

This document contains the comments the MPCA received during the Request for Comments public comment period July 24, 2023, through September 22, 2023, for the planned amendments to rules governing Air Quality (Air Toxics Emissions Reporting Rule), Revisor ID # R-4599.

39354 Minnesota Pollution Control Agency Request for Comments on Air Toxics Emissions Reporting Rule

Closed Sep 22, 2023 · Discussion · 2 Participants · 1 Topics · 2 Answers · 0 Replies · 0 Votes

2

PARTICIPANTS

1

TOPICS

2

ANSWERS

0

REPLIES

0

VOTES

SUMMARY OF TOPICS

SUBMIT A COMMENT

 2 Answers · 0 Replies

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Tony Kwilas · Citizen · (Postal Code: unknown) · Sep 21, 2023 3:34 pm

 0 Votes

The Minnesota Chamber of Commerce comments are attached

Mike Karbo · Citizen · (Postal Code: unknown) · Sep 22, 2023 9:25 am

 0 Votes

Please find the American Petroleum Institute's comments attached.



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



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 related to air toxics 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.

As indicated below, 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 cumulative impacts analysis and air toxics emissions reporting, 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 deliberate 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.

Overview

The Chamber supports efforts to ensure facilities do not operate in a manner that creates public health risks. We understand the importance of maintaining public trust in operating facilities. Importantly, the MPCA is not writing on a clean slate. Air toxics have been subject to regulation since the passage of the Federal Clean Air Act in 1970. The 1990 amendments to the Clean Air Act established a comprehensive program regulating all major sources of hazardous air pollutants (HAP) in the United States and requiring compliance with technology-based standards, such as the maximum achievable control technology (MACT) and generally achievable control technology (GACT) rules in 40 CFR Part 63 to reduce emissions at both major and non-major sources of HAP, regardless of risk.

The 1990 amendments also required that sources subject to MACT standards undergo a comprehensive regulatory review to ensure those facilities posed no residual risk requiring additional regulation. That process has led to additional requirements based on the United States Environmental Protection Agency's (US EPA's) risk-based evaluation. We believe this comprehensive federal program (particularly the residual risk component), which has been in place for 33 years, provides the proper assurance that sources are well-regulated.



Finally, these regulations create the possibility of a significant regulatory burden without substantial benefit. As always, we believe that any new requirements need to strike the proper balance between regulatory objectives and the continued economic vitality of the state.

With these preliminary comments in mind, the Chamber provides the following specific comments:

The Current Legislation does not Mandate a Comprehensive Air Toxics Regulatory Program.

Our understanding is that Section 5 of HF 2310 was a relatively late addition to Article 8 of that bill. We further understand that the intent of Section 5 was to provide the MPCA with the tools necessary to implement the remainder of Article 8. Article 8 is captioned “Environmental Justice,” and thus, Section 5 must be read in that context. This is further reinforced by the fact that the rulemaking authorization in Section 5 has no legislatively specified location in the Minnesota Statutes. This is in contrast with Sections 1 (Minn. Stat. §16A.151), 2 (§116.062), 3 (§116.065), and 4 (§116.07). Generally, we believe this should be interpreted to mean that any authorization set forth in Section 5 is ancillary to the other sections of Article 8. Finally, the MPCA acknowledges the direct connection to the rest of Article 8 in its RFC when it indicates the persons affected by the rule are “[p]eople living in environmental justice areas.”

Section 5, as written, contains no express authorization or requirement for the MPCA to adopt a comprehensive air toxics program independent of the rest of Article 8. The authorization is to “adopt rules” to “implement and govern regulation of facilities that emit air toxics.” Section 5, Subd. 3. The only specific and actionable mandate is found in Subd. 4(a). There, in parts (3) through (7), the legislature requires testing, monitoring, reporting, recordkeeping, and inspections – all items that are in furtherance of the rest of Article 8 and directly relate to the implementation of Section 2 and enforcement of any requirements in Section 3.

Subd. 4(b) reinforces this narrow mandate: “In developing the rules, the commissioner must establish **testing, monitoring, reporting, recordkeeping, and inspection** requirements for facilities . . .” (emphasis added).

This is not a broad obligation for the sort of regulatory program the MPCA appears to be contemplating in its RFC. The Chamber supports the incremental approach that is provided for in the legislation, wherein the MPCA first develops more fully the tools to characterize and understand the nature of any air toxic emissions. At that point, the agency can determine if it deems additional regulation necessary – or, as described below, utilize an existing process such as MNRISKS to prioritize efforts.

Importantly, the Chamber believes that any broader interpretation of the MPCA’s mandate (or the agency’s statistical broadening of the definition of Environmental Justice Area as addressed below) creates the risk of diluting the primary purpose of this legislation, which is to address impacts on potentially overburdened areas. Expanding the focus of this mission will, among other things, divert already scarce agency resources away from the focus on environmental justice.

The Information Required by Statute Should First be used to Support the MPCA’s MNRISKS Effort.

We believe the MPCA already has in place a tool for understanding and addressing public health issues associated with toxic air emissions. The legislative mandate for testing, monitoring, reporting, recordkeeping, and inspection set forth above should first be used to support that effort. For example, MNRISKS data may suggest certain pollutants and/or areas are of concern. The MPCA specifications of testing, recordkeeping, and reporting may focus on those issues instead of broad new requirements that do not incorporate learning and priorities from MNRISKS. If refined data do not alleviate concerns about specific areas or pollutants, the MPCA may consider whether additional regulation is required.

If the MPCA considers new requirements or program elements related to air toxics, those requirements should not be standalone programs but an outgrowth of federal and Minnesota work in the area over the decades. The MPCA has managed a state air toxics emissions inventory for thirty or more years, collaborating with other Midwest states and the US EPA on procedures, software, and data. As noted above, the US EPA has enacted many programs regulating air toxics over the same period. Minnesota has gone beyond federal and state law by enacting policies that examine the potential impact of air toxics during facility permitting and/or other environmental reviews. The MPCA built MNRISKS, a multimedia risk assessment model that uses available data to describe the state of knowledge on air toxics risks in the state. The MPCA has completed short- and long-term ambient monitoring studies to characterize concentrations at various geographic levels. In short, the MPCA has spent significant time and resources studying air toxics. Any potential new programs should build upon that work and aim for targeted improvements in the context of all this Minnesota-specific work. The MPCA should consult with other states on best practices for air toxics management and decide which of those practices would be relevant and effective in Minnesota.

Guideposts for a Regulatory Program

If the MPCA were to proceed beyond the mandate in Section 5, the Chamber believes there are important guideposts the MPCA (and an advisory committee) should observe. These suggestions are not intended to include all Chamber comments on a potential program.

Any toxics program should provide certainty to the community and the regulated entities.

Any regulatory program should not be overly complex or ambiguous or create a substantial “back-and-forth” process with an uncertain outcome between the agency and facilities. A program could be efficient and effective in multiple ways:

- A toxics program should exempt sources already subject to the federal regulatory program for HAP as described above. These sources are already regulated and subject to risk review. In addition, there should be a “bright line” screening of emissions levels that require no further action. The rules should also consider other means of streamlining, including establishing de minimis levels below which the regulations do not apply.

- Any rule should also establish an ambient monitoring “exit ramp” from additional regulation. Any source that agrees to implement an approved ambient monitoring program for air toxic pollutants of concern in the area should be exempt from a modeling analysis requirement that the rule may otherwise require.
- Also, any rule should include “safe harbor” provisions exempting sources from additional review unless a facility is being modified in a manner inconsistent with any prior evaluation. Such a provision makes it clear that compliance with the rule satisfies any environmental review obligations and creates an exemption for any source that has already undergone an MPCA air emissions risk analysis (AERA) and has not been modified.
- Finally, we believe any dispersion modeling evaluation provided by the rule should be performed on an actual emissions basis, not a theoretical potential to emit basis, and should consider only normal facility operations exclusive of startup, shutdown, or malfunction scenarios. From the experience of our members who have undertaken an AERA or similar process for air toxics emissions, starting such an evaluation with potential emissions or evaluating hypothetical worst-case emissions scenarios leads to skewed results and a lengthy iterative process with the agency that requires substantial resources and does not lead to any different risk determination nor any benefit to the community. Additionally, given the inherent conservatism built into any modeling projections, any modeling required by the rule should be validated by comparing results to available monitored values.

