reporting Requirements (AERR) alignment. It should update the draft rule before final publication to match the AERR to the maximum extent possible.
- The proposed language in Minn. R. 7019.3020, subps. 9 and 10, add new requirements for the use of specific control efficiencies. Current voluntary submittals likely use control efficiencies determined by regulated facilities. MPCA-specified efficiencies are less likely to represent specific equipment and operations than facility data. MPCA's rule should allow for facility specific control efficiencies. These data will better represent real world emissions. Outside of the scope of this rule, some regulatory applicability analyses may require conservative assumptions as a factor of safety. This reporting rule is

intended to represent actual emissions. Conservative assumptions that lead to higher emission estimates would not serve the purpose of the rule.

- MPCA includes some de minimis allowances based on material safety data sheets. That is positive.
- With an expanded list of reportable materials, MPCA should clarify its expectations for pollutant testing and certifications of submittals. For example, many facilities do not add per-or polyfluoroalkyl substances (PFAS) materials to their processes, but there may be trace amounts in raw materials or incoming water. MPCA must clarify whether companies will be expected to test for PFAS or other materials that are not part of their process or otherwise expected to be present. Are other speciation methods (e.g., safety data sheet information) subject to the requirements of the calculation hierarchy available for toxics reporting instead of testing?

Repeal of the Emergency Affirmative Defense Provisions

The Chamber incorporates and reasserts its May 1, 2024, comments to the MPCA regarding its proposed repeal of the emergency affirmative defense provisions in Minn. R. 7007.1850 and the referencing conditions to the air permit program in Minn. R. 7007.0800, subp. 6, item F, and Minn. R. 7007.1146, subp. 5, item A, subitem (1).[1] The MPCA states that the proposal to repeal the emergency affirmative defense provisions is in response to the EPA's July 21, 2023, final rule that removed emergency affirmative defense provisions from the Clean Air Act Title V operating permit program regulations, herein referred to as the "T5-AD rule change."[2]

The Title V affirmative defense is important for subject facilities in Minnesota. In Minn. R. 7007.1850, an "emergency" is defined as "any situation arising from sudden and reasonably unforeseeable events beyond the control of the owners and operators of the stationary source, including an act of God, that requires immediate corrective action to restore normal operation, and that causes the stationary source to exceed a technology-based emission limitation under the permit, due to unavoidable increases in emissions attributable to the emergency." A facility must demonstrate an affirmative defense of emergency by satisfying several conditions listed in item C of the rule with corresponding evidence. The Chamber believes retaining these provisions to the extent practical and legal is imperative. Sources should not be held liable for emissions noncompliance resulting from an emergency situation beyond their control.

The Chamber continues to recommend not proceeding with the notice of intent to repeal the emergency affirmative defense provisions in chapter 7007. The proposed repeal should be delayed until active litigation between intervenors and the US EPA is concluded.[3] Final briefs on this litigation were submitted to the court in November 2024, and oral arguments are scheduled for January 14, 2025. A court decision on the issue is expected before August 21, 2025, which is MPCA's current EPA-approved deadline to remove the T5-AD rule change language from the state rules. Because the outcome of this litigation—which could include a potential stay or vacatur–may impact the disposition of the T5-AD rule change, the Chamber reiterates that the only prudent thing to do is for MPCA to await final disposition of this challenge. If necessary, MPCA should seek another extension to the current repeal deadline to allow for both parties to adhere to the court's decision rather than risk actions that may run afoul of that decision.

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[1] May 1, 2024, letter, from Tony Kwilas of the Minnesota Chamber of Commerce to Administrative Law Judge Jessica Palmer-Denig, OAH Docket No. 71-9003-39354.

[2] 88 Fed. Reg. 47029 (July 21, 2023).

[3] *SSM Litigation Group v. EPA*, filed September 19, 2023, in the United States Court of Appeals for the District Of Columbia Circuit, case number 23-1267.

As noted in the Chamber's May 1, 2024, comments, waiting for the outcome of active litigation on this matter may avoid a repeat of the 2015 startup, shutdown, and malfunction (SSM) State Implementation Plan (SIP) "call." In that case, EPA ordered a number of states—including Minnesota—to revise those parts of their SIPs that included defenses or exemptions related to emission exceedances during SSM events. The MPCA repealed Minn. R. 7011.1415 shortly thereafter. The D.C. Circuit Court of Appeals overturned most of the bases for the EPA's 2015 SIP call.[4] Had the MPCA not rushed to repeal its SSM rule, it may have avoided the need to do so. The 2015 SIP call underscores the need for slower and more careful consideration, particularly given that the litigation regarding the T5-AD rule change is still ongoing. Accordingly, if the MPCA preemptively repeals the rule and the litigation on the T5-AD rule change results in a stay or vacatur of the repeal, the MPCA should immediately reinstate the emergency affirmative defense provisions to be consistent with the Clean Air Act. MPCA (and EPA) would be better advised to wait for a final resolution this time before proceeding prematurely, as was the case with the 2015 SIP call. EPA would surely appreciate the prudence of such a position, if MPCA does find it necessary to seek another extension of its repeal deadline.

The MPCA also asserts that repealing the emergency affirmative defense provision would directly impact only one facility's permit and that "it is reasonable to repeal rules that are not used."

If or when the MPCA decides to repeal these provisions, it should retain them for air permits not issued pursuant to the Clean Air Act Title V operating permit program regulations. Since the MPCA permitting rules combine both the non-Title V and Title V operating permit programs, it is unclear how the removal or modification of the affirmative defense provisions will affect non-Title V facilities or why such a repeal would even be necessary. Minn. R. 7007.1850 does not disassociate the use of the affirmative defense between these types of permitted facilities, but the EPA's rule revoking the affirmative defense applies only to Title V permits. There is no basis for removing this provision for non-Title V permitted facilities.

Thank you for the opportunity to provide comments and participate in this rulemaking.

Sincerely,

Andrew Morley
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[4] *Environmental Committee of the Florida Electric Power Coordinating Group, Inc. v. Environmental Protection Agency*, 94 F. 4th 77 (D.C. Cir. 2024).

MINNESOTA CHAMBER OF COMMERCE
GROWING MINNESOTA

September 21, 2023

Administrative Law Judge James Mortenson
Minnesota Office of Administrative Hearings

Comments submitted electronically through OAH's website

The Minnesota Chamber of Commerce (Chamber) submits these comments in response to the Minnesota Pollution Control Agency's (MPCA or Agency) request for comments (RFC) on the Agency's planned rulemaking for air toxics emissions reporting for facilities that emit air toxics and are located in the counties of Anoka, Carver, Dakota, Hennepin, Ramsey, Scott, and Washington. The Chamber represents members that the rulemaking will impact.

The Chamber welcomes this opportunity to share its point of view regarding the proposed regulations. The Chamber recognizes that these rules, in conjunction with associated rules for air toxics regulation and cumulative impacts analysis, pose the possibility of a significant impact on the economic vitality of the areas subject to the rules. We believe that the MPCA also recognizes this concern. As such, the Chamber urges the MPCA to be deliberative and consultative in its approach.

Toward that end, and as a preliminary matter, the Chamber urges creating an advisory committee of key stakeholders to consult with the Agency before publishing draft rules. These stakeholders should include significant representation from parties that will be subject to new legal requirements under this rule. Such a process would help drive consensus around key issues and help the MPCA avoid (or at least narrow the scope of) potential rule challenges.

In its initial RFC, the MPCA referenced enabling legislation from the 2023 Minnesota legislative session that directs the MPCA to develop and issue rules that will:

1. Establish the requirements for air toxics emissions reporting for permitted facilities on an annual basis.
2. Identify the air toxics to be reported.
3. Amend permit and reporting processes to align with annual air toxics emissions reporting.

The Chamber's comments follow those elements and reference the Chamber's comments submitted for other planned rulemakings (attached below).

1. Establish the requirements for air toxics emissions reporting for permitted facilities on an annual basis.

The Chamber generally believes any new requirements for reporting should be aligned with existing data and conclusions. New or expanded reporting requirements should address specific public health priorities supported by the data. Please see the sections on "Data Utility" and "Reporting Burden" in the attached Chamber letter from August 6, 2020.

2. Identify the air toxics to be reported.

If air toxics will be further regulated and additional reporting required, the Chamber supports the MPCA's adoption of a list of air toxics in a rule. The list may be modified, as needed, through rulemaking and public comment in the future. Please see the section on “Guideposts for a Regulatory Program” in the attached Chamber letter dated September 21, 2023.

3. Amend permit and reporting processes to align with annual air toxics emissions reporting.

In line with our comments under item 1 above, the MPCA should only amend permits for facilities emitting priority pollutants or in designated areas. The MPCA should establish reporting thresholds and practical ways for potential reporters to determine applicability. Please see the “Streamlining Reporting” section in the attached Chamber letter from August 6, 2020.

The attached Chamber letters include additional policy and technical suggestions that go beyond the three issues the MPCA listed in the request for comments on the rule. Please consider those elements as the MPCA develops initial rulemaking.

In July 2023, the United States Environmental Protection Agency (US EPA) proposed updates to its Air Emissions Reporting Requirements (AERR). These changes would allow US EPA to collect annual hazardous air pollutant (HAP) emissions data starting in 2027. The MPCA should align any Minnesota rulemaking on air toxics / HAPs with US EPA requirements to avoid redundant reporting in multiple systems or to multiple government agencies.

Thank you for the opportunity to provide comments and participate in this rulemaking. As the rulemaking process proceeds, the Chamber and its members are available for further consultation.

Sincerely,

Tony Kwilas
Director, Environmental Policy
Minnesota Chamber of Commerce
tkwilas@mnchamber.com
651-292-4668

MINNESOTA CHAMBER OF COMMERCE
GROWING MINNESOTA

August 6, 2020

Dear Ms. Maggie Wenger:

On July 16th, 2020, the Minnesota Pollution Control Agency (MPCA) organized an online meeting to discuss potential changes to air toxics reporting, primarily an agency interest in making emissions reporting mandatory. The Minnesota Chamber of Commerce (Chamber) has members across the state, many of whom hold air quality permits or are subject to air quality rules. This letter contains the Chamber's initial comments and questions on the issue of air toxics emissions reporting.

MPCA asked the following questions. We will organize our comments around them.

- Would you use the information we collect? How?
- Do you have concerns or questions about reporting burden? How does this reporting burden change when the inventory is not voluntary but mandatory?
- What would help simplify reporting?
- How should MPCA create the list of Air Toxics and maintain it over time? How to balance emerging pollutants of concern with a fixed list of air toxics in a rule? What should be the process for adding a pollutant to the list?
- What other states' toxics inventory and/or control programs should the MPCA look at?

Data Utility

MPCA's existing suite of air pollution-focused online tools and databases provide useful information for the public to understand trends and relative concentrations across geographies. As MPCA points out, the data fidelity is limited for determining neighborhood-scale concentrations and changes over time.

If MPCA's goal is to better understand community level emissions trends and potential health impacts, it seems unlikely that an incremental improvement in one sector's data would help with that goal. The emissions data from "point sources," while voluntary, have historically been of higher quality than the data for distributed, smaller sources or mobile sources of air pollution. Emissions from some categories of small sources were calculated using population-based emission factors at the county level. Improvements in calculations for those sources probably would bring more "bang for the buck" than additional requirements for industrial sources.

MPCA may also consider targeted air quality monitoring to better understand local conditions or specific pollutant concentrations. According to section 5.2 of the MPCA's 2021 Air Monitoring Network Plan for Minnesota, the MPCA monitors 10 metals at 18 TSP sites, and 7 carbonyls and 58 individual VOCs at 19 sites. The MPCA then converts these monitored concentrations into risk values and reports them online.

These efforts cannot answer every question but they seem to be better and more focused than mandatory reporting for the entire regulated community.

Even neighborhood-scale monitors may not completely characterize public health risks. Retired MPCA research scientist Greg Pratt collaborated with other researchers on many papers related to human exposure to air pollution. Two are attached. In these studies, comparisons of monitoring data at various scales showed that people's real exposures were driven by the micro-environments they experienced throughout their days.

We encourage MPCA to broadly consider potential efforts to understand concentrations of air toxics and weigh their relative effectiveness. If the goal is to provide useful data for policymakers and citizens, improvements to the most uncertain data that feed our inventories and models are likely the best path. In addition, studies that compare modeled NATA results to monitoring data may provide better targets for data improvements.

Reporting Burden

Some facilities are already required to calculate emissions of hazardous air pollutants (HAPs) or air toxics. For these facilities, a routine, voluntary submittal can be manageable. For facilities that are not required to calculate and track emissions, the reporting burden can be significant.

- The number of pollutants is large (187 HAPs plus numerous air toxics).
- Calculation methods are not always available.
- Facilities may not have information necessary to calculate such emissions. For example, the information on Safety Data Sheets may not provide information at the desired level of detail (compositional data can be (i) missing, especially if below de minimus levels, (ii) conservatively high, (iii) expressed as a wide range, and/or (iv) not identified by CAS number (which can make it difficult to identify HAPs).
- Adding air toxics reporting in the Q1 timeframe is especially challenging because this is already a very busy time for reporting under other programs.

A mandatory program may increase the burden in ways that are difficult to predict. Under a voluntary program, a facility may submit available data in good faith. Once the program becomes mandatory, we are concerned with new requirements that could impose regulatory penalties for reporting errors or require analytical testing to characterize specific emissions. A stack test may cost $5,000 to $10,000 per pollutant per stack.

Increasing the reporting frequency from every three years to every year would also increase the burden for all affected facilities, including those already submitting emissions information for HAPs and air toxics, due to the effort spent entering data into MPCA's CEDR / e-Services system. Chamber members would prefer to keep the current triennial frequency to minimize this burden.

Any increases in reporting rigor or frequency would be associated with costs for staff time to research and calculate emissions. If MPCA intends to process these emissions estimates and enter them into dispersion modeling analyses every year instead of every three years that would also lead to increased program costs that would likely be passed along to fee-paying permit holders.

Before proceeding with any related rulemaking, the Chamber requests that MPCA conduct a cost analysis for the proposed rule. The analysis should consider the likely data collection costs for regulated facilities and the staff costs for MPCA to administer the program and process the data. MPCA could look at various scenarios, from an "everybody reports" option to a targeted program that focused on geographies or pollutants. However, as noted above, a targeted analysis may be better completed by conducting ambient monitoring than an emissions-modeling-risk assessment approach.

In general, Chamber members believe that it is in the best interests of companies to report accurate data and that a shift to mandatory reporting may have a minimal effect on the overall public health information available. Before embarking on a new rule, MPCA should better characterize the expected improvements and the related costs.

Streamlining Reporting

For many facilities, compiling and submitting data for the current voluntary effort may take a week or more of real working time. A significant amount of that time is spent hard-keying the information into MPCA's CEDR / e-Services system. Many states, including Minnesota, have improved systems for uploading water quality discharge monitoring reports. An improved interface that allowed direct import of data would simplify reporting and improve accuracy.
Reporting could also be streamlined by maintaining consistency on reporting requirements over time.

Pollutant Lists

Any rule requiring reporting should establish clear guidelines on relevant compounds, *de minimis* reporting thresholds, and applicable sources. As described above, a rule could start with a limited set of sources and compounds in order to target the most important public health issues. Such an approach would add predictability and reduce the overall reporting burden.

The establishment of *de minimis* levels is not straightforward. If a facility does not have available emissions data, there may be no simple way to demonstrate that a particular compound is emitted below relevant thresholds. Facilities would be stuck in a chicken-and-egg scenario for small sources or compounds unlikely to be emitted.

MPCA should consider how to treat unique sources in any future program. Exemptions for research and development or temporary sources would be useful for permit holders and avoid extensive work to characterize sources that may not be significant.
The provision of detailed lists of compounds at a process level also creates challenges for the protection of confidential business information. MPCA should include provisions that allow sources to protect sensitive, process-specific data and formulations.

Relevant program details, including lists of compounds, should be explicitly listed in any rule and require notice-and-comment rulemaking to modify the list. In states where lists may be changed without notice, new compounds create unexpected technical challenges for regulated facilities.

State Examples

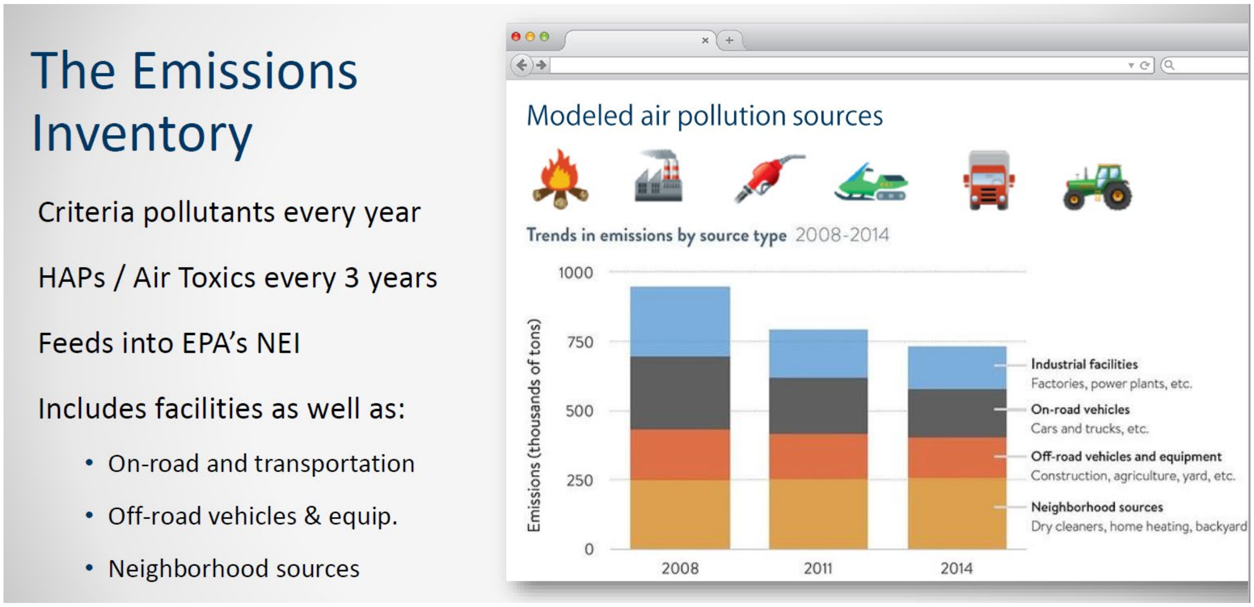
Each state's air toxics program is unique. For US EPA Region 5 states, Wisconsin is one example of a well-defined program, with pollutants and screening modeling thresholds included in rule. There are limitations to that program but it has the advantage of being predictable.

Many other states have policy-based programs, with minimal details included in rule. These programs are difficult for permit holders to manage during specific projects. We are not aware of examples of easily identified improvements to local pollutant concentrations or public health outcomes that can be attributed to these programs.

Other Comments

Chamber members are generally against increased reporting requirements as part of the MPCA's air toxics emissions inventory. Many of the most significant sources are regulated by federal NESHAPs. A number of the NESHAPs have recently undergone or will be subject to Residual Risk and Technology (RTR) reviews, which are required to demonstrate that facilities' HAP emission limits are protective of human health and the environment, with an adequate margin of safety.

Many of the MPCA's own reports state that emissions from industrial sources, both as a percent of total pollution and in absolute terms, are decreasing. A recent MPCA presentation on online air pollution tools showed this point.



The Emissions Inventory

Criteria pollutants every year

HAPs / Air Toxics every 3 years

Feeds into EPA's NEI

Includes facilities as well as:

- On-road and transportation
- Off-road vehicles & equip.
- Neighborhood sources

MPCA highlighted several improvements that would potentially result from mandatory reporting, including better data quality and useful information for future program changes. However, more information is needed that links the specific proposal to these outcomes. Better data is a means to an end and a more targeted approach for certain sources or compounds may accomplish the same goal with reduced effort.

Chamber members continue to be frustrated with the timeliness of MPCA approval of permits and environmental review submittals. Reporting changes would increase the work required from key staff (e.g., dispersion modelers, risk assessors, possibly stack test coordinators) who are already in high demand. It is not a good trade off to reduce staff assigned to core regulatory programs to marginally improve data quality for emissions inventories.

Finally, as MPCA considers how to leverage existing programs to better serve communities and reduce exposure to air pollution, the Chamber reiterates its support for Clean Air Minnesota (CAM) programs and outcomes. While incremental data improvements are good, the overarching goal should be real improvements for real people, and that is where CAM excels. MPCA is already very involved with CAM and the Chamber appreciates MPCA's strong engagement and direct support for the collaborative effort. Further ramping up MPCA support for CAM projects related to clean cars, wood-burning stoves, diesel engines, and community businesses would lead to direct improvements in the air people breathe and may be a better way to spend our collective time on air quality issues.

Thank you for the opportunity to comment on the MPCA's potential changes to air toxics emissions reporting. The Chamber and its members are available for further consultation as these efforts proceed.

Respectfully submitted,

Tony Kwilas
Director, Environmental Policy
Minnesota Chamber of Commerce

Enclosures: 2
Evaluating Differences between Measured Personal Exposures to Volatile Organic Compounds and Concentrations in Outdoor and Indoor Air
Comparison of Personal, Indoor, and Outdoor Exposures to Hazardous Air Pollutants in Three Urban Communities

Environ. Sci. Technol. **2004**, *38,* 423−430

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^2 with a population density of 2000−8000 per km^2. 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^2 and a population density of 1000−4000 per km^2. 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^2 and has a population density of 500−2000 per km^2. 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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10.1021/es030319u CCC: $27.50

TABLE 1. Summary of Valid, Matched, VOC Samples[a] 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

[a] 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 ≤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

	outdoor (ug/m³)						indoor (ug/m³)						personal (ug/m³)					
VOC	*n*	%det[b]	mean	median	Q10	Q90	*n*	%det[b]	mean	median	Q10	Q90	*n*	%det[b]	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
p-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
d-limonene	121[a]	86.8	0.3	0.2	0.1	0.6	262[a]	99.6	16.1	9.0	2.2	30.7	258[a]	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
a-pinene	121[a]	74.4	0.2	0.2	0.1	0.4	262[a]	99.6	6.7	2.5	0.7	12.4	258[a]	99.6	6.6	2.7	0.9	14.6
b-pinene	121[a]	9.1	0.1	0.1	0.1	0.1	262[a]	71.0	3.3	1.2	0.1	5.2	258[a]	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
o-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
m-/*p*-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

[a] Fewer valid samples were available because of calibration problems. [b] Percentage of samples with instrument readings above zero.

