

*This document contains the comments the MPCA received during the Dual Notice of Intent to Adopt Rules public comment period November 25, 2024, through January 15, 2025, for the planned amendments to rules governing Air Quality (Air Toxics Emissions Reporting Rule), Revisor ID # R-4599.*

# 39354 Minnesota Pollution Control Agency Dual Notice of Intent to Adopt Rules

Closed Jan 15, 2025 · Discussion · 4 Participants · 1 Topics · 7 Answers · 0 Replies · 0 Votes

4

PARTICIPANTS

1

TOPICS

7

ANSWERS

0

REPLIES

0

VOTES

## SUMMARY OF TOPICS

### SUBMIT A COMMENT

 7 Answers · 0 Replies

Important: All comments will be made available to the public. Please only submit information that you wish to make available publicly. The Office of Administrative Hearings does not edit or delete submissions that include personal information. We reserve the right to remove any comments we deem offensive, intimidating, belligerent, harassing, or bullying, or that contain any other inappropriate or aggressive behavior without prior notification.

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**Andrew Morley** · Citizen · (Postal Code: unknown) · Jan 15, 2025 10:09 am

 0 Votes

Please see the attached letter from the Minnesota Chamber of Commerce.

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**Andrew Morley** · Citizen · (Postal Code: unknown) · Jan 15, 2025 10:23 am

 0 Votes

Please find the attached petition to hold a public hearing.

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**Shalini Gupta** · Citizen · (Postal Code: unknown) · Jan 15, 2025 11:19 am

 0 Votes

Please see attached comment to require reporting of sulfuryl fluoride as an air toxic.

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**Andrew Morley** · Citizen · (Postal Code: unknown) · Jan 15, 2025 1:58 pm

 0 Votes

Please find the updated petition to hold a public hearing.

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**Andrew Morley** · Citizen · (Postal Code: unknown) · Jan 15, 2025 2:15 pm

 0 Votes

## 39354 Minnesota Pollution Control Agency Dual Notice of Intent to Adopt Rules

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Please find an addendum to the Chamber's initial comments, originally posted at 10:23 AM CT.

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**Jill Van Noord** · Citizen · (Postal Code: unknown) · Jan 15, 2025 3:13 pm

 0 Votes

Please see the attached comments from Northern States Power Company - Minnesota

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**Brendan Mascarenhas** · Citizen · (Postal Code: unknown) · Jan 15, 2025 4:29 pm

 0 Votes

Please see the attached comments from the American Chemistry Council.



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).<sup>1</sup> 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."<sup>2</sup>

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.<sup>3</sup> 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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<sup>1</sup> 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.

<sup>2</sup> 88 Fed. Reg. 47029 (July 21, 2023).

<sup>3</sup> *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.<sup>4</sup> 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  
Director, Environmental Policy  
Minnesota Chamber of Commerce  
[amorley@mnchamber.com](mailto:amorley@mnchamber.com)  
763-221-7523

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<sup>4</sup> *Environmental Committee of the Florida Electric Power Coordinating Group, Inc. v. Environmental Protection Agency*, 94 F. 4<sup>th</sup> 77 (D.C. Cir. 2024).



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



August 6, 2020

Dear Ms. Maggie Wenger:

On July 16<sup>th</sup>, 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

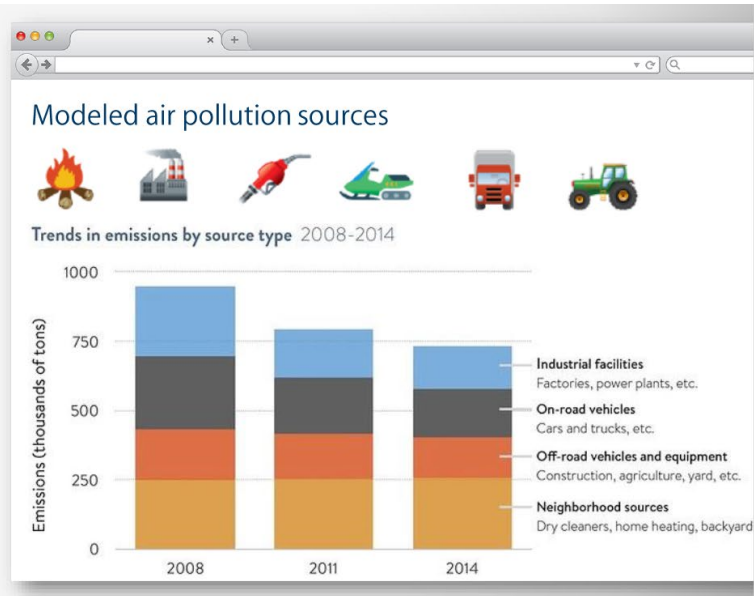
Criteria pollutants every year

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,

A handwritten signature in dark ink, appearing to read 'Tony Kwilas', is written over a faint, light-colored background.

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



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

KEN SEXTON,\*<sup>†</sup> JOHN L. ADGATE,<sup>†</sup>  
GURUMURTHY RAMACHANDRAN,<sup>†</sup>  
GREGORY C. PRATT,<sup>‡</sup>  
STEVEN J. MONGIN,<sup>†</sup>  
THOMAS H. STOCK,<sup>§</sup> AND  
MARIA T. MORANDIS<sup>§</sup>

*Division of Environmental and Occupational Health,  
School of Public Health, University of Minnesota,  
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University of Texas, Houston, Texas 77030*

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

## Introduction

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

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

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

## Study Design

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

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

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

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

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

<sup>a</sup> Without duplicates.

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

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

## Methods

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

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

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

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

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

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

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

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

## Results

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

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

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

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

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

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

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

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

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

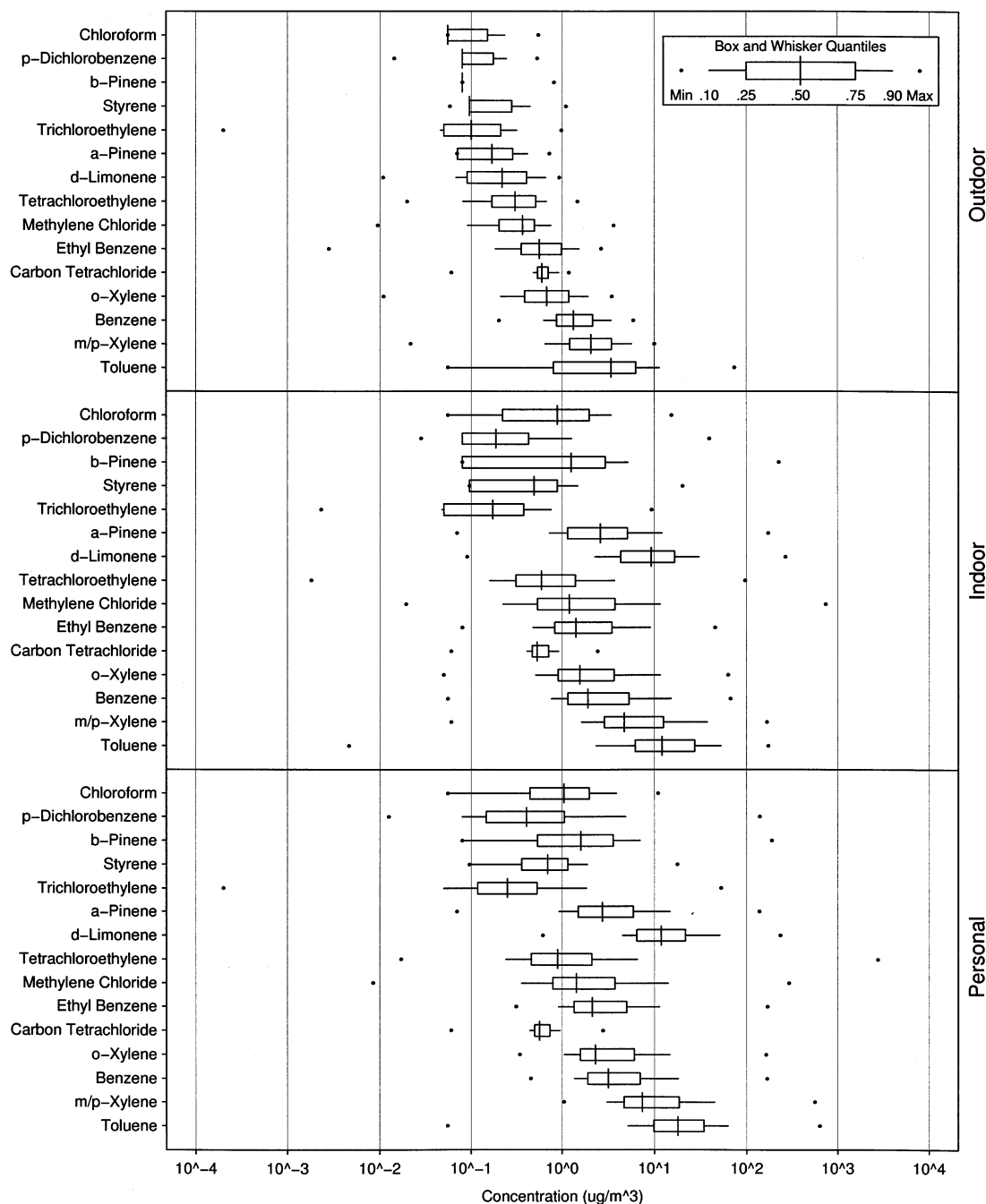


FIGURE 1. Distributions of all valid, matched VOC concentrations for outdoor, indoor, and personal samples

