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Silicone Wristbands as Passive Samplers for Quantitative Measurement of Wood Smoke Exposure

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Silicone Wristbands as Passive Samplers for Quantitative Measurement of Wood Smoke Exposure

Thesis Paper

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Abstract

Human exposure to biomass smoke is a health concern worldwide. Although many studies have measured particulate matter in wood smoke as a health concern, exposure to mutagenic and carcinogenic volatile and semivolatile compounds remains understudied. This research introduces a novel method of quantitative measurement of exposure to these compounds using silicone wristbands. The study developed a method to extract analytes of interest from the wristbands and quantify a few volatile organic compounds and polycyclic aromatic hydrocarbons with known ill health effects, and then performed linear regressions between extracted levels and exposure to those analytes using controlled exposure studies. Results indicate good and statistically significant correlations between recovered analytes from the wristbands and average exposure over time, making these wristbands a potentially useful tool for quantitatively testing exposure to wood smoke.

Chapter One: Introduction and Background

Introduction

Human exposure to wood smoke remains a major health concern both domestically and internationally[1,2]. Although hazardous industrial emissions receive the bulk of environmental attention, wood smoke emissions pose serious health risks through exposure to compounds both volatile and solid. This is especially true in rural areas and developing communities that primarily rely on wood stoves or cooking fires for heat and food preparation, or in communities that experience air quality problems from wild fires.

Though solid compounds in the form of particulate matter (PM) have been the main focus of research in wood smoke exposure, volatile and semivolatile organic compounds, such as polycyclic aromatic hydrocarbons (PAHs) or other small aromatic volatile organic compounds (VOCs), also pose risks with their carcinogenic and/or mutagenic properties.

Measuring individual exposure to these volatilized compounds poses difficulties. Previous techniques that have been employed, such as breath condensate, blood analysis, urine analysis, and skin wipes, are at best a hassle and at worst invasive. Additionally, inconsistencies in metabolism between subjects means these techniques are usually more qualitative than quantitative. Mechanical passive and active samplers have also been used, but are often expensive, fragile, and difficult to carry. This research proposes and tests a novel passive sampler, a silicone wristband, for the measurement of carcinogenic VOCs in wood smoke. The wristband is convenient, lightweight, and analytically sound, as well as being already familiar to potential test subjects.

This research develops a method for using silicone wristbands to quantitatively measure carcinogen exposure from wood smoke, and then tests that method against controlled exposure in a closed wood smoke chamber.

Background Information

Composition and Effect of Wood Smoke

Wood smoke is composed of hundreds of distinct chemical species[3]. Wood smoke's health effects have been thoroughly documented; inhalation of wood smoke components causes inflammation, oxidative stress, and allergenic and carcinogenic effects[4]. Numerous studies show that large-scale vegetation fires in proximity of population groups have correlations to increased emergency room and physician visits related to respiratory symptoms and diseases, and exacerbation of respiratory disease like asthma or COPD[4]. Wood smoke exposure has also been associated with increased mortality[5].

One of the most abundant involatile components of wood smoke is levoglucosan, a sugar anhydride that is considered unique to woodsmoke, as it originates from the pyrolysis of cellulose[6,78]. Levoglucosan exists in woodsmoke as a primary component of PM[9]. Most studies linking health effects to wood smoke are done using measurement of PM, but these measurements alone do not take into account the impact of lower-concentration components, such as PAHs and VOCs.

PAHs are released by the incomplete combustion of biomass, and are a common low-concentration component of woodsmoke[10], especially under low-flame smoldering conditions[11]. PAHs come with unfortunate health impacts; many are known carcinogens and mutagens. Effects range from the acute—vomiting, respiratory symptoms, oxidative stress—to the longer

term—low birth weight and unfavorable pregnancy outcomes, pulmonary and respiratory disease, DNA damage, and increased risk of many different cancers[12]. In general, PAHs with high molecular weight, such as pyrene, tend to be more carcinogenic and mutagenic, while PAHs with low molecular weight, such as naphthalene, tend to be more toxic in nature[13]. The more toxic PAHs tend to fall into the category of volatile organic compounds (VOCs) or semivolatile organic compounds (SVOCs).

Wood smoke is primarily sourced from wildland burning, where exposure is a concern for people living in the vicinity of wildfires, but especially for firefighting personnel. Exposure of the latter group has been understudied, despite their increased risk through long hours of exertion in close proximity of the fires. Another significant source of woodsmoke is heating stoves and cooking fires[2]. Because these stoves are used in enclosed or partially enclosed spaces, they often have an immediate impact on human health. In rural areas, where wood is a primary fuel for cooking and/or heating, wood smoke exposure and its associated health effects are of particular concern.