15 VOCs. Rather than present all 405 combinations (3 × 3 × 3 × 15) with inferential statements about each, key marginal distributions are examined ("marginal" here referring to the margins of this 3 × 3 × 3 × 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, tetrachloroehylene, *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 ($\mu g/m^3$) 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 ug/m^3, which is derived from 0.7 ug/m^3 (for BCK in SPRG) × 2.0 (effect modifier for ESP) × 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

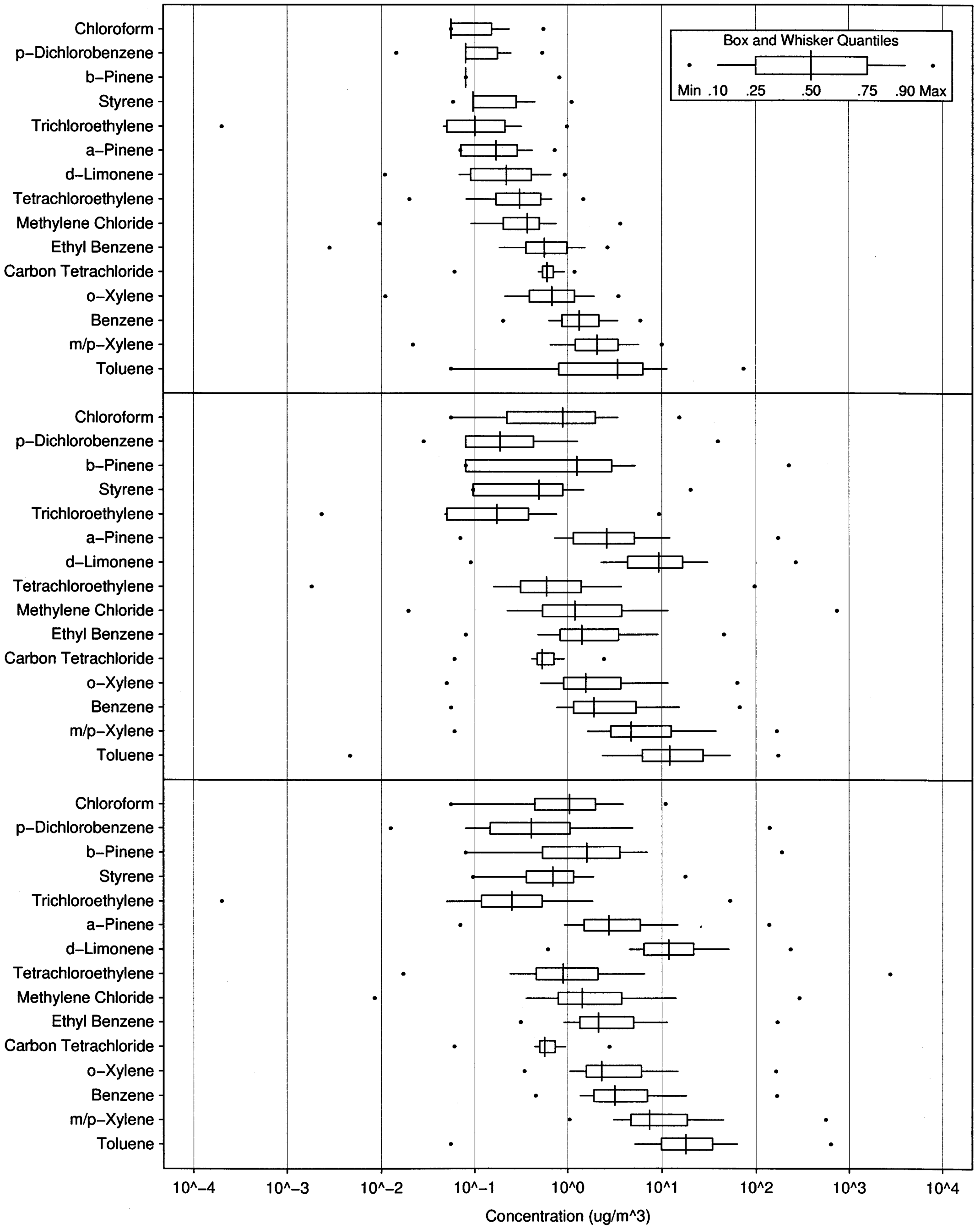

FIGURE 1. Distributions of all valid, matched VOC concentrations for outdoor, indoor, and personal samples

derived by multiplying 6.9 (P/O ERC for benzene in BCK in SPRG) × 0.3 (ESP effect modifier) × 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 $\cong$ 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

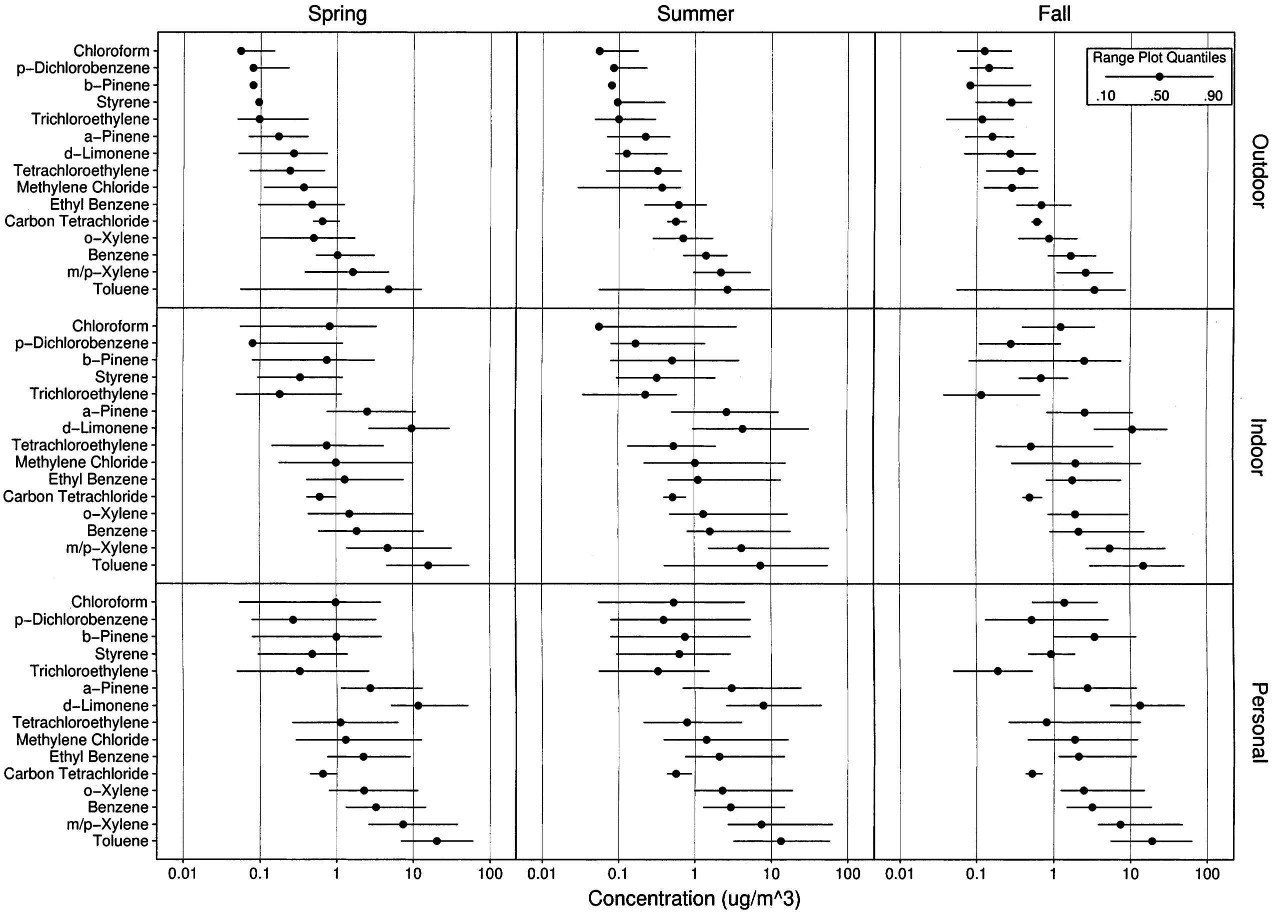

FIGURE 2. Distributions of all valid, matched VOC concentrations by monitor location and season

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 ≅ 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 ≅ I ≅ 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 soley from indoor sources, and nine (benzene, ethyl benzene, methylene chloride, styrene, toluene, trichloroethylene, tetrachloro-

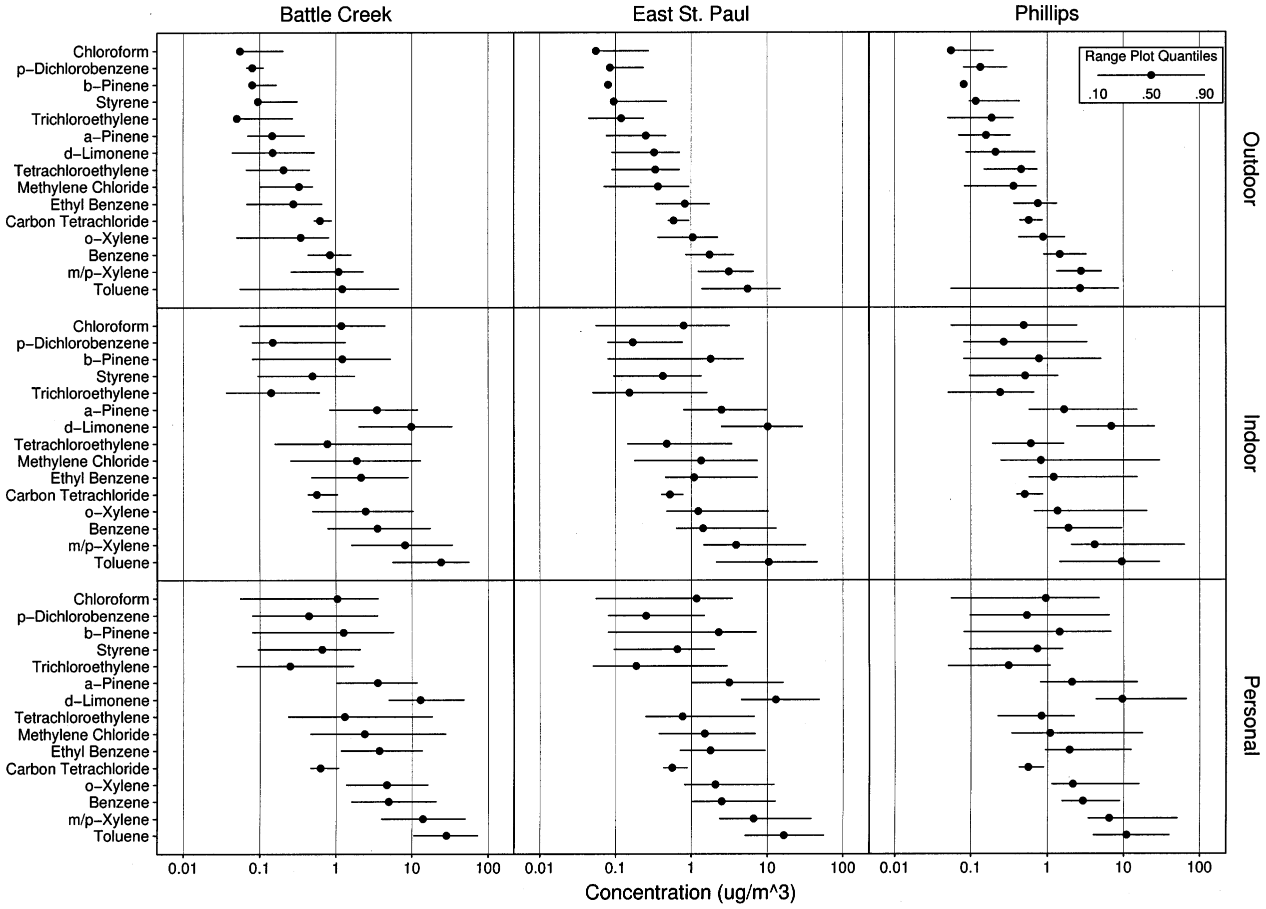

FIGURE 3. Distributions of all valid, matched VOC concentrations by monitor location and community

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

voc	*n*	est. (ug/m^3) 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[b], 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[a]	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[a]	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[a]	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)

[a] Fewer valid samples were available because of calibration problems. [b] 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

					community and season ERC effect modifiers (relative to BCK in SPRG)							
		ERC for BCK in SPRG			P/O				I/O			
VOC	*n*	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[a]	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[a]	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[a]	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)

[a] 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 $\mu g/m^3$)

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

[a] Estimated lifetime excess cancer risk (95th percentile upper-bound) of 1×10^{-5} (1 in 100 000) for an individual exposed to this concentration for a 70-year lifetime. [b] Minnesota Health Risk Value (HRV). [c] U. S. Environmental Protection Agency IRIS (Integrated Risk Information System) Value. [d] 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 ($\mu g/m^3$), 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 1×10^{-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 ug/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.

Acknowledgments

This research was funded by a STAR (Science to Achieve Results) Grant (R825241) from the U.S. Environmental Protection Agency, National Center for Environmental Research. We also benefited from a grant from the Academic Health Center at the University of Minnesota. We thank the individuals who participated in the study and acknowledge the contributions of the field team. We also thank the 3M Corporation for donating some of the organic vapor monitors used in this study. The help and support provided by the Minnesota Pollution Control Agency was essential to the success of this project.

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Received for review January 15, 2003. Revised manuscript received October 27, 2003. Accepted November 4, 2003.

ES030319U

Environ. Sci. Technol. **2004**, *38,* 2593−2602

Evaluating Differences between Measured Personal Exposures to Volatile Organic Compounds and Concentrations in Outdoor and Indoor Air

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Accurate estimation of human exposures to volatile organic compounds (VOCs) is a key element of strategies designed to protect public health from the adverse effects of hazardous air pollutants. The focus here is on examining the capability of three different exposure metrics (outdoor community concentrations, indoor residential concentrations, and a simple time-weighted model) to estimate observed personal exposures to 14 VOCs. The analysis is based on 2-day average concentrations of individual VOCs measured concurrently in outdoor (O) air in three urban neighborhoods, indoor (I) air in participant's residences, and personal (P) air near the breathing zone of 71 healthy, nonsmoking adults. A median of four matched P−I−O samples was collected for each study participant in Minneapolis/St. Paul over three seasons (spring, summer, and fall) in 1999 using charcoal-based passive air samplers (3M model 3500 organic vapor monitors). Results show a clear pattern for the 14 VOCs, with P > I > O concentrations. Intra-individual variability typically spanned at least an order of magnitude, and inter-individual variability spanned 2 or more orders of magnitude for each of the 14 VOCs. Although both O and I concentrations generally underestimated personal exposures, I concentrations provided a substantially better estimate of measured P concentrations. Mean squared error (MSE) as well as correlation measures were used to assess estimator performance at the subject-specific level, and hierarchical, mixed effects models were used to estimate the bias and variance components of MSE by tertile of personal exposure. Bias and variance both tended to increase in the upper third of the P exposure distribution for O versus P and I versus P. A simple time-weighted model incorporating measured concentrations in both outdoor community air and indoor residential air provided no improvement over I concentration alone for the estimation of P exposure.

Introduction

Concentrations of hazardous air pollutants in a person's breathing zone for a defined period of time are typically referred to as *personal* exposures (*1*, *2*). An individual's personal exposure for a particular time period (e.g., 48 h) depends on pollutant concentrations in the indoor and outdoor microenvironments through which he or she moves during routine daily activities and on the time spent in each of these locations. From a public health perspective, it is often important to estimate the distribution of personal exposures in a population or to distinguish between individuals with high versus low exposure. But measuring personal exposures for a large number of people (including potentially vulnerable groups such as the young, the elderly, and the infirm) can be burdensome, time-consuming, expensive, and, in many cases, impractical. It is imperative, therefore, to gain a clear understanding of the value of more easily obtained metrics, such as measurements at outdoor community sites or indoor residential locations, for estimating personal exposures.

Although volatile organic compounds (VOCs) are common constituents of outdoor (*3*−*6*) and indoor (*7*−*9*) air, comparatively little is known about personal exposures. The relatively few personal monitoring studies that have been conducted suggest that personal exposures tend generally to be higher than indoor residential concentrations, which tend typically to be higher than outdoor community concentrations (*10*−*15*). Other personal exposure studies have concentrated on exposure of specific subpopulations to one or few individual VOCs, with many focused on exposure to benzene. This paper examines the ability of fixed indoor residential and outdoor monitors, in combination with time−activity data, to estimate personal exposures to 14 individual VOCs for 71 nonsmoking adults 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 (*13*). A secondary objective was to measure $PM_{2.5}$ exposures for a subset of the subjects, results of which have been published previously (*16*−*19*). Three urban neighborhoods (Phillips, East St. Paul, and Battle Creek) with different outdoor VOC concentration profiles based on modeling results (*13, 20, 21*) were selected for the exposure monitoring study.

Phillips (PHI) is an economically disadvantaged, predominantly minority inner-city neighborhood in south central Minneapolis. 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. VOC concentrations were predicted to be relatively high, primarily as a result of emissions from nearby manufacturing plants. Battle Creek (BCK) is a predominantly white, affluent neighborhood on the eastern edge of St. Paul. Predicted VOC concentrations were relatively low as compared to the other two neighborhoods.

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10.1021/es030607q CCC: $27.50

A centralized outdoor monitoring site (community site) was established in each neighborhood. Approximately 25 healthy, nonsmoking adults were recruited from each neighborhood using house-to-house canvassing and direct solicitation (informed consent was obtained). Matched 2-day samples were collected outdoors at the three community monitoring sites, indoors in participants' residences (room where they spent most of their waking hours), and near participants' breathing zones, all using passive dosimeters. Participants also completed time−activity logs recording the time they spent in seven microenvironments (indoors at home, work, other; outdoors at home, work, other; in transit) and the time they were in close proximity to environmental tobacco smoke. 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).

Methods

VOC Collection and Analysis. All VOC concentrations (O, I, and P) were 2-day (approximately 48-h) 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. (*22*, *23*). These investigators have also described the determination of extraction efficiencies and the calculation of method detection limits. 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, and Vectra 486 computer with EnvironQuant Chem-Station 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 (*23*). Duplicate O, I, and P badges were collected periodically during the study (total $n = 80$), and correlation coefficients for the positive measurements were >0.95 for all individual VOCs except styrene (0.94) and chloroform (0.95). We define the median relative absolute difference (MRAD) as the median of the ratios of within-pair absolute differences divided by the within-pair mean. MRAD was <0.18 for all VOCs except trichloroethylene (0.44).

Statistical Analyses. All statistical analyses were performed using SAS (*24*) and S-plus (*25*). Concentrations less than the method detection limit (MDL) were included in the calculations. "Nondetectable" measurements (i.e., samples with no analytical response or those with values ≤ 0 after blank subtraction) were assigned a value of one-half the analytical detection limit (ADL).

Three estimators of personal exposure are evaluated:

$$\hat{P}_{[O]ij} = O_{ij} \tag{1}$$

$$\hat{P}_{[I]ij} = I_{ij} \tag{2}$$

$$\hat{P}_{[OI]ij} = O_{ij}t_{[O]ij} + I_{ij}t_{[I]ij} \tag{3}$$

where O_{ij} and I_{ij} denote the observed concentration for the ith subject on the jth occasion, from O and I, respectively; $t_{[O]ij}$ and $t_{[I]ij}$ represent the (time) fraction of the 2-day monitoring period spent in the O and I environments, respectively. For the purposes of this analysis, we let $\hat{P}_{[O]}$, $\hat{P}_{[I]}$, and $\hat{P}_{[OI]}$ represent $\hat{P}_{[O]ij}$, $\hat{P}_{[I]ij}$, and $\hat{P}_{[OI]ij}$ for all subjects and all times. In the simple time-weighted model (eq 3), the proportion of time in O was defined to be the complement of the proportion of time in I (i.e., $t_{[O]ij} = 1 - t_{[I]ij}$). Thus, the model implicitly assumes that individuals not in their homes are exposed uniformly to the measured O concentration regardless of whether they are indoors or out (a likely underestimate of actual exposures).

The mean squared error (MSE) was computed for each estimator of P (see Discussion). To maintain the original scale of measurement, the root mean squared error (RMSE) is reported instead of the MSE, and the variance is represented by its square root as the standard deviation (SD). For $\hat{P}_{[O]}$ and $\hat{P}_{[I]}$, both RMSE and longitudinal correlations are first presented, based on estimation of each statistic for each subject. Geometric means of all duplicate samples are used to facilitate comparison with previous studies. To maximize the information available from our sample, no lower limit on the number of repeated measurements was applied in the calculation of these subject-specific RMSEs or longitudinal correlations (R) except for the mathematical limit imposed by the statistics themselves. For example, a longitudinal correlation cannot be calculated for subjects with only one data point. We report medians with upper and lower deciles to illustrate the inter-subject distributions of RMSE and R and to give a sense of their inherent variation.

To further analyze the MSE by its component bias and variance, mixed effects models were used (*26*, *27*). These models accommodate duplicate data explicitly, making use of information on measurement error, and obviating the need to take means of duplicates. Moreover, mixed effects models handle variation in numbers of measurements across subjects by downweighting those with fewer measurements. To allow for heterogeneity of variance and to more flexibly model bias, the range of all P exposures was divided into its three tertiles, and a separate model was fitted for each.

Results

Selected sociodemographic characteristics and exposure-related attributes for the 71 participants in the study are summarized in Table 1. Seventy-seven percent were female, and more than half (56%) were between the ages of 40−65 years. Only one person had less than a high school education, while 37% had some college, 18% were college graduates, and 34% reported some post-graduate education. More than half (51%) had an annual household income of $40 000 or more, with 8% earning between $75 000 and $100 000, and 3% earning more than $100 000. Eighty-five percent were white, 7% were African American, 3% were Native American, 1% was Asian/Pacific Islander, and 3% were other. Most participants (69%) worked outside the home, only 7% lived with a smoker, and 34% had attached garages. Overall, the participants were predominantly white, female, well-educated, relatively affluent, and unlikely to be exposed to environmental tobacco smoke at home. As expected, participants from PHI had the highest percentage of minorities and the lowest household incomes.

A total of 284 valid, matched P and O sample sets with time−activity diaries were obtained from the 71 participants. The number collected for each participant varied from 1 (2 people) to 11 (1 person), with a median of 4 (Q25 = 3 and Q75 = 6). This variability in the number of P samples for each individual results from the fact that some participants dropped out of the study early, while others continued to participate. Furthermore, some of the P samples were invalid because of protocol errors, monitor malfunctions, or analytical problems. The range of P VOC concentrations for each participant is displayed graphically in Figure 1, and the range of I VOC concentrations for each participant is presented in Figure 2. For individual VOCs, each line in these range plots represents one of the 71 participants and spans the range of concentrations measured for that person. Within each VOC, the line segments are ordered by maximum concentration, and the vertical ordering of the VOCs themselves is deter-

TABLE 1. Summary of Sociodemographic Information for Participants in the Study

parameter	*n* (%)			
	Battle Creek	**East St. Paul**	**Phillips**	**all communities**
no. of participants	25 (35%)	22 (31%)	24 (34%)	71 (100%)
gender				
male	7 (10%)	2 (3%)	7 (10%)	16 (23%)
female	18 (25%)	20 (28%)	17 (24%)	55 (77%)
age				
18−39 yr	6 (8%)	12 (17%)	11 (15%)	29 (41%)
40−65 yr	17 (24%)	10 (14%)	13 (18%)	40 (56%)
>65 yr	1 (1%)	0 (0%)	0 (0%)	1 (1%)
missing	1 (1%)	0 (0%)	0 (0%)	1 (1%)
education				
less than high school	0 (0%)	1 (1%)	0 (0%)	1 (1%)
high school	2 (3%)	2 (3%)	3 (4%)	7 (10%)
some college	7 (10%)	13 (18%)	6 (8%)	26 (37%)
college graduate	6 (8%)	2 (3%)	5 (7%)	13 (18%)
post-graduate education	10 (14%)	4 (6%)	10 (14%)	24 (34%)
annual household income				
$10 000−$19 999	2 (3%)	1 (1%)	3 (4%)	6 (8%)
$20 000−$29 999	0 (0%)	4 (6%)	9 (13%)	13 (18%)
$30 000−$39 999	4 (6%)	3 (4%)	3 (4%)	10 (14%)
$40 000−$49 999	2 (3%)	6 (8%)	1 (1%)	9 (13%)
$50 000−$74 999	9 (13%)	5 (7%)	5 (7%)	19 (27%)
$75 000−$99 999	2 (3%)	3 (4%)	1 (1%)	6 (8%)
≥$100 000	2 (3%)	0 (0%)	0 (0%)	2 (3%)
refused or missing	4 (6%)	0 (0%)	2 (3%)	6 (8%)
race				
white	24 (34%)	22 (31%)	14 (20%)	60 (85%)
African American	1 (1%)	0 (0%)	4 (6%)	5 (7%)
Native American	0 (0%)	0 (0%)	2 (3%)	2 (3%)
Asian/Pacific Islander	0 (0%)	0 (0%)	1 (1%)	1 (1%)
other	0 (0%)	0 (0%)	2 (3%)	2 (3%)
refused	0 (0%)	0 (0%)	1 (1%)	1 (1%)
work outside the home				
yes	17 (24%)	13 (18%)	19 (27%)	49 (69%)
no	8 (11%)	9 (13%)	5 (7%)	22 (31%)
live with a smoker				
yes	1 (1%)	3 (4%)	1 (1%)	5 (7%)
no	24 (34%)	19 (27%)	23 (32%)	66 (93%)
attached garage				
yes	18 (25%)	3 (4%)	3 (4%)	24 (34%)
no	7 (10%)	19 (27%)	21 (30%)	47 (66%)

mined by the median of these maximum values. Minimum values appear to be truncated in some cases (for example, β-pinene, chloroform, and styrene in Figure 1) because many samples were zero or below.