These suggestions aim to guide the program toward sources that may require additional characterization or engagement and avoid duplicative work on sources that are already well-regulated and characterized.

The MPCA Must Adopt the List of Regulated Toxics by Rule

Although the legislation defines “air toxics,” it does so in a way that requires additional rulemaking. The legislative definition incorporates compounds currently established only in guidance and not otherwise established by rule. For example, the definition includes compounds for which the Minnesota Department of Health (MDH) has developed health-based values or risk assessment advice and compounds that are addressed in the federal Integrated Risk Information System (IRIS) process. Most ambiguously, it includes “chemicals reported by facilities in the agency’s most recent triennial emissions inventory.”

As part of any MPCA rulemaking effort and consistent with general principles of administrative law, the MPCA must adopt an initial list of air toxics consistent with the legislative definitions and then, by rule, periodically modify the list as necessary, consistent with Subd. 4(a)(1).

The MPCA should use a Legislatively Consistent Definition of “Environmental Justice Area.”



Section 3 and Section 5 of Article 8 include similar definitions of “environmental justice area,” but they are not exactly the same – Section 3 includes the word “decennial” before “census data.” Importantly, neither definition implies that the census data should be modified statistically to create a confidence interval. While the Chamber has no indication at this point that the MPCA contemplates making a statistical adjustment to the Census data, the MPCA has done so on one of its current web pages. The Chamber would oppose such an approach in implementing the Article 8 rules.

Not only is such an adjustment contrary to the express language of the legislation, but it also is inconsistent with the approach utilized by other states (e.g., New Jersey, New York, Colorado) that administer air toxics programs. To artificially inflate the number of environmental justice areas dilutes the effectiveness, focus, and credibility of the environmental justice effort. Please see the Attachment for an additional technical description of this issue and concern.

As the attached analysis indicates, to include a statistical adjustment (i.e., a margin of error) inappropriately skews the definition of “environmental justice area” based solely on the confidence interval employed in one direction only – to increase the percentage. Further, the data show that the confidence interval changes based on the number of census respondents because a confidence interval may be greater for any given year’s data if fewer people respond. The U.S. Census data (as presented in the Attachment) illustrates this point.

The direct result of the unidirectional statistical adjustment substantially increases the number of environmental justice areas based solely on that confidence interval. Thus, the data indicates that using a confidence interval can almost double the number of potential environmental justice areas in the Twin Cities metropolitan area. As the number of respondents decreased during the COVID-19 pandemic, the statistical confidence intervals increased, almost tripling the number of environmental justice areas.

Such an approach not only inflates the number of environmental justice areas in any year, it also creates greater variability in possible environmental justice areas year-to-year. For example, an area with consistent actual reported data on a year-to-year basis could become an environmental justice area because there was a low number of respondents in any given year. If the number of respondents increases the next year, the area will once again not be listed as an environmental justice area. To meet the legislation’s intent, any process for identifying environmental justice areas should aim for accuracy rather than maximization.

Summary

The Chamber believes the legislation requiring this rulemaking requires a limited air toxics program focused on environmental justice areas. Within that scope, the Chamber further suggests that the MPCA use its decades of data on air toxic emissions and concentrations to target any regulatory program on pollutants and areas of potential concern, not on permitted sources and pollutants generally. A focused approach is most likely to identify and improve any elevated risks to public health.

We welcome the opportunity to participate in an advisory committee to help guide the MPCA's efforts as it moves forward with these rules.

Sincerely,

A handwritten signature in blue ink, appearing to read "Tony Kwilas".

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



August 6, 2020

Dear Ms. Maggie Wenger:

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

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

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

Data Utility

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

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

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

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

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

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

Reporting Burden

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

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

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

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

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

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

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

Streamlining Reporting

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

Reporting could also be streamlined by maintaining consistency on reporting requirements over time.

Pollutant Lists

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

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

MPCA should consider how to treat unique sources in any future program. Exemptions for research and development or temporary sources would be useful for permit holders and avoid extensive work to characterize sources that may not be significant.

The provision of detailed lists of compounds at a process level also creates challenges for the protection of confidential business information. MPCA should include provisions that allow sources to protect sensitive, process-specific data and formulations.

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

State Examples

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

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

Other Comments

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

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

The Emissions Inventory

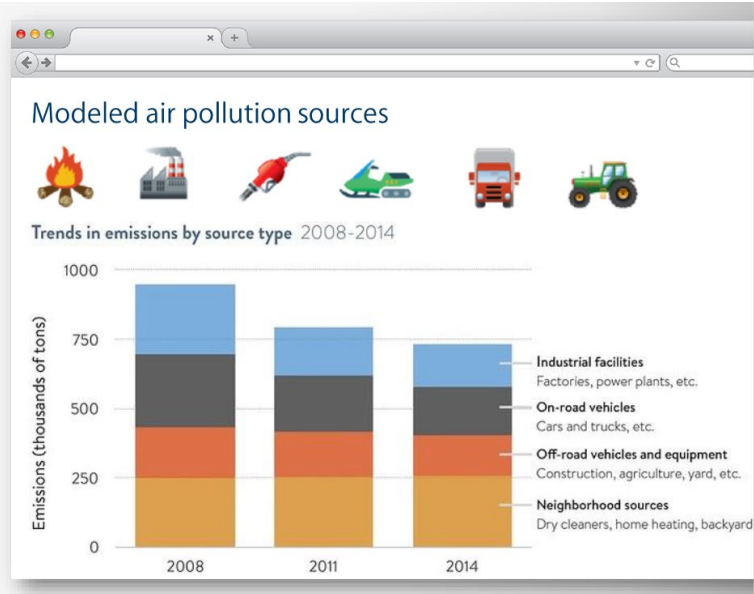
Criteria pollutants every year

HAPs / Air Toxics every 3 years

Feeds into EPA's NEI

Includes facilities as well as:

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



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

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

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

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

Respectfully submitted,



Tony Kwilas
Director, Environmental Policy
Minnesota Chamber of Commerce

Enclosures: 2

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

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

KEN SEXTON,*† JOHN L. ADGATE,†
GURUMURTHY RAMACHANDRAN,†
GREGORY C. PRATT,‡
STEVEN J. MONGIN,†
THOMAS H. STOCK,§ AND
MARIA T. MORANDI§

*Division of Environmental and Occupational Health,
School of Public Health, University of Minnesota,
Minneapolis, Minnesota 55455, Minnesota Pollution Control
Agency, 520 Lafayette Road, St. Paul, Minnesota 55155, and
School of Public Health, Houston Health Science Center,
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 km² with a population density of 2000–8000 per km². 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 km² and a population density of 1000–4000 per km². 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 km² and has a population density of 500–2000 per km². 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

* Corresponding author phone: (956)554-5168; fax: (956)554-5152; e-mail: ksexton@utb.edu.

† University of Minnesota.

‡ Minnesota Pollution Control Agency.

§ University of Texas.

TABLE 1. Summary of Valid, Matched, VOC Samples^a by Community, Season, and Monitor Location

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

^a Without duplicates.

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

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

Methods

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

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

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

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

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

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

15 VOCs. Rather than present all 405 combinations ($3 \times 3 \times 3 \times 15$) 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