Most studies of the effects of woodsmoke on human health have been epidemiological, either large-scale survey-style studies that rely on self-reported data, or studies on individuals who already have chronic respiratory illnesses[4,14,15]. Few studies have been done on individual health impacts on otherwise healthy individuals[14]. The limited number of studies means that knowledge of health effects is limited to extreme cases, of very high exposure or extreme effect, with little specificity. For individual effects to be measured, however, individual exposure must be measurable.

Current Sampling Methods

Several sampling methods have been used to test human exposure to wood smoke. Biological sampling methods include blood samples, urine samples, skin wipes, and breath condensate, among others. In all cases, the nature of biological sampling requires several regular timely samples[16]. Such methods are typically costly and often invasive and inconvenient. If samples are collected by a researcher, participants are less available and more unlikely to participate to begin with. If samples are taken by a participant, there is risk of inaccurate sampling and contamination. Furthermore, analysis of biological samples faces the added challenge of parsing metabolomics, as even physically similar individuals metabolize chemical exposures at different rates and to different extents. In the case of wood smoke, many important analytes are converted into completely different compounds, or confounded by similar or identical compounds introduced by diet[17,18]. Finding an adequate number of subjects willing to submit to biological sampling is difficult, but finding an adequate number to then draw significant conclusions from results is even more challenging.

Passive samplers, unlike active sampling methods, are often cheaper to both purchase and process, less invasive, and more convenient. The core difficulty of passive samplers tends to be maintaining consistent and reliable results. Passive samplers must be able to pick up very low levels of analytes, and therefore often require long exposure periods in order to be effective. Therefore passive samplers for human exposure must be very portable for ease of use, exposed to the ambient air, and relatively simple to analyze.

Many passive samplers are currently in use to measure exposure to air pollutants and particles. Some, like the Radiello passive sampler or the Analyst passive sampler, collect air samples through a membrane and onto an adsorbant bed, often made of charcoal[16]. Such devices

have changed over time to be more efficient and less expensive, but the overall design has largely remained the same for the last fifty years[16]. Such devices are effective, but fragile, and sometimes expensive to deploy, especially to a statistically significant number of people. A more technological active sampling option is to use laser-aided particle counters, such as Dusttrak personal aerosol monitors or the Lighthouse Solair portable particle counters. These counters are more sensitive and reliable, but tend to be bulky and awkward to carry around. The awkwardness tends to hamper subjects' normal movement, leading to a skewed representation of woodsmoke exposure, as well as subject noncompliance with sampling protocols. Furthermore, they are significantly more expensive than biological sampling methods.

Many research groups are attempting to develop smaller and simpler passive sampling devices. Such devices show comparable performance to traditional passive sampling methods, particularly those made of silicone[19].

Silicone Personal Sampling Setups

The idea of using silicone wristbands as passive samplers has gained headway in recent years due to the work of Kim A. Anderson at Oregon State University[20,21]. The company MyExposome, headed by two researchers associated with Anderson's group, claims to be able to qualitatively test for over 1400 discreet chemical species[22]. Examples of analytical research conducted with these wristbands include testing for pesticide exposure in Senegalese farmers and children's exposure to flame retardants in an American elementary school[23,24]. In this work, we use the same tactic, employing silicone rubber wristbands as passive samplers, to study exposure to woodsmoke on an individual basis.

Silicone rubber is an optimal material for this purpose[25]. Some research is already available on their consistency as samplers[25]. One study found that of thirteen polymers, silicone

rubber picked up the widest range and largest concentration of hydrophobic organic contaminants. Silicone passive samplers have also been tested quantitatively for exposure to PAHs, although their use has so far been restricted to aqueous environments[26]. MyExposome claims to be able to test qualitatively for several of the VOCs of interest to this project, and the ones that remain untested have structures analogous to previously tested compounds[22].

Combined with the convenience of a lightweight wristband, silicone rubber is a fitting sampler to study individual exposure to woodsmoke.

Chapter Two: Experimental Methods

Extraction and Quantification of Analytes from Exposed Wristbands

This study focused on quantitatively determining exposure to the analytes in Table 1.

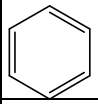
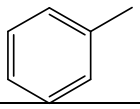
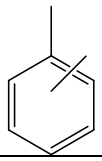
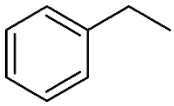
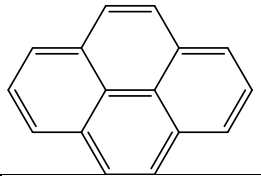
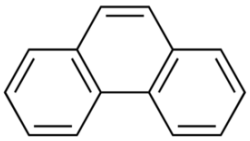
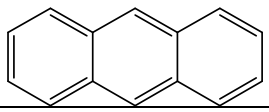
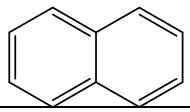
Compound	Structure	Mass (g/mol)	Reference
Benzene		78.11	[1,3,20]
Toluene		92.14	[3,20]
Xylenes		106.16	[3,20]
Ethyl Benzene		106.17	[3,20]
Pyrene		202.25	[20]
Phenanthrene		178.23	[3,20,27]
Anthracene		178.23	[3,20,27]
Naphthalene		128.17	[3,27]

Table 1: The analytes of interest.