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

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

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

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

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

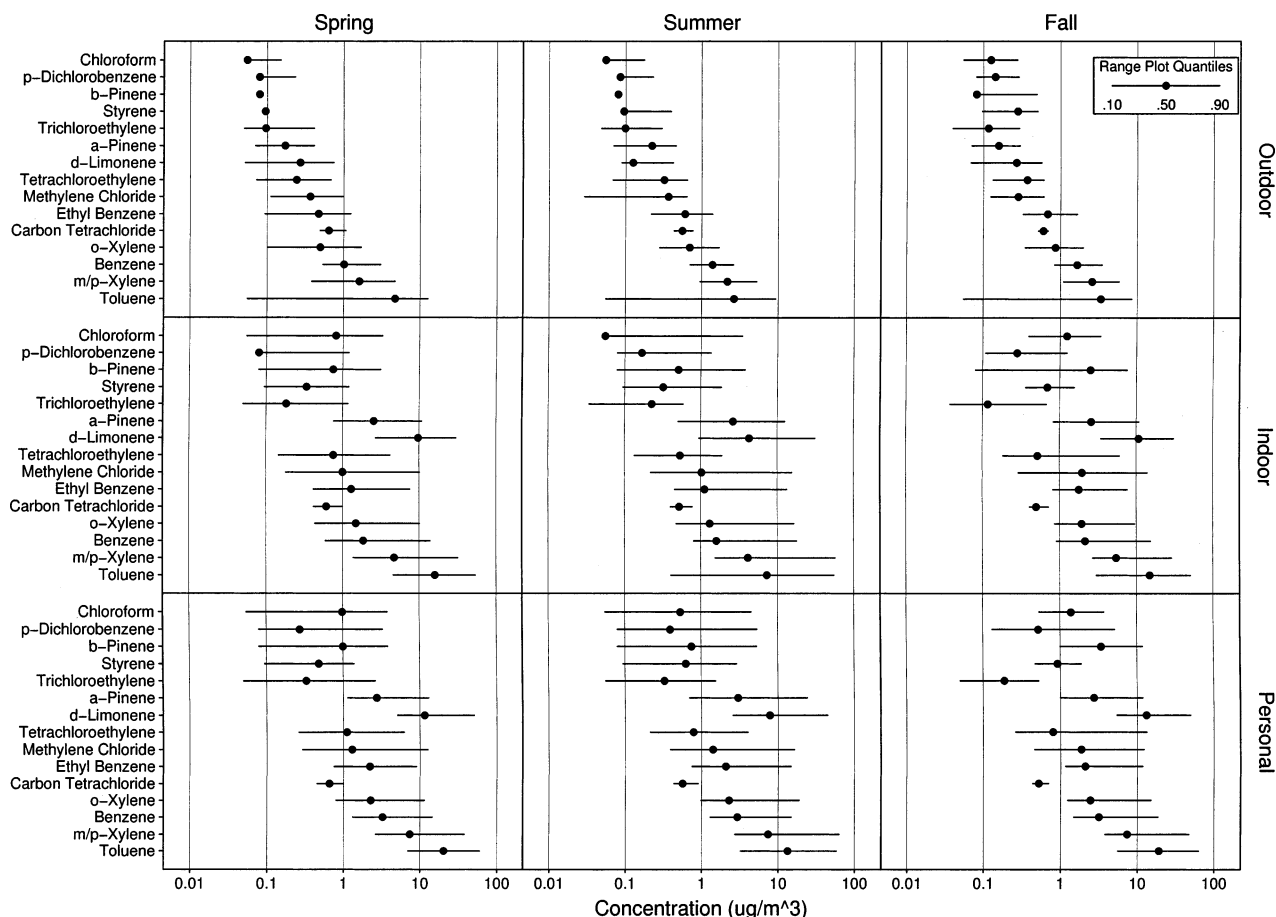


FIGURE 2. Distributions of all valid, matched VOC concentrations by monitor location and season

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

## Discussion

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

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

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

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

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



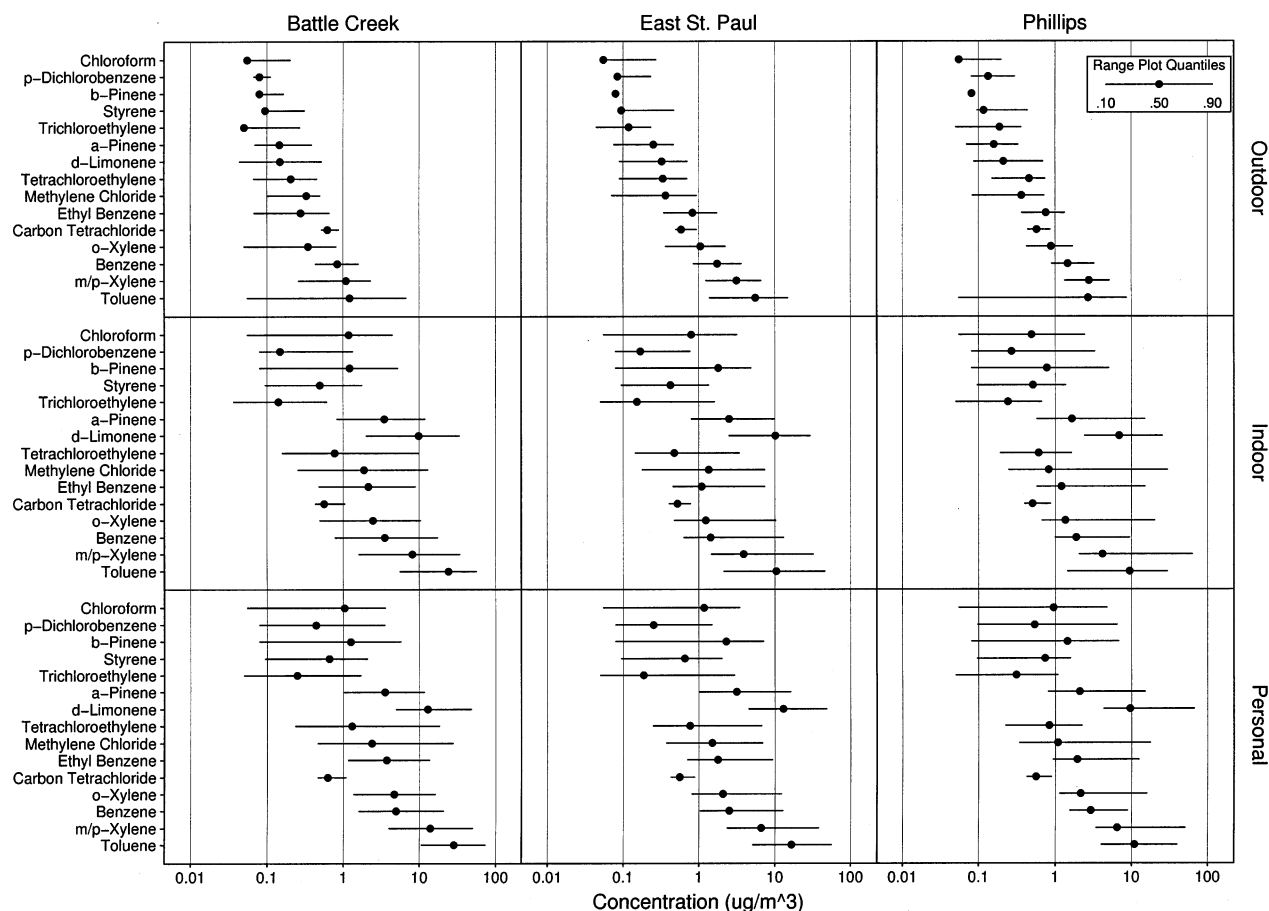


FIGURE 3. Distributions of all valid, matched VOC concentrations by monitor location and community

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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## Literature Cited