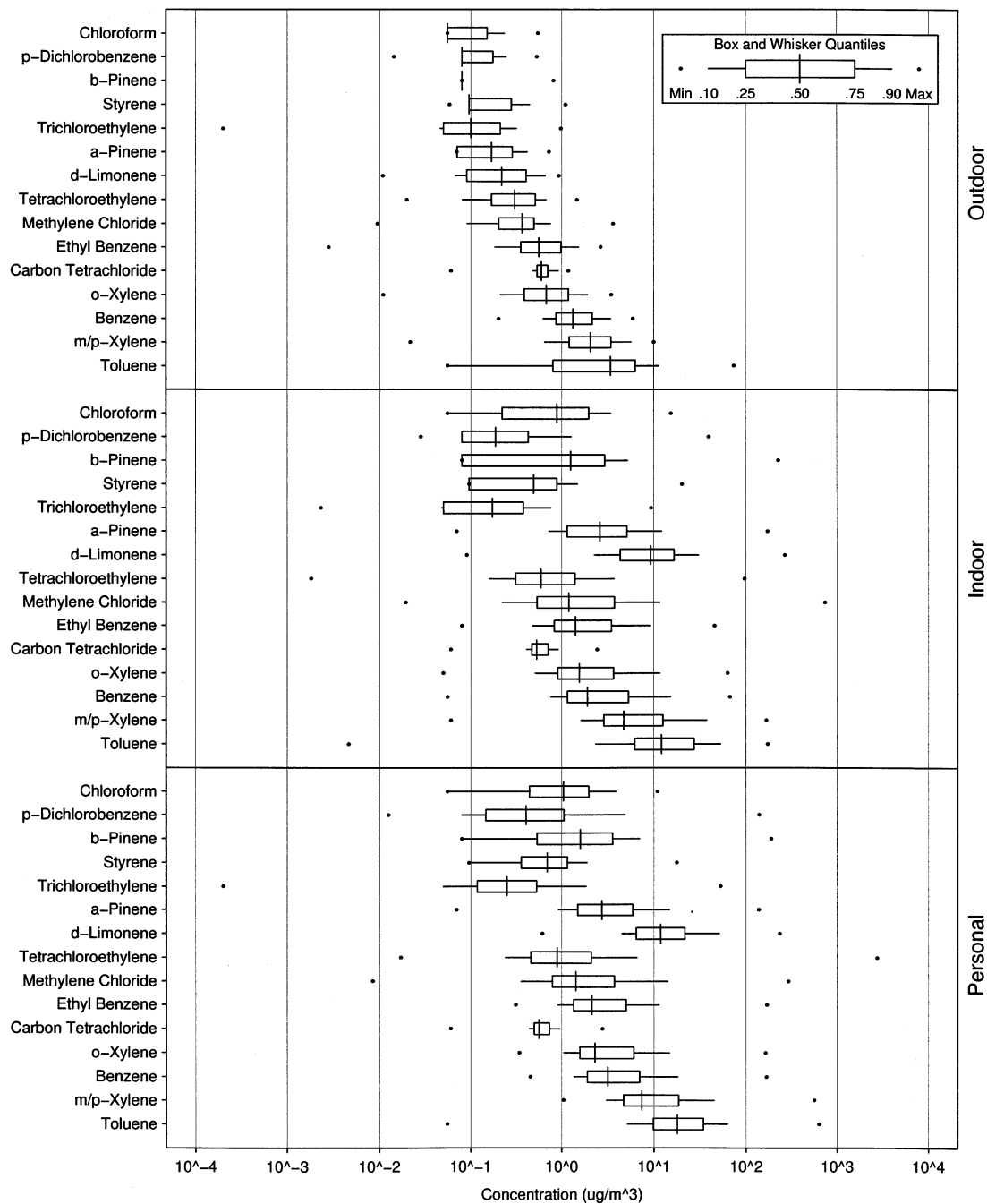


FIGURE 1. Distributions of all valid, matched VOC concentrations for outdoor, indoor, and personal samples

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

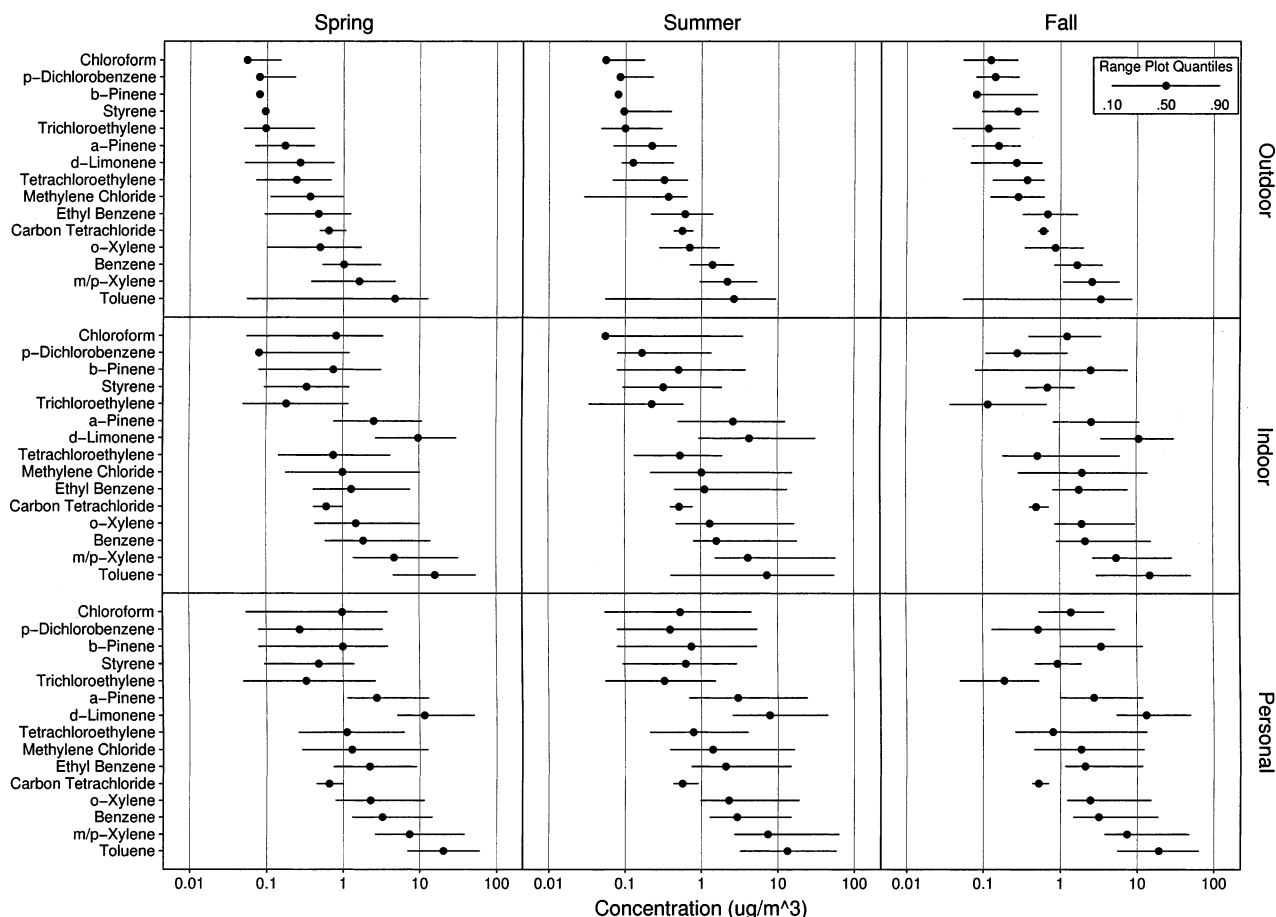


FIGURE 2. Distributions of all valid, matched VOC concentrations by monitor location and season

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 ≈ 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-