As shown in Figure 1, a participant's P exposure to individual VOCs over multiple monitoring periods (within-person variability) often spanned 1 or more orders of magnitude. Moreover, the difference between participants' with the lowest maximum P values and those with the highest (between-person variability) often spanned 2 or more orders of magnitude. This same pattern also held true for participants' I concentrations (Figure 2), which were generally lower than matched P exposures. The evidence indicates that for these 14 VOCs there was substantial within-person variability and between-person variability for both P exposures and I concentrations.

Two subject-level criteria for characterizing the performance of $\hat{P}_{[O]}$ are provided in Table 2. The RMSE and *R* were calculated for each subject with a sufficient number of samples for each measure (≥1 for RMSE, ≥2 for *R*). RMSE is a measure of the magnitude and variation of the difference ($\mu g/m^3$) between measured O concentrations and P exposures, while *R* is a measure of the linear association between O and P. Compared to *R* and for the aims of this study, RMSE is a more direct measure of performance of these estimators (see Discussion); however, we present both to facilitate their comparison. The median value for RMSE and *R* across all subjects along with 10th and 90th percentiles are presented.

Looking at the overall results, the median RMSE for $\hat{P}_{[O]}$ was between 0.2 and 1.8 $\mu g/m^3$ for 9 VOCs, between 2.5 and 4.8 $\mu g/m^3$ for 3 VOCs (α-pinene, β-pinene, and *m*-/*p*-xylene), 13.4 $\mu g/m^3$ for D-limonene, and 16.3 $\mu g/m^3$ for toluene. It should be noted that RMSE is expected to be elevated for those VOCs found at higher concentrations, since their variance is usually higher as well. For all 14 VOCs, $\hat{P}_{[O]}$ underestimated P exposure. The RMSE of $\hat{P}_{[O]}$ for 6 VOCs (benzene, ethyl benzene, methylene chloride, toluene, *o*-xylene, *m*-/*p*-xylene) was substantially higher in BCK than in ESP and PHI. This is not surprising given that O concentrations in BCK tended to be slightly but consistently lower than in the other two neighborhoods, while P exposures tended to be slightly higher (hence a greater underestimation of P exposures in BCK). Overall, correlation coefficients were generally unremarkable, with median *R* for 9 VOCs between −0.08 and 0.24 and between 0.43 and 0.59 for the other 5 VOCs (benzene, ethyl benzene, styrene, *o*-xylene, *m*-/*p*-xylene). With the exceptions of D-limonene and tetrachloroethylene in ESP and benzene, styrene, and *m*-/*p*-xylene in BCK, *R* values were generally comparable across the three neighborhoods.

Analogous performance measures for $\hat{P}_{[I]}$ by neighborhood are provided in Table 3. Comparing $\hat{P}_{[I]}$ to $\hat{P}_{[O]}$ overall, there was a reduction in RMSE for 13 of the 14 VOCs (trichloroethylene remained unchanged). The most dramatic reductions were observed for D-limonene (from 13.4 to 4.7 $\mu g/m^3$) and toluene (from 16.3 to 8.3 $\mu g/m^3$). Generally, $\hat{P}_{[I]}$ also

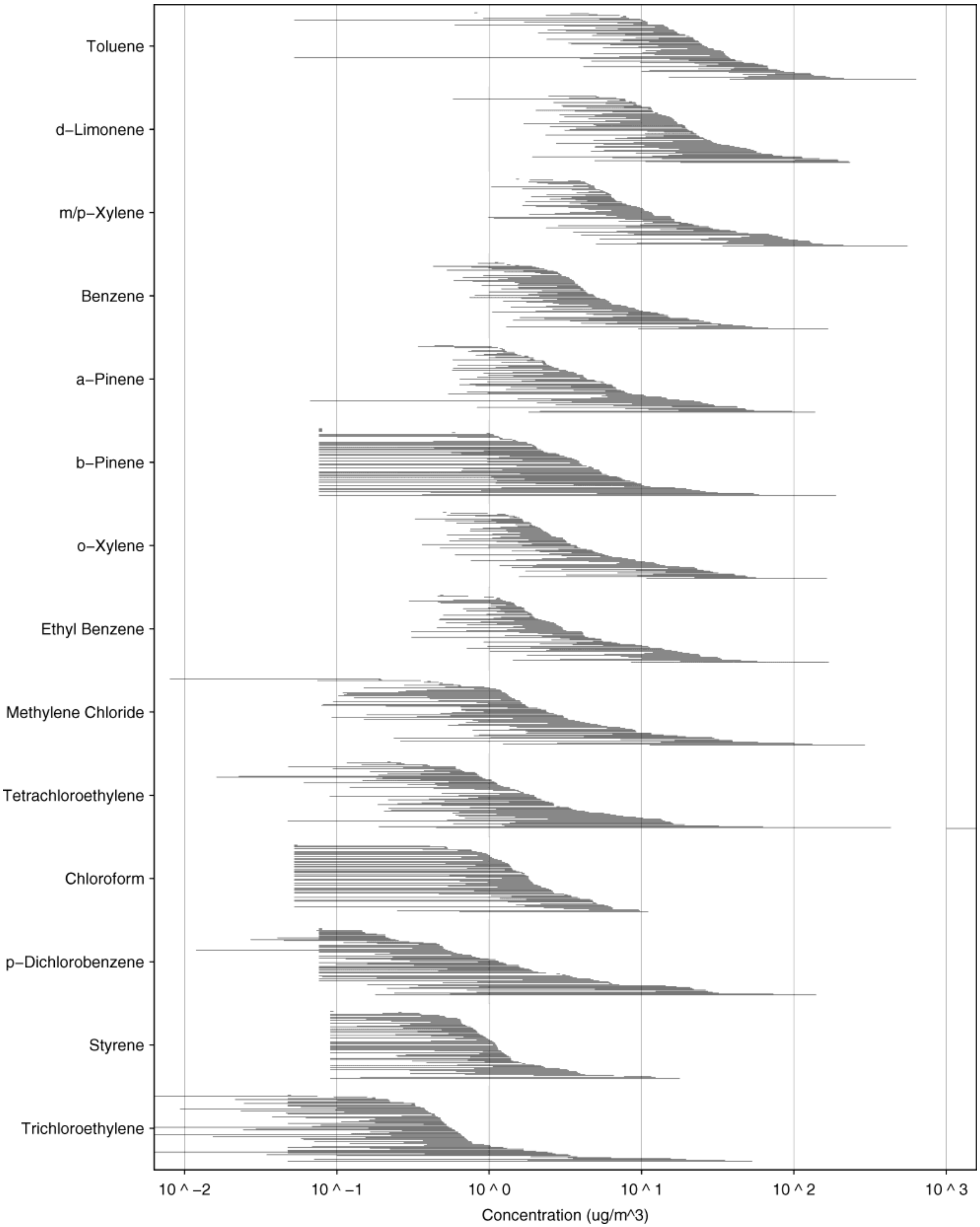

FIGURE 1. Range plot of measured personal VOC exposures for each study participant.

tended to underestimate P exposures, but not as much or as consistently as $\hat{P}_{[O]}$. Compared to $\hat{P}_{[O]}$, reduced RMSE occurred similarly across neighborhoods, and for benzene, toluene, *o*-xylene, and *m*-/*p*-xylene remained higher in BCK as compared to ESP and PHI (similar to the pattern observed for $\hat{P}_{[O]}$). Correlation coefficients improved dramatically for all VOCs, with $R > 0.85$ for 8 VOCs (benzene, chloroform, D-limonene, methylene chloride, α-pinene, β-pinene, *o*-xylene, *m*-/*p*-xylene), and $0.57 \leq R \leq 0.83$ for the remaining 6 VOCs. Relatively consistent *R* values for individual VOCs were observed across neighborhoods, with the exception of *p*-dichlorobenzene (0.16) in BCK and trichloroethylene (0.40) in PHI.

The improved performance of I over O concentrations is illustrated graphically in Figure 3 using three VOCs as examples. It is clear from the scatter plots that O concentra-

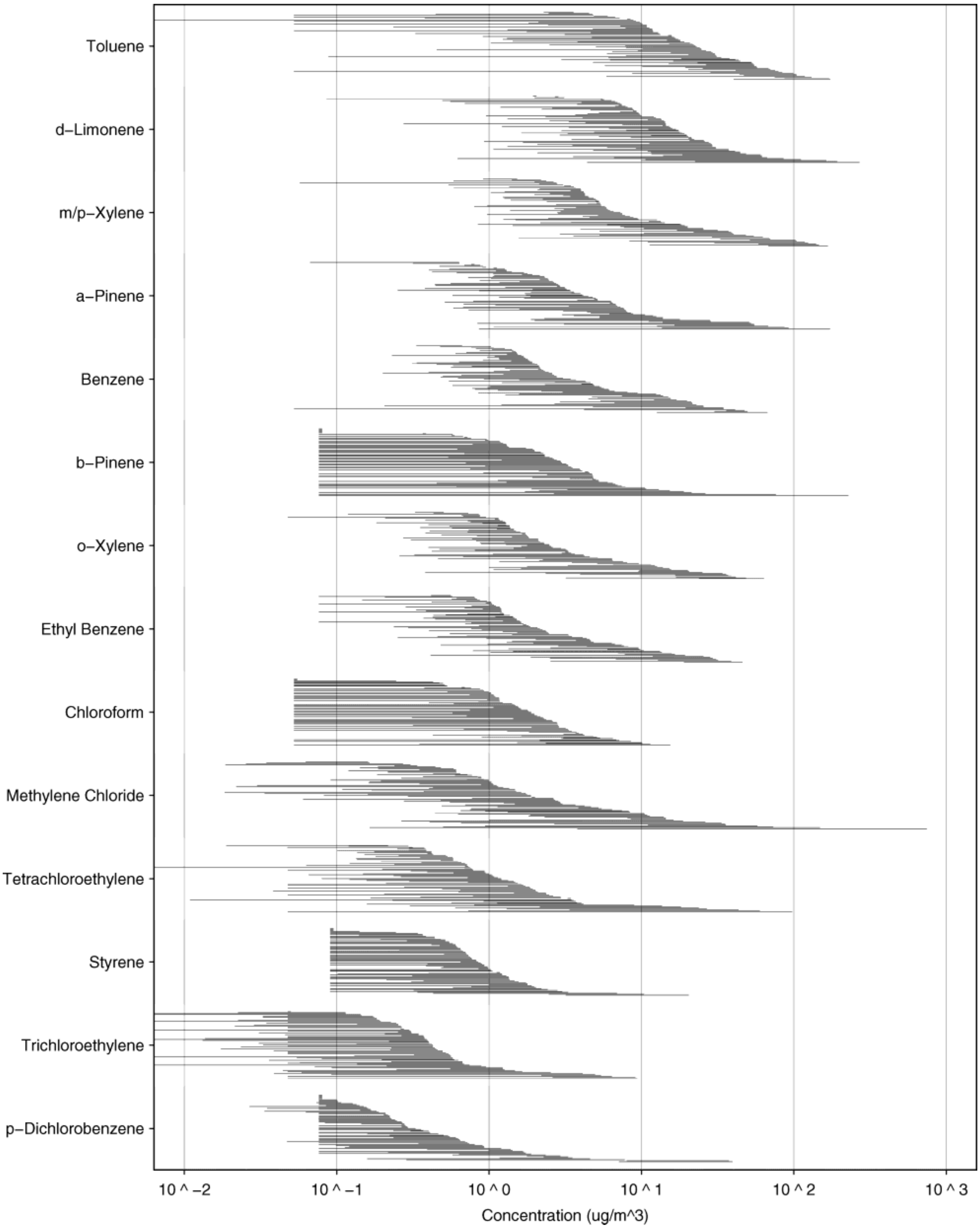

FIGURE 2. Range plot of measured indoor residential VOC concentrations for each study participant.

tions underestimate P exposure in the majority of cases for benzene, methylene chloride, and toluene. I concentrations, on the other hand, provide a noticeable improvement in estimating P exposure, although the tendency is still to underestimate. Overall, for this population and under the conditions of the study, matched I concentrations provided a substantially better estimate of personal VOC exposure than matched O concentrations for all 14 VOCs measured.

To further investigate the nature of RMSE for $\hat{P}_{[O]}$ and $\hat{P}_{[I]}$, we divided the domains of measured P exposures into lower, middle, and upper tertiles and then estimated the two components of MSE, bias (squared) and variance, using the mixed effects model. We distinguish the vector of all numerical observations of personal exposures by $\mathbf{P}$. An estimate of bias is obtained for each tertile by estimating the mean of $\hat{P}_{[O]} - \mathbf{P}$ (Table 4) or the mean of $\hat{P}_{[I]} - \mathbf{P}$ (Table 5).

TABLE 2. Comparison of Matched (Outdoor Community, Personal) VOC Concentrations for Individual Participants in the Study

	Battle Creek		East St. Paul		Phillips		all communities	
compound	RMSE[a]	R[b]	RMSE	R	RMSE	R	RMSE	R
benzene	4.9	0.02	1.4	0.79	1.5	0.68	1.8	0.59
	(0.9, 19.4)[c]	(−0.92, 0.89)[c]	(0.9, 7.8)	(−0.37, 1.00)	(0.7, 8.5)	(−0.92, 1.00)	(0.7, 16.3)	(−0.85, 1.00)
chloroform	1.1	0.00	1.4	0.31	1.5	0.00	1.8	0.00
	(0.3, 3.3)	(−0.51, 1.00)	(0.6, 4.6)	(−0.16, 0.92)	(0.5, 4.2)	(−0.54, 0.98)	(0.5, 3.9)	(−0.50, 0.99)
p-dichlorobenzene	0.6	0.00	0.3	0.15	0.9	−0.01	0.7	0.00
	(0.1, 9.5)	(−0.54, 0.58)	(0.1, 8.4)	(−0.73, 0.82)	(0.1, 13.5)	(−0.78, 1.00)	(0.1, 9.8)	(−0.72, 0.98)
ethyl benzene	3.7	0.41	1.1	0.51	1.1	0.65	1.5	0.53
	(1.0, 14.3)	(−0.47, 1.00)	(0.5, 13.4)	(−0.76, 1.00)	(0.6, 12.3)	(0.01, 1.00)	(0.5, 14.3)	(−0.52, 1.00)
D-limonene	12.7	0.43	17.5	−0.31	12.2	0.34	13.4	0.15
	(6.3, 36.2)	(−0.64, 1.00)	(7.6, 86.5)	(−0.97, 1.00)	(6.9, 40.6)	(−1.00, 1.00)	(7.0, 57.2)	(−1.00, 1.00)
methylene chloride	3.3	0.14	1.5	0.11	0.8	0.38	1.3	0.14
	(0.2, 32.0)	(−0.93, 0.96)	(0.4, 8.3)	(−0.90, 0.84)	(0.4, 8.3)	(−0.76, 1.00)	(0.3, 12.4)	(−0.86, 1.00)
α-pinene	3.6	−0.04	3.6	0.12	2.0	−0.17	3.0	−0.08
	(1.2, 17.9)	(−0.93, 0.95)	(1.1, 15.4)	(−0.87, 0.96)	(1.2, 14.6)	(−1.00, 0.75)	(1.2, 17.3)	(−1.00, 0.95)
β-pinene	1.8	0.00	3.6	0.00	1.9	0.28	2.5	0.00
	(0.1, 8.8)	(−0.13, 0.98)	(1.5, 9.5)	(−0.40, 0.87)	(0.8, 7.2)	(0.00, 1.00)	(0.8, 9.4)	(−0.16, 0.99)
styrene	0.6	0.08	0.5	0.74	0.6	0.40	0.6	0.55
	(0.2, 2.1)	(−0.20, 0.99)	(0.2, 2.3)	(0.20, 0.98)	(0.4, 1.7)	(−0.82, 0.90)	(0.2, 2.0)	(−0.23, 0.98)
tetrachloroethylene	1.3	−0.15	1.0	0.62	0.6	0.17	0.9	0.24
	(0.2, 25.3)	(−0.75, 1.00)	(0.1, 8.7)	(−0.64, 0.99)	(0.2, 3.7)	(−1.00, 0.98)	(0.2, 8.9)	(−0.91, 1.00)
toluene	29.9	−0.11	13.8	0.06	10.0	0.33	16.3	0.02
	(9.6, 85.2)	(−0.99, 1.00)	(7.4, 50.4)	(−0.65, 0.87)	(5.1, 19.3)	(−0.49, 1.00)	(6.1, 64.5)	(−0.90, 0.99)
trichloroethylene	0.2	0.16	0.2	0.43	0.2	0.20	0.2	0.24
	(0.1, 1.1)	(−0.65, 1.00)	(0.1, 1.5)	(−0.16, 0.98)	(0.1, 0.5)	(−0.92, 0.98)	(0.1, 1.3)	(−0.79, 0.99)
o-xylene	4.2	0.26	1.3	0.44	1.3	0.67	1.6	0.43
	(1.2, 17.3)	(−0.94, 0.96)	(0.5, 16.5)	(−0.78, 0.97)	(0.6, 16.3)	(0.13, 1.00)	(0.6, 19.0)	(−0.72, 1.00)
m-/*p*-xylene	14.1	0.19	3.8	0.50	3.7	0.70	4.8	0.47
	(3.4, 57.4)	(−0.75, 0.98)	(1.5, 51.9)	(−0.76, 0.99)	(1.8, 54.0)	(0.08, 1.00)	(2.0, 63.4)	(−0.69, 1.00)

[a] Median root mean squared error (μg/m^3); *n* for number of research subjects = 25 for Battle Creek, 22 for East St. Paul, and 24 for Phillips. [b] Median correlation coefficient; *n* for number of research subjects varies from 20 to 23 for Battle Creek, *n* = 22 for East St. Paul, and *n* varies from 21 to 22 for Phillips. [c] 10th and 90th percentiles.

In addition, an estimate of standard deviation (SD) is obtained from the square root of the variance resulting from application of the same mixed model.

The results from Table 4 show that both the bias and the SD of $\hat{P}_{[O]}$ tend to increase from the lower to the middle and from the middle to the upper tertile of the distribution of P exposures. For example, in the lower tertile the range of $\hat{P}_{[O]} - \mathbf{P}$ values for individual VOCs is between −1.9 and 0.0; in the middle tertile it is between −13.2 and −0.1; and in the upper tertile it is between −62.7 and −2.0. These data suggest that $\hat{P}_{[O]}$ typically underestimates P exposures in all cases and that the magnitude of this underestimation increases with higher P exposures. In terms of variance, the range of SDs for individual VOCs in the lower tertile is 0.1−9.9, 0.2−6.4 in the middle tertile, and 1.9−360 in the upper-tertile. Again, the data indicate that the variance of $\hat{P}_{[O]}$ generally increases with higher P exposures.

The pattern is similar for I versus P in Table 5, with both bias and variance of $\hat{P}_{[I]}$ increasing from lower to middle to higher tertiles of P exposures. For example, the range of $\hat{P}_{[I]} - \mathbf{P}$ values for the 14 individual VOCs is −0.9 to 0.4 in the lower tertile, −3.3 to 1.1 in the middle tertile, and −55.8 to 3.9 in the upper tertile. The evidence suggests that $\hat{P}_{[I]}$ tends to underestimate P exposures for 12 of the 14 VOCs, especially in upper tertile of the distribution of P exposures. $\hat{P}_{[I]}$ tends to overestimate, particularly in the upper tertile, for methylene chloride and α-pinene. Similarly, the range of SDs for individual VOCs increases from 0.1 to 5.2 in the lower tertile, from 0.2 to 10.2 in the middle tertile, and from 1.7 to 351 in the upper tertile, which suggests that variance in $\hat{P}_{[I]}$ also tends to increase with higher P exposures.

We investigated the time-weighted estimator $\hat{P}_{[OI]}$ by examining the RMSE for the model where P exposure equals the time fraction of the 2-day monitoring period spent indoors at home ($t_{[I]}$) times the measured I concentration plus the complement of the time fraction indoors at home ($1 - t_{[I]}$) times the measured O concentration (see eq 3). Because the measured O concentration is likely to be less than or equal to unmeasured concentrations in the other microenvironments, it represents quasi-baseline conditions (i.e., minimal exposures) when participants were not inside their homes. In Table 6, the RMSE for this model is apportioned into bias and SD using the same approach as for $\hat{P}_{[O]}$ and $\hat{P}_{[I]}$ (Tables 4 and 5).

As found for $\hat{P}_{[O]}$ and $\hat{P}_{[I]}$, the bias (the expected difference between the estimator and P exposure) to noise (SD) ratio for $\hat{P}_{[OI]}$ in Table 6 is relatively low. Nevertheless, it is apparent that the estimated bias of $\hat{P}_{[OI]}$ was similar to that for $\hat{P}_{[I]}$ (Table 5) in the lower and middle tertiles. At the higher tertile, the bias was greater for the time-weighted estimator in every instance except methylene chloride. The SD was generally similar between $\hat{P}_{[I]}$ and the time-weighted model across all three tertiles.