- (1) Kelly, T. J.; Mukund, R.; Spicer, C. W.; et al. *Environ. Sci. Technol.* **1994**, *28*, 378A–387A.
- (2) LaGrone, F. S. *Environ. Sci. Technol.* **1991**, *25*, 366–368.
- (3) Morello-Frosch, R. A.; Woodruff, T. J.; Axelrad, D. A.; et al. *Risk Anal.* **2000**, *20*, 273–291.
- (4) Woodruff, T. J.; Axelrad, D. A.; Caldwell, J.; et al. *Environ. Health Perspect.* **1998**, *106*, 245–251.
- (5) U. S. Environmental Protection Agency, Integrated Risk Information System (IRIS), [www.epa.gov/iris/](http://www.epa.gov/iris/).
- (6) Spengler, J. D.; Sexton, K. *Science* **1983**, *221*, 9–17.
- (7) Samet, J. M.; Spengler, J. D. Eds. *Indoor Air Pollution: A Health Perspective*; The Johns Hopkins University Press: Baltimore, MD, 1991.
- (8) Wallace, L. A. *Annu. Rev. Energy Environ.* **2001**, *26*, 269–301.
- (9) Wallace, L. A.; Pellizzari, E. D.; Hartwell, T.; et al. *Atmos. Environ.* **1985**, *19*, 1651–1661.
- (10) Wallace, L. A.; Pellizzari, E. D.; Hartwell, T.; et al. *Atmos. Environ.* **1988**, *22*, 2141–2143.
- (11) Wallace, L. A.; Nelson, W. C.; Ziegenfuss, R.; et al. *J. Expo. Anal. Environ. Epidemiol.* **1991**, *12*, 37–72.
- (12) Adgate, J. L.; Ramachandran, G.; Pratt, G. C.; Waller, L. A.; Sexton, K. *Atmos. Environ.* **2002**, *36*, 3255–3265.
- (13) Adgate, J. L.; Ramachandran, G.; Pratt, G. C.; Waller, L. A.; Sexton, K. *Atmos. Environ.* **2003**, *37*, 993–1002.
- (14) Ramachandran, G.; Adgate, J. L.; Hill, N.; et al. *Air Waste Manage. Assoc.* **2000**, *50*, 1157–1166.
- (15) Ramachandran, G.; Adgate, J. L.; Pratt, G. C.; et al. *Aerosol Sci. Technol.* **2003**, *37*, 37, 33–45.
- (16) Pratt, G. C.; McCourtney, M.; Wu, C. Y.; et al. *Proceedings of a Specialty Conference co-sponsored by the Air and Waste Management Association and U. S. Environmental Protection Agency*, Cary, NC, 1998; Vol II, pp 64–72.
- (17) Chung, C.; Morandi, M. T.; Stock, T. H.; Afshar, M. *Environ. Sci. Technol.* **1999**, *33*, 3661–3665.
- (18) Chung, C.; Morandi, M. T.; Stock, T. H.; Afshar, M. *Environ. Sci. Technol.* **1999**, *33*, 3666–3671.
- (19) SAS Institute, Inc. SAS OnlineDoc, Version 8; SAS Institut: Cary, NC, 1999.
- (20) MathSoft, Inc. 2000, S-PLUS 6.0 Guide to Statistics, Volume 1; Data Analysis Division, MathSoft: Seattle, WA.
- (21) Laird, N. M.; Ware, J. H. *Biometrics* **1982**, *38*, 963–974.
- (22) Lindstrom, M. J.; Bates, D. M. *J. Am. Stat. Assoc.* **1988**, *83*, 1014–1022.
- (23) California Environmental Protection Agency, Office of Environmental Health Hazard Assessment, Sacramento, CA; [www.oehha.org/air.html](http://www.oehha.org/air.html).
- (24) Minnesota Pollution Control Agency, Health Risk Values, Minnesota Rules, sections 4717.8000 to 4717.8600; St. Paul, MN; [www.revisor.leg.state.mn.us/arule/4717](http://www.revisor.leg.state.mn.us/arule/4717).
- (25) National Research Council. *Human Exposure Assessment for Airborne Pollutants*; National Academy Press: Washington, DC, 1991.
- (26) Sexton, K.; Callahan, M. A.; Bryan, E. F. *Environ. Health Perspect.* **1995**, *103* (Supplement 3), 13–29.

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# 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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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  $\leq 0$  after blank subtraction) were assigned a value of one-half the analytical detection limit (ADL).

Three estimators of personal exposure are evaluated:

$$\hat{P}_{[O]ij} = O_{ij} \quad (1)$$

$$\hat{P}_{[I]ij} = I_{ij} \quad (2)$$

$$\hat{P}_{[O+I]ij} = O_{ij}t_{[O]ij} + I_{ij}t_{[I]ij} \quad (3)$$

where  $O_{ij}$  and  $I_{ij}$  denote the observed concentration for the  $i$ th subject on the  $j$ th 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  $\hat{P}_{[O]ij}$ ,  $\hat{P}_{[I]ij}$ , and  $\hat{P}_{[O+I]ij}$  represent  $\hat{P}_{[O]ij}$ ,  $\hat{P}_{[I]ij}$ , and  $\hat{P}_{[O+I]ij}$  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  $\hat{P}_{[O]ij}$  and  $\hat{P}_{[I]ij}$ , 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 ( $Q_{25} = 3$  and  $Q_{75} = 6$ ). 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,  $\beta$ -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 ( $\geq 1$  for RMSE,  $\geq 2$  for  $R$ ). RMSE is a measure of the magnitude and variation of the difference ( $\mu\text{g}/\text{m}^3$ ) 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  $\mu\text{g}/\text{m}^3$  for 9 VOCs, between 2.5 and 4.8  $\mu\text{g}/\text{m}^3$  for 3 VOCs ( $\alpha$ -pinene,  $\beta$ -pinene, and  $m$ -/ $p$ -xylene), 13.4  $\mu\text{g}/\text{m}^3$  for D-limonene, and 16.3  $\mu\text{g}/\text{m}^3$  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  $\mu\text{g}/\text{m}^3$ ) and toluene (from 16.3 to 8.3  $\mu\text{g}/\text{m}^3$ ). Generally,  $\hat{P}_{[I]}$  also

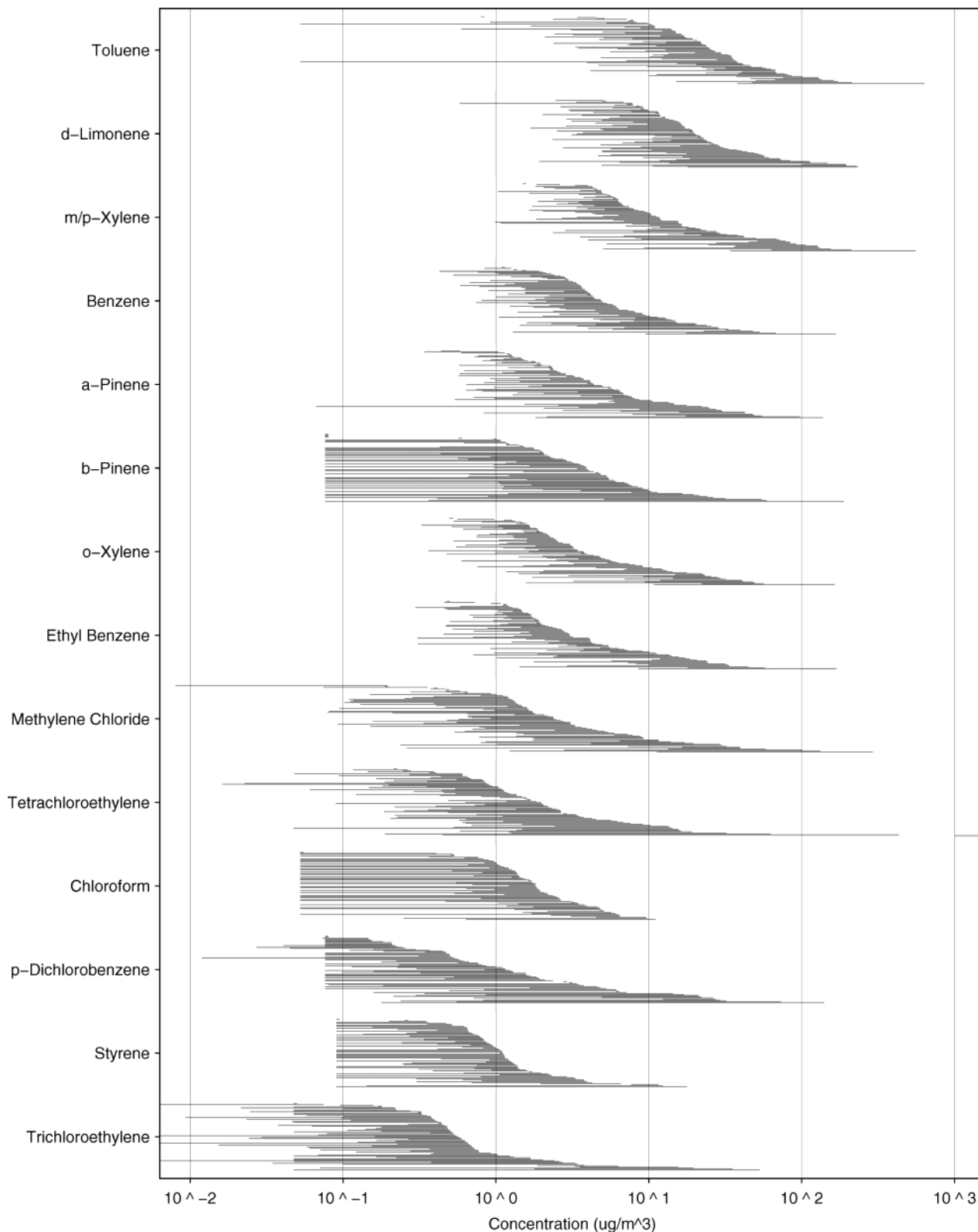


FIGURE 1. Range plot of measured personal VOC exposures for each study participant.