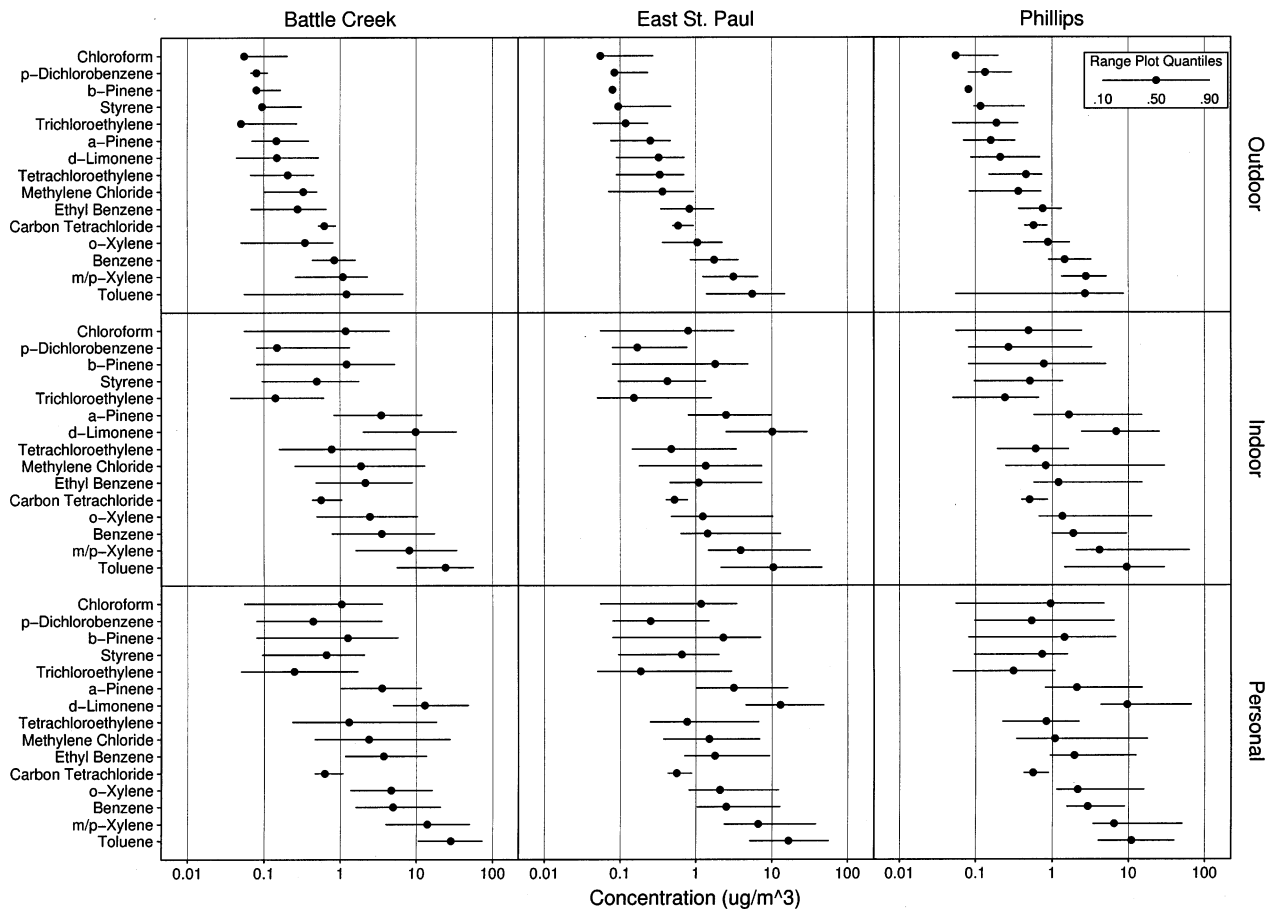


FIGURE 3. Distributions of all valid, matched VOC concentrations by monitor location and community

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

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

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

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

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

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

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 ^a	73.8 (45.0, 121.0)	54.8 (33.5, 89.8)	1.3 (1.1, 1.6)	0.6 (0.3, 1.2)	0.8 (0.4, 1.5)	1.0 (0.6, 1.7)	1.2 (0.8, 2.0)	0.6 (0.3, 1.2)	0.7 (0.4, 1.2)	0.9 (0.5, 1.5)	1.3 (0.8, 2.0)
methylene chloride	636	5.8 (3.1, 10.8)	4.4 (2.4, 8.2)	1.3 (1.1, 1.6)	0.5 (0.2, 1.3)	0.4 (0.2, 1.0)	2.0 (1.2, 3.1)	2.0 (1.3, 3.0)	0.5 (0.2, 1.2)	0.5 (0.2, 1.0)	2.0 (1.3, 3.2)	2.3 (1.5, 3.5)
a-pinene	570 ^a	20.5 (12.9, 32.5)	20.2 (12.8, 32.1)	1.0 (0.9, 1.2)	0.7 (0.4, 1.3)	0.7 (0.4, 1.3)	0.9 (0.6, 1.4)	1.3 (0.9, 1.8)	0.6 (0.3, 1.2)	0.6 (0.3, 1.1)	0.9 (0.6, 1.3)	1.3 (0.9, 1.9)
b-pinene	570 ^a	6.5 (4.0, 10.5)	6.4 (4.0, 10.4)	1.0 (0.7, 1.4)	1.8 (1.0, 3.4)	1.0 (0.5, 1.9)	0.8 (0.5, 1.4)	3.0 (2.0, 4.5)	1.2 (0.7, 2.3)	0.6 (0.3, 1.2)	0.9 (0.5, 1.4)	2.7 (1.8, 4.1)
styrene	636	4.3 (2.9, 6.2)	3.2 (2.2, 4.6)	1.3 (1.1, 1.7)	0.9 (0.6, 1.5)	0.8 (0.5, 1.3)	1.1 (0.8, 1.5)	1.1 (0.8, 1.4)	0.8 (0.5, 1.2)	0.8 (0.5, 1.4)	1.0 (0.7, 1.3)	1.1 (0.9, 1.5)
tetrachloroethylene	636	9.4 (5.5, 16.3)	5.5 (3.2, 9.4)	1.7 (1.4, 2.2)	0.4 (0.2, 0.8)	0.3 (0.1, 0.6)	0.7 (0.5, 1.1)	0.7 (0.5, 1.1)	0.4 (0.2, 0.9)	0.3 (0.2, 0.7)	0.7 (0.5, 1.0)	0.8 (0.5, 1.1)
toluene	636	27.1 (13.1, 56.4)	20.8 (10.0, 43.2)	1.3 (1.0, 1.6)	0.1 (0.0, 0.2)	0.1 (0.1, 0.3)	1.5 (0.7, 3.4)	2.0 (1.0, 4.2)	0.1 (0.0, 0.2)	0.1 (0.1, 0.4)	1.0 (0.4, 2.1)	1.9 (0.9, 3.9)
trichloroethylene	636	3.0 (1.8, 5.2)	1.6 (0.9, 2.8)	1.9 (1.4, 2.5)	1.0 (0.5, 1.9)	0.6 (0.3, 1.3)	1.1 (0.6, 1.9)	0.8 (0.5, 1.3)	1.1 (0.6, 2.2)	0.9 (0.4, 1.7)	1.1 (0.6, 1.9)	1.0 (0.6, 1.6)
o-xylene	636	18.0 (11.7, 27.8)	11.0 (7.2, 17.0)	1.6 (1.4, 2.0)	0.2 (0.1, 0.3)	0.2 (0.1, 0.4)	0.8 (0.6, 1.1)	0.7 (0.5, 1.0)	0.2 (0.1, 0.3)	0.2 (0.1, 0.4)	0.7 (0.5, 1.0)	0.8 (0.6, 1.1)
m-p-xylene	636	19.2 (12.5, 29.7)	12.4 (8.1, 19.2)	1.5 (1.3, 1.9)	0.2 (0.1, 0.3)	0.2 (0.1, 0.3)	0.8 (0.6, 1.1)	0.8 (0.6, 1.0)	0.2 (0.1, 0.3)	0.2 (0.1, 0.3)	0.7 (0.5, 1.0)	0.8 (0.6, 1.1)

^a Fewer valid samples were available because of calibration problems.

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

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

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

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

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

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

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

study that are designated human carcinogens (5, 23, 24). The established risk threshold in Minnesota (24) is the airborne concentration ($\mu\text{g}/\text{m}^3$), 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 1×10^{-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.

Acknowledgments

This research was funded by a STAR (Science to Achieve Results) Grant (R825241) from the U.S. Environmental Protection Agency, National Center for Environmental

Research. We also benefited from a grant from the Academic Health Center at the University of Minnesota. We thank the individuals who participated in the study and acknowledge the contributions of the field team. We also thank the 3M Corporation for donating some of the organic vapor monitors used in this study. The help and support provided by the Minnesota Pollution Control Agency was essential to the success of this project.

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

ES030319U

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

KEN SEXTON,^{*,†} JOHN L. ADGATE,[‡]
STEVEN J. MONGIN,[‡]
GREGORY C. PRATT,[§]
GURUMURTHY RAMACHANDRAN,[‡]
THOMAS H. STOCK,^{||} AND
MARIA T. MORANDI^{||}

School of Public Health, University of Texas, Brownsville Regional Campus, RAHC Building, 80 Fort Brown, Brownsville, Texas 78520, Division of Environmental & Occupational Health, School of Public Health, University of Minnesota, Minneapolis, Minnesota 55455, Minnesota Pollution Control Agency, 520 Lafayette Road, St. Paul, Minnesota 55155, and School of Public Health, University of Texas, Houston Health Science Center, Houston, Texas 77030

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.

* Corresponding author phone: (956)554-5165; fax: (956)554-5152; e-mail: ksexton@utb.edu.