These analytes are all VOCs and/or PAHs with known ill health effects and are byproducts of the incomplete combustion of wood or biomass.

Wristband Specifications

Wristbands were used from multiple sources, but were all entirely made of silicone rubber dyed with unreactive dyes. Wristbands were cleaned by submerging in successive two-hour solvent baths, placed in an orbital shaker at 30°C and 75 rpm. The solvent baths consisted of three rounds of ethyl acetate and hexane (1:1 v:v, 30 mL per wristband), and two rounds of ethyl acetate and methanol (1:1 v:v, 30 mL per wristband). This removed contaminants from production and transport, as well as any loose low molecular weight siloxane compounds in the wristband's structure. The cleaned wristbands were kept at room temperature in a sealed jar with a Teflon-lined lid until use. When ready for use, wristbands did not come in contact with bare skin and were exposed to no more ambient air than absolutely necessary. After exposure, wristbands were stored in individual amber glass 100 mL jars with Teflon lids at approximately -15°C until extraction.

If wristbands were exposed to wood smoke (as opposed to those which were used for method development and optimization with standard concentrations), they were briefly rinsed after exposure and before extraction of analytes, twice in distilled water and once in isopropyl alcohol. This wash removed PM on the surface of the wristbands and other incidental debris.

Extraction of Analytes

After being washed for debris and before extraction, each wristband was spiked with 5 µg of an internal standard, naphthalene d-10, to account for losses in extraction, sample manipulation, or evaporation, either volatilizing during the extraction process or evaporated off during the evaporation process.

Extraction of the wristbands took place in the same jars in which they were stored, in order to minimize loss from contact with the glass. 100 mL of ethyl acetate was added to the jar,

which was placed on an orbital shaker for two hours at room temperature and 75rpm. After two hours, the extract was removed and replaced with an additional 100 mL of ethyl acetate for another two hours. These were combined into an Erlenmeyer flask for evaporation.

Each extract was evaporated down to 1-3 mL under a stream of cool, filtered air, and placed in a conical vial. Erlenmeyer flasks were rinsed with an additional 3-5 mL of ethyl acetate that was also added to the conical vial, and then evaporated down to 2 mL.

Analysis by Gas Chromatography-Mass Spectrometry

Extracts were run on GC-MS. The gas chromatograph used helium carrier gas, splitless injection (2µL), and a temperature gradient to separate the analytes of interest. The gradient begins at 33°C, holding for five minutes, then increasing at a rate of 10°C/min to 200°C, holding for one minute, and then increasing again at a rate of 10°C/min to 300° and holding for another five minutes. The method takes approximately 37 minutes. The flow of gas is constant at 1mL/min, and the mass spectrometer's electron impact mode is set to 70 eV. This method is adapted from ones found in the literature[23–25,28,29] to include the full range of analytes of interest. Peaks were located for each analyte using ion extraction of that analyte's standard ion at the mass specified in Table 1, and areas under the peaks were compared to a calibration curve run previously. Ethyl benzene and o-xylene emerged at the same time on the spectrograph, and the two were grouped along with the other xylenes.

Standards were prepared in 1.0 mL of ethyl acetate (VWR Chemical, 99.5%) having 0.1-35µg of each analyte: benzene (VWR Scientific, 99.8%), toluene (JT Baker Chemicals, 99.5%), xylenes (Fischer Scientific, 99.9%), naphthalene (Acros Organics, 99.0%), anthracene (Sigma-Aldrich, 99.0%), phenanthrene (Sigma-Aldrich, TraceCERT certified reference), and pyrene (Sigma-Aldrich, TraceCERT certified reference), and 5µg of naphthalene d-10 (Sigma-Aldrich,

≥98%). The GC-MS was calibrated using these standards and integrated extracted ion chromatograms at the masses specified in Table 1. The relative area of the standard ion to that of naphthalene d-10 was plotted as a function of standard concentration.

Recoveries from non-exposed spiked wristbands were calculated by comparing the area of the standard ion from the wristbands (multiplied by two account for the dilution to 2mL) to that of an equivalent standard run the same day. The resulting proportion was considered the percent recovery for the purposes of method development.

Mass of each analyte from exposed wristbands, spiked with the internal standard, were calculated by comparing the area of the standard ion relative to the area of the internal standard Naphthalene-10. Masses were then calculated using the calibration function of standard concentration.