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,  $\alpha$ -pinene,

$\beta$ -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-

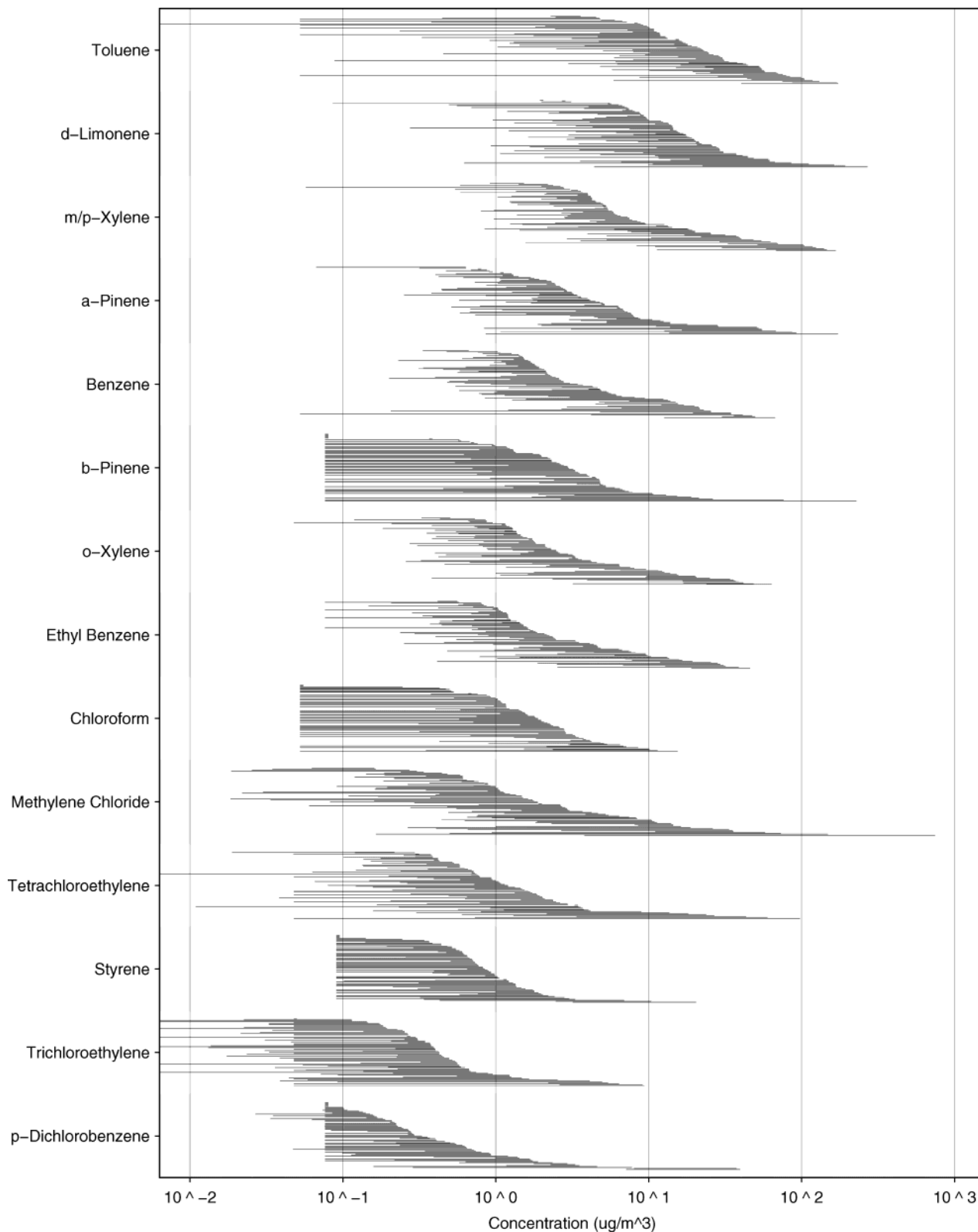


FIGURE 2. Range plot of measured indoor residential VOC concentrations for each study participant.

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

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

<sup>a</sup> Median root mean squared error ( $\mu\text{g}/\text{m}^3$ ); *n* for number of research subjects = 25 for Battle Creek, 22 for East St. Paul, and 24 for Phillips.

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

<sup>a</sup> Median root mean squared error ( $\mu\text{g}/\text{m}^3$ );  $n$  for number of research subjects = 25 for Battle Creek, 22 for East St. Paul, and 24 for Phillips.

<sup>b</sup> 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. <sup>c</sup> 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

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

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

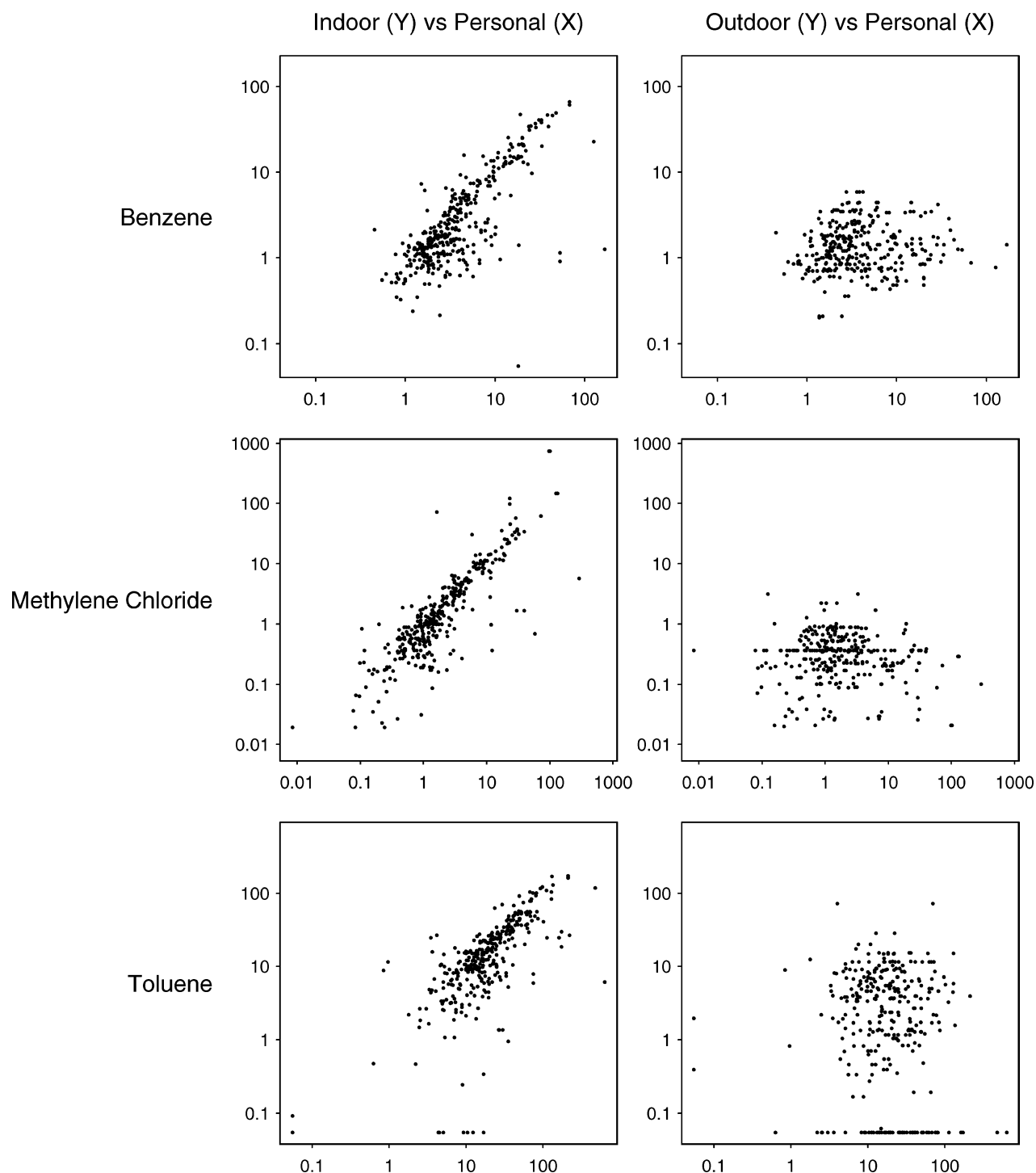


FIGURE 3. Plots of (a) indoor residential concentrations ( $\mu\text{g}/\text{m}^3$ ) and (b) outdoor community concentrations vs personal exposures to benzene, methylene chloride, and toluene for participants in the study. As described in the text, nondetectable measurements (i.e., samples with no analytical 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  $\hat{\mathbf{P}}_{\bullet}$  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.:

$$\text{bias}[\hat{p}_{ij}; p_{ij}] = E[\hat{p}_{ij}] - p_{ij} \quad (4)$$

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<sup>a</sup>**

chemical	personal exposure distribution				
	lower tertile	1st tertile cutpoint	middle tertile	2nd tertile cutpoint	upper tertile
benzene	-0.3 <sup>b</sup> (0.7) <sup>c</sup>	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)
<i>p</i> -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)
<i>l</i> -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)
$\alpha$ -pinene	-0.9 (0.4)	1.8	-2.6 (0.8)	4.2	-15.8 (20.6)
$\beta$ -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)
<i>o</i> -xylene	-0.4 (0.6)	1.7	-1.6 (0.9)	3.8	-14.5 (20.4)
<i>m/p</i> -xylene	-1.3 (1.7)	5.4	-5.1 (2.8)	12.4	-45.9 (66.2)