Discussion

Chronic exposure to relatively low levels of airborne VOCs is an inescapable reality for residents of the United States. This class of chemicals is ubiquitous in occupational and nonoccupational settings, including both indoor and outdoor environments. Not only are VOCs released into the air from industrial processes, internal combustion engines, cigarette smoking, and bathing or showering in chlorinated water, they are also common constituents in cleaning and degreasing agents, deordorizers, dry-cleaning processes, paints, pesticides, personal care products, and solvents (*2, 7−15*). Of the 14 VOCs measured in this study, five originate from primarily indoor sources (chloroform, *p*-dichlorobenzene, D-limonene, and α- and β-pinene), while nine are emitted by a combination of indoor and outdoor sources (benzene,

TABLE 3. Comparison of Matched (Indoor Residential, Personal) VOC Concentrations for Individual Participants in the Study

compound	Battle Creek RMSE[a]	Battle Creek R^b	East St. Paul RMSE	East St. Paul R	Phillips RMSE	Phillips R	all communities RMSE	all communities R
benzene	2.5	0.86	1.6	0.89	1.1	0.78	1.7	0.86
	(0.5, 9.7)[c]	(0.12, 1.00)[c]	(0.4, 6.0)	(0.10, 1.00)	(0.6, 4.4)	(−0.98, 1.00)	(0.4, 8.1)	(−0.26, 1.00)
chloroform	0.4	0.89	0.6	0.90	0.5	0.70	0.5	0.88
	(0.2, 1.5)	(0.06, 1.00)	(0.3, 1.7)	(−0.19, 0.99)	(0.3, 2.7)	(−0.32, 1.00)	(0.2, 1.7)	(−0.05, 1.00)
p-dichlorobenzene	0.5	0.16	0.2	0.64	0.5	0.62	0.3	0.57
	(0.1, 9.0)	(−0.42, 0.99)	(0.1, 8.3)	(−0.48, 0.99)	(0.1, 6.8)	(−0.88, 1.00)	(0.0, 9.0)	(−0.54, 1.00)
ethyl benzene	1.4	0.69	0.8	0.85	0.8	0.73	1.0	0.75
	(0.3, 11.0)	(−0.94, 0.99)	(0.2, 3.0)	(−0.26, 1.00)	(0.3, 15.6)	(−0.13, 1.00)	(0.3, 11.1)	(−0.39, 1.00)
D-limonene	4.2	0.96	5.8	0.98	4.7	0.94	4.7	0.96
	(2.1, 18.9)	(0.34, 1.00)	(2.5, 36.3)	(0.26, 1.00)	(1.8, 45.0)	(−0.84, 1.00)	(2.1, 36.4)	(0.11, 1.00)
methylene chloride	1.3	0.95	0.6	0.93	0.8	0.81	0.8	0.90
	(0.3, 26.2)	(−0.37, 1.00)	(0.2, 1.8)	(0.37, 1.00)	(0.2, 5.7)	(−0.09, 1.00)	(0.2, 8.7)	(−0.04, 1.00)
α-pinene	1.3	0.98	0.8	0.92	1.0	0.92	1.0	0.95
	(0.3, 7.2)	(0.34, 1.00)	(0.3, 6.3)	(0.61, 1.00)	(0.2, 14.0)	(−0.51, 1.00)	(0.2, 7.6)	(−0.42, 1.00)
β-pinene	0.9	0.98	1.2	0.96	1.1	0.97	1.0	0.97
	(0.1, 2.8)	(0.00, 1.00)	(0.3, 4.9)	(0.15, 1.00)	(0.4, 2.9)	(0.00, 1.00)	(0.2, 4.1)	(0.00, 1.00)
styrene	0.4	0.65	0.3	0.70	0.4	0.77	0.4	0.71
	(0.1, 1.2)	(−0.19, 1.00)	(0.2, 1.3)	(0.01, 0.99)	(0.2, 1.1)	(0.01, 1.00)	(0.2, 1.2)	(−0.12, 1.00)
tetrachloroethylene	0.8	0.83	0.6	0.90	0.4	0.77	0.7	0.83
	(0.2, 25.1)	(−0.32, 1.00)	(0.1, 6.4)	(−0.19, 1.00)	(0.2, 3.0)	(−0.12, 1.00)	(0.2, 6.5)	(−0.30, 1.00)
toluene	12.5	0.65	7.3	0.86	7.5	0.83	8.3	0.77
	(2.3, 43.4)	(−0.98, 0.98)	(1.8, 18.5)	(0.22, 0.99)	(3.3, 23.8)	(−0.25, 1.00)	(2.7, 26.9)	(−0.67, 1.00)
trichloroethylene	0.2	0.88	0.2	0.88	0.2	0.40	0.2	0.69
	(0.0, 2.5)	(0.23, 1.00)	(0.1, 2.5)	(−0.17, 1.00)	(0.1, 0.5)	(−0.64, 0.99)	(0.1, 1.0)	(−0.26, 1.00)
o-xylene	2.0	0.92	0.9	0.92	0.7	0.82	1.1	0.90
	(0.4, 12.5)	(−0.09, 1.00)	(0.3, 4.0)	(−0.17, 1.00)	(0.4, 16.0)	(−0.24, 1.00)	(0.4, 12.9)	(−0.20, 1.00)
m-/*p*-xylene	5.6	0.90	3.1	0.93	2.2	0.71	3.5	0.86
	(0.9, 40.1)	(−0.16, 1.00)	(0.6, 11.8)	(−0.40, 1.00)	(1.3, 58.3)	(−0.26, 1.00)	(1.0, 40.1)	(−0.30, 1.00)

[a] Median root mean squared error ($\mu g/m^3$); *n* for number of research subjects = 25 for Battle Creek, 22 for East St. Paul, and 24 for Phillips. [b] Median correlation coefficient; *n* for number of research subjects varies from 20 to 23 for Battle Creek, *n* = 22 for East St. Paul, and *n* varies from 21 to 22 for Phillips. [c] 10th and 90th percentiles.

ethyl benzene, methylene chloride, styrene, toluene, trichloroethylene, tetrachloroethylene, *o*-xylene, and *m*-/*p*-xylene).

Measuring P exposures is the only way to determine unequivocally the magnitude, duration, and frequency of actual exposures experienced by people as they move through a variety of indoor and outdoor locations during their normal daily activities (*1*, *2*). Consequently, P exposure is the de facto "gold standard" for assessment of individual and population exposures to VOCs. But because it is usually impractical and prohibitively expensive to measure P VOC exposures for everyone (or even a large sample of the population of interest), there is a continuing need to develop and validate practical and cost-effective surrogate estimators that are suitably accurate and precise. In this paper, we have examined the performance of three candidate estimators of P exposure: outdoor community concentration, indoor residential concentration, and a simple time-weighted model.

The evidence indicates that, consistent with previous studies in urban areas (*10*−*15*), P exposures tended to be higher than measured indoor concentrations, which tended to be higher than measured outdoor concentrations. The data for P and I concentrations also show that within-person variability for the 14 VOCs measured in this study typically spanned 1 or more orders of magnitude, while between-person variability usually spanned 2 or more orders of magnitude. These findings suggest that a substantial number of people and a substantial number of P and I measurements for each person may be necessary to adequately characterize VOC exposures for a particular population.

One of the novel aspects of this study was the use of MSE as well as correlation measures to assess the performance of multiple estimators (O, I, simple time-weighted model) for P exposure. To appreciate the value of MSE as a comparison metric at the subject-specific level, it is important to recognize the inherent limitations of *R*, a more traditional means of comparing exposure estimators.

To examine and compare estimators of P exposures, we assumed a set of measured P concentrations from a group of *m* subjects represented their actual exposures to an individual VOC. The vector of these observations is denoted as

$$\mathbf{P} = [p_{11} \cdots p_{1n_1}, p_{21} \cdots p_{2n_2}, \ldots, p_{m1} \cdots p_{mn_m}]$$

where p_{ij} gives the observed P exposure for the *i*th subject on the *j*th occasion. A candidate estimator of $\mathbf{P}$, denoted as $\hat{\mathbf{P}}_*$, is a vector of the same structure as $\mathbf{P}$ but with some function of the data at element $\hat{p}_{*ij}$. Metrics for assessing the ability of $\hat{\mathbf{P}}_*$ to estimate $\mathbf{P}$ traditionally include the sample correlation coefficient, *R* (*28*), which may be estimated for each subject over time or jointly for all subjects, where *R* takes values within the interval $[-1, +1]$.

Although *R* is a common metric for analyzing associations between P exposures and O or I concentrations, it is only a measure of the linear association between $\hat{\mathbf{P}}_*$ and $\mathbf{P}$ (*29*). To the extent that $\hat{\mathbf{P}}_*$ is an unbiased and precise estimator of $\mathbf{P}$, *R* approaches +1. However, *R* also approaches +1 in many other cases. For example, if $\hat{p}_{*ij} = (1/2)p_{ij}$ for all *j*, then $R_i = +1$ despite the fact that $\hat{\mathbf{P}}_*$ underestimates $\mathbf{P}$ by a factor of 2.

Another problem with *R* is its dependence on the distribution of $\mathbf{P}$ values. Despite having the same MSE in estimating $\mathbf{P}$, it can be shown that an estimator $\hat{\mathbf{P}}_*$ will yield potentially very different values of *R*, depending on the distribution of values of $\mathbf{P}$ that are sampled or selected for the study. Thus it is not possible to compare an estimator from one study with one from a different study, unless the sets of $\mathbf{P}$ measurements are the same or at least have similar distributions. Absent these common features, therefore, we cannot answer the question of which estimator is better.

In the calculation of a separate, longitudinal correlation coefficient for each subject, this dependence on the $\mathbf{P}$ distribution adversely affects the usefulness of the resulting

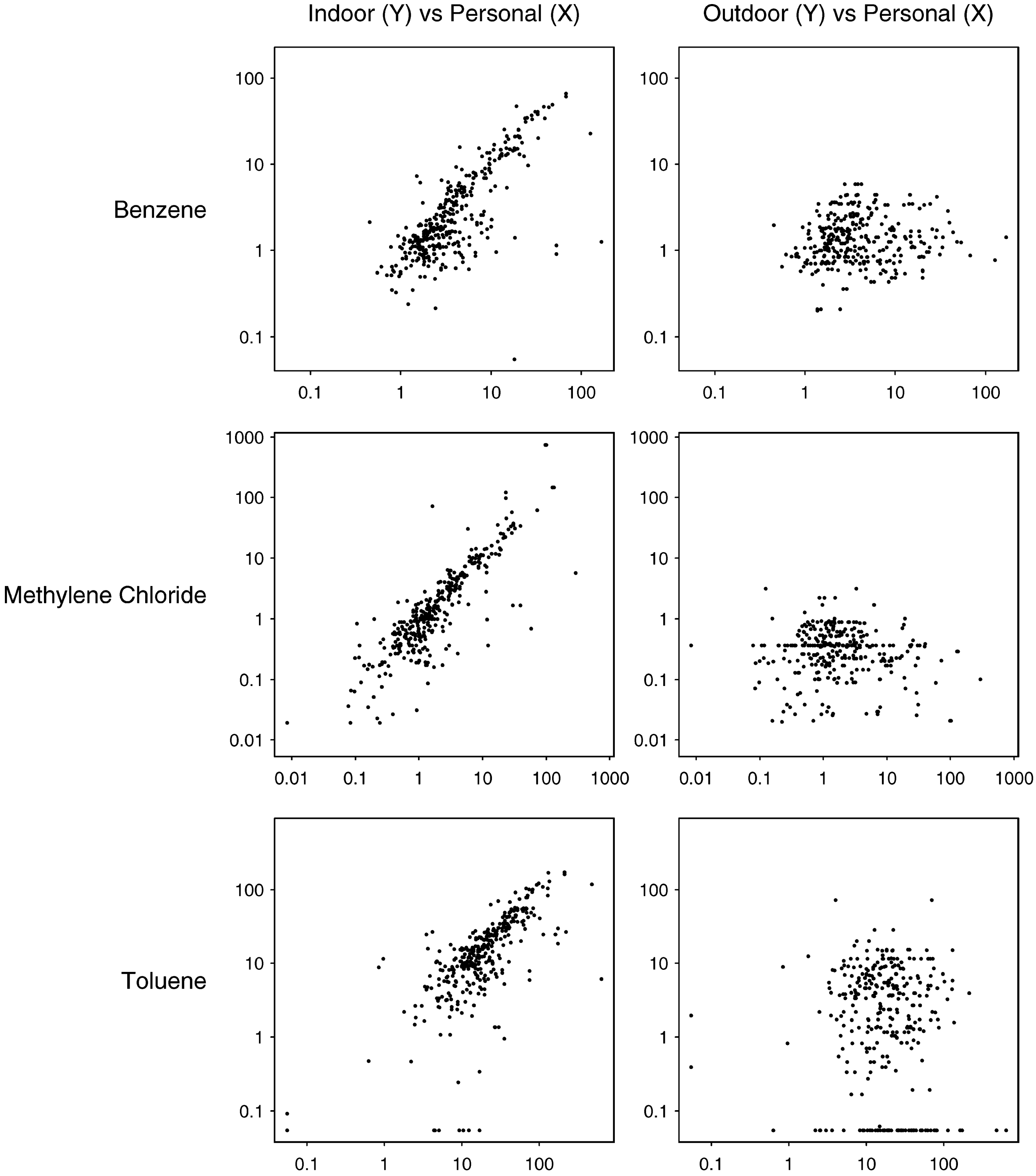

FIGURE 3. Plots of (a) indoor residential concentrations (μg/m^3) and (b) outdoor community concentrations vs personal exposures to benzene, methylene chloride, and toluene for participants in the study. As described in the text, nondetectable measurements (i.e., samples with no analytical response, or those with values $\leq$ 0 after blank subtraction) are represented with a value of half the analytical detection limit.

set of R_i values. The number and distribution of measured personal exposures will inevitably vary across subjects, but these factors should not bear on the assessment of the performance of, say, a monitor located at some central site. While the performance of this central site monitor may in fact be identical for all subjects, their own variation in personal exposure and compliance with the sampling effort can yield large differences in their longitudinal correlations. Finally, the use of longitudinal correlation as a comparison metric also means that subjects with only one measured VOC value cannot contribute an R_i. But in reality there is no reason a single observation should not add to our understanding of the ability of $\hat{\mathbf{P}}_*$ to estimate $\mathbf{P}$.

For these reasons, we also assessed estimators of $\mathbf{P}$ in terms of MSE and its constituents: bias and variance. For the estimator of a specific element p_{ij} of $\mathbf{P}$, the bias of $\hat{p}_{*ij}$ for p_{ij} is the difference between the expected value of $\hat{p}_{*ij}$ and p_{ij}, i.e.:

$$\mathrm{bias}[\hat{p}_{*ij}:p_{ij}] = E[\hat{p}_{*ij}] - p_{ij} \qquad (4)$$

where the $E[\ ]$ denotes the expectation operator. The variance

TABLE 4. Using Outdoor Community Concentrations To Predict Measured Personal Exposures: Estimated Bias and Variance (Presented as Standard Deviation in Parentheses) for the Lower, Middle, and Upper Tertiles of the Personal Exposure Distribution[a]

	personal exposure distribution				
chemical	lower tertile	1st tertile cutpoint	middle tertile	2nd tertile cutpoint	upper tertile
benzene	−0.3[b] (0.7)[c]	2.2	−1.5 (1.4)	4.7	−14.4 (21.9)
chloroform	−0.2 (0.2)	0.7	−1.0 (0.3)	1.7	−3.2 (1.9)
p-dichlorobenzene	0.0 (0.1)	0.2	−0.3 (0.2)	0.7	−7.8 (19.2)
ethyl benzene	−0.4 (0.5)	1.6	−1.5 (0.7)	3.5	−12.2 (19.3)
D-limonene	−4.9 (1.6)	7.7	−11.5 (2.7)	16.6	−47.3 (51.1)
methylene chloride	−0.1 (0.5)	1.0	−1.2 (0.6)	2.9	−17.1 (35.7)
α-pinene	−0.9 (0.4)	1.8	−2.6 (0.8)	4.2	−15.8 (20.6)
β-pinene	−0.2 (0.3)	0.8	−1.5 (0.5)	2.7	−10.9 (23.4)
styrene	−0.1 (0.1)	0.5	−0.5 (0.2)	1.0	−2.0 (2.8)
tetrachloroethylene	0.0 (0.3)	0.6	−0.6 (0.4)	1.5	−62.7 (360.4)
toluene	−1.9 (9.9)	12.1	−13.2 (6.4)	25.1	−57.8 (79.8)
trichloroethylene	0.0 (0.1)	0.2	−0.1 (0.2)	0.4	−2.4 (7.5)
o-xylene	−0.4 (0.6)	1.7	−1.6 (0.9)	3.8	−14.5 (20.4)
m-/*p*-xylene	−1.3 (1.7)	5.4	−5.1 (2.8)	12.4	−45.9 (66.2)

[a] All estimates and cutpoints in units of μg/m^3. [b] Bias estimated by the mean difference of predictor and personal exposure. [c] Variance estimated by the variance of the differences of predictor and personal exposure; with square root applied to present in terms of standard deviation (SD).

TABLE 5. Using Indoor Residential Concentrations To Predict Measured Personal Exposures: Estimated Bias and Variance (Presented as Standard Deviation in Parentheses) for the Lower, Middle, and Upper Tertiles of the Personal Exposure Distribution[a]

	personal exposure distribution				
chemical	lower tertile	1st tertile cutpoint	middle tertile	2nd tertile cutpoint	upper tertile
benzene	−0.2[b] (1.0)[c]	2.2	−0.6 (2.1)	4.7	−3.8 (20.8)
chloroform	0.4 (1.8)	0.7	−0.1 (0.6)	1.7	−0.5 (1.7)
p-dichlorobenzene	0.0 (0.2)	0.2	−0.2 (0.2)	0.7	−5.5 (19.4)
ethyl benzene	−0.2 (0.4)	1.6	−0.4 (1.1)	3.5	−4.7 (19.5)
D-limonene	−0.9 (2.0)	7.7	−1.6 (5.8)	16.6	−13.2 (50.1)
methylene chloride	0.0 (0.3)	1.0	1.1 (10.2)	2.9	3.9 (74.2)
α-pinene	0.0 (0.7)	1.8	0.0 (0.9)	4.2	0.8 (10.4)
β-pinene	0.3 (0.8)	0.8	−0.2 (0.9)	2.7	−2.1 (10.2)
styrene	0.1 (0.4)	0.5	−0.1 (0.3)	1.0	−0.8 (3.1)
tetrachloroethylene	0.0 (0.3)	0.6	−0.3 (0.4)	1.5	−55.8 (350.5)
toluene	0.2 (5.2)	12.1	−3.3 (8.2)	25.1	−19.9 (77.1)
trichloroethylene	0.0 (0.1)	0.2	0.1 (0.8)	0.4	−1.7 (7.6)
o-xylene	−0.2 (0.6)	1.7	−0.5 (1.2)	3.8	−5.3 (20.5)
m-/*p*-xylene	−0.6 (1.6)	5.4	−1.7 (3.9)	12.4	−17.0 (66.6)

[a] All estimates and cutpoints in units of μg/m^3. [b] Bias estimated by the mean difference of predictor and personal exposure. [c] Variance estimated by the variance of the differences of predictor and personal exposure; with square root applied to present in terms of standard deviation (SD).

TABLE 6. Using a Simple Time-Weighted Model To Predict Measured Personal Exposures: Estimated Bias and Variance (Presented as Standard Deviation in Parentheses) for the Lower, Middle, and Upper Tertiles of the Personal Exposure Distribution[a]

	personal exposure distribution				
chemical	lower tertile	1st tertile cutpoint	middle tertile	2nd tertile cutpoint	upper tertile
benzene	−0.2[b] (0.8)[c]	2.2	−0.8 (1.4)	4.7	−7.5 (21.0)
chloroform	0.2 (1.1)	0.7	−0.4 (0.4)	1.7	−1.2 (1.5)
p-dichlorobenzene	0.0 (0.1)	0.2	−0.2 (0.2)	0.7	−6.6 (19.4)
ethyl benzene	−0.3 (0.4)	1.6	−0.7 (0.8)	3.5	−6.9 (19.4)
D-limonene	−2.1 (1.8)	7.7	−4.4 (4.6)	16.6	−20.8 (48.6)
methylene chloride	0.0 (0.3)	1.0	0.5 (7.9)	2.9	−3.3 (48.2)
α-pinene	−0.3 (0.5)	1.8	−0.7 (0.7)	4.2	−4.8 (9.4)
β-pinene	0.1 (0.6)	0.8	−0.6 (0.7)	2.7	−5.6 (12.0)
styrene	0.0 (0.3)	0.5	−0.2 (0.2)	1.0	−1.2 (2.8)
tetrachloroethylene	0.0 (0.2)	0.6	−0.4 (0.3)	1.5	−60.9 (363.5)
toluene	0.0 (5.7)	12.1	−6.2 (5.9)	25.1	−30.6 (78.6)
trichloroethylene	0.0 (0.1)	0.2	0.0 (0.6)	0.4	−2.0 (7.7)
o-xylene	−0.3 (0.5)	1.7	−0.8 (0.9)	3.8	−8.1 (20.2)
m-/*p*-xylene	−0.8 (1.6)	5.4	−2.7 (2.7)	12.4	−26.0 (66.0)

[a] All estimates and cutpoints in units of μg/m^3. [b] Bias estimated by the mean difference of predictor and personal exposure. [c] Variance estimated by the variance of the differences of predictor and personal exposure; with square root applied to present in terms of standard deviation (SD).

of $\hat{p}_{*ij}$ does not depend functionally on p_{ij} and may be expressed as

$$\mathrm{var}[\hat{p}_{*ij}] = E[(\hat{p}_{*ij} - E[\hat{p}_{*ij}])^2] \tag{5}$$

The MSE is yet another linear operator comprising these constituents as

$$\mathrm{MSE}[\hat{p}_{*ij}{:}p_{ij}] = (\mathrm{bias}[\hat{p}_{*ij}{:}p_{ij}])^2 + \mathrm{var}[\hat{p}_{*ij}] \tag{6}$$

The bias and variance describe different characteristics of the estimator $\hat{p}_{*ij}$. Bias describes the extent to which $\hat{p}_{*ij}$ under- or overestimates p_{ij}. Variance conveys the precision of $\hat{p}_{*ij}$; the precision of a statistic is sometimes defined specifically as the inverse of its variance.

Based on MSE as well as R (Tables 2 and 3), I concentrations were a better estimator of P exposure than O concentrations for all 14 VOCs, although both consistently underestimated P exposure. There are several reasons for this. First, personal exposures tended to be higher than matched indoor residential concentrations, which tended to be higher than matched outdoor community concentrations. For example, median and 90th percentile values for benzene were 3.2 and 18.3 μg/m^3 in personal air, 1.9 and 15.3 μg/m^3 in indoor air, and 1.3 and 3.3 μg/m^3 in outdoor air (*13*). Second, most participants typically spent the majority of their time indoors at home (and relatively little outside). Results from the participants' 2-day time−activity logs show that, on average, participants spent 34 h (70.9%) indoors at home. The rest of the time was spent indoors at work or school (6 h or 12.6%), indoors in other locations (2.6 h or 5.5%), outside at home (1.7 h or 3.5%), outside at work or school (0.3 h or 0.6%), outside at other locations (1.1 h or 2.4%), and in transit (2.2 h or 4.5%). In addition, participants were in close proximity to a smoker for an average of only 0.5 h (0.9%) over a typical 2-day monitoring period. Third, the measured indoor concentrations may be an underestimate of what people were actually exposed to during their time inside at home. The monitors collected a 2-day integrated sample, but concentrations may have been highest when people were cooking and carrying on other routine activities. And fourth, it is possible that concentrations in other microenvironments through which participants moved during the 2-day monitoring period were relatively high as compared to measured I and O concentrations. Thus, although participants spent a relatively small proportion of their time indoors at work/school, indoors in other locations, outside at work/school, outside at other locations, and in transit, concentrations in these microenvironments appear to make a significant contribution to measured P exposure.

The bias and variance of all three estimators (indoor, outdoor, and time-weighted model) tended to increase in the upper third of the P exposure distribution. This means that common exposure estimators, such as measured indoor and outdoor concentrations and time-weighted models, tend to be less accurate and precise just where we need them most—for estimating exposures at the upper end of the exposure distribution. Future research should investigate whether these same patterns and relationships hold for (a) communities with higher outdoor levels of VOCs, (b) a more diverse sample of adults (race/ethnicity, socioeconomic status, occupation), and (c) vulnerable segments of the population (pregnant women and their fetuses, children, the elderly, the infirm).