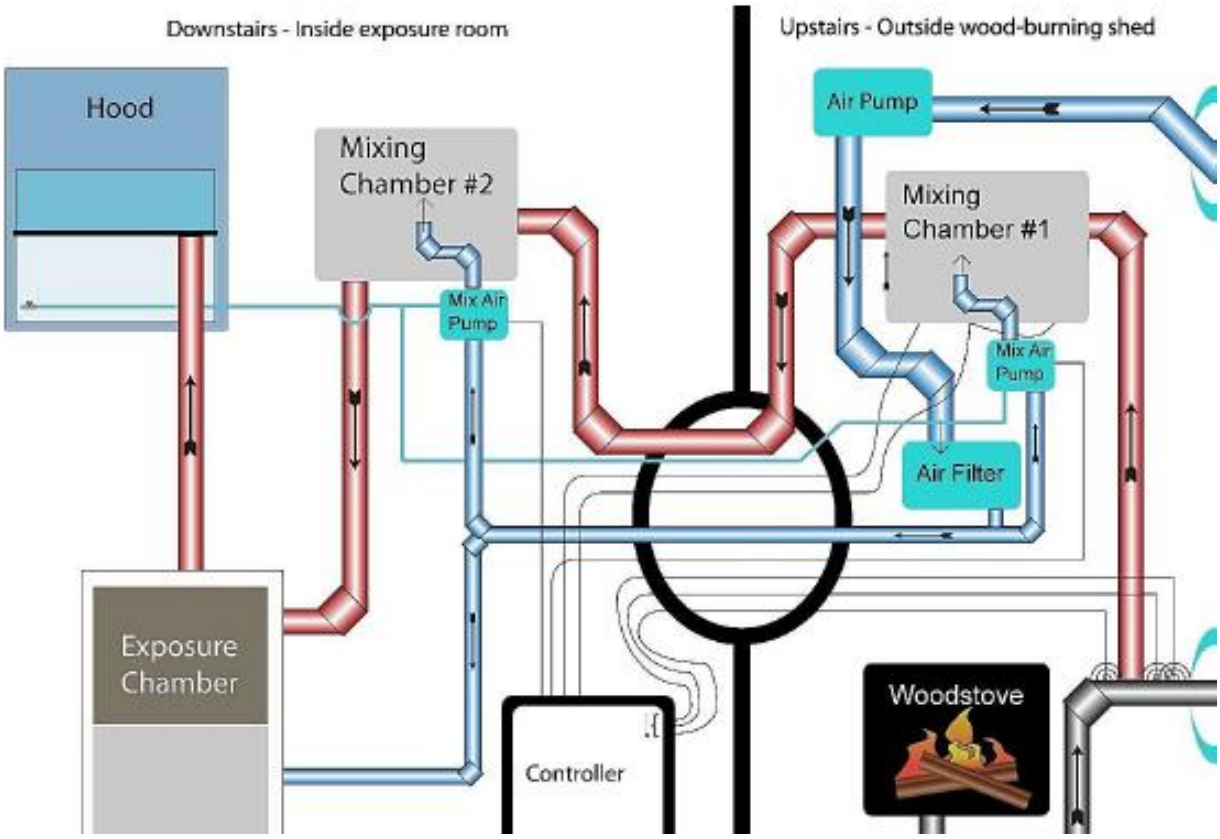


Figure 1: Diagram of the Exposure Chamber.

Exposure of Wristbands to Wood Smoke in Controlled Exposure Chamber

Experimental Design

For this research, controlled exposure was facilitated by the exposure chamber built and maintained by the Center for Environmental Health Sciences at the University of Montana.

The chamber consists of a sealed box into which wood smoke is piped from a woodstove, located in a separate room. Concentration of the smoke's $PM_{2.5}$ is monitored by an active sampling program, and concentration of the $PM_{2.5}$ is modified using air pumped into the mixing chambers of the system. A diagram of the exposure chamber is shown in Figure 1[30].

By controlling air flow into the mixing chambers, the exposure chamber could aim for particular concentrations of $PM_{2.5}$, although actual averages varied from the aim slightly. Actual averages were recorded for each test. Flow rate through the exposure chamber is between 10-20L/min,

Trial #	**length of exposure**	**Aimed-for $PM_{2.5}$ concentration (mg/m^3)**	**Actual $PM_{2.5}$ concentration (mg/m^3)**	**Notes**
1	2hrs	3.0	5.20	Vent malfunction; aimed conc. changed to compensate
1	4hrs	3.0	4.24	
2	2hrs	5.0	4.60	Repeating first 2hr test to compensate for unusual data due to malfunction
3	2hrs	3.0	2.20	
3	4hrs	3.0	2.90	
4	2hrs	4.2	3.00	
4	4hrs	4.2	3.10	
5	2hrs	3.0	3.14	*No PTR-MS measurements.*
6	2hrs	1.5	1.54	*"*
6	4hrs	1.5	1.54	*"*
7	2hrs	0.75	0.87	*"*
7	4hrs	0.75	0.83	*"*

Table 2: Description of exposure trials in exposure chamber.

closer to 20L/min unless the air in the air-smoke mixture is decreased to increase smoke concentration. To establish a background reading on the wristbands, a few wristbands were placed in the lower part of the exposure chamber (see Figure 2) and exposed only to fresh air for the duration of the exposure trials.