[†] University of Texas, Brownsville.

[‡] University of Minnesota.

[§] Minnesota Pollution Control Agency.

^{||} University of Texas, Houston.

A centralized outdoor monitoring site (community site) was established in each neighborhood. Approximately 25 healthy, nonsmoking adults were recruited from each neighborhood using house-to-house canvassing and direct solicitation (informed consent was obtained). Matched 2-day samples were collected outdoors at the three community monitoring sites, indoors in participants' residences (room where they spent most of their waking hours), and near participants' breathing zones, all using passive dosimeters. Participants also completed time-activity logs recording the time they spent in seven microenvironments (indoors at home, work, other; outdoors at home, work, other; in transit) and the time they were in close proximity to environmental tobacco smoke. All outdoor community site (O), indoor residential (I), and personal (P) samples were collected during three monitoring sessions in 1999: spring (April 26–June 20); summer (June 21–August 11); and fall (September 23–November 21).

Methods

VOC Collection and Analysis. All VOC concentrations (O, I, and P) were 2-day (approximately 48-h) average values obtained with 3M model 3500 organic vapor monitors (3500 OVMs), which are charcoal-based passive air samplers. The suitability of these VOC badges for outdoor, indoor, and personal sampling has been demonstrated by Chung et al. (22, 23). These investigators have also described the determination of extraction efficiencies and the calculation of method detection limits. The extraction solvent consisted of a 2:1 v/v mix of acetone and carbon disulfide, which provided a very low background for target analytes. All extracts were analyzed by GC/MS with a Hewlett-Packard 5890 series II Plus GC with an HP 5972 MS detector, HP 18593B autosampler, and Vectra 486 computer with EnvironQuant ChemStation Software and NBS75K Spectra Library, using an RTX-1/60 m/0.25 mm i.d./1 mm film thickness capillary column. Analytical and internal standards were prepared, and VOC concentrations were calculated as described previously (23). Duplicate O, I, and P badges were collected periodically during the study (total $n = 80$), and correlation coefficients for the positive measurements were >0.95 for all individual VOCs except styrene (0.94) and chloroform (0.95). We define the median relative absolute difference (MRAD) as the median of the ratios of within-pair absolute differences divided by the within-pair mean. MRAD was <0.18 for all VOCs except trichloroethylene (0.44).

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

Three estimators of personal exposure are evaluated:

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

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

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

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 $\hat{P}_{[O]}$, $\hat{P}_{[I]}$, and $\hat{P}_{[O|I]}$ 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 $\hat{P}_{[O]}$ and $\hat{P}_{[I]}$, both RMSE and longitudinal correlations are first presented, based on estimation of each statistic for each subject. Geometric means of all duplicate samples are used to facilitate comparison with previous studies. To maximize the information available from our sample, no lower limit on the number of repeated measurements was applied in the calculation of these subject-specific RMSEs or longitudinal correlations (R) except for the mathematical limit imposed by the statistics themselves. For example, a longitudinal correlation cannot be calculated for subjects with only one data point. We report medians with upper and lower deciles to illustrate the inter-subject distributions of RMSE and R and to give a sense of their inherent variation.

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

Results

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

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

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

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

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

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

Two subject-level criteria for characterizing the performance of $\hat{P}_{[O]}$ are provided in Table 2. The RMSE and R were calculated for each subject with a sufficient number of samples for each measure (≥ 1 for RMSE, ≥ 2 for R). RMSE is a measure of the magnitude and variation of the difference ($\mu\text{g}/\text{m}^3$) 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 (α -pinene, β -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

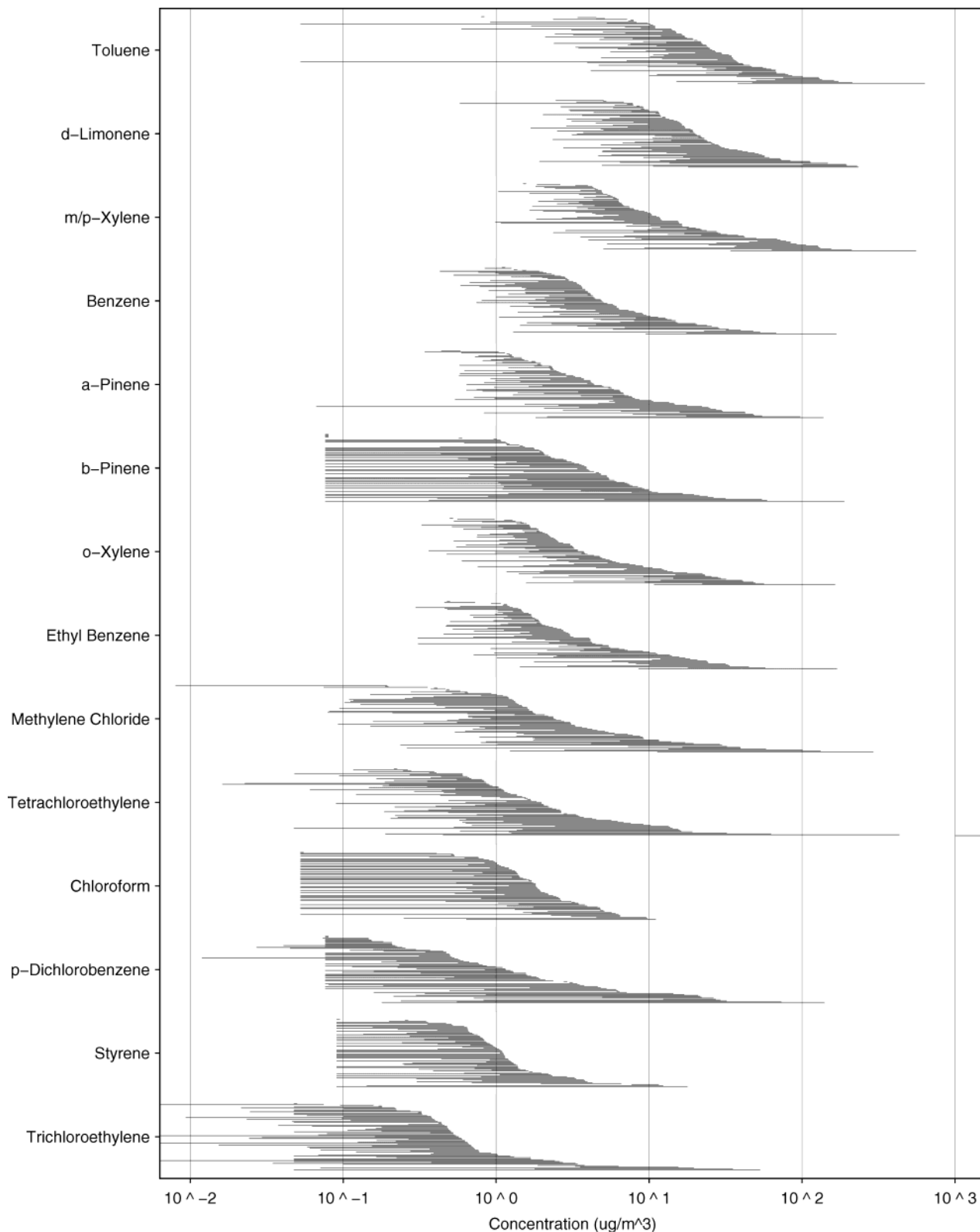


FIGURE 1. Range plot of measured personal VOC exposures for each study participant.

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, α -pinene,

β -pinene, *o*-xylene, *m*-/*p*-xylene), and $0.57 \leq R \leq 0.83$ for the remaining 6 VOCs. Relatively consistent R values for individual VOCs were observed across neighborhoods, with the exception of *p*-dichlorobenzene (0.16) in BCK and trichloroethylene (0.40) in PHI.