Acknowledgments

This research was funded by a STAR (Science to Achieve Results) Grant (R825241) from the U.S. Environmental Protection Agency, National Center for Environmental Research. We also benefited from a grant from the Academic Health Center at the University of Minnesota. We thank the individuals who participated in the study and acknowledge the contributions of the field team. We also thank the 3M Corporation for donating some of the organic vapor monitors used in this study. The help and support provided by the Minnesota Pollution Control Agency was essential to the success of this project. K.S. was a member of the Division of Environmental and Occupational Health at the University of Minnesota School of Public Health when this study was conducted.

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Received for review August 25, 2003. Revised manuscript received February 10, 2004. Accepted February 12, 2004.

ES030607Q

MINNESOTA CHAMBER OF COMMERCE
GROWING MINNESOTA

January 15, 2025

Administrative Law Judge Jessica Palmer-Denig
Minnesota Office of Administrative Hearings
600 N. Robert Street
St. Paul, Minnesota 55101
OAH Docket No. 71-9003-39354

Comments submitted electronically through OAH's website
https://minnesotaoah.granicusideas.com/discussions/39354-minnesota-pollution-control-agency-dual-notice-of-intent-to-adopt-rules

Your Honor:

On behalf of the Minnesota Chamber of Commerce (Chamber), a statewide organization representing 6,300 businesses and more than a half million employees throughout Minnesota, we appreciate the opportunity to submit this letter in response to the Minnesota Pollution Control Agency's (MPCA) request for comments regarding the proposed amendments to rules known as the "Air toxics emissions reporting rule", which was directed by *Minnesota Statutes*, section 116.062. The Chamber represents members that the rulemaking will impact. This letter is being submitted as a supplement to an initial comment letter submitted earlier today to provide additional comments on behalf of our members.

In general, the Chamber reiterates many of the comments and themes from the Chamber's September 21, 2023 letter and attachments submitted on the planned rulemaking at the time. That particularly includes the comments related to data utility, reporting burden, and establishing a limited set of pollutants in order to target the most important public health issues. In contrast, the November 2024 Statement of Need and Reasonableness (SONAR), Exhibit 1, proposes a 26-page list of just over 900 pollutants to be reported annually. In the SONAR, as a key point in the statement of general need, the MPCA notes with reference to Figure 1 that "78% of block groups (a subset of census tracts) are above health benchmarks for air toxics pollution." The reference appears to mean 78% of block groups within the seven metropolitan counties addressed by the proposed amendments. The header for Figure 1 reads "Data from 2017 MNRISKS modeling depicts emissions from all sources including transportation, point sources, wood smoke, etc. and estimated areas of concern for environmental justice in the seven metropolitan counties."

What neither the SONAR nor the underlying legislation acknowledges nor connects is that transportation and an extensive list of non-point sources, including wood smoke, are large drivers of human health risk in the seven metropolitan counties.

The SONAR indicates that "By requiring air toxics emissions data on an annual basis, the MPCA will be able to provide current data that accurately represents air quality within the state." In fact, unless MPCA develops an inventory of non-point and transportation sources that also accounts for the proposed list of air toxics to be reported in the SONAR Exhibit 1, MPCA will only be able to provide the contribution of permitted, or point, sources to air quality within the state. Only accounting for the list of air toxic emissions and their associated risks from point sources will be an incomplete picture and will inaccurately bias the risk associated with point sources. This could lead to the MPCA focusing on point source risk reductions with inconsequential relative impact because those risks could be dwarfed by risks associated with transportation or non-point source contributions of the same pollutants.

If the intent is truly to address disproportionate exposure to air toxics and to improve the health impacts to more vulnerable populations, MPCA needs to acknowledge the disproportionate contribution of health impacts from transportation and non-point sources and focus characterization and reduction on those sources. Unless and until MPCA can commit to a similarly robust inventory of the Exhibit 1 pollutants from transportation and non-point sources, MPCA should not require the reporting of such an extensive list of pollutants for permitted sources.

In the SONAR section on “Pollutant lists reviewed”, MPCA notes that it was “directed to review the pollutant lists found in Minn. Stat. § 116.062 that include chemicals that may or may not be important for the purpose of air toxics reporting and risks to human health and the environment.” As such, MPCA acknowledges that some of the pollutants may not be important for the purpose of air toxics reporting and risks to human health. However, based on the SONAR, there appears to have been no effort to screen for the ones that are important. Therefore, there could be significant effort by permittees collectively to characterize and report emission levels that may not have consequential impacts to human health and the environment.

As noted in the SONAR section addressing “Differences with other state standards”, Tables 6 and 7 indicate that most neighboring and EPA Region 5 states require annual reporting of a more limited number of hazardous air pollutants. They include the 188 Federal hazardous air pollutants (HAPs) that EPA has focused on because, as noted on EPA’s website, they are “known or suspected to cause cancer or other serious health effects, such as reproductive effects or birth defects, or adverse environmental effects.” That is also the pollutant list that is addressed under EPA’s 2023 proposed revisions to the Air Emissions Reporting Requirements (AERR).

In order to focus the health improvements for vulnerable communities in the seven metropolitan counties, and to be consistent with other states approaches for permitted facilities, the Chamber would support a regulation that requires annual reporting of the more concise list of air toxics pollutants in EPA’s Federal HAP list. In the future, if EPA’s Air Emissions Reporting Requirements include compounds beyond the list of Federal HAPs, MPCA can modify the list of pollutants to be reported by the seven metropolitan county permittees.

The Chamber appreciates the opportunity to comment on this important stage of the air toxics reporting rulemaking.

Sincerely,

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MINNESOTA CHAMBER OF COMMERCE
GROWING MINNESOTA

September 21, 2023

Administrative Law Judge James Mortenson
Minnesota Office of Administrative Hearings

Comments submitted electronically through OAH's website

The Minnesota Chamber of Commerce (Chamber) submits these comments in response to the Minnesota Pollution Control Agency's (MPCA or Agency) request for comments (RFC) on the Agency's planned rulemaking for air toxics emissions reporting for facilities that emit air toxics and are located in the counties of Anoka, Carver, Dakota, Hennepin, Ramsey, Scott, and Washington. The Chamber represents members that the rulemaking will impact.

The Chamber welcomes this opportunity to share its point of view regarding the proposed regulations. The Chamber recognizes that these rules, in conjunction with associated rules for air toxics regulation and cumulative impacts analysis, pose the possibility of a significant impact on the economic vitality of the areas subject to the rules. We believe that the MPCA also recognizes this concern. As such, the Chamber urges the MPCA to be deliberative and consultative in its approach.

Toward that end, and as a preliminary matter, the Chamber urges creating an advisory committee of key stakeholders to consult with the Agency before publishing draft rules. These stakeholders should include significant representation from parties that will be subject to new legal requirements under this rule. Such a process would help drive consensus around key issues and help the MPCA avoid (or at least narrow the scope of) potential rule challenges.

In its initial RFC, the MPCA referenced enabling legislation from the 2023 Minnesota legislative session that directs the MPCA to develop and issue rules that will:

1. Establish the requirements for air toxics emissions reporting for permitted facilities on an annual basis.
2. Identify the air toxics to be reported.
3. Amend permit and reporting processes to align with annual air toxics emissions reporting.

The Chamber's comments follow those elements and reference the Chamber's comments submitted for other planned rulemakings (attached below).

1. Establish the requirements for air toxics emissions reporting for permitted facilities on an annual basis.

The Chamber generally believes any new requirements for reporting should be aligned with existing data and conclusions. New or expanded reporting requirements should address specific public health priorities supported by the data. Please see the sections on "Data Utility" and "Reporting Burden" in the attached Chamber letter from August 6, 2020.

2. Identify the air toxics to be reported.

If air toxics will be further regulated and additional reporting required, the Chamber supports the MPCA's adoption of a list of air toxics in a rule. The list may be modified, as needed, through rulemaking and public comment in the future. Please see the section on “Guideposts for a Regulatory Program” in the attached Chamber letter dated September 21, 2023.

3. Amend permit and reporting processes to align with annual air toxics emissions reporting.

In line with our comments under item 1 above, the MPCA should only amend permits for facilities emitting priority pollutants or in designated areas. The MPCA should establish reporting thresholds and practical ways for potential reporters to determine applicability. Please see the “Streamlining Reporting” section in the attached Chamber letter from August 6, 2020.

The attached Chamber letters include additional policy and technical suggestions that go beyond the three issues the MPCA listed in the request for comments on the rule. Please consider those elements as the MPCA develops initial rulemaking.

In July 2023, the United States Environmental Protection Agency (US EPA) proposed updates to its Air Emissions Reporting Requirements (AERR). These changes would allow US EPA to collect annual hazardous air pollutant (HAP) emissions data starting in 2027. The MPCA should align any Minnesota rulemaking on air toxics / HAPs with US EPA requirements to avoid redundant reporting in multiple systems or to multiple government agencies.

Thank you for the opportunity to provide comments and participate in this rulemaking. As the rulemaking process proceeds, the Chamber and its members are available for further consultation.

Sincerely,

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MINNESOTA CHAMBER OF COMMERCE
GROWING MINNESOTA

August 6, 2020

Dear Ms. Maggie Wenger:

On July 16th, 2020, the Minnesota Pollution Control Agency (MPCA) organized an online meeting to discuss potential changes to air toxics reporting, primarily an agency interest in making emissions reporting mandatory. The Minnesota Chamber of Commerce (Chamber) has members across the state, many of whom hold air quality permits or are subject to air quality rules. This letter contains the Chamber's initial comments and questions on the issue of air toxics emissions reporting.

MPCA asked the following questions. We will organize our comments around them.

- Would you use the information we collect? How?
- Do you have concerns or questions about reporting burden? How does this reporting burden change when the inventory is not voluntary but mandatory?
- What would help simplify reporting?
- How should MPCA create the list of Air Toxics and maintain it over time? How to balance emerging pollutants of concern with a fixed list of air toxics in a rule? What should be the process for adding a pollutant to the list?
- What other states' toxics inventory and/or control programs should the MPCA look at?

Data Utility

MPCA's existing suite of air pollution-focused online tools and databases provide useful information for the public to understand trends and relative concentrations across geographies. As MPCA points out, the data fidelity is limited for determining neighborhood-scale concentrations and changes over time.

If MPCA's goal is to better understand community level emissions trends and potential health impacts, it seems unlikely that an incremental improvement in one sector's data would help with that goal. The emissions data from "point sources," while voluntary, have historically been of higher quality than the data for distributed, smaller sources or mobile sources of air pollution. Emissions from some categories of small sources were calculated using population-based emission factors at the county level. Improvements in calculations for those sources probably would bring more "bang for the buck" than additional requirements for industrial sources.

MPCA may also consider targeted air quality monitoring to better understand local conditions or specific pollutant concentrations. According to section 5.2 of the MPCA's 2021 Air Monitoring Network Plan for Minnesota, the MPCA monitors 10 metals at 18 TSP sites, and 7 carbonyls and 58 individual VOCs at 19 sites. The MPCA then converts these monitored concentrations into risk values and reports them online.

These efforts cannot answer every question but they seem to be better and more focused than mandatory reporting for the entire regulated community.

Even neighborhood-scale monitors may not completely characterize public health risks. Retired MPCA research scientist Greg Pratt collaborated with other researchers on many papers related to human exposure to air pollution. Two are attached. In these studies, comparisons of monitoring data at various scales showed that people's real exposures were driven by the micro-environments they experienced throughout their days.

We encourage MPCA to broadly consider potential efforts to understand concentrations of air toxics and weigh their relative effectiveness. If the goal is to provide useful data for policymakers and citizens, improvements to the most uncertain data that feed our inventories and models are likely the best path. In addition, studies that compare modeled NATA results to monitoring data may provide better targets for data improvements.

Reporting Burden

Some facilities are already required to calculate emissions of hazardous air pollutants (HAPs) or air toxics. For these facilities, a routine, voluntary submittal can be manageable. For facilities that are not required to calculate and track emissions, the reporting burden can be significant.

- The number of pollutants is large (187 HAPs plus numerous air toxics).
- Calculation methods are not always available.
- Facilities may not have information necessary to calculate such emissions. For example, the information on Safety Data Sheets may not provide information at the desired level of detail (compositional data can be (i) missing, especially if below de minimus levels, (ii) conservatively high, (iii) expressed as a wide range, and/or (iv) not identified by CAS number (which can make it difficult to identify HAPs).
- Adding air toxics reporting in the Q1 timeframe is especially challenging because this is already a very busy time for reporting under other programs.

A mandatory program may increase the burden in ways that are difficult to predict. Under a voluntary program, a facility may submit available data in good faith. Once the program becomes mandatory, we are concerned with new requirements that could impose regulatory penalties for reporting errors or require analytical testing to characterize specific emissions. A stack test may cost $5,000 to $10,000 per pollutant per stack.

Increasing the reporting frequency from every three years to every year would also increase the burden for all affected facilities, including those already submitting emissions information for HAPs and air toxics, due to the effort spent entering data into MPCA's CEDR / e-Services system. Chamber members would prefer to keep the current triennial frequency to minimize this burden.

Any increases in reporting rigor or frequency would be associated with costs for staff time to research and calculate emissions. If MPCA intends to process these emissions estimates and enter them into dispersion modeling analyses every year instead of every three years that would also lead to increased program costs that would likely be passed along to fee-paying permit holders.

Before proceeding with any related rulemaking, the Chamber requests that MPCA conduct a cost analysis for the proposed rule. The analysis should consider the likely data collection costs for regulated facilities and the staff costs for MPCA to administer the program and process the data. MPCA could look at various scenarios, from an “everybody reports” option to a targeted program that focused on geographies or pollutants. However, as noted above, a targeted analysis may be better completed by conducting ambient monitoring than an emissions-modeling-risk assessment approach.

In general, Chamber members believe that it is in the best interests of companies to report accurate data and that a shift to mandatory reporting may have a minimal effect on the overall public health information available. Before embarking on a new rule, MPCA should better characterize the expected improvements and the related costs.

Streamlining Reporting

For many facilities, compiling and submitting data for the current voluntary effort may take a week or more of real working time. A significant amount of that time is spent hard-keying the information into MPCA’s CEDR / e-Services system. Many states, including Minnesota, have improved systems for uploading water quality discharge monitoring reports. An improved interface that allowed direct import of data would simplify reporting and improve accuracy.
Reporting could also be streamlined by maintaining consistency on reporting requirements over time.

Pollutant Lists

Any rule requiring reporting should establish clear guidelines on relevant compounds, *de minimis* reporting thresholds, and applicable sources. As described above, a rule could start with a limited set of sources and compounds in order to target the most important public health issues. Such an approach would add predictability and reduce the overall reporting burden.

The establishment of *de minimis* levels is not straightforward. If a facility does not have available emissions data, there may be no simple way to demonstrate that a particular compound is emitted below relevant thresholds. Facilities would be stuck in a chicken-and-egg scenario for small sources or compounds unlikely to be emitted.

MPCA should consider how to treat unique sources in any future program. Exemptions for research and development or temporary sources would be useful for permit holders and avoid extensive work to characterize sources that may not be significant.
The provision of detailed lists of compounds at a process level also creates challenges for the protection of confidential business information. MPCA should include provisions that allow sources to protect sensitive, process-specific data and formulations.

Relevant program details, including lists of compounds, should be explicitly listed in any rule and require notice-and-comment rulemaking to modify the list. In states where lists may be changed without notice, new compounds create unexpected technical challenges for regulated facilities.

State Examples

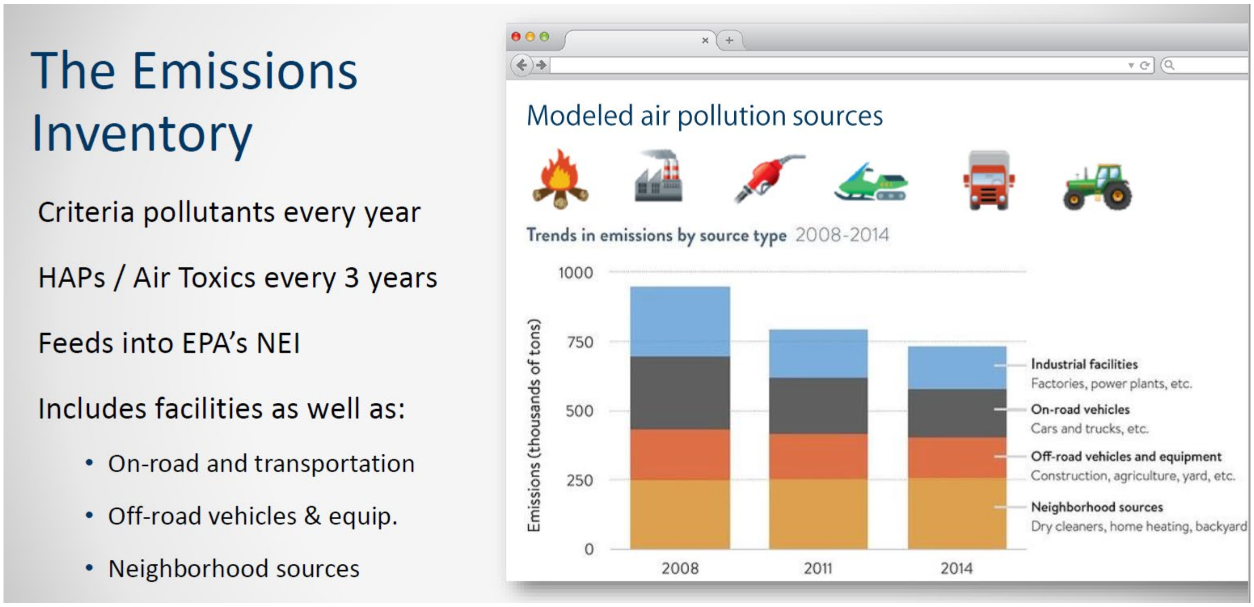
Each state's air toxics program is unique. For US EPA Region 5 states, Wisconsin is one example of a well-defined program, with pollutants and screening modeling thresholds included in rule. There are limitations to that program but it has the advantage of being predictable.

Many other states have policy-based programs, with minimal details included in rule. These programs are difficult for permit holders to manage during specific projects. We are not aware of examples of easily identified improvements to local pollutant concentrations or public health outcomes that can be attributed to these programs.

Other Comments

Chamber members are generally against increased reporting requirements as part of the MPCA's air toxics emissions inventory. Many of the most significant sources are regulated by federal NESHAPs. A number of the NESHAPs have recently undergone or will be subject to Residual Risk and Technology (RTR) reviews, which are required to demonstrate that facilities' HAP emission limits are protective of human health and the environment, with an adequate margin of safety.

Many of the MPCA's own reports state that emissions from industrial sources, both as a percent of total pollution and in absolute terms, are decreasing. A recent MPCA presentation on online air pollution tools showed this point.



The Emissions Inventory

Criteria pollutants every year

HAPs / Air Toxics every 3 years

Feeds into EPA's NEI

Includes facilities as well as:

- On-road and transportation
- Off-road vehicles & equip.
- Neighborhood sources

MPCA highlighted several improvements that would potentially result from mandatory reporting, including better data quality and useful information for future program changes. However, more information is needed that links the specific proposal to these outcomes. Better data is a means to an end and a more targeted approach for certain sources or compounds may accomplish the same goal with reduced effort.

Chamber members continue to be frustrated with the timeliness of MPCA approval of permits and environmental review submittals. Reporting changes would increase the work required from key staff (e.g., dispersion modelers, risk assessors, possibly stack test coordinators) who are already in high demand. It is not a good trade off to reduce staff assigned to core regulatory programs to marginally improve data quality for emissions inventories.

Finally, as MPCA considers how to leverage existing programs to better serve communities and reduce exposure to air pollution, the Chamber reiterates its support for Clean Air Minnesota (CAM) programs and outcomes. While incremental data improvements are good, the overarching goal should be real improvements for real people, and that is where CAM excels. MPCA is already very involved with CAM and the Chamber appreciates MPCA's strong engagement and direct support for the collaborative effort. Further ramping up MPCA support for CAM projects related to clean cars, wood-burning stoves, diesel engines, and community businesses would lead to direct improvements in the air people breathe and may be a better way to spend our collective time on air quality issues.

Thank you for the opportunity to comment on the MPCA's potential changes to air toxics emissions reporting. The Chamber and its members are available for further consultation as these efforts proceed.

Respectfully submitted,

Tony Kwilas
Director, Environmental Policy
Minnesota Chamber of Commerce

Enclosures: 2
Evaluating Differences between Measured Personal Exposures to Volatile Organic Compounds and Concentrations in Outdoor and Indoor Air
Comparison of Personal, Indoor, and Outdoor Exposures to Hazardous Air Pollutants in Three Urban Communities

Environ. Sci. Technol. **2004**, *38,* 423−430

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^2 with a population density of 2000−8000 per km^2. 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^2 and a population density of 1000−4000 per km^2. 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^2 and has a population density of 500−2000 per km^2. 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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10.1021/es030319u CCC: $27.50

TABLE 1. Summary of Valid, Matched, VOC Samples[a] 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

[a] 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 ≤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

	outdoor (ug/m^3)						indoor (ug/m^3)						personal (ug/m^3)					
VOC	*n*	%det[b]	mean	median	Q10	Q90	*n*	%det[b]	mean	median	Q10	Q90	*n*	%det[b]	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
p-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
d-limonene	121[a]	86.8	0.3	0.2	0.1	0.6	262[a]	99.6	16.1	9.0	2.2	30.7	258[a]	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
a-pinene	121[a]	74.4	0.2	0.2	0.1	0.4	262[a]	99.6	6.7	2.5	0.7	12.4	258[a]	99.6	6.6	2.7	0.9	14.6
b-pinene	121[a]	9.1	0.1	0.1	0.1	0.1	262[a]	71.0	3.3	1.2	0.1	5.2	258[a]	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
o-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
m-/*p*-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

[a] Fewer valid samples were available because of calibration problems. [b] Percentage of samples with instrument readings above zero.