<sup>a</sup> All estimates and cutpoints in units of  $\mu\text{g}/\text{m}^3$ . <sup>b</sup> Bias estimated by the mean difference of predictor and personal exposure. <sup>c</sup> 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<sup>a</sup>**

chemical	personal exposure distribution				
	lower tertile	1st tertile cutpoint	middle tertile	2nd tertile cutpoint	upper tertile
benzene	-0.2 <sup>b</sup> (1.0) <sup>c</sup>	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)
<i>p</i> -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)
<i>l</i> -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)
$\alpha$ -pinene	0.0 (0.7)	1.8	0.0 (0.9)	4.2	0.8 (10.4)
$\beta$ -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)
<i>o</i> -xylene	-0.2 (0.6)	1.7	-0.5 (1.2)	3.8	-5.3 (20.5)
<i>m/p</i> -xylene	-0.6 (1.6)	5.4	-1.7 (3.9)	12.4	-17.0 (66.6)

<sup>a</sup> All estimates and cutpoints in units of  $\mu\text{g}/\text{m}^3$ . <sup>b</sup> Bias estimated by the mean difference of predictor and personal exposure. <sup>c</sup> 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<sup>a</sup>**

chemical	personal exposure distribution				
	lower tertile	1 <sup>st</sup> tertile cutpoint	middle tertile	2 <sup>nd</sup> tertile cutpoint	upper tertile
benzene	-0.2 <sup>b</sup> (0.8) <sup>c</sup>	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)
<i>p</i> -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)
<i>l</i> -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)
$\alpha$ -pinene	-0.3 (0.5)	1.8	-0.7 (0.7)	4.2	-4.8 (9.4)
$\beta$ -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)
<i>o</i> -xylene	-0.3 (0.5)	1.7	-0.8 (0.9)	3.8	-8.1 (20.2)
<i>m/p</i> -xylene	-0.8 (1.6)	5.4	-2.7 (2.7)	12.4	-26.0 (66.0)

<sup>a</sup> All estimates and cutpoints in units of  $\mu\text{g}/\text{m}^3$ . <sup>b</sup> Bias estimated by the mean difference of predictor and personal exposure. <sup>c</sup> 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

$$\text{var}[\hat{p}_{ij}] = E[(\hat{p}_{ij} - E[\hat{p}_{ij}])^2] \quad (5)$$

The MSE is yet another linear operator comprising these constituents as

$$\text{MSE}[\hat{p}_{ij}; p_{ij}] = (\text{bias}[\hat{p}_{ij}; p_{ij}])^2 + \text{var}[\hat{p}_{ij}] \quad (6)$$

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  $\mu\text{g}/\text{m}^3$  in personal air, 1.9 and 15.3  $\mu\text{g}/\text{m}^3$  in indoor air, and 1.3 and 3.3  $\mu\text{g}/\text{m}^3$  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).

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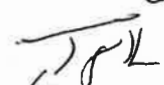
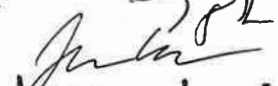
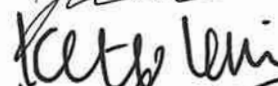



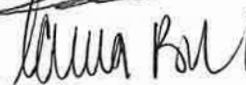
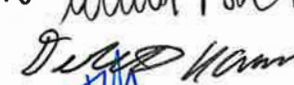










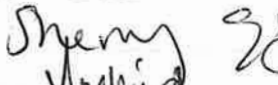
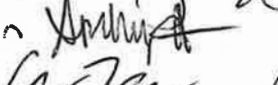




## Literature Cited

- (1) Sexton, K.; Ryan, P. B. Assessment of Human Exposure to Air Pollutants: Methods, Measurements, and Models. In *Air Pollution, the Automobile, and Public Health*; Watson, A. Y., Bates, R. R., Kennedy, D., Eds.; National Academy Press: Washington, DC, 1988.
- (2) National Research Council. *Human Exposure Assessment for Airborne Pollutants: Advance and Opportunities*; National Academy Press: Washington, DC, 1991.
- (3) Kelly, T. J.; Mukund, R.; Spicer, C. W.; et al. *Environ. Sci. Technol.* **1994**, *28*, 378A–387A.
- (4) LaGrone, F. S. *Environ. Sci. Technol.* **1991**, *25*, 366–368.
- (5) Morello-Frosch, R. A.; Woodruff, T. J.; Axelrad, D. A.; et al. *Risk Anal.* **2000**, *20*, 273–291.
- (6) Woodruff, T. J.; Axelrad, D. A.; Caldwell, J.; et al. *Environ. Health Perspect.* **1998**, *106*, 245–251.
- (7) Spengler, J. D.; Sexton, K. *Science* **1983**, *221*, 9–17.
- (8) Samet, J. M.; Spengler, J. D., Eds. *Indoor Air Pollution: A Health Perspective*; Johns Hopkins University Press: Baltimore, MD, 1991.
- (9) Wallace, L. A. *Annu. Rev. Energy Environ.* **2001**, *26*, 269–301.
- (10) Wallace, L. A.; Pellizzari, E. D.; Hartwell, T.; et al. *Atmos. Environ.* **1985**, *19*, 1651–1661.
- (11) Wallace, L. A.; Pellizzari, E. D.; Hartwell, T.; et al. *Atmos. Environ.* **1988**, *22*, 2141–2143.
- (12) Wallace, L. A.; Nelson, W. C.; Ziegenfuss, R.; et al. *J. Exposure Anal. Environ. Epidemiol.* **1991**, *12*, 37–72.
- (13) Sexton, K.; Adgate, J. L.; Ramachandran, G.; Pratt, G. C.; Mongin, S. J.; Stock, T. H.; Morandi, M. T. *Environ. Sci. Technol.* **2004**, *38*, 423–430.
- (14) Adgate, J. L.; Eberly, L. E.; Stroebel, C.; Pellizzari, E. D.; Sexton, K. *J. Exposure Anal. Environ. Epidemiol.* (in press).
- (15) Kim, Y. M.; Harrad, S.; Harrison, R. M. *Environ. Sci. Technol.* **2002**, *36*, 5405–5410.
- (16) Adgate, J. L.; Ramachandran, G.; Pratt, G. C.; Waller, L. A.; Sexton, K. *Atmos. Environ.* **2002**, *36*, 3255–3265.
- (17) Adgate, J. L.; Ramachandran, G.; Pratt, G. C.; Waller, L. A.; Sexton, K. *Atmos. Environ.* **2003**, *37* (7), 993–1002.
- (18) Ramachandran, G.; Adgate, J. L.; Hill, N.; et al. *Air Waste Manage. Assoc.* **2000**, *50*, 1157–1166.
- (19) Ramachandran, G.; Adgate, J. L.; Pratt, G. C.; et al. *Aerosol Sci. Technol.* **2003**, *37*, 33–45.
- (20) Pratt, G. C.; McCourtney, M.; Wu, C. Y.; et al. *Proceedings of a Specialty Conference*, co-sponsored by the Air and Waste Management Association and U.S. Environmental Protection Agency, Cary, NC, 1998; Vol. II, pp 64–72.
- (21) Pratt, G. C.; Wu, C. Y.; Bock, D.; Adgate, J. L.; Ramachandran, G.; Stock, T. H.; Morandi, M. T.; Sexton, K. *Environ. Sci. Technol.* (submitted for publication).
- (22) Chung, C.; Morandi, M. T.; Stock, T. H.; Afshar, M. *Environ. Sci. Technol.* **1999**, *33*, 3661–3665.
- (23) Chung, C.; Morandi, M. T.; Stock, T. H.; Afshar, M. *Environ. Sci. Technol.* **1999**, *33*, 3666–3671.
- (24) SAS Institute, Inc. *SAS OnlineDoc*, Version 8; SAS Institute: Cary, NC, 1999.
- (25) MathSoft, Inc. *S-PLUS 6.0 Guide to Statistics*, Vol. 1; Data Analysis Division, MathSoft: Seattle, WA, 2000.
- (26) Laird, N. M.; Ware, J. H. *Biometrics* **1982**, *38*, 963–974.
- (27) Lindstrom, M. J.; Bates, D. M. *J. Am. Stat. Assoc.* **1988**, *83*, 1014–1022.
- (28) Janssen, N. A.; Hoek, G.; Harssema, H.; Brunekreef, B. *Occup. Environ. Med.* **1997**, *54* (12), 888–894.
- (29) Draper, N. R.; Smith, H. *Applied Regression Analysis*, 2nd ed.; John Wiley Press: New York, 1981.