The trials were varied in length of exposure time in circumstances as close to constant as possible, in order to test how much analytes collected over time, and whether the total amount of analyte was correlated to the total time exposed. Trials were also varied in amount of exposure, at levels found commonly in wildfire situations (although higher than levels typical of indoor wood stoves), in order to test how the total mass of analyte collected correlated with the level of exposure.

Wristbands were hung from steel hooks inside the exposure chamber, not touching the walls or rack inside, to minimize exposure to analytes stuck to the chamber itself and to maximize surface area exposed to the smoke. For tests 1-4, in addition to PM concentration, the analytes of interest were also measured via Proton Transfer Reaction-Mass Spectrometry.

Proton Transfer Reaction-Mass Spectrometry Analysis

Proton Transfer Reaction-Mass Spectrometry (PTR-MS) is a real-time, highly sensitive mass spectrometry technique, with a detection limit that can extend down to 1pptv. The PTR-MS instrument used in this research, kindly lent by the Lu Hu group at the

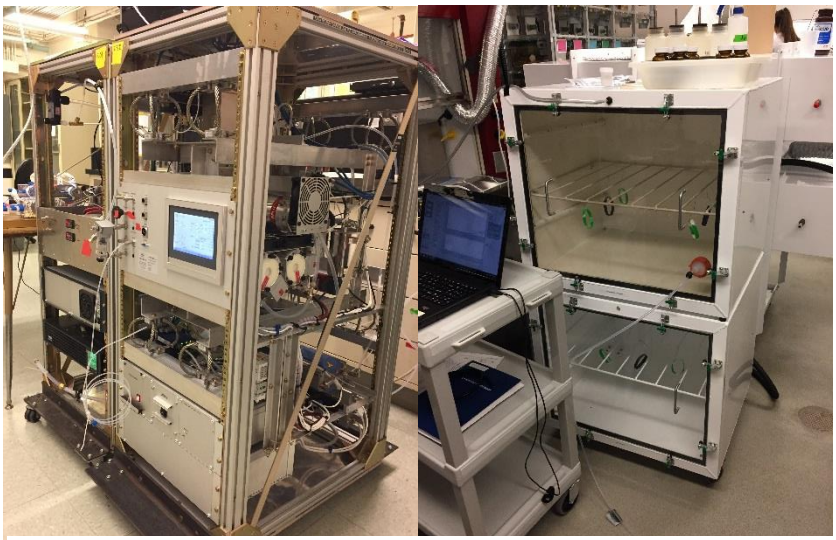


Figure 2: The PTR-MS (left), and the exposure chamber (right).

University of Montana, is a PTR-TOF-MS 4000 (IONICON Analytik).

The intake of the PTR-MS was inserted through a sealed port in the door of the exposure chamber. Intake came through a 2 µm filter to remove PM and ash. Concentration measurements of the analytes of interest were taken and recorded every thirty seconds during the time of exposure. Total flow intake was 0.7-1.1 L/min, a fraction of which (20 cm^3) was run for analytes. PTR-MS was calibrated after each exposure trial using standard VOC gas dynamically diluted into a catalyst-generated zero air, sourced from the exposure chamber when no smoke was present. Background measurements were taken before, after, and approximately every ninety minutes during each trial. During background measurements, detection of analytes dropped to zero. To compensate for this, points along the curve were approximated using values between the points when detection stopped and resumed.

Figure 3: Close-up of exposure chamber, showing wristbands and the PTR-MS intake with filter.

Because the PTR-MS differentiates between molar masses but not chemical structures, for the purposes of this research, all o-, m-, and p-xylene as well as ethyl benzene were collected and analyzed together and grouped as "xylenes," and anthracene and phenanthrene were collected and analyzed together. Measurements taken from the PTR-MS were plotted as functions of parts per billion (ppb) of each analyte over time for each trial. The average mass of each analyte detected by PTR-MS over time was taken, as well as the total mass of each analyte the wristband was exposed to during the trial, found by integration under the plot for the time of

exposure. The plots were also integrated at five minute intervals for the last thirty minutes of each wristband's exposure.

Predicted Exposure from Correlations

Tests of linear regression were conducted between the measurements of exposure from the PTR-MS and the total mass recovered from the wristbands in trials 1-4 to find correlations, if any existed. Regressions were conducted with the y-intercept set to zero, as zero exposure was expected to yield no analyte on the wrist band. Using the best correlations, approximate exposures were predicted for wristbands in trials 5-7, with error propagated using standard uncertainty from those correlations. Predicted values were checked against correlations drawn between the best measurement of exposure for each analyte and the average measured $PM_{2.5}$ for each trial.