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

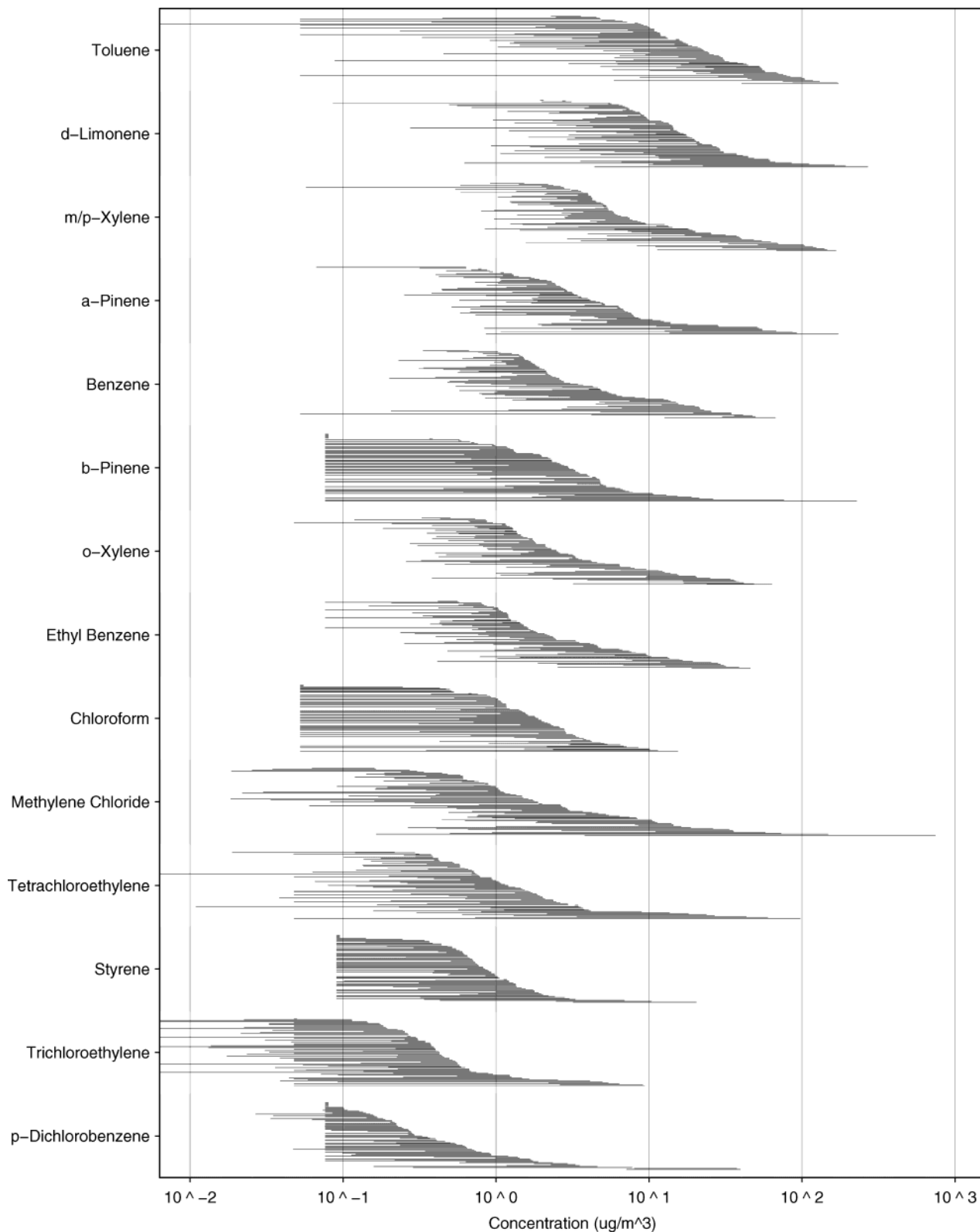


FIGURE 2. Range plot of measured indoor residential VOC concentrations for each study participant.

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

To further investigate the nature of RMSE for $\hat{P}_{[0]}$ and $\hat{P}_{[1]}$, 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 $\hat{P}_{[0]} - \mathbf{P}$ (Table 4) or the mean of $\hat{P}_{[1]} - \mathbf{P}$ (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 ^a	R ^b	RMSE	R	RMSE	R	RMSE	R
benzene	4.9 (0.9, 19.4) ^c	0.02 (-0.92, 0.89) ^c	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)
α -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)
β -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)

^a 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.

^b Median correlation coefficient; *n* for number of research subjects varies from 20 to 23 for Battle Creek, *n* = 22 for East St. Paul, and *n* varies from 21 to 22 for Phillips. ^c 10th and 90th percentiles.

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

The results from Table 4 show that both the bias and the SD of $\hat{P}_{[O]}$ tend to increase from the lower to the middle and from the middle to the upper tertile of the distribution of *P* exposures. For example, in the lower tertile the range of $\hat{P}_{[O]} - P$ 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 α -pinene. Similarly, the range of SDs for individual VOCs increases from 0.1 to 5.2 in the lower tertile, from 0.2 to 10.2 in the middle tertile, and from 1.7 to 351 in the upper tertile, which suggests that variance in $\hat{P}_{[I]}$ also tends to increase with higher *P* exposures.

We investigated the time-weighted estimator $\hat{P}_{[OI]}$ by examining the RMSE for the model where *P* exposure equals the time fraction of the 2-day monitoring period spent indoors

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

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

Discussion

Chronic exposure to relatively low levels of airborne VOCs is an inescapable reality for residents of the United States. This class of chemicals is ubiquitous in occupational and nonoccupational settings, including both indoor and outdoor environments. Not only are VOCs released into the air from industrial processes, internal combustion engines, cigarette smoking, and bathing or showering in chlorinated water, they are also common constituents in cleaning and degreasing agents, 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 α - and β -pinene), while nine are emitted by a combination of indoor and outdoor sources (benzene,

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

compound	Battle Creek		East St. Paul		Phillips		all communities	
	RMSE ^a	R ^b	RMSE	R	RMSE	R	RMSE	R
benzene	2.5 (0.5, 9.7) ^c	0.86 (0.12, 1.00) ^c	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)
α -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)
β -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)

^a 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. ^b Median correlation coefficient; *n* for number of research subjects varies from 20 to 23 for Battle Creek, *n* = 22 for East St. Paul, and *n* varies from 21 to 22 for Phillips. ^c 10th and 90th percentiles.

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

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

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

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

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

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

where p_{ij} gives the observed P exposure for the *i*th subject on the *j*th occasion. A candidate estimator of P, denoted as $\hat{\mathbf{P}}$, is a vector of the same structure as P but with some function of the data at element \hat{p}_{ij} . Metrics for assessing the ability of $\hat{\mathbf{P}}$ to estimate 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 P (29). To the extent that $\hat{\mathbf{P}}$ is an unbiased and precise estimator of 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 P by a factor of 2.

Another problem with *R* is its dependence on the distribution of P values. Despite having the same MSE in estimating 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 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 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 P distribution adversely affects the usefulness of the resulting