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## REQUEST PUBLIC HEARING FOR REVISOR'S ID R-4599, OAH DOCKET NUMBER 71-9003-39354

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21	Solveig Erickson		4135 Quail Ave. N Robbinsdale MN 55422
22	Clarissa Tracy		2565 Franklin Ave St. Paul MN 55114
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24	Vicki Shte		10825 STINSON AVE. Chisago, MN 55013
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January 15<sup>th</sup>, 2025

To: Minnesota Pollution Control Agency  
From: Shalini Gupta, Environmental Justice Consultant  
Re: Require Reporting of Sulfuryl Fluoride as an Air Toxic

---

Dear MPCA:

The MPCA should require reporting of sulfuryl fluoride as an air toxic. It can be emitted from permitted sources and it is toxic.

Sulfural fluoride is not a hazardous air pollutant under the Clean Air Act and is not a VOC. Therefore, sulfuryl fluoride emissions have not previously been reported to the MPCA.

However, it is toxic, can be used as a replacement for other fumigants that are listed as HAPs under the CAA, and may be emitted at sources that are regulated, or could reasonably be regulated, by MPCA.

The State of New Jersey determined that sulfuryl fluoride is emitted at sources that should be regulated under their air permitting program. The state of New Jersey has developed two general permits to regulate fumigants, including sulfuryl fluoride. New Jersey cites the CALEPA's review process toxicity values as their part of their reasoning for adding sulfuryl fluoride to the pollutants regulated at the state level.

New Jersey general permits:

Indoors Fumigation Operations of Cocoa Bean Products

<https://dep.nj.gov/wp-content/uploads/boss/general-permits/gp-021a.pdf>

Outdoor Fumigation Operation of Containerized Commodities

<https://dep.nj.gov/wp-content/uploads/boss/proposed-gp-021b-03-05-24.pdf>

NJ FAQ on Air Toxics Rule Implementation:

<https://dep.nj.gov/wp-content/uploads/boss/permitting-guidance/fumigation-faq-2-1-2023-update.pdf>

NJ Fact Sheet:

Revision to NJDEP Division of Air Quality Risk Screening Worksheet for Carcinogenic Effects and Noncarcinogenic Long-Term and Short-Term Effects (Worksheet) as Listed in Technical Manual 1003 "Guidance on Preparing a Risk Assessment for Air Contaminant Emissions"

[https://www.nj.gov/dep/aqpp/archived/RSWorksheet/Risk%20Screening%20Worksheet%20Fact%20Sheet\\_June%202022.pdf](https://www.nj.gov/dep/aqpp/archived/RSWorksheet/Risk%20Screening%20Worksheet%20Fact%20Sheet_June%202022.pdf)

This fact sheet states the following.

**Sulfuryl fluoride (SF) will be added to the Risk Screening Worksheet with the following reference concentrations: Averaging time of 24 hours 3,128 micrograms per cubic meter ( $\mu\text{g}/\text{m}^3$ ); and Long-term or chronic 50  $\mu\text{g}/\text{m}^3$ .**

Sulfuryl fluoride (SF) is being proposed as an addition to the risk screening worksheet based on SF's high toxicity and its significant use in fumigation operations. The addition of SF will also



provide certainty and consistency within the permitting review process. The California Environmental Protection Agency (CalEPA) is currently in the process of reviewing a 24-hour short term reference concentration range of 0.25 - 0.75 parts per million by volume (ppmv) to identify a final Sulfuryl fluoride 24-hour reference concentration. The New Jersey Department of Environmental Protection's Division of Air Quality is proposing to use CalEPA's upper range number of 0.75ppmv (3,128 µg/m<sup>3</sup>) as a temporary short-term Reference concentration (RfC) and a long-term/chronic RfC of 0.012ppmv (50 µg/m<sup>3</sup>) until CalEPA can finalize the individual RfC's. Additional information on the previous development of these concentrations can be found at "Sulfuryl Fluoride (Vikane) Risk Characterization Document, Volume II, Exposure Assessment, June, 2006" ([https://www.cdpr.ca.gov/docs/emon/pubs/tac/tacpdfs/sulfluor/final\\_rcd\\_vol2.pdf](https://www.cdpr.ca.gov/docs/emon/pubs/tac/tacpdfs/sulfluor/final_rcd_vol2.pdf)), "Establishing Sulfuryl Fluoride Uncertainty Factors for Acute and Short-term Exposures, March 3, 2017, CalEPA" ([https://www.cdpr.ca.gov/docs/risk/rcd/establishing\\_sulfuryl\\_fluoride.pdf](https://www.cdpr.ca.gov/docs/risk/rcd/establishing_sulfuryl_fluoride.pdf)), "Addendum to the 2006 Risk Characterization Document Update of the Toxicology and Reference Concentrations, May 2020" ([https://www.cdpr.ca.gov/docs/risk/rcd/sulfuryl-fluoride\\_addendum.pdf](https://www.cdpr.ca.gov/docs/risk/rcd/sulfuryl-fluoride_addendum.pdf)) and "SULFURYL FLUORIDE STRUCTURAL FUMIGATION MITIGATION SCOPING DOCUMENT", January 2021, CalDPR ([https://www.cdpr.ca.gov/docs/whs/pdf/sulfuryl\\_fluoride\\_mitigation\\_012221.pdf](https://www.cdpr.ca.gov/docs/whs/pdf/sulfuryl_fluoride_mitigation_012221.pdf)).

Based on sulfuryl fluoride being toxic, having the potential to be emitted from air permitted sources, and NJ determining that an air permit is required for fumigation of specific sources in their state, the MPCA should at least require reporting of sulfuryl fluoride emissions from facilities.

As additional evidence of the reasonableness, EPA wrote this notice on their next steps to regulate sulfuryl fluoride in the fumigation of residential homes. The notice cites at least 11 deaths and two serious injuries during residential fumigation in California and Florida that have occurred since 2002, stating the deaths and serious injuries occurred after homes had been "cleared" for re-entry. <https://www.epa.gov/pesticides/epa-announces-next-steps-protect-people-sulfuryl-fluoride-used-fumigate-residential>

While neither MPCA nor EPA regulate sulfuryl fluoride in air permits because it is not a listed HAP and is not a VOC, this EPA notice about residential fumigation acknowledges the real risk posed by the pollutant. Again, at a minimum, MPCA should require reporting of sulfuryl fluoride emissions.

Sincerely,

Shalini Gupta  
Environmental Justice Consultant  
Minneapolis, MN  
[www.sgupta.org](http://www.sgupta.org)

Name:

Andrew Morley

Address:

2235 Thomas Lane

White Bear Lake, MN

55110




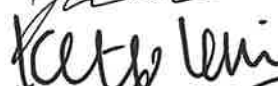




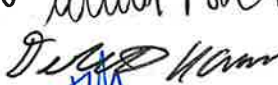





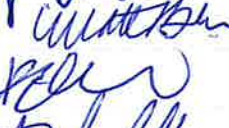
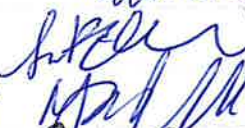




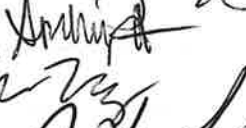




Part of rule(s) objecting to:

I object to and request a hearing on the entirety of 39354 Minnesota Pollution Control Agency Dual Notice of Intent to Adopt Rules (Office of Administrative Hearings Docket No. 71-9003-39354), which includes:

- Proposed Amendment to Rules Governing Air Quality, *Minnesota Rules*, chapters 7002, 7005, 7007, and 7019. Revisor's ID Number R-4599
- Proposed Repeal to Rules Governing Air Quality, *Minnesota Rules*, chapter 7007.1850.