15 VOCs. Rather than present all 405 combinations (3 × 3 × 3 × 15) with inferential statements about each, key marginal distributions are examined ("marginal" here referring to the margins of this 3 × 3 × 3 × 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, tetrachloroehylene, *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 ($\mu g/m^3$) 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 ug/m^3, which is derived from 0.7 ug/m^3 (for BCK in SPRG) × 2.0 (effect modifier for ESP) × 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

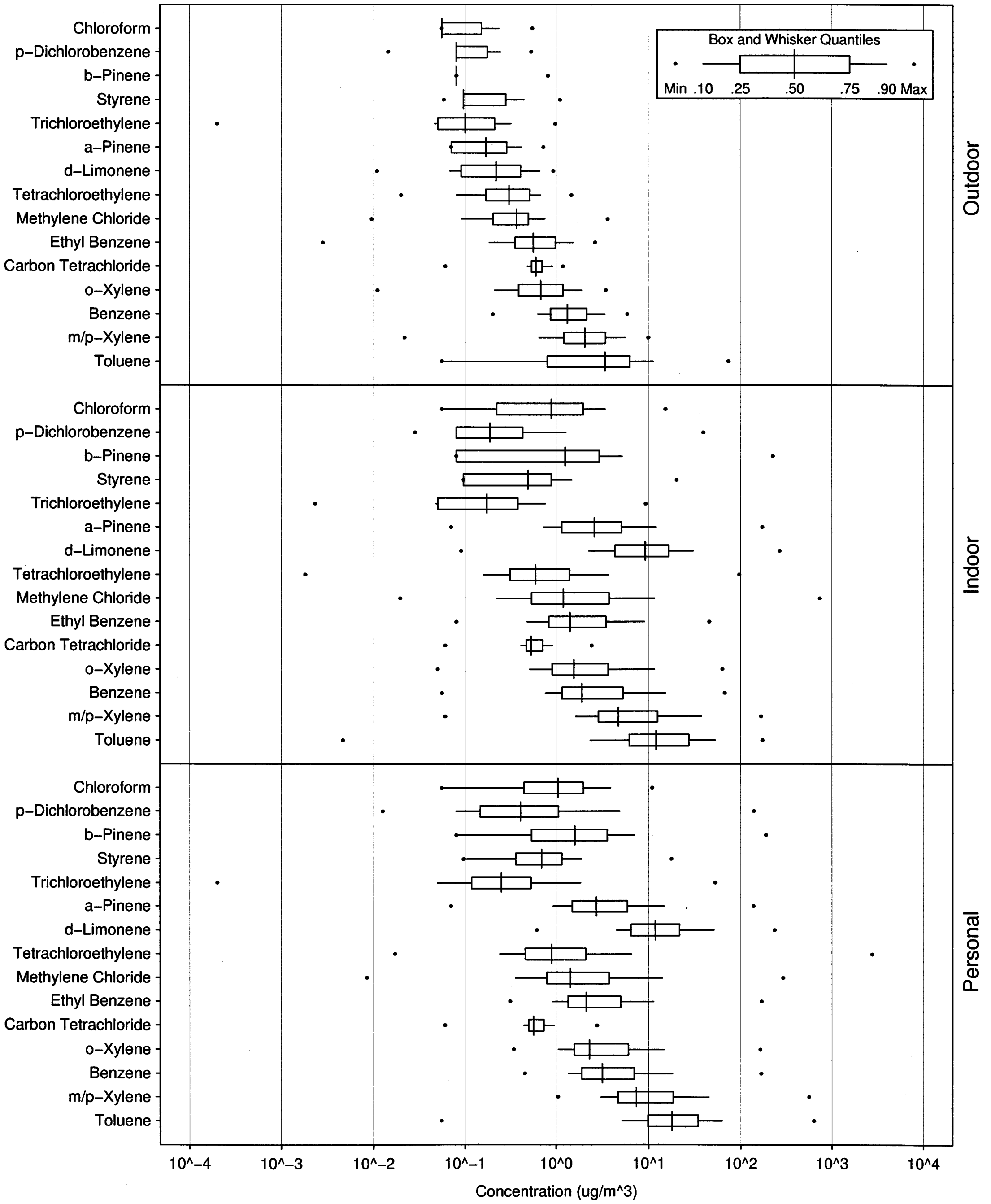

FIGURE 1. Distributions of all valid, matched VOC concentrations for outdoor, indoor, and personal samples

derived by multiplying 6.9 (P/O ERC for benzene in BCK in SPRG) × 0.3 (ESP effect modifier) × 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 ≅ 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 ≥ 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

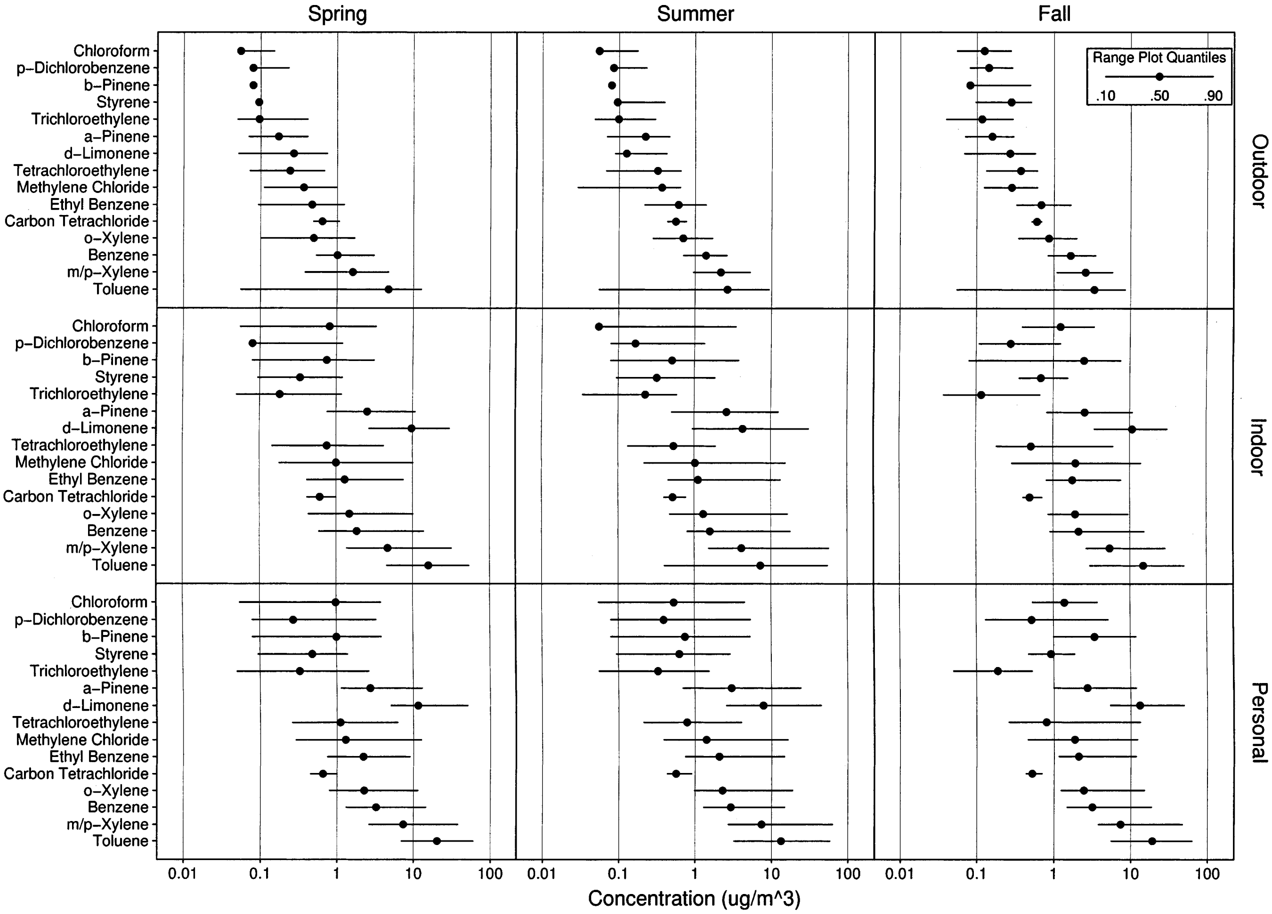

FIGURE 2. Distributions of all valid, matched VOC concentrations by monitor location and season

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 ≅ 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 ≅ I ≅ 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 soley from indoor sources, and nine (benzene, ethyl benzene, methylene chloride, styrene, toluene, trichloroethylene, tetrachloro-

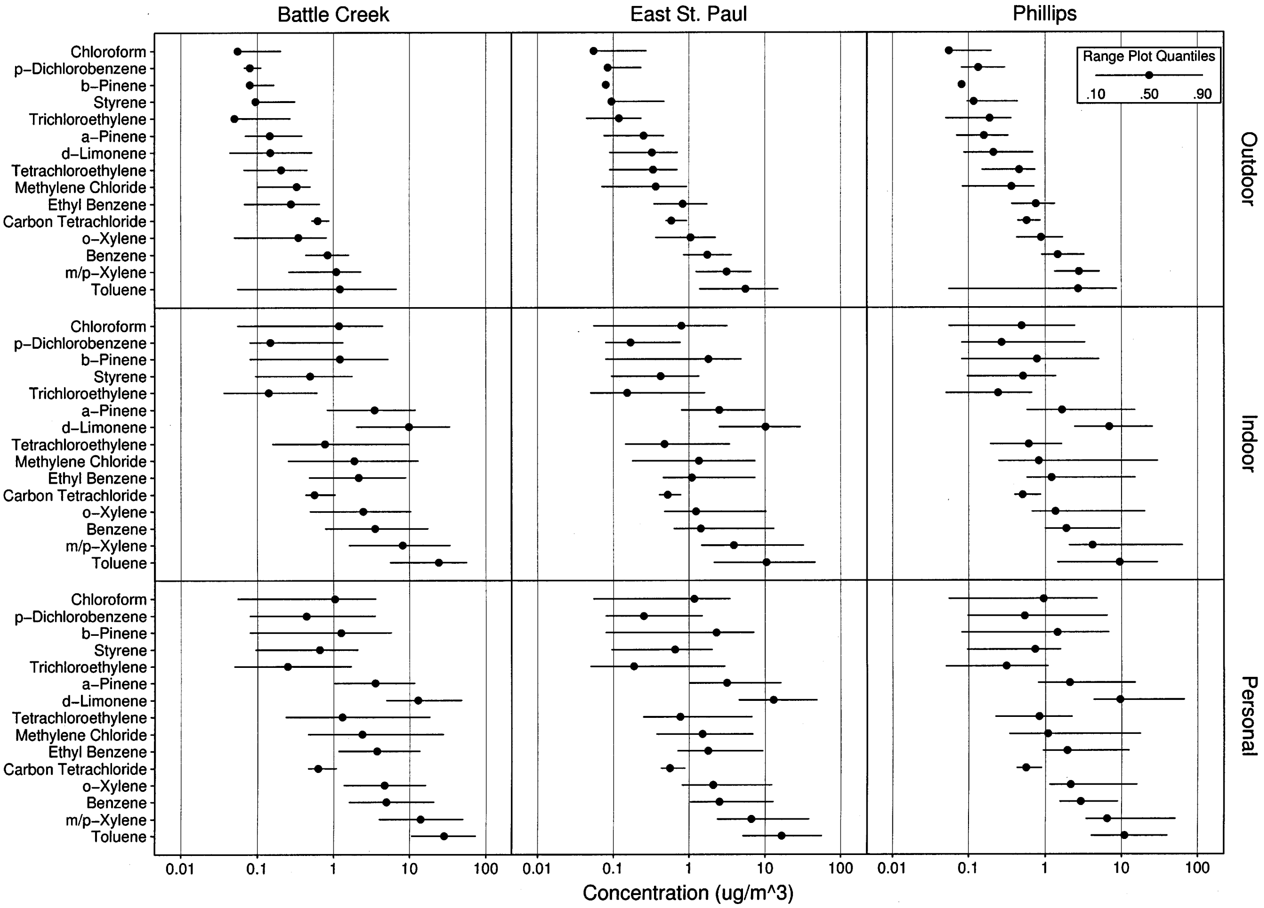

FIGURE 3. Distributions of all valid, matched VOC concentrations by monitor location and community

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

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

[a] Fewer valid samples were available because of calibration problems. [b] 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	ERC for BCK in SPRG			community and season ERC effect modifiers (relative to 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[a]	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[a]	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[a]	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)

[a] 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 $\mu g/m^3$)

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

[a] Estimated lifetime excess cancer risk (95th percentile upper-bound) of 1×10^{-5} (1 in 100 000) for an individual exposed to this concentration for a 70-year lifetime. [b] Minnesota Health Risk Value (HRV). [c] U. S. Environmental Protection Agency IRIS (Integrated Risk Information System) Value. [d] 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 ($\mu g/m^3$), 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 1×10^{-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 ug/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.

Acknowledgments

This research was funded by a STAR (Science to Achieve Results) Grant (R825241) from the U.S. Environmental Protection Agency, National Center for Environmental Research. We also benefited from a grant from the Academic Health Center at the University of Minnesota. We thank the individuals who participated in the study and acknowledge the contributions of the field team. We also thank the 3M Corporation for donating some of the organic vapor monitors used in this study. The help and support provided by the Minnesota Pollution Control Agency was essential to the success of this project.

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Received for review January 15, 2003. Revised manuscript received October 27, 2003. Accepted November 4, 2003.

ES030319U

Environ. Sci. Technol. **2004**, *38,* 2593−2602

Evaluating Differences between Measured Personal Exposures to Volatile Organic Compounds and Concentrations in Outdoor and Indoor Air

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Accurate estimation of human exposures to volatile organic compounds (VOCs) is a key element of strategies designed to protect public health from the adverse effects of hazardous air pollutants. The focus here is on examining the capability of three different exposure metrics (outdoor community concentrations, indoor residential concentrations, and a simple time-weighted model) to estimate observed personal exposures to 14 VOCs. The analysis is based on 2-day average concentrations of individual VOCs measured concurrently in outdoor (O) air in three urban neighborhoods, indoor (I) air in participant's residences, and personal (P) air near the breathing zone of 71 healthy, nonsmoking adults. A median of four matched P−I−O samples was collected for each study participant in Minneapolis/St. Paul over three seasons (spring, summer, and fall) in 1999 using charcoal-based passive air samplers (3M model 3500 organic vapor monitors). Results show a clear pattern for the 14 VOCs, with P > I > O concentrations. Intra-individual variability typically spanned at least an order of magnitude, and inter-individual variability spanned 2 or more orders of magnitude for each of the 14 VOCs. Although both O and I concentrations generally underestimated personal exposures, I concentrations provided a substantially better estimate of measured P concentrations. Mean squared error (MSE) as well as correlation measures were used to assess estimator performance at the subject-specific level, and hierarchical, mixed effects models were used to estimate the bias and variance components of MSE by tertile of personal exposure. Bias and variance both tended to increase in the upper third of the P exposure distribution for O versus P and I versus P. A simple time-weighted model incorporating measured concentrations in both outdoor community air and indoor residential air provided no improvement over I concentration alone for the estimation of P exposure.

Introduction

Concentrations of hazardous air pollutants in a person's breathing zone for a defined period of time are typically referred to as *personal* exposures (*1*, *2*). An individual's personal exposure for a particular time period (e.g., 48 h) depends on pollutant concentrations in the indoor and outdoor microenvironments through which he or she moves during routine daily activities and on the time spent in each of these locations. From a public health perspective, it is often important to estimate the distribution of personal exposures in a population or to distinguish between individuals with high versus low exposure. But measuring personal exposures for a large number of people (including potentially vulnerable groups such as the young, the elderly, and the infirm) can be burdensome, time-consuming, expensive, and, in many cases, impractical. It is imperative, therefore, to gain a clear understanding of the value of more easily obtained metrics, such as measurements at outdoor community sites or indoor residential locations, for estimating personal exposures.

Although volatile organic compounds (VOCs) are common constituents of outdoor (*3*−*6*) and indoor (*7*−*9*) air, comparatively little is known about personal exposures. The relatively few personal monitoring studies that have been conducted suggest that personal exposures tend generally to be higher than indoor residential concentrations, which tend typically to be higher than outdoor community concentrations (*10*−*15*). Other personal exposure studies have concentrated on exposure of specific subpopulations to one or few individual VOCs, with many focused on exposure to benzene. This paper examines the ability of fixed indoor residential and outdoor monitors, in combination with time−activity data, to estimate personal exposures to 14 individual VOCs for 71 nonsmoking adults 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 (*13*). A secondary objective was to measure $PM_{2.5}$ exposures for a subset of the subjects, results of which have been published previously (*16*−*19*). Three urban neighborhoods (Phillips, East St. Paul, and Battle Creek) with different outdoor VOC concentration profiles based on modeling results (*13, 20, 21*) were selected for the exposure monitoring study.

Phillips (PHI) is an economically disadvantaged, predominantly minority inner-city neighborhood in south central Minneapolis. 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. VOC concentrations were predicted to be relatively high, primarily as a result of emissions from nearby manufacturing plants. Battle Creek (BCK) is a predominantly white, affluent neighborhood on the eastern edge of St. Paul. Predicted VOC concentrations were relatively low as compared to the other two neighborhoods.

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10.1021/es030607q CCC: $27.50

A centralized outdoor monitoring site (community site) was established in each neighborhood. Approximately 25 healthy, nonsmoking adults were recruited from each neighborhood using house-to-house canvassing and direct solicitation (informed consent was obtained). Matched 2-day samples were collected outdoors at the three community monitoring sites, indoors in participants' residences (room where they spent most of their waking hours), and near participants' breathing zones, all using passive dosimeters. Participants also completed time−activity logs recording the time they spent in seven microenvironments (indoors at home, work, other; outdoors at home, work, other; in transit) and the time they were in close proximity to environmental tobacco smoke. 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).

Methods

VOC Collection and Analysis. All VOC concentrations (O, I, and P) were 2-day (approximately 48-h) 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. (*22*, *23*). These investigators have also described the determination of extraction efficiencies and the calculation of method detection limits. 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, and 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 (*23*). Duplicate O, I, and P badges were collected periodically during the study (total $n = 80$), and correlation coefficients for the positive measurements were >0.95 for all individual VOCs except styrene (0.94) and chloroform (0.95). We define the median relative absolute difference (MRAD) as the median of the ratios of within-pair absolute differences divided by the within-pair mean. MRAD was <0.18 for all VOCs except trichloroethylene (0.44).

Statistical Analyses. All statistical analyses were performed using SAS (*24*) and S-plus (*25*). Concentrations less than the method detection limit (MDL) were included in the calculations. "Nondetectable" measurements (i.e., samples with no analytical response or those with values ≤ 0 after blank subtraction) were assigned a value of one-half the analytical detection limit (ADL).

Three estimators of personal exposure are evaluated:

$$\hat{P}_{[O]ij} = O_{ij} \tag{1}$$

$$\hat{P}_{[I]ij} = I_{ij} \tag{2}$$

$$\hat{P}_{[OI]ij} = O_{ij}t_{[O]ij} + I_{ij}t_{[I]ij} \tag{3}$$

where O_{ij} and I_{ij} denote the observed concentration for the ith subject on the jth occasion, from O and I, respectively; $t_{[O]ij}$ and $t_{[I]ij}$ represent the (time) fraction of the 2-day monitoring period spent in the O and I environments, respectively. For the purposes of this analysis, we let $\hat{P}_{[O]}$, $\hat{P}_{[I]}$, and $\hat{P}_{[OI]}$ represent $\hat{P}_{[O]ij}$, $\hat{P}_{[I]ij}$, and $\hat{P}_{[OI]ij}$ for all subjects and all times. In the simple time-weighted model (eq 3), the proportion of time in O was defined to be the complement of the proportion of time in I (i.e., $t_{[O]ij} = 1 - t_{[I]ij}$). Thus, the model implicitly assumes that individuals not in their homes are exposed uniformly to the measured O concentration regardless of whether they are indoors or out (a likely underestimate of actual exposures).

The mean squared error (MSE) was computed for each estimator of P (see Discussion). To maintain the original scale of measurement, the root mean squared error (RMSE) is reported instead of the MSE, and the variance is represented by its square root as the standard deviation (SD). For $\hat{P}_{[O]}$ and $\hat{P}_{[I]}$, both RMSE and longitudinal correlations are first presented, based on estimation of each statistic for each subject. Geometric means of all duplicate samples are used to facilitate comparison with previous studies. To maximize the information available from our sample, no lower limit on the number of repeated measurements was applied in the calculation of these subject-specific RMSEs or longitudinal correlations (R) except for the mathematical limit imposed by the statistics themselves. For example, a longitudinal correlation cannot be calculated for subjects with only one data point. We report medians with upper and lower deciles to illustrate the inter-subject distributions of RMSE and R and to give a sense of their inherent variation.

To further analyze the MSE by its component bias and variance, mixed effects models were used (*26*, *27*). These models accommodate duplicate data explicitly, making use of information on measurement error, and obviating the need to take means of duplicates. Moreover, mixed effects models handle variation in numbers of measurements across subjects by downweighting those with fewer measurements. To allow for heterogeneity of variance and to more flexibly model bias, the range of all P exposures was divided into its three tertiles, and a separate model was fitted for each.

Results

Selected sociodemographic characteristics and exposure-related attributes for the 71 participants in the study are summarized in Table 1. Seventy-seven percent were female, and more than half (56%) were between the ages of 40−65 years. Only one person had less than a high school education, while 37% had some college, 18% were college graduates, and 34% reported some post-graduate education. More than half (51%) had an annual household income of \$40 000 or more, with 8% earning between \$75 000 and \$100 000, and 3% earning more than \$100 000. Eighty-five percent were white, 7% were African American, 3% were Native American, 1% was Asian/Pacific Islander, and 3% were other. Most participants (69%) worked outside the home, only 7% lived with a smoker, and 34% had attached garages. Overall, the participants were predominantly white, female, well-educated, relatively affluent, and unlikely to be exposed to environmental tobacco smoke at home. As expected, participants from PHI had the highest percentage of minorities and the lowest household incomes.

A total of 284 valid, matched P and O sample sets with time−activity diaries were obtained from the 71 participants. The number collected for each participant varied from 1 (2 people) to 11 (1 person), with a median of 4 (Q25 = 3 and Q75 = 6). This variability in the number of P samples for each individual results from the fact that some participants dropped out of the study early, while others continued to participate. Furthermore, some of the P samples were invalid because of protocol errors, monitor malfunctions, or analytical problems. The range of P VOC concentrations for each participant is displayed graphically in Figure 1, and the range of I VOC concentrations for each participant is presented in Figure 2. For individual VOCs, each line in these range plots represents one of the 71 participants and spans the range of concentrations measured for that person. Within each VOC, the line segments are ordered by maximum concentration, and the vertical ordering of the VOCs themselves is deter-

TABLE 1. Summary of Sociodemographic Information for Participants in the Study

	n (%)			
parameter	Battle Creek	East St. Paul	Phillips	all communities
no. of participants	25 (35%)	22 (31%)	24 (34%)	71 (100%)
gender				
male	7 (10%)	2 (3%)	7 (10%)	16 (23%)
female	18 (25%)	20 (28%)	17 (24%)	55 (77%)
age				
18−39 yr	6 (8%)	12 (17%)	11 (15%)	29 (41%)
40−65 yr	17 (24%)	10 (14%)	13 (18%)	40 (56%)
>65 yr	1 (1%)	0 (0%)	0 (0%)	1 (1%)
missing	1 (1%)	0 (0%)	0 (0%)	1 (1%)
education				
less than high school	0 (0%)	1 (1%)	0 (0%)	1 (1%)
high school	2 (3%)	2 (3%)	3 (4%)	7 (10%)
some college	7 (10%)	13 (18%)	6 (8%)	26 (37%)
college graduate	6 (8%)	2 (3%)	5 (7%)	13 (18%)
post-graduate education	10 (14%)	4 (6%)	10 (14%)	24 (34%)
annual household income				
\$10 000−\$19 999	2 (3%)	1 (1%)	3 (4%)	6 (8%)
\$20 000−\$29 999	0 (0%)	4 (6%)	9 (13%)	13 (18%)
\$30 000−\$39 999	4 (6%)	3 (4%)	3 (4%)	10 (14%)
\$40 000−\$49 999	2 (3%)	6 (8%)	1 (1%)	9 (13%)
\$50 000−\$74 999	9 (13%)	5 (7%)	5 (7%)	19 (27%)
\$75 000−\$99 999	2 (3%)	3 (4%)	1 (1%)	6 (8%)
≥\$100 000	2 (3%)	0 (0%)	0 (0%)	2 (3%)
refused or missing	4 (6%)	0 (0%)	2 (3%)	6 (8%)
race				
white	24 (34%)	22 (31%)	14 (20%)	60 (85%)
African American	1 (1%)	0 (0%)	4 (6%)	5 (7%)
Native American	0 (0%)	0 (0%)	2 (3%)	2 (3%)
Asian/Pacific Islander	0 (0%)	0 (0%)	1 (1%)	1 (1%)
other	0 (0%)	0 (0%)	2 (3%)	2 (3%)
refused	0 (0%)	0 (0%)	1 (1%)	1 (1%)
work outside the home				
yes	17 (24%)	13 (18%)	19 (27%)	49 (69%)
no	8 (11%)	9 (13%)	5 (7%)	22 (31%)
live with a smoker				
yes	1 (1%)	3 (4%)	1 (1%)	5 (7%)
no	24 (34%)	19 (27%)	23 (32%)	66 (93%)
attached garage				
yes	18 (25%)	3 (4%)	3 (4%)	24 (34%)
no	7 (10%)	19 (27%)	21 (30%)	47 (66%)

mined by the median of these maximum values. Minimum values appear to be truncated in some cases (for example, β-pinene, chloroform, and styrene in Figure 1) because many samples were zero or below.