Chapter Three: Effectiveness of the Extraction Method

Recovery of Analytes from the Wristbands

The first step in evaluating the effectiveness of the extraction method was measuring the recovery of analytes from non-exposed spiked wristbands. Extraction effectiveness was tested in three iterations of 4-5 different spikes. As mentioned above, recovery from these wristbands was calculated from the quotient of the area of the analyte's standard ion as recovered from the wristband, and the area of the analyte's standard ion in a standard of equivalent mass run on the same day. Outliers were tested for by q-test and removed from datasets as appropriate. The averages of those recoveries are in Table 3.

Analyte of Interest	**Average % Recovery (A_x/A_{stdx} x 100)**	**Standard Deviation**
Toluene	39.4	31.3
Xylenes	75.3	21.5
Naphthalene	134.2	18.7
Phenanthrene/Anthracene	55.5	15.1
Pyrene	45.9	17.0

Table 3: Average % Recovery of analytes from spiked wristbands.

Benzene is not included on this table. In early trials, not even trace amounts of benzene were recovered from wristbands, and so it was excluded from further spike testing. The most likely explanation for this is that benzene's boiling point (80.1 °C) and vapor pressure is too similar to the ethyl acetate (77.1 °C) from which it was evaporated, and it was thus volatilized along with the ethyl acetate rather than concentrated.

Based on the results above, we see that recovery is poor for all analytes except for naphthalene, which has an impossibly large recovery that is most likely due to human error. For the purposes of this study, because we are trying to quantify exposure rather than collect all of each of the analytes the wristbands were exposed to, total recovery matters much less than

reproducibility. However, the large standard deviations for these averages suggest that reproducibility is a problem. The extraction and subsequent evaporation process are involved and take several hours, so the introduction of uncertainty to the process is almost inevitable. To determine at what point, evaporation or extraction, and to what extent this uncertainty was introduced, a test was done by introducing mixtures of standards directly to 200mL of ethyl acetate, and evaporating immediately.

Sources of Uncertainty

Evaporation was tested in five iterations each of 4-5 different spikes, with recovery calculated as before and outliers tested for by q-test and removed from datasets as appropriate. It might be expected that average recovery of analytes would be higher than for the entire process, but that was not the case (Table 4).

Analyte of Interest	**Average % Recovery (A_x/A_{stdx} x 100)**	**Standard Deviation**
Toluene	24.1	11.5
Xylenes	75.2	32.8
Naphthalene	102.9	35.3
Phenanthrene/Anthracene	116.2	26.4
Pyrene	110.1	25.5

Table 4: Average % Recovery of analytes from spiked evaporants.

While the larger PAHs, phenanthrene, anthracene, and pyrene, do show higher recoveries for the evaporation than for the entire method (albeit improbably high), recoveries for the other three analytes are actually lower, and the standard deviation for all averages except for toluene is much higher. Upon further analysis, toluene also presents a pattern when average percent

recoveries are plotted against the concentrations of their respective spikes (Figure 4). The mass

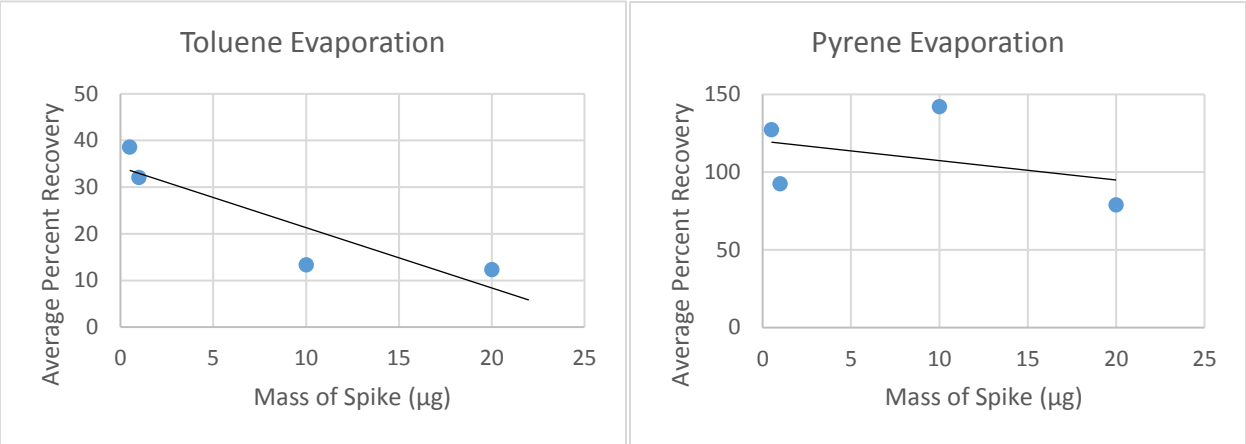


Figure 4: Plots of percent recovery of analyte given spikes of a particular mass. Toluene (left) shows a weak but clear inverse relationship, while the other analytes, such as Pyrene (right) show no such correlation.

of toluene present in the spike is inversely related to the amount recovered off of the wristband. No other analyte showed such a pattern; in fact, recoveries were generally uncorrelated and messy (Figure 4).