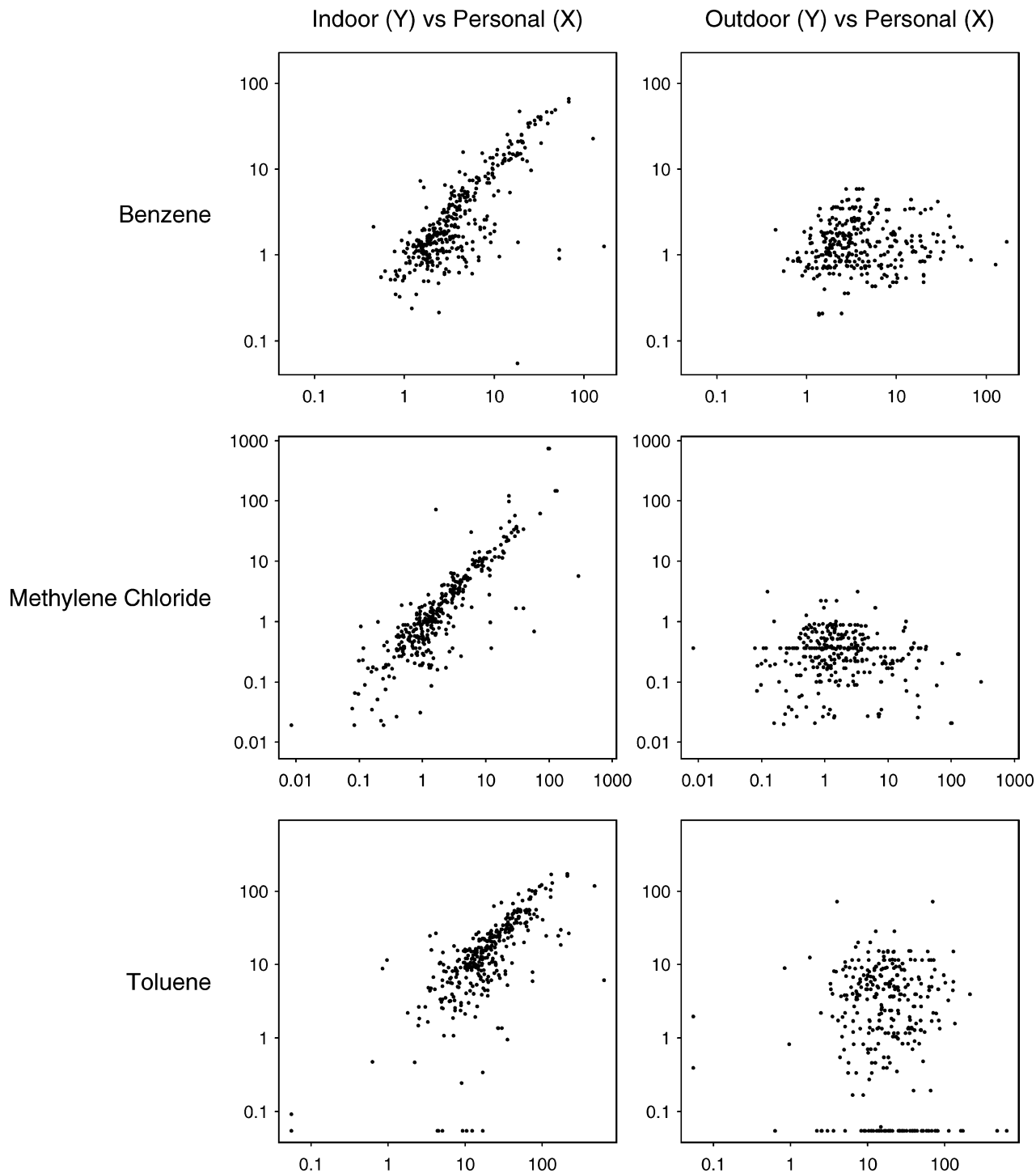


FIGURE 3. Plots of (a) indoor residential concentrations ($\mu\text{g}/\text{m}^3$) and (b) outdoor community concentrations vs personal exposures to benzene, methylene chloride, and toluene for participants in the study. As described in the text, nondetectable measurements (i.e., samples with no analytical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

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

reason a single observation should not add to our understanding of the ability of $\hat{\mathbf{P}}$ to estimate \mathbf{P} .

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

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

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^a

chemical	personal exposure distribution				
	lower tertile	1st tertile cutpoint	middle tertile	2nd tertile cutpoint	upper tertile
benzene	-0.3 ^b (0.7) ^c	2.2	-1.5 (1.4)	4.7	-14.4 (21.9)
chloroform	-0.2 (0.2)	0.7	-1.0 (0.3)	1.7	-3.2 (1.9)
<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)
α -limonene	-4.9 (1.6)	7.7	-11.5 (2.7)	16.6	-47.3 (51.1)
methylene chloride	-0.1 (0.5)	1.0	-1.2 (0.6)	2.9	-17.1 (35.7)
α -pinene	-0.9 (0.4)	1.8	-2.6 (0.8)	4.2	-15.8 (20.6)
β -pinene	-0.2 (0.3)	0.8	-1.5 (0.5)	2.7	-10.9 (23.4)
styrene	-0.1 (0.1)	0.5	-0.5 (0.2)	1.0	-2.0 (2.8)
tetrachloroethylene	0.0 (0.3)	0.6	-0.6 (0.4)	1.5	-62.7 (360.4)
toluene	-1.9 (9.9)	12.1	-13.2 (6.4)	25.1	-57.8 (79.8)
trichloroethylene	0.0 (0.1)	0.2	-0.1 (0.2)	0.4	-2.4 (7.5)
<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)

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

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

chemical	personal exposure distribution				
	lower tertile	1st tertile cutpoint	middle tertile	2nd tertile cutpoint	upper tertile
benzene	-0.2 ^b (1.0) ^c	2.2	-0.6 (2.1)	4.7	-3.8 (20.8)
chloroform	0.4 (1.8)	0.7	-0.1 (0.6)	1.7	-0.5 (1.7)
<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)
α -limonene	-0.9 (2.0)	7.7	-1.6 (5.8)	16.6	-13.2 (50.1)
methylene chloride	0.0 (0.3)	1.0	1.1 (10.2)	2.9	3.9 (74.2)
α -pinene	0.0 (0.7)	1.8	0.0 (0.9)	4.2	0.8 (10.4)
β -pinene	0.3 (0.8)	0.8	-0.2 (0.9)	2.7	-2.1 (10.2)
styrene	0.1 (0.4)	0.5	-0.1 (0.3)	1.0	-0.8 (3.1)
tetrachloroethylene	0.0 (0.3)	0.6	-0.3 (0.4)	1.5	-55.8 (350.5)
toluene	0.2 (5.2)	12.1	-3.3 (8.2)	25.1	-19.9 (77.1)
trichloroethylene	0.0 (0.1)	0.2	0.1 (0.8)	0.4	-1.7 (7.6)
<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)

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

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

chemical	personal exposure distribution				
	lower tertile	1 st tertile cutpoint	middle tertile	2 nd tertile cutpoint	upper tertile
benzene	-0.2 ^b (0.8) ^c	2.2	-0.8 (1.4)	4.7	-7.5 (21.0)
chloroform	0.2 (1.1)	0.7	-0.4 (0.4)	1.7	-1.2 (1.5)
<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)
α -limonene	-2.1 (1.8)	7.7	-4.4 (4.6)	16.6	-20.8 (48.6)
methylene chloride	0.0 (0.3)	1.0	0.5 (7.9)	2.9	-3.3 (48.2)
α -pinene	-0.3 (0.5)	1.8	-0.7 (0.7)	4.2	-4.8 (9.4)
β -pinene	0.1 (0.6)	0.8	-0.6 (0.7)	2.7	-5.6 (12.0)
styrene	0.0 (0.3)	0.5	-0.2 (0.2)	1.0	-1.2 (2.8)
tetrachloroethylene	0.0 (0.2)	0.6	-0.4 (0.3)	1.5	-60.9 (363.5)
toluene	0.0 (5.7)	12.1	-6.2 (5.9)	25.1	-30.6 (78.6)
trichloroethylene	0.0 (0.1)	0.2	0.0 (0.6)	0.4	-2.0 (7.7)
<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)

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

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

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

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).

Acknowledgments

This research was funded by a STAR (Science to Achieve Results) Grant (R825241) from the U.S. Environmental Protection Agency, National Center for Environmental Research. We also benefited from a grant from the Academic Health

Center at the University of Minnesota. We thank the individuals who participated in the study and acknowledge the contributions of the field team. We also thank the 3M Corporation for donating some of the organic vapor monitors used in this study. The help and support provided by the Minnesota Pollution Control Agency was essential to the success of this project. K.S. was a member of the Division of Environmental and Occupational Health at the University of Minnesota School of Public Health when this study was conducted.

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

ES030607Q



Mike Karbo
Associate Director, Midwest Region
445 Minnesota Street, Suite 1500
St. Paul MN 55401
karbom@api.org

Filed electronically: OAH.Webmaster@state.mn.us.

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

September 22, 2023

Re: American Petroleum Institute Comments on planned amendments to air quality rules, Minnesota Rules Chapters 7002 (Permit Fees), 7005 (Definitions and Abbreviations), 7007 (Permits and Offsets), 7008 (Conditionally Exempt Stationary Sources and Conditionally Insignificant Activities), 7011 (Standards for Stationary Sources), 7017 (Monitoring and Testing Requirements), and 7019 (Emission Inventory Requirements).

Revisor number: R-04599

To Whom It May Concern:

The American Petroleum Institute (“API”) is pleased to submit the following comments on planned amendments to air quality rules, Minnesota Rules Chapters 7002 (Permit Fees), 7005 (Definitions and Abbreviations), 7007 (Permits and Offsets), 7008 (Conditionally Exempt Stationary Sources and Conditionally Insignificant Activities), 7011 (Standards for Stationary Sources), 7017 (Monitoring and Testing Requirements), and 7019 (Emission Inventory Requirements). This rulemaking is referred to as the Air Toxics Emissions Reporting Rule published at Revisor number: R-04599 (“Proposed Rule”).