As shown in Figure 1, a participant's P exposure to individual VOCs over multiple monitoring periods (within-person variability) often spanned 1 or more orders of magnitude. Moreover, the difference between participants' with the lowest maximum P values and those with the highest (between-person variability) often spanned 2 or more orders of magnitude. This same pattern also held true for participants' I concentrations (Figure 2), which were generally lower than matched P exposures. The evidence indicates that for these 14 VOCs there was substantial within-person variability and between-person variability for both P exposures and I concentrations.

Two subject-level criteria for characterizing the performance of $\hat{P}_{[O]}$ are provided in Table 2. The RMSE and *R* were calculated for each subject with a sufficient number of samples for each measure (≥1 for RMSE, ≥2 for *R*). RMSE is a measure of the magnitude and variation of the difference ($\mu g/m^3$) between measured O concentrations and P exposures, while *R* is a measure of the linear association between O and P. Compared to *R* and for the aims of this study, RMSE is a more direct measure of performance of these estimators (see Discussion); however, we present both to facilitate their comparison. The median value for RMSE and *R* across all subjects along with 10th and 90th percentiles are presented.

Looking at the overall results, the median RMSE for $\hat{P}_{[O]}$ was between 0.2 and 1.8 $\mu g/m^3$ for 9 VOCs, between 2.5 and 4.8 $\mu g/m^3$ for 3 VOCs (α-pinene, β-pinene, and *m*-/*p*-xylene), 13.4 $\mu g/m^3$ for D-limonene, and 16.3 $\mu g/m^3$ for toluene. It should be noted that RMSE is expected to be elevated for those VOCs found at higher concentrations, since their variance is usually higher as well. For all 14 VOCs, $\hat{P}_{[O]}$ underestimated P exposure. The RMSE of $\hat{P}_{[O]}$ for 6 VOCs (benzene, ethyl benzene, methylene chloride, toluene, *o*-xylene, *m*-/*p*-xylene) was substantially higher in BCK than in ESP and PHI. This is not surprising given that O concentrations in BCK tended to be slightly but consistently lower than in the other two neighborhoods, while P exposures tended to be slightly higher (hence a greater underestimation of P exposures in BCK). Overall, correlation coefficients were generally unremarkable, with median *R* for 9 VOCs between −0.08 and 0.24 and between 0.43 and 0.59 for the other 5 VOCs (benzene, ethyl benzene, styrene, *o*-xylene, *m*-/*p*-xylene). With the exceptions of D-limonene and tetrachloroethylene in ESP and benzene, styrene, and *m*-/*p*-xylene in BCK, *R* values were generally comparable across the three neighborhoods.

Analogous performance measures for $\hat{P}_{[I]}$ by neighborhood are provided in Table 3. Comparing $\hat{P}_{[I]}$ to $\hat{P}_{[O]}$ overall, there was a reduction in RMSE for 13 of the 14 VOCs (trichloroethylene remained unchanged). The most dramatic reductions were observed for D-limonene (from 13.4 to 4.7 $\mu g/m^3$) and toluene (from 16.3 to 8.3 $\mu g/m^3$). Generally, $\hat{P}_{[I]}$ also

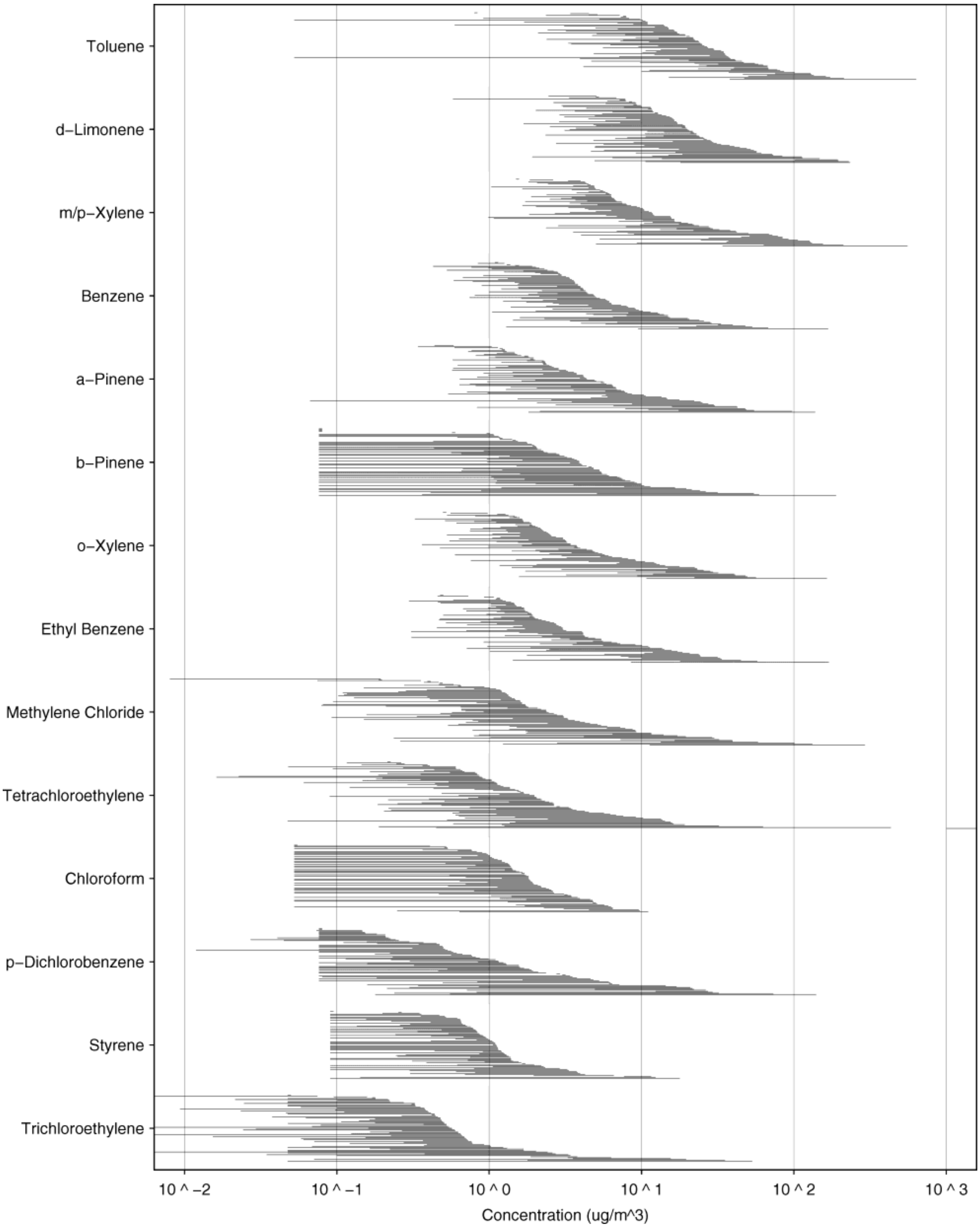

FIGURE 1. Range plot of measured personal VOC exposures for each study participant.

tended to underestimate P exposures, but not as much or as consistently as $\hat{P}_{[O]}$. Compared to $\hat{P}_{[O]}$, reduced RMSE occurred similarly across neighborhoods, and for benzene, toluene, *o*-xylene, and *m*-/*p*-xylene remained higher in BCK as compared to ESP and PHI (similar to the pattern observed for $\hat{P}_{[O]}$). Correlation coefficients improved dramatically for all VOCs, with $R > 0.85$ for 8 VOCs (benzene, chloroform, D-limonene, methylene chloride, α-pinene, β-pinene, *o*-xylene, *m*-/*p*-xylene), and $0.57 \le R \le 0.83$ for the remaining 6 VOCs. Relatively consistent *R* values for individual VOCs were observed across neighborhoods, with the exception of *p*-dichlorobenzene (0.16) in BCK and trichloroethylene (0.40) in PHI.

The improved performance of I over O concentrations is illustrated graphically in Figure 3 using three VOCs as examples. It is clear from the scatter plots that O concentra-

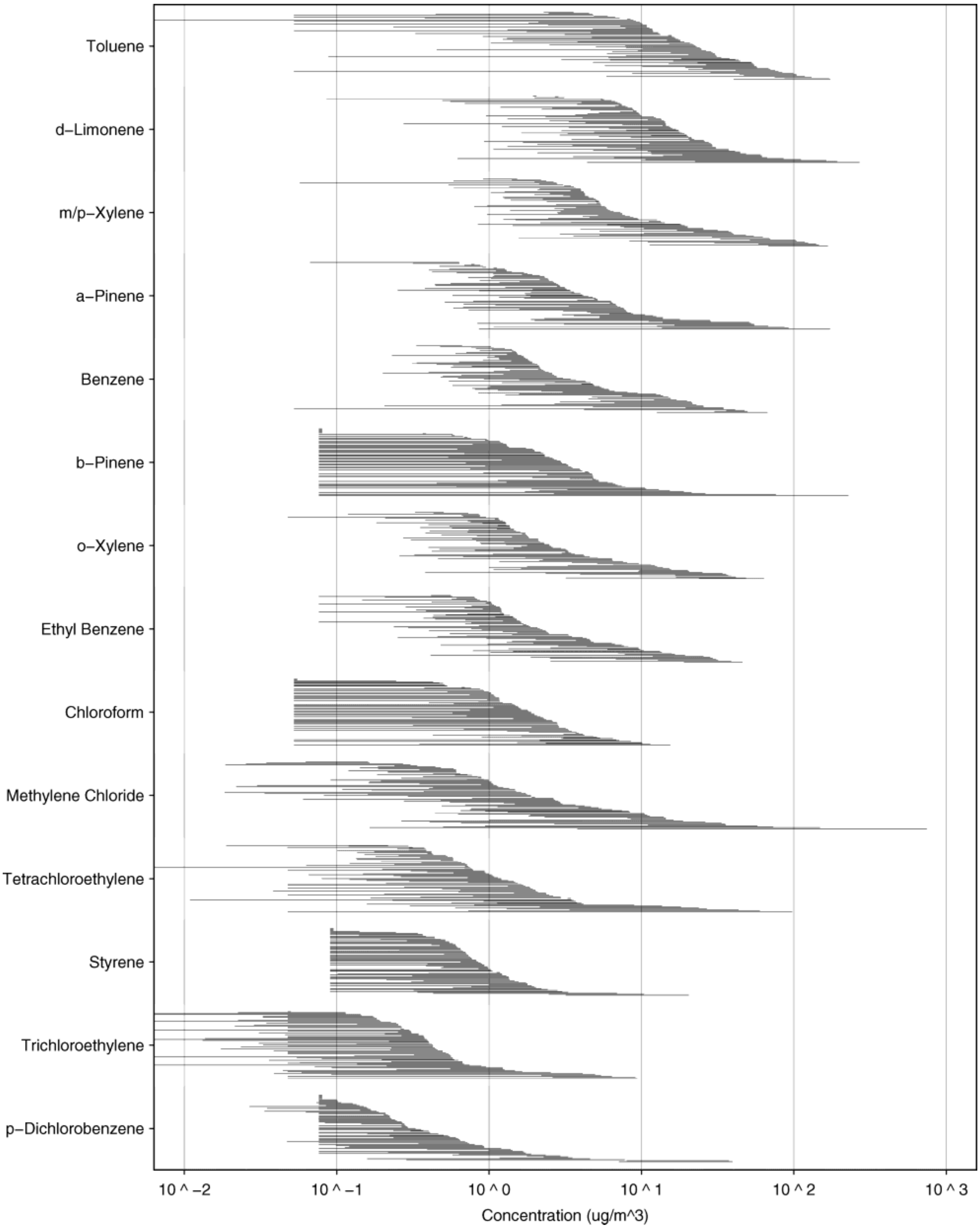

FIGURE 2. Range plot of measured indoor residential VOC concentrations for each study participant.

tions underestimate P exposure in the majority of cases for benzene, methylene chloride, and toluene. I concentrations, on the other hand, provide a noticeable improvement in estimating P exposure, although the tendency is still to underestimate. Overall, for this population and under the conditions of the study, matched I concentrations provided a substantially better estimate of personal VOC exposure than matched O concentrations for all 14 VOCs measured.

To further investigate the nature of RMSE for $\hat{P}_{[O]}$ and $\hat{P}_{[I]}$, we divided the domains of measured P exposures into lower, middle, and upper tertiles and then estimated the two components of MSE, bias (squared) and variance, using the mixed effects model. We distinguish the vector of all numerical observations of personal exposures by $\mathbf{P}$. An estimate of bias is obtained for each tertile by estimating the mean of $\hat{P}_{[O]} - \mathbf{P}$ (Table 4) or the mean of $\hat{P}_{[I]} - \mathbf{P}$ (Table 5).

TABLE 2. Comparison of Matched (Outdoor Community, Personal) VOC Concentrations for Individual Participants in the Study

	Battle Creek		East St. Paul		Phillips		all communities	
compound	RMSE[a]	R[b]	RMSE	R	RMSE	R	RMSE	R
benzene	4.9	0.02	1.4	0.79	1.5	0.68	1.8	0.59
	(0.9, 19.4)[c]	(−0.92, 0.89)[c]	(0.9, 7.8)	(−0.37, 1.00)	(0.7, 8.5)	(−0.92, 1.00)	(0.7, 16.3)	(−0.85, 1.00)
chloroform	1.1	0.00	1.4	0.31	1.5	0.00	1.8	0.00
	(0.3, 3.3)	(−0.51, 1.00)	(0.6, 4.6)	(−0.16, 0.92)	(0.5, 4.2)	(−0.54, 0.98)	(0.5, 3.9)	(−0.50, 0.99)
p-dichlorobenzene	0.6	0.00	0.3	0.15	0.9	−0.01	0.7	0.00
	(0.1, 9.5)	(−0.54, 0.58)	(0.1, 8.4)	(−0.73, 0.82)	(0.1, 13.5)	(−0.78, 1.00)	(0.1, 9.8)	(−0.72, 0.98)
ethyl benzene	3.7	0.41	1.1	0.51	1.1	0.65	1.5	0.53
	(1.0, 14.3)	(−0.47, 1.00)	(0.5, 13.4)	(−0.76, 1.00)	(0.6, 12.3)	(0.01, 1.00)	(0.5, 14.3)	(−0.52, 1.00)
D-limonene	12.7	0.43	17.5	−0.31	12.2	0.34	13.4	0.15
	(6.3, 36.2)	(−0.64, 1.00)	(7.6, 86.5)	(−0.97, 1.00)	(6.9, 40.6)	(−1.00, 1.00)	(7.0, 57.2)	(−1.00, 1.00)
methylene chloride	3.3	0.14	1.5	0.11	0.8	0.38	1.3	0.14
	(0.2, 32.0)	(−0.93, 0.96)	(0.4, 8.3)	(−0.90, 0.84)	(0.4, 8.3)	(−0.76, 1.00)	(0.3, 12.4)	(−0.86, 1.00)
α-pinene	3.6	−0.04	3.6	0.12	2.0	−0.17	3.0	−0.08
	(1.2, 17.9)	(−0.93, 0.95)	(1.1, 15.4)	(−0.87, 0.96)	(1.2, 14.6)	(−1.00, 0.75)	(1.2, 17.3)	(−1.00, 0.95)
β-pinene	1.8	0.00	3.6	0.00	1.9	0.28	2.5	0.00
	(0.1, 8.8)	(−0.13, 0.98)	(1.5, 9.5)	(−0.40, 0.87)	(0.8, 7.2)	(0.00, 1.00)	(0.8, 9.4)	(−0.16, 0.99)
styrene	0.6	0.08	0.5	0.74	0.6	0.40	0.6	0.55
	(0.2, 2.1)	(−0.20, 0.99)	(0.2, 2.3)	(0.20, 0.98)	(0.4, 1.7)	(−0.82, 0.90)	(0.2, 2.0)	(−0.23, 0.98)
tetrachloroethylene	1.3	−0.15	1.0	0.62	0.6	0.17	0.9	0.24
	(0.2, 25.3)	(−0.75, 1.00)	(0.1, 8.7)	(−0.64, 0.99)	(0.2, 3.7)	(−1.00, 0.98)	(0.2, 8.9)	(−0.91, 1.00)
toluene	29.9	−0.11	13.8	0.06	10.0	0.33	16.3	0.02
	(9.6, 85.2)	(−0.99, 1.00)	(7.4, 50.4)	(−0.65, 0.87)	(5.1, 19.3)	(−0.49, 1.00)	(6.1, 64.5)	(−0.90, 0.99)
trichloroethylene	0.2	0.16	0.2	0.43	0.2	0.20	0.2	0.24
	(0.1, 1.1)	(−0.65, 1.00)	(0.1, 1.5)	(−0.16, 0.98)	(0.1, 0.5)	(−0.92, 0.98)	(0.1, 1.3)	(−0.79, 0.99)
o-xylene	4.2	0.26	1.3	0.44	1.3	0.67	1.6	0.43
	(1.2, 17.3)	(−0.94, 0.96)	(0.5, 16.5)	(−0.78, 0.97)	(0.6, 16.3)	(0.13, 1.00)	(0.6, 19.0)	(−0.72, 1.00)
m-/*p*-xylene	14.1	0.19	3.8	0.50	3.7	0.70	4.8	0.47
	(3.4, 57.4)	(−0.75, 0.98)	(1.5, 51.9)	(−0.76, 0.99)	(1.8, 54.0)	(0.08, 1.00)	(2.0, 63.4)	(−0.69, 1.00)

[a] Median root mean squared error ($\mu g/m^3$); *n* for number of research subjects = 25 for Battle Creek, 22 for East St. Paul, and 24 for Phillips. [b] Median correlation coefficient; *n* for number of research subjects varies from 20 to 23 for Battle Creek, *n* = 22 for East St. Paul, and *n* varies from 21 to 22 for Phillips. [c] 10th and 90th percentiles.

In addition, an estimate of standard deviation (SD) is obtained from the square root of the variance resulting from application of the same mixed model.

The results from Table 4 show that both the bias and the SD of $\hat{P}_{[O]}$ tend to increase from the lower to the middle and from the middle to the upper tertile of the distribution of P exposures. For example, in the lower tertile the range of $\hat{P}_{[O]} - \mathbf{P}$ values for individual VOCs is between −1.9 and 0.0; in the middle tertile it is between −13.2 and −0.1; and in the upper tertile it is between −62.7 and −2.0. These data suggest that $\hat{P}_{[O]}$ typically underestimates P exposures in all cases and that the magnitude of this underestimation increases with higher P exposures. In terms of variance, the range of SDs for individual VOCs in the lower tertile is 0.1−9.9, 0.2−6.4 in the middle tertile, and 1.9−360 in the upper-tertile. Again, the data indicate that the variance of $\hat{P}_{[O]}$ generally increases with higher P exposures.

The pattern is similar for I versus P in Table 5, with both bias and variance of $\hat{P}_{[I]}$ increasing from lower to middle to higher tertiles of P exposures. For example, the range of $\hat{P}_{[I]} - \mathbf{P}$ values for the 14 individual VOCs is −0.9 to 0.4 in the lower tertile, −3.3 to 1.1 in the middle tertile, and −55.8 to 3.9 in the upper tertile. The evidence suggests that $\hat{P}_{[I]}$ tends to underestimate P exposures for 12 of the 14 VOCs, especially in upper tertile of the distribution of P exposures. $\hat{P}_{[I]}$ tends to overestimate, particularly in the upper tertile, for methylene chloride and α-pinene. Similarly, the range of SDs for individual VOCs increases from 0.1 to 5.2 in the lower tertile, from 0.2 to 10.2 in the middle tertile, and from 1.7 to 351 in the upper tertile, which suggests that variance in $\hat{P}_{[I]}$ also tends to increase with higher P exposures.

We investigated the time-weighted estimator $\hat{P}_{[OI]}$ by examining the RMSE for the model where P exposure equals the time fraction of the 2-day monitoring period spent indoors at home ($t_{[I]}$) times the measured I concentration plus the complement of the time fraction indoors at home ($1 - t_{[I]}$) times the measured O concentration (see eq 3). Because the measured O concentration is likely to be less than or equal to unmeasured concentrations in the other microenvironments, it represents quasi-baseline conditions (i.e., minimal exposures) when participants were not inside their homes. In Table 6, the RMSE for this model is apportioned into bias and SD using the same approach as for $\hat{P}_{[O]}$ and $\hat{P}_{[I]}$ (Tables 4 and 5).

As found for $\hat{P}_{[O]}$ and $\hat{P}_{[I]}$, the bias (the expected difference between the estimator and P exposure) to noise (SD) ratio for $\hat{P}_{[OI]}$ in Table 6 is relatively low. Nevertheless, it is apparent that the estimated bias of $\hat{P}_{[OI]}$ was similar to that for $\hat{P}_{[I]}$ (Table 5) in the lower and middle tertiles. At the higher tertile, the bias was greater for the time-weighted estimator in every instance except methylene chloride. The SD was generally similar between $\hat{P}_{[I]}$ and the time-weighted model across all three tertiles.