When the same tactic—plotting mass of the spikes against the corresponding percent recoveries—is applied to the extraction method trials, the patterns that emerge are more distinctive. Again, toluene shows an inverse relationship between the mass in the spike and the mass recovered off the wristband, as do the xylenes, while the larger PAHs, phenanthrene/anthracene and pyrene show direct relationships (Figure 5). Naphthalene is the notable exception, showing little trend or correlation.

The trends in the smaller VOCs might be explained by their relatively low boiling points. It's clear that a significant portion is lost to evaporation, but the trend may indicate that as concentration, and therefore vapor pressure, decreased, less mass of both was lost. The lack of trend and consistency in the naphthalene recoveries is more puzzling, but may be due to naphthalene's relatively high vapor pressure, which allows it to sublimate at room temperature, making its volatility a little more unpredictable.

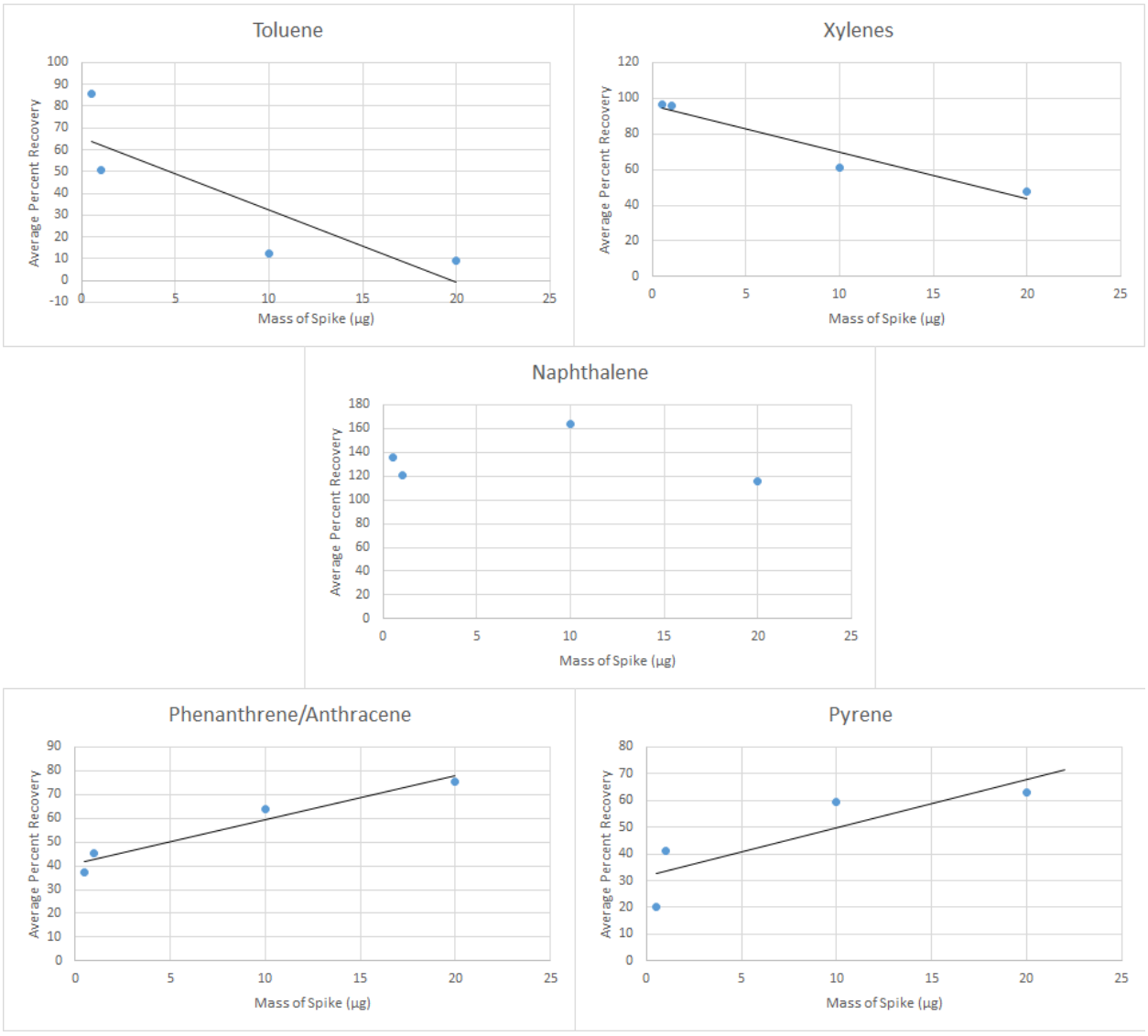


Figure 5: Relationships between average percent recovery and the orignal mass of the spikes for each analyte.