API is the national trade association representing America’s oil and natural gas industry. Our industry supports more than 11 million U.S. jobs and accounts for nearly 8 percent of U.S. Gross Domestic Product. API’s approximately 600 members, from fully integrated oil and natural gas companies to independent companies, comprise all segments of the industry. API’s members are producers, refiners, suppliers, retailers, pipeline operators, and marine transporters, as well as service and supply companies, providing much of our nation’s energy. API was formed in 1919 as a standards-setting organization and is the global leader in convening subject matter experts across the industry to establish, maintain, and distribute consensus standards for the oil and natural gas industry. API has developed more than 800 standards to enhance operational safety, environmental protection, and sustainability in the industry.

API has numerous members that will be affected by these planned amendments to Rules Governing Air Quality, Minnesota Rules, chapters 7002, 7005, 7007, 7008, 7011, 7017, and 7019 by way of emissions guidelines, reporting, and corresponding state standards implemented under this action. For example, there are API member companies that own and operate refineries and distribution terminals which would be subject to these proposed regulatory standards. Thus, API and its members will be impacted by the regulatory changes that MPCA makes for air toxics program requirements.

We offer the following comments on the Proposed Rule.

1. Air Toxics Reporting Rule is duplicative of the current AERR initiative by EPA. MPCA should be aligned with AERR, therefore ensuring synergy of efforts by regulated sources.

API recommends MPCA align the Air Toxics Reporting rule with the current Air Emission Reporting Requirements (AERR) initiative by the EPA. The proposed amendments to AERR were published August 9, 2023 and may require changes to “current regulations of State, local, and certain tribal air agencies; would require these agencies to report emissions data to the EPA using different approaches from current requirements; and would require owners/operators of some facilities to report additional emissions data.” The proposed amendments will require certain sources to report Hazardous Air Pollutants, criteria air pollutants, and their precursors in addition to other requirements. MPCA’s alignment with AERR will prevent duplicative efforts and ensure consistency across reporting requirements for the state.

Alignment with the federal emission reporting effort will result in a reporting process that minimizes burden on Minnesota facilities while still enabling MPCA to collect accurate and complete data on air toxics. One consistent reporting process will reduce the effort required to reconcile data across multiple reporting formats, protocols, and structures. One reporting process will also result in consistent data reporting across the state, and will not be limited to Anoka, Carver, Dakota, Hennepin, Ramsey, Scott, and Washington counties. Statewide alignment with AERR is beneficial to Minnesota facilities and the MPCA.

2. Air Toxics inventory reporting should be limited to the federal list.

API recommends that Air Toxics Inventory Reporting requirements be limited to the federal list of HAPS and Criteria Air Pollutants. There are three substantial challenges that are likely to arise if the Air Toxic Emission Reporting requirements are not limited to the federal list of HAPS and Criteria Air Pollutants. First, Minnesota Statute 116.062(c) currently defines air toxics as “chemical compounds or compound classes that are emitted into the air by a permitted facility and that are: (1) hazardous air pollutants listed under the federal Clean Air Act, United States Code, title 42, section 7412, as amended; (2) chemicals reported as released into the atmosphere by a facility located in the state for the Toxic Release Inventory under the federal Emergency Planning and Community Right-to-Know Act, United States Code, title 42, section 11023, as amended; (3) chemicals for which the Department of Health has developed health-based values or risk assessment advice; (4) chemicals for which the risk to human health has been assessed by either the federal Environmental Protection Agency's Integrated Risk Information System; or (5) chemicals reported by facilities in the agency's most recent triennial emissions inventory.” This expansive list of air toxics creates challenges for facilities in Minnesota that will

have to either develop a method of calculation or directly measure the components for annual emission reporting. The second challenge is that the above-referenced Minnesota Statute allows for air toxics to be added to the list without means for notification to affected facilities. Lastly, facilities would be required to develop methods for accurate reporting of emissions, which in turn implies that facilities would be required to comply with 7019.3020 (Calculating Actual Emissions for Emission Inventory) for each air toxic.

If Minnesota pursues air toxic reporting as defined in Minnesota Statute 116.062(c), MPCA should adopt the list of Air Toxics into rule. This will provide notice for facilities to investigate and develop emission estimation methods and provide accurate and complete emission reporting. It is recommended that Minnesota limits air toxics included in the mandatory emission inventories to the federal list of HAPs and Criteria Air Pollutants, or those finalized in the EPA's AERR.

3. The term “insignificant” should be defined, and thresholds for reporting should be consistent with EPA’s AERR.

API recommends MPCA require reporting for major sources of air toxics consistent with Section 112 (insert correct reference) which will also be consistent with existing Part 61 and Part 63 NEHSAP standards. Alternatively, MPCA must align with thresholds for reporting that are consistent with EPA’s AERR. Additional consideration should be given to air toxics that are not included in the AERR when establishing de minimis thresholds to prevent undue burden for facilities that would be required to report exceedingly small amounts or investigate impurities. Establishing methods for estimating these quantities would be increasingly difficult if facilities would be required to meet the standard set by 7019.3020, which can require performance testing, process studies and modeling, and sampling – if an alternative method must be used, the facility would need to comply with 7019.3100, which requires the facility’s proposed alternative method to be approved by the commissioner every five years:

The owner or operator of an emission reporting facility may propose an alternative method for calculating actual emissions if the owner or operator can demonstrate to the satisfaction of the commissioner either:

(1) that the proposed method is more accurate than the methods in parts 7019.3040 to 7019.3090; or

(2) that none of the methods in parts 7019.3040 to 7019.3090 is technically or economically feasible and the proposed method is accurate.

It should be noted that the additional resources required for emission reporting are significant – performance testing at a source can cost \$5-10,000 per pollutant per source. Establishing a targeted list of air toxics with minimum thresholds would reduce the significant burden that would be required to calculate and report accurate emissions.

4. MPCA should incorporate alternative emission estimation methods for air toxic emission reporting.

API recommends an alternative process for calculating air toxics. Minnesota currently provides a hierarchy for methods of calculations for criteria pollutants; (1) Continuous Emission

Monitor Data; (2) Performance Test Data; (3) VOC Material Balance, Mercury Material Balance, SO₂ Material Balance, Emission Factor, Enforceable Limitations; (4) Facility Proposal. These methods have defined procedures within 7019, which will result in significant reporting burden.

The emission estimations required for reporting will be significant because the number of pollutants is large – the current list of pollutants for Minnesota air toxic emission inventory includes 500 components, with 187 of those being federal HAPs. Existing calculations are not available for all of those components, and facilities may not have the information required to calculate the emissions. For components that have existing reporting requirements for federal standards, the same methodologies should be accepted for Minnesota emissions reporting. For components that may not meet this criterion, to reduce the burden, facilities should be able to use engineering and process knowledge to complete estimations. These estimates should not be required to comply with 7019.3100, which requires the facility to submit the proposal to the commissioner for approval every five years. Exclusion of this requirement would ease the burden for facilities and MPCA.

5. Timing of inventory should be no earlier than AERR.

API recommends MPCA's Air Toxic Emission Inventory Reporting align with EPA's Air Emission Reporting Requirements for the reporting timelines, with mandatory reporting starting consistent with the final AERR rule. Reconciliation of report timing will allow for the advancements of reporting tools or software and will prevent developments that may conflict with AERR.

6. MPCA should incorporate certifications for Air Toxic Reporting if it wishes to include data quality assurance.

MPCA has indicated interest in pursuing a pathway for data quality assurance. If they do so, the method of achieving this should be a requirement for certifications upon submittal of air toxic emission reporting similar to that of the emission inventory under 7019.3000 Subpart 1(A), with the exclusion of the language specific to fee payment. This would be consistent with requirements in other states for Air Toxic Reporting (LAC 33:III.5107.A.2 and N.J.A.C. 7:27-21.8(a)). If MPCA requires certification for air toxic emission reporting, MPCA should additionally allow for error correction consistent with that detailed in 7019.3000 Subpart 2, with the exclusion of the language specific to emission fee correction.

Thank you again for the opportunity to submit these comments on the Proposed Rule. Please do not hesitate to contact me if you have questions or need more information.

Sincerely,

Mike Karbo
Associate Director, Midwest Region
American Petroleum Institute