# REQUEST PUBLIC HEARING FOR REVISOR'S ID R-4599, OAH

## DOCKET NUMBER 71-9003-39354

- 1 Andrew Moray  763-721-  
H35 Thomas Lane, White Bear Lake 55120 75523
- 2 Tony Kwikas  11688 Iny Woods TRAIL WOODBURY
- 3 Jenna Nelson  259 POINT DOUGLAS RD N, ST. PAUL, MN 55106
- 4 Katie Klein  9000 City Place Blvd Unit 2427 Woodbury
- 5 Laura Stein  4026 Cedar Grove Ln Eagan 55122
- 6  640 Main St N #21 Stillwater, MN 55082
- 7 Brian Cook  1814 Oregon Ave S St. Louis Park, MN 55426
- 8 Laura Borenstein  1308 HERMAN AVE, ST. PAUL, MN 55116
- 9 Derek Nannman  15750 Rockford Rd. A220, Plymouth MN 55446
- 10 BENTLEY GRAVES  5980 CHARLETON CIR., EXCELSIOR, MN 55331
- 11 Jack Dwyer  2560 Dorothy Ave, White Bear Lake, MN 55110
- 12 Annette Kojetik  824 Great Oaks Trail, Eagan MN 55123
- 13 Anne Morton  2235 Thomas Ln WBL MN 55116
- 14 Whitney Herring  8207 Jergen Ave Cottage Grove 55008
- 15 Matt Bohm  3912 Magnolia Ln, Vadnais Heights 55127
- 16 Sarah Erickson  3416 NE Cleveland, Minneapolis, MN
- 17 Megan Newlander  8930 Olive Ln N, Maple Grove, MN 55311
- 18 Chance Gaddy  6297 MacLynn Ave NE Otsego MN 55301
- 19 Taylor Schmidt  345 E MAIN ST, Waconia MN, 55389
- 20 Elizabeth Sherry  9287 Jody Lane S. Cottage Grove MN 55016
- 21 Selvig Erickson  4135 Quail Ave. N Robbinsdale MN 55422
- 22 Clarissa Tracy  2565 Franklin Ave St. Paul MN 55114
- 23 Jennifer Munn  14414 Ervater Ave N, Hugo, MN 55038
- 24 Vicki Sute  10825 STINSON AVE. Chisago, MN 55013
- 25 Bayert Salverdi  2202 E 32nd St MPLS, MN, 55407



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,

A handwritten signature in black ink, appearing to read "A. Morley", with a stylized flourish at the end.

Andrew Morley  
Director, Environmental Policy  
Minnesota Chamber of Commerce  
[amorley@mnchamber.com](mailto:amorley@mnchamber.com)  
763-221-7523



January 15, 2025

Office of Administrative Hearings  
Attn: William Moore  
Minnesota Pollution Control Agency  
600 North Robert Street  
P.O. Box 64620  
St. Paul, MN 55164-0620

**RE: Comments of the American Chemistry Council on Minnesota Pollution Control Proposed Amendment to Rules Governing Air Quality, Minnesota Rules, chapters 7002, 7005, 7007, and 7019; Proposed Repeal to Rules Governing Air Quality, Minnesota Rules, chapter 7007.1850.**

**Submitted electronically**

Dear Mr. Moore,

The American Chemistry Council (ACC) appreciates the opportunity to submit comments to Minnesota Pollution Control Agency (MPCA) on its request for comments in advance of its proposed amendments to existing air quality rules chapters 7002, 7005, 7007, and 7019, and repeal of rules at chapter 7007.1850. ACC appreciates MPCA's approach to amend and introduce new potentially significant regulatory requirements that address air emissions from facilities in the state.

ACC member companies are an important part of Minnesota's broader economy, contributing to innovation, job creation, and the production of essential products that support various sectors, including agriculture, healthcare, transportation, and technology. Through several chemical manufacturing facilities located within the state, ACC and its members directly and indirectly support thousands of jobs and generate significant economic output and essential products for the state and country as a whole.

As responsible stewards of environmental health and safety, our members operate under stringent regulations and continuously improve practices to reduce emissions and mitigate environmental impacts. We demonstrate this commitment to strong sustainability goals and environmental/health and safety policies through ACC's Responsible Care® program, under which ACC members work to continually improve their systems for addressing health, safety, and environmental performance. Additionally, our members' facilities are subject to numerous existing local, state, and federal statutory and regulatory requirements, including permit conditions approved by state regulators and administered under the Clean Air Act (CAA), Clean Water Act, Resource Conservation and Recovery Act, and others. Through operating regulatory and voluntary programs, ACC members recognize the important role that industry can play in our surrounding communities as corporate stewards of the local environment.

For these reasons, ACC appreciates MPCA's overall goal to implement regulations aimed at reducing air toxic emissions. ACC believes that appropriately designed emissions requirements are an essential component for public health, and we recognize the importance of scientifically supported and technically

feasible clear emissions standards for facility operations. As such, we submitted comments to MPCA in October 2024 on its pre-proposal for potential updates to Chapter 60 of the current air toxics regulations.<sup>1</sup> We continue to believe that it is crucial for any new regulatory requirements strike a balance between protecting public health and enabling the continued viability of critical industries.

As MPCA moves forward, we urge the state to consider not only existing requirements, but also the potential economic impacts of new regulations on industries that are vital to the state's economy. Regulatory certainty and a balanced approach will ensure that industries can continue to operate, innovate, and provide high-quality jobs while meeting environmental goals. Collaboration between the state, industry, and community stakeholders is key to achieving these outcomes.

#### **A. MPCA Should Ensure that Any New Requirements Avoid Overly Burdensome Impacts on State Facilities and Duplicative Reporting Obligations.**

As part of the proposed amendments, MPCA follows Minn. Stat. § 116.062 to require annual reporting of air toxics emissions. MPCA supports this change by noting the increased frequency will “help identify and prioritize areas of concern.”<sup>2</sup> Unfortunately, it is unclear if MPCA provides any additional rationale to support this significantly more burdensome reporting schedule.

As stated in our October 2024 comments, ACC recognizes the importance of transparency and data collection in the establishment of technically feasible and consistent monitoring and reporting requirements. ACC also cautions that requirements that are overly burdensome or duplicative may result in expensive time and personnel burdens on facility staff, hindering the ability of facilities to operate efficiently. MPCA should thoughtfully consider the creation of any new air emissions requirements and associated reporting schedules, which should be designed to provide meaningful data without imposing unnecessary administrative burdens.

ACC is concerned that MPCA's proposed shift to annual reporting requirements may impose significant administrative and operational burdens on facilities without demonstrable public health benefits. Additionally, it is unclear how MPCA will coordinate any new requirements and reporting schedules to avoid overlapping conflict and duplication with existing federal reporting frameworks, such as those under Clean Air Act (detailed further below) and the Toxics Release Inventory (TRI). Any additional state-level requirements should align with these programs to avoid redundancy, minimize operational burdens, and avoid creating unnecessary costs.

To mitigate these concerns, we believe that MPCA should clearly define the objectives and anticipated benefits of annual reporting. The state should also ensure reporting requirements are streamlined, consistent with and don't duplicate federal standards and reporting requirements. If MPCA proceeds with this reporting schedule, it will be critical to provide necessary flexibility in reporting mechanisms to accommodate varying facility sizes and operational complexities. Through a flexible and balanced approach, MPCA can help address its data collection and transparency goals while minimizing disruptions to industry operations.

As mentioned above, several current federal standards and regulatory programs provide rigorous controls of potential emissions with comprehensive monitoring and reporting requirements. Any new requirements from MPCA risk overlapping provisions that could lead to unnecessary inefficiencies, increased



costs, and avoidable confusion for industry stakeholders, all while yielding little to no additional public health or environmental benefits.

ACC member facilities in the state already operate under many federal programs that address emissions of hazardous air pollutants (HAPs), including:

- **National Emission Standards for Hazardous Air Pollutants (NESHAPs):** Under CAA Section 112, EPA applies NESHAPs that are designed to control emissions of HAPs from specific industrial source categories. NESHAPs establish technology-based standards for new and existing sources to ensure that emission levels reflect the best available control technologies. NESHAPs set health- and technology-based emissions standards for both major sources (stationary sources with 10 tons per year for a single HAP or 25 tons per year of any combination of HAPs) and smaller area sources.
- **Title V Operating Permits:** CAA Title V mandates that any major source of air pollution, including those with HAP emissions, obtain operating permits. These permits consolidate all applicable federal permits and ensure that facilities comply with air toxics emission standards through ongoing monitoring, recordkeeping, and reporting requirements.

Together, these federal programs regulate sources of industrial hazardous air pollutants in the state, including chemical manufacturing facilities. As such, we urge MPCA to first consider the regulatory programs that already address hazardous air pollutant emissions and avoid duplicative requirements that would result in unnecessary burdens on regulated facilities.

## B. Screening Values and Regulatory Thresholds

MPCA should provide clear and science-based guidelines on emission thresholds to help ensure the rule is effective and manageable for both regulators and industry and results in an air toxics regulatory program that is grounded in sound science. Therefore, ACC recommends that new reporting requirements should apply only to pollutants with risk values that have been formally reviewed and approved through a regulatory process.

Many of the health risk benchmarks referenced in the current regulation have not been officially adopted by rule and some of the proposed additional substances do not have health risk benchmarks. If MPCA intends to rely on these benchmarks to trigger regulatory obligations, we believe they should first be adopted through a transparent rulemaking process that allows for full stakeholder input on the supporting science for each benchmark. This is particularly relevant given the proposal to utilize lists, such as the TRI, that are not intended to inform determinations of risk associated with substances but instead serve as an information collection mechanism. ACC continues to emphasize that regulatory thresholds should prioritize the principles of best available science and risk-based decision-making, using toxicological data and risk assessments to meaningfully address risk in an appropriate and technologically feasible manner.

## C. Toxics Release Inventory (TRI) Substances

As noted above, to help ensure that any new requirements are effective, provide meaningful information, and are manageable for both regulators and the regulated community, the rule should focus only on substances with established risk values. This should not include TRI listed substances as these do not represent risk values.