Discussion

Chronic exposure to relatively low levels of airborne VOCs is an inescapable reality for residents of the United States. This class of chemicals is ubiquitous in occupational and nonoccupational settings, including both indoor and outdoor environments. Not only are VOCs released into the air from industrial processes, internal combustion engines, cigarette smoking, and bathing or showering in chlorinated water, they are also common constituents in cleaning and degreasing agents, deordorizers, dry-cleaning processes, paints, pesticides, personal care products, and solvents (*2, 7−15*). Of the 14 VOCs measured in this study, five originate from primarily indoor sources (chloroform, *p*-dichlorobenzene, D-limonene, and α- and β-pinene), while nine are emitted by a combination of indoor and outdoor sources (benzene,

TABLE 3. Comparison of Matched (Indoor Residential, Personal) VOC Concentrations for Individual Participants in the Study

	Battle Creek		East St. Paul		Phillips		all communities	
compound	RMSE[a]	R[b]	RMSE	R	RMSE	R	RMSE	R
benzene	2.5	0.86	1.6	0.89	1.1	0.78	1.7	0.86
	(0.5, 9.7)[c]	(0.12, 1.00)[c]	(0.4, 6.0)	(0.10, 1.00)	(0.6, 4.4)	(−0.98, 1.00)	(0.4, 8.1)	(−0.26, 1.00)
chloroform	0.4	0.89	0.6	0.90	0.5	0.70	0.5	0.88
	(0.2, 1.5)	(0.06, 1.00)	(0.3, 1.7)	(−0.19, 0.99)	(0.3, 2.7)	(−0.32, 1.00)	(0.2, 1.7)	(−0.05, 1.00)
p-dichlorobenzene	0.5	0.16	0.2	0.64	0.5	0.62	0.3	0.57
	(0.1, 9.0)	(−0.42, 0.99)	(0.1, 8.3)	(−0.48, 0.99)	(0.1, 6.8)	(−0.88, 1.00)	(0.0, 9.0)	(−0.54, 1.00)
ethyl benzene	1.4	0.69	0.8	0.85	0.8	0.73	1.0	0.75
	(0.3, 11.0)	(−0.94, 0.99)	(0.2, 3.0)	(−0.26, 1.00)	(0.3, 15.6)	(−0.13, 1.00)	(0.3, 11.1)	(−0.39, 1.00)
D-limonene	4.2	0.96	5.8	0.98	4.7	0.94	4.7	0.96
	(2.1, 18.9)	(0.34, 1.00)	(2.5, 36.3)	(0.26, 1.00)	(1.8, 45.0)	(−0.84, 1.00)	(2.1, 36.4)	(0.11, 1.00)
methylene chloride	1.3	0.95	0.6	0.93	0.8	0.81	0.8	0.90
	(0.3, 26.2)	(−0.37, 1.00)	(0.2, 1.8)	(0.37, 1.00)	(0.2, 5.7)	(−0.09, 1.00)	(0.2, 8.7)	(−0.04, 1.00)
α-pinene	1.3	0.98	0.8	0.92	1.0	0.92	1.0	0.95
	(0.3, 7.2)	(0.34, 1.00)	(0.3, 6.3)	(0.61, 1.00)	(0.2, 14.0)	(−0.51, 1.00)	(0.2, 7.6)	(−0.42, 1.00)
β-pinene	0.9	0.98	1.2	0.96	1.1	0.97	1.0	0.97
	(0.1, 2.8)	(0.00, 1.00)	(0.3, 4.9)	(0.15, 1.00)	(0.4, 2.9)	(0.00, 1.00)	(0.2, 4.1)	(0.00, 1.00)
styrene	0.4	0.65	0.3	0.70	0.4	0.77	0.4	0.71
	(0.1, 1.2)	(−0.19, 1.00)	(0.2, 1.3)	(0.01, 0.99)	(0.2, 1.1)	(0.01, 1.00)	(0.2, 1.2)	(−0.12, 1.00)
tetrachloroethylene	0.8	0.83	0.6	0.90	0.4	0.77	0.7	0.83
	(0.2, 25.1)	(−0.32, 1.00)	(0.1, 6.4)	(−0.19, 1.00)	(0.2, 3.0)	(−0.12, 1.00)	(0.2, 6.5)	(−0.30, 1.00)
toluene	12.5	0.65	7.3	0.86	7.5	0.83	8.3	0.77
	(2.3, 43.4)	(−0.98, 0.98)	(1.8, 18.5)	(0.22, 0.99)	(3.3, 23.8)	(−0.25, 1.00)	(2.7, 26.9)	(−0.67, 1.00)
trichloroethylene	0.2	0.88	0.2	0.88	0.2	0.40	0.2	0.69
	(0.0, 2.5)	(0.23, 1.00)	(0.1, 2.5)	(−0.17, 1.00)	(0.1, 0.5)	(−0.64, 0.99)	(0.1, 1.0)	(−0.26, 1.00)
o-xylene	2.0	0.92	0.9	0.92	0.7	0.82	1.1	0.90
	(0.4, 12.5)	(−0.09, 1.00)	(0.3, 4.0)	(−0.17, 1.00)	(0.4, 16.0)	(−0.24, 1.00)	(0.4, 12.9)	(−0.20, 1.00)
m-/*p*-xylene	5.6	0.90	3.1	0.93	2.2	0.71	3.5	0.86
	(0.9, 40.1)	(−0.16, 1.00)	(0.6, 11.8)	(−0.40, 1.00)	(1.3, 58.3)	(−0.26, 1.00)	(1.0, 40.1)	(−0.30, 1.00)

[a] Median root mean squared error (μg/m^3); *n* for number of research subjects = 25 for Battle Creek, 22 for East St. Paul, and 24 for Phillips. [b] Median correlation coefficient; *n* for number of research subjects varies from 20 to 23 for Battle Creek, *n* = 22 for East St. Paul, and *n* varies from 21 to 22 for Phillips. [c] 10th and 90th percentiles.

ethyl benzene, methylene chloride, styrene, toluene, trichloroethylene, tetrachloroethylene, *o*-xylene, and *m*-/*p*-xylene).

Measuring P exposures is the only way to determine unequivocally the magnitude, duration, and frequency of actual exposures experienced by people as they move through a variety of indoor and outdoor locations during their normal daily activities (*1*, *2*). Consequently, P exposure is the de facto "gold standard" for assessment of individual and population exposures to VOCs. But because it is usually impractical and prohibitively expensive to measure P VOC exposures for everyone (or even a large sample of the population of interest), there is a continuing need to develop and validate practical and cost-effective surrogate estimators that are suitably accurate and precise. In this paper, we have examined the performance of three candidate estimators of P exposure: outdoor community concentration, indoor residential concentration, and a simple time-weighted model.

The evidence indicates that, consistent with previous studies in urban areas (*10*−*15*), P exposures tended to be higher than measured indoor concentrations, which tended to be higher than measured outdoor concentrations. The data for P and I concentrations also show that within-person variability for the 14 VOCs measured in this study typically spanned 1 or more orders of magnitude, while between-person variability usually spanned 2 or more orders of magnitude. These findings suggest that a substantial number of people and a substantial number of P and I measurements for each person may be necessary to adequately characterize VOC exposures for a particular population.

One of the novel aspects of this study was the use of MSE as well as correlation measures to assess the performance of multiple estimators (O, I, simple time-weighted model) for P exposure. To appreciate the value of MSE as a comparison metric at the subject-specific level, it is important to recognize the inherent limitations of *R*, a more traditional means of comparing exposure estimators.

To examine and compare estimators of P exposures, we assumed a set of measured P concentrations from a group of *m* subjects represented their actual exposures to an individual VOC. The vector of these observations is denoted as

$$\mathbf{P} = [p_{11} \cdots p_{1n_1}, p_{21} \cdots p_{2n_2}, \ldots, p_{m1} \cdots p_{mn_m}]$$

where p_{ij} gives the observed P exposure for the *i*th subject on the *j*th occasion. A candidate estimator of $\mathbf{P}$, denoted as $\hat{\mathbf{P}}_*$, is a vector of the same structure as $\mathbf{P}$ but with some function of the data at element $\hat{p}_{*ij}$. Metrics for assessing the ability of $\hat{\mathbf{P}}_*$ to estimate $\mathbf{P}$ traditionally include the sample correlation coefficient, *R* (*28*), which may be estimated for each subject over time or jointly for all subjects, where *R* takes values within the interval $[-1, +1]$.

Although *R* is a common metric for analyzing associations between P exposures and O or I concentrations, it is only a measure of the linear association between $\hat{\mathbf{P}}_*$ and $\mathbf{P}$ (*29*). To the extent that $\hat{\mathbf{P}}_*$ is an unbiased and precise estimator of $\mathbf{P}$, *R* approaches +1. However, *R* also approaches +1 in many other cases. For example, if $\hat{p}_{*ij} = (1/2)p_{ij}$ for all *j*, then $R_i = +1$ despite the fact that $\hat{\mathbf{P}}_*$ underestimates $\mathbf{P}$ by a factor of 2.

Another problem with *R* is its dependence on the distribution of $\mathbf{P}$ values. Despite having the same MSE in estimating $\mathbf{P}$, it can be shown that an estimator $\hat{\mathbf{P}}_*$ will yield potentially very different values of *R*, depending on the distribution of values of $\mathbf{P}$ that are sampled or selected for the study. Thus it is not possible to compare an estimator from one study with one from a different study, unless the sets of $\mathbf{P}$ measurements are the same or at least have similar distributions. Absent these common features, therefore, we cannot answer the question of which estimator is better.

In the calculation of a separate, longitudinal correlation coefficient for each subject, this dependence on the $\mathbf{P}$ distribution adversely affects the usefulness of the resulting

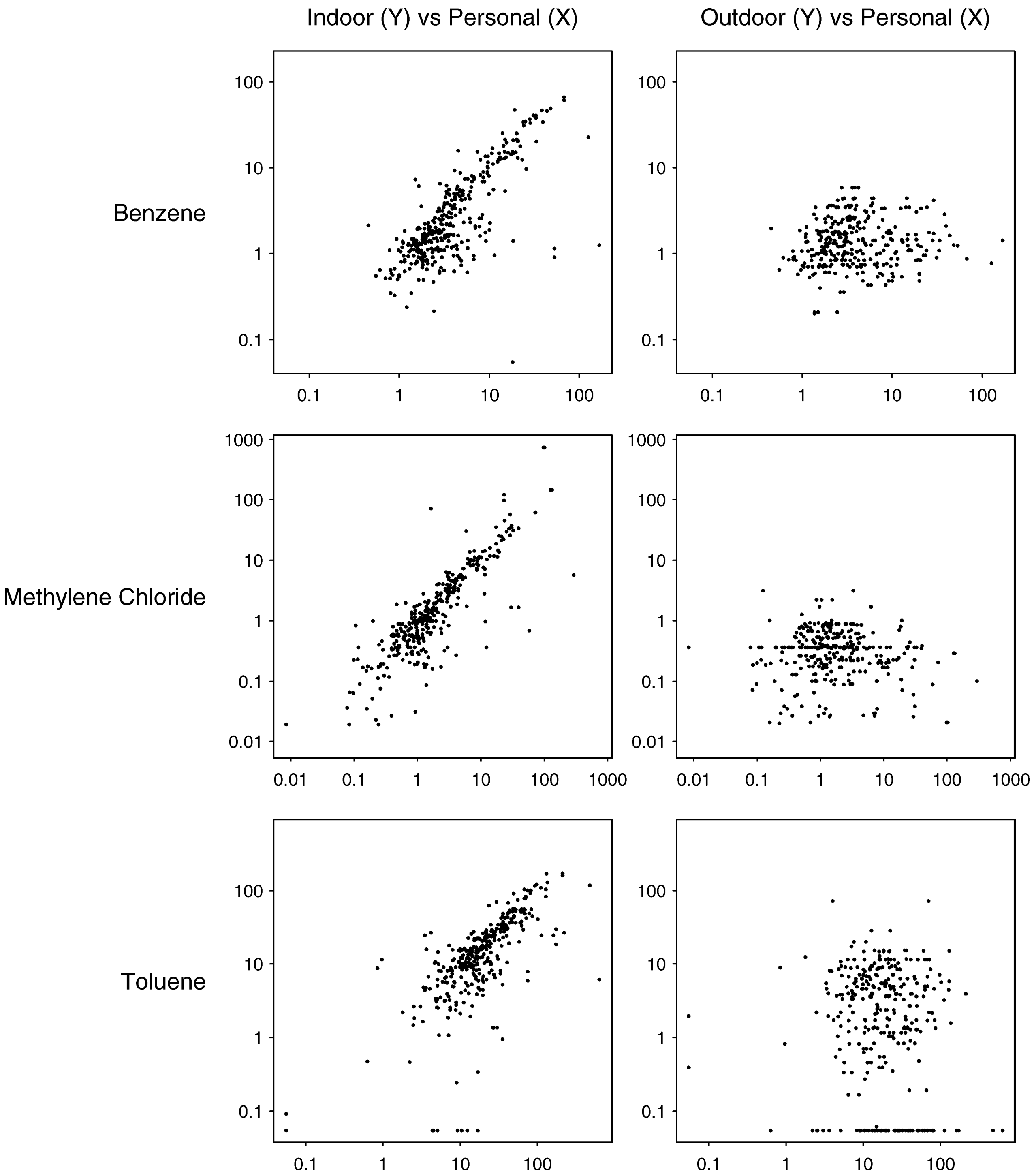

FIGURE 3. Plots of (a) indoor residential concentrations (μg/m^3) and (b) outdoor community concentrations vs personal exposures to benzene, methylene chloride, and toluene for participants in the study. As described in the text, nondetectable measurements (i.e., samples with no analytical response, or those with values $\leq$ 0 after blank subtraction) are represented with a value of half the analytical detection limit.

set of R_i values. The number and distribution of measured personal exposures will inevitably vary across subjects, but these factors should not bear on the assessment of the performance of, say, a monitor located at some central site. While the performance of this central site monitor may in fact be identical for all subjects, their own variation in personal exposure and compliance with the sampling effort can yield large differences in their longitudinal correlations. Finally, the use of longitudinal correlation as a comparison metric also means that subjects with only one measured VOC value cannot contribute an R_i. But in reality there is no reason a single observation should not add to our understanding of the ability of $\hat{\mathbf{P}}_*$ to estimate $\mathbf{P}$.

For these reasons, we also assessed estimators of $\mathbf{P}$ in terms of MSE and its constituents: bias and variance. For the estimator of a specific element p_{ij} of $\mathbf{P}$, the bias of $\hat{p}_{*ij}$ for p_{ij} is the difference between the expected value of $\hat{p}_{*ij}$ and p_{ij}, i.e.:

$$\mathrm{bias}[\hat{p}_{*ij}{:}p_{ij}] = E[\hat{p}_{*ij}] - p_{ij} \qquad (4)$$

where the $E[\ ]$ denotes the expectation operator. The variance

TABLE 4. Using Outdoor Community Concentrations To Predict Measured Personal Exposures: Estimated Bias and Variance (Presented as Standard Deviation in Parentheses) for the Lower, Middle, and Upper Tertiles of the Personal Exposure Distribution[a]

	personal exposure distribution				
chemical	lower tertile	1st tertile cutpoint	middle tertile	2nd tertile cutpoint	upper tertile
benzene	−0.3[b] (0.7)[c]	2.2	−1.5 (1.4)	4.7	−14.4 (21.9)
chloroform	−0.2 (0.2)	0.7	−1.0 (0.3)	1.7	−3.2 (1.9)
p-dichlorobenzene	0.0 (0.1)	0.2	−0.3 (0.2)	0.7	−7.8 (19.2)
ethyl benzene	−0.4 (0.5)	1.6	−1.5 (0.7)	3.5	−12.2 (19.3)
D-limonene	−4.9 (1.6)	7.7	−11.5 (2.7)	16.6	−47.3 (51.1)
methylene chloride	−0.1 (0.5)	1.0	−1.2 (0.6)	2.9	−17.1 (35.7)
α-pinene	−0.9 (0.4)	1.8	−2.6 (0.8)	4.2	−15.8 (20.6)
β-pinene	−0.2 (0.3)	0.8	−1.5 (0.5)	2.7	−10.9 (23.4)
styrene	−0.1 (0.1)	0.5	−0.5 (0.2)	1.0	−2.0 (2.8)
tetrachloroethylene	0.0 (0.3)	0.6	−0.6 (0.4)	1.5	−62.7 (360.4)
toluene	−1.9 (9.9)	12.1	−13.2 (6.4)	25.1	−57.8 (79.8)
trichloroethylene	0.0 (0.1)	0.2	−0.1 (0.2)	0.4	−2.4 (7.5)
o-xylene	−0.4 (0.6)	1.7	−1.6 (0.9)	3.8	−14.5 (20.4)
m-/*p*-xylene	−1.3 (1.7)	5.4	−5.1 (2.8)	12.4	−45.9 (66.2)

[a] All estimates and cutpoints in units of μg/m^3. [b] Bias estimated by the mean difference of predictor and personal exposure. [c] Variance estimated by the variance of the differences of predictor and personal exposure; with square root applied to present in terms of standard deviation (SD).

TABLE 5. Using Indoor Residential Concentrations To Predict Measured Personal Exposures: Estimated Bias and Variance (Presented as Standard Deviation in Parentheses) for the Lower, Middle, and Upper Tertiles of the Personal Exposure Distribution[a]

	personal exposure distribution				
chemical	lower tertile	1st tertile cutpoint	middle tertile	2nd tertile cutpoint	upper tertile
benzene	−0.2[b] (1.0)[c]	2.2	−0.6 (2.1)	4.7	−3.8 (20.8)
chloroform	0.4 (1.8)	0.7	−0.1 (0.6)	1.7	−0.5 (1.7)
p-dichlorobenzene	0.0 (0.2)	0.2	−0.2 (0.2)	0.7	−5.5 (19.4)
ethyl benzene	−0.2 (0.4)	1.6	−0.4 (1.1)	3.5	−4.7 (19.5)
D-limonene	−0.9 (2.0)	7.7	−1.6 (5.8)	16.6	−13.2 (50.1)
methylene chloride	0.0 (0.3)	1.0	1.1 (10.2)	2.9	3.9 (74.2)
α-pinene	0.0 (0.7)	1.8	0.0 (0.9)	4.2	0.8 (10.4)
β-pinene	0.3 (0.8)	0.8	−0.2 (0.9)	2.7	−2.1 (10.2)
styrene	0.1 (0.4)	0.5	−0.1 (0.3)	1.0	−0.8 (3.1)
tetrachloroethylene	0.0 (0.3)	0.6	−0.3 (0.4)	1.5	−55.8 (350.5)
toluene	0.2 (5.2)	12.1	−3.3 (8.2)	25.1	−19.9 (77.1)
trichloroethylene	0.0 (0.1)	0.2	0.1 (0.8)	0.4	−1.7 (7.6)
o-xylene	−0.2 (0.6)	1.7	−0.5 (1.2)	3.8	−5.3 (20.5)
m-/*p*-xylene	−0.6 (1.6)	5.4	−1.7 (3.9)	12.4	−17.0 (66.6)

[a] All estimates and cutpoints in units of μg/m^3. [b] Bias estimated by the mean difference of predictor and personal exposure. [c] Variance estimated by the variance of the differences of predictor and personal exposure; with square root applied to present in terms of standard deviation (SD).

TABLE 6. Using a Simple Time-Weighted Model To Predict Measured Personal Exposures: Estimated Bias and Variance (Presented as Standard Deviation in Parentheses) for the Lower, Middle, and Upper Tertiles of the Personal Exposure Distribution[a]

	personal exposure distribution				
chemical	lower tertile	1st tertile cutpoint	middle tertile	2nd tertile cutpoint	upper tertile
benzene	−0.2[b] (0.8)[c]	2.2	−0.8 (1.4)	4.7	−7.5 (21.0)
chloroform	0.2 (1.1)	0.7	−0.4 (0.4)	1.7	−1.2 (1.5)
p-dichlorobenzene	0.0 (0.1)	0.2	−0.2 (0.2)	0.7	−6.6 (19.4)
ethyl benzene	−0.3 (0.4)	1.6	−0.7 (0.8)	3.5	−6.9 (19.4)
D-limonene	−2.1 (1.8)	7.7	−4.4 (4.6)	16.6	−20.8 (48.6)
methylene chloride	0.0 (0.3)	1.0	0.5 (7.9)	2.9	−3.3 (48.2)
α-pinene	−0.3 (0.5)	1.8	−0.7 (0.7)	4.2	−4.8 (9.4)
β-pinene	0.1 (0.6)	0.8	−0.6 (0.7)	2.7	−5.6 (12.0)
styrene	0.0 (0.3)	0.5	−0.2 (0.2)	1.0	−1.2 (2.8)
tetrachloroethylene	0.0 (0.2)	0.6	−0.4 (0.3)	1.5	−60.9 (363.5)
toluene	0.0 (5.7)	12.1	−6.2 (5.9)	25.1	−30.6 (78.6)
trichloroethylene	0.0 (0.1)	0.2	0.0 (0.6)	0.4	−2.0 (7.7)
o-xylene	−0.3 (0.5)	1.7	−0.8 (0.9)	3.8	−8.1 (20.2)
m-/*p*-xylene	−0.8 (1.6)	5.4	−2.7 (2.7)	12.4	−26.0 (66.0)

[a] All estimates and cutpoints in units of μg/m^3. [b] Bias estimated by the mean difference of predictor and personal exposure. [c] Variance estimated by the variance of the differences of predictor and personal exposure; with square root applied to present in terms of standard deviation (SD).

of $\hat{p}_{*ij}$ does not depend functionally on p_{ij} and may be expressed as

$$\mathrm{var}[\hat{p}_{*ij}] = E[(\hat{p}_{*ij} - E[\hat{p}_{*ij}])^2] \tag{5}$$

The MSE is yet another linear operator comprising these constituents as

$$\mathrm{MSE}[\hat{p}_{*ij}{:}p_{ij}] = (\mathrm{bias}[\hat{p}_{*ij}{:}p_{ij}])^2 + \mathrm{var}[\hat{p}_{*ij}] \tag{6}$$

The bias and variance describe different characteristics of the estimator $\hat{p}_{*ij}$. Bias describes the extent to which $\hat{p}_{*ij}$ under- or overestimates p_{ij}. Variance conveys the precision of $\hat{p}_{*ij}$; the precision of a statistic is sometimes defined specifically as the inverse of its variance.

Based on MSE as well as *R* (Tables 2 and 3), I concentrations were a better estimator of P exposure than O concentrations for all 14 VOCs, although both consistently underestimated P exposure. There are several reasons for this. First, personal exposures tended to be higher than matched indoor residential concentrations, which tended to be higher than matched outdoor community concentrations. For example, median and 90th percentile values for benzene were 3.2 and 18.3 μg/m^3 in personal air, 1.9 and 15.3 μg/m^3 in indoor air, and 1.3 and 3.3 μg/m^3 in outdoor air (*13*). Second, most participants typically spent the majority of their time indoors at home (and relatively little outside). Results from the participants' 2-day time−activity logs show that, on average, participants spent 34 h (70.9%) indoors at home. The rest of the time was spent indoors at work or school (6 h or 12.6%), indoors in other locations (2.6 h or 5.5%), outside at home (1.7 h or 3.5%), outside at work or school (0.3 h or 0.6%), outside at other locations (1.1 h or 2.4%), and in transit (2.2 h or 4.5%). In addition, participants were in close proximity to a smoker for an average of only 0.5 h (0.9%) over a typical 2-day monitoring period. Third, the measured indoor concentrations may be an underestimate of what people were actually exposed to during their time inside at home. The monitors collected a 2-day integrated sample, but concentrations may have been highest when people were cooking and carrying on other routine activities. And fourth, it is possible that concentrations in other microenvironments through which participants moved during the 2-day monitoring period were relatively high as compared to measured I and O concentrations. Thus, although participants spent a relatively small proportion of their time indoors at work/school, indoors in other locations, outside at work/school, outside at other locations, and in transit, concentrations in these microenvironments appear to make a significant contribution to measured P exposure.

The bias and variance of all three estimators (indoor, outdoor, and time-weighted model) tended to increase in the upper third of the P exposure distribution. This means that common exposure estimators, such as measured indoor and outdoor concentrations and time-weighted models, tend to be less accurate and precise just where we need them most—for estimating exposures at the upper end of the exposure distribution. Future research should investigate whether these same patterns and relationships hold for (a) communities with higher outdoor levels of VOCs, (b) a more diverse sample of adults (race/ethnicity, socioeconomic status, occupation), and (c) vulnerable segments of the population (pregnant women and their fetuses, children, the elderly, the infirm).

Acknowledgments

This research was funded by a STAR (Science to Achieve Results) Grant (R825241) from the U.S. Environmental Protection Agency, National Center for Environmental Research. We also benefited from a grant from the Academic Health Center at the University of Minnesota. We thank the individuals who participated in the study and acknowledge the contributions of the field team. We also thank the 3M Corporation for donating some of the organic vapor monitors used in this study. The help and support provided by the Minnesota Pollution Control Agency was essential to the success of this project. K.S. was a member of the Division of Environmental and Occupational Health at the University of Minnesota School of Public Health when this study was conducted.

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Received for review August 25, 2003. Revised manuscript received February 10, 2004. Accepted February 12, 2004.

ES030607Q