In addition, many of the proposed substances for addition to the MPCA reporting requirements have not been formally evaluated for consistency with the underlying criteria and listing requirements outlined in the Emergency Planning and Community Right-to-Know Act (EPCRA), which authorizes the TRI program in Section 313. These substances were added to TRI based on unique provisions outlined the Fiscal Year 2020 National Defense Authorization Act and as such are not appropriate for inclusion in the rule's separate reporting requirements. To the extent MPCA opts to consider TRI substances, any consideration should be limited to those substances that have established risk values and have been formally evaluated against the underlying EPCRA criteria.

#### **D. De minimis Standard**

The de minimis standard should be maintained. The de minimis standard is a long-standing policy that is designed to help generate meaningful information and focus on priority levels of substances. It also provides for the minimization of unreasonable burdens to quantify minute amounts of a chemical substance. MPCA's proposed elimination of these common-sense exemptions serves no purpose; quantification of individual substances would become highly impractical and compliance nearly infeasible. Elimination of the de minimis standard will make the proposed rule unworkable and undermine the objectives of providing meaningful information. In addition, in many cases, there are no approved analytical methods for measuring certain chemicals in complex mixtures, which would be required if these provisions were removed. Unfortunately, any proposed removal would only serve to create substantial uncertainty, significant burdens, and impractical compliance challenges for limited or no environmental benefit.

#### **E. Compliance Issues**

It is critical that MPCA include clear, reasonable, and achievable permit and enforcement mechanisms in any future rulemaking. Future regulatory compliance timelines must be realistic and provide sufficient time for facilities to implement the necessary control technologies. We also ask that the MPCA provide support and clear, detailed guidance during the compliance phase to facilitate smooth transitions for affected facilities.

\*\*\*\*\*

ACC appreciates the MPCA's efforts to address air emissions in the state and we appreciate a collaborative approach to developing regulations that protect public health and the environment while supporting a thriving economy. We encourage the MPCA to consider the importance of Minnesota's chemical manufacturing sector and to adopt regulations that are both effective and economically sustainable. We welcome further dialogue on this issue and look forward to continued participation as the regulatory process moves forward. If you have any questions, please feel free to reach to out to me at [Brendan\\_Mascarenhas@americanchemistry.com](mailto:Brendan_Mascarenhas@americanchemistry.com) or via phone at (202) 249-6423.

Sincerely,

Brendan Mascarenhas  
Senior Director, Environment  
American Chemistry Council



January 15, 2025

*Submitted electronically via OAH Comment Portal at  
<https://minnesotaoah.granicusideas.com>*

**Re: Minnesota Pollution Control Agency's Proposed Rule re: Proposed Amendment to Rules Governing Air Quality, Minnesota Rules, chapters 7002, 7005, 7007, and 7019 and Proposed Repeal to Rules Governing Air Quality, Minnesota Rules, chapter 7007.1850**

**OAH Docket No. 71-9003-39354**

Northern States Power Company-Minnesota (NSPM) respectfully submits the following comments in response to the Minnesota Pollution Control Agency's (MPCA) Proposed Amendment to Rules Governing Air Quality, Minnesota Rules, chapters 7002, 7005, 7007, and 7019 and Proposed Repeal to Rules Governing Air Quality, Minnesota Rules, chapter 7007.1850 (Proposed Rules). The Proposed Rules cover both the establishment of air toxics reporting requirements and repeal of emergency affirmative defense provisions.

NSPM is a wholly owned subsidiary of Xcel Energy that provides electricity and gas to Minnesota cities and townships, as well as unincorporated communities and wholesale customers. Xcel Energy is a major U.S. energy company that provides a comprehensive portfolio of energy-related products and services to 3.8 million electricity customers and 2.2 million natural gas customers across Colorado, Michigan, Minnesota, New Mexico, North Dakota, South Dakota, Texas, and Wisconsin.

Our company is the first major U.S. energy provider to announce aggressive goals for reducing greenhouse gas emissions across three large sectors of the economy: electricity, natural gas use in buildings, and transportation. For nearly two decades, Xcel Energy has led the transition to cleaner energy sources and was the first large power provider with a vision to deliver 100% carbon-free electricity by 2050. We will fully exit from coal by the end of 2030. These efforts have significantly reduced emissions from our generating sources in Minnesota and across our fleet.

NSPM operates several generating units located in the in Anoka, Carver, Dakota, Hennepin, Ramsey, Scott, or Washington County that would be subject to the proposed air toxics reporting rule. Furthermore, NSPM's resources around the state will be impacted by the repeal of the emergency affirmative defense provisions.



NSPM provides the following comments on the Proposed Rules:

- **The Air Toxics Report Timing Should Align with TRI Reporting Requirements.**

NSPM recommends that the reporting deadline be moved back a short time to allow for better alignment with the TRI reporting requirements. The Proposed Rules set an annual reporting deadline of April 1 to report emissions from the previous calendar year. In contrast, annual TRI reports are due by July 1 following the reporting calendar year. More closely aligning these report dates will reduce undue administrative burdens and help ensure consistent reporting. Specifically, we request a July 1 reporting deadline for the air toxics.

The TRI reporting requirements follow an annual cycle that allows for development and distribution of updated reporting instructions and updates to the reporting software.<sup>1</sup> The reporting software reflects updates made to TRI reporting requirements, such as updated thresholds or emission factors, for that reporting year. To aid in reporting from power plants, we work with Electric Power Research Institute (EPRI) to utilize their TRI for Power Plants (TRIPP) software that incorporates the EPA-required information into a program developed specifically for utilities to estimate, track, and report releases of TRI chemicals and then allows for merging into the EPA reporting software. This software typically is released in the March to April timeframe to meet the TRI July 1 reporting deadline. With an April 1 deadline, it is unlikely that the software will be available to meet the deadline. Therefore, for the chemicals included in both reporting sets, we will need to utilize two separate mechanisms to analyze chemical amounts for the same reporting year. Under the proposed rule, with a proposed deadline of April 1 there would be no time to reconcile data reported under the two separate programs, potentially leading to inconsistent reporting. This creates unnecessary and undue burden in creating duplicative and potentially inconsistent reporting requirements.

EPA also recognized the relationship between HAP reporting and TRI in the 2023 Air Emissions Reporting Requirements proposed rule. In proposing new reporting deadlines, EPA noted the connection between the two programs and proposed a phase-in period of earlier reporting, with the reporting deadline of March 31 for the first five years. See 88 Fed. Reg. 54118, 54160 (Aug. 9, 2023). NSPM encourages MPCA to consider a similar approach for the air toxics reporting if it does not set a July 1 deadline.

- **The Air Toxics Reporting Regulations Should Establish Reporting Thresholds for Each Air Toxic.**

NSPM recommends that reporting thresholds be included for the air toxics. As proposed, the list of air toxics is extensive and the reporting will require a significant effort. Without reporting or de minimis thresholds, reporting entities will be attempting to quantify extremely small quantities. Reporting thresholds can – and should – be tailored to the

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<sup>1</sup> See TRI Program website: <https://www.epa.gov/toxics-release-inventory-tri-program/basics-tri-reporting#fourth>



specific characteristics and potential human health and environmental impact of each air toxic. In addition, reporting thresholds provide context against which to compare reported emissions.

MPCA should rely on already developed reporting thresholds where available. Reporting thresholds have been established by the EPA in various contexts that can provide a basis for setting reporting thresholds on the federally regulated pollutants. In addition, EPA proposed reporting thresholds for certain pollutants in the AERR proposed rule. Other states, such as California, also have established reporting thresholds. Where thresholds have been established, MPCA can build on those efforts.

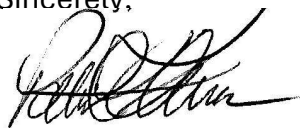
Overall, reporting thresholds provide a mechanism to focus reporting efforts on providing the most accurate and meaningful data. We encourage MPCA to establish reporting thresholds based on the best available data, building on the efforts of other states and EPA.

- **The Emergency Affirmative Defense Provisions Should be Maintained as “State-Only” Rather Than Fully Repealed.**

Rather than a complete repeal of the emergency defense provisions from Minnesota regulations, MPCA should adopt regulations that clarify that the emergency defense provisions apply to state-only provisions of permits and only apply to enforcement actions of state law only. As raised by other commenters in this rulemaking process, EPA has specifically endorsed this option as a pathway for states. See 88 Fed. Reg. 47029, 47049 (July 21, 2023) (EPA, Removal of Title V Emergency Affirmative Defense Provisions From State Operating Permit Programs and Federal Operating Permit Program, Final Rule). NSPM encourages MPCA to take the path laid out by EPA and retain these provisions as applied to state-only permit provisions.

Thank you for the opportunity to comment on the Proposed Rules. Please reach out if you have any questions or would like more information or clarification on these comments.

Sincerely,

A handwritten signature in black ink, appearing to read 'Patrick Flowers', with a stylized, cursive script.

Patrick Flowers  
Director, Environmental Services  
Xcel Energy Services Inc.  
On behalf of Northern States Power Company