Evidently, likely because of the lack of control over temperature and airflow speed in the described method, the evaporation step is the source of the most uncertainty in method development and the greatest losses in recovery of volatile analytes. As for why extraction showed patterns that evaporation did not, it is possible that spiked mixtures for evaporation were improperly mixed, and the uneven loss of analyte reflects a lack of homogeneity in the evaporant. If that is the case, then it makes sense that patterns emerged in the entire extraction that were not present in the evaporation step; the spikes on the wristbands had time to soak into the structure of the silicone, and therefore the extracted evaporant was much more homogenous. This would also explain the relatively low recoveries of the larger PAHs from the entire extraction as compared to the evaporation step. Most likely, the large nonpolar PAHs were not completely extracted by the slightly polar ethyl acetate, and a portion of the spike was left behind in the structure of the silicone. Thus the recovery of the PAHs, much slower to volatilize than the smaller VOCs, show a direct relationship to the mass of PAHs in the corresponding spike.

These trends, while interesting, underline that the recovery of analytes cannot be reliably measured against an outside standard; the internal standard must be used in order to control for unpredictable evaporation loss, as will be seen in the next chapter. Furthermore, better recoveries and reproducibilities could likely be achieved if deuterated standards were used for each target analyte, rather than relying on naphthalene d-10 as the sole internal standard.

Chapter Four: Results of the Exposure Trials

Correlations Between PTR-MS Measurements and Extracted Analytes

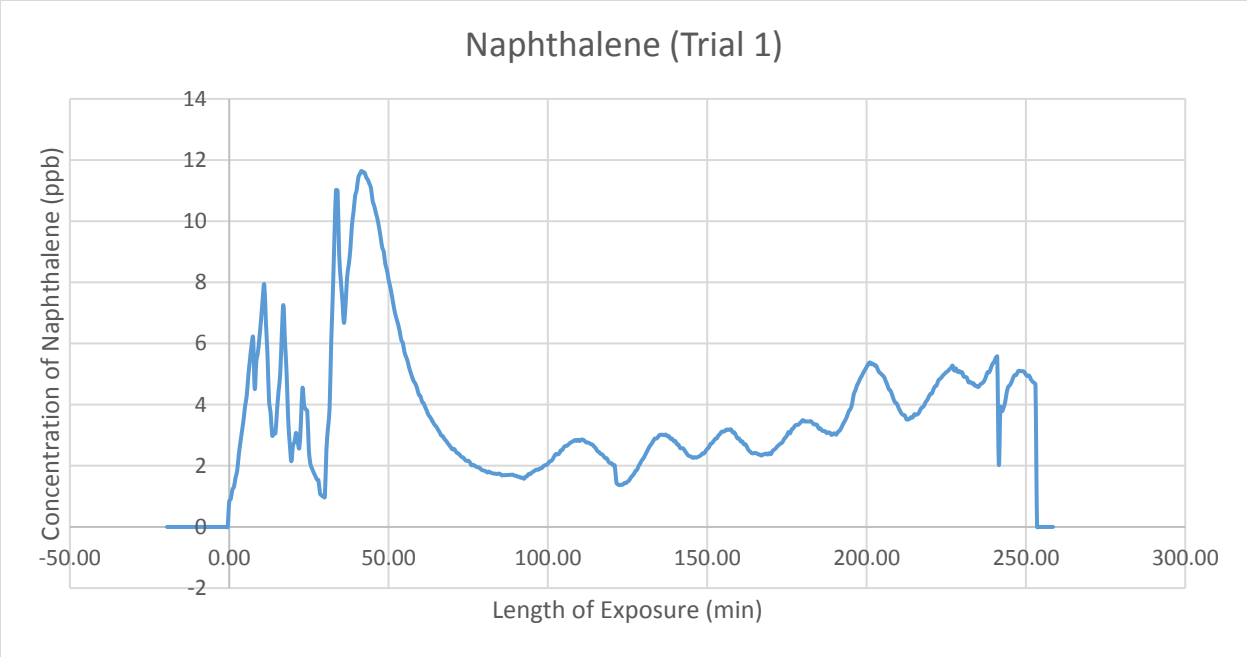


Figure 6: Naphthalene measured over four hours by PTR-MS in the exposure trial done on April 25th (avg. PM: 4.24 mg/m3). All plots of PTR-MS data can be found in Appendix A.

The following measurements of exposure were gleaned from the PTR-MS data collected for each analyte and each exposure trial: time-integrated exposure over the full length of the trial (referred to as "total"), average exposure over time, and time-integrated exposure after the last thirty, twenty-five, twenty, fifteen, ten, and five minutes of exposure. Each measurement was compared to the amount of analyte extracted from the wristband exposed during the trial to check for possible correlations. The extracted measurements were corrected by the internal standard as outlined in Chapter Two, by comparing the area under the standard ion to the area under the naphthalene d-10 spike (A_x/A_{IS}). Recovered masses were then calculated based on the internal standard calibration curve. Phenanthrene and Anthracene were not included in these results, because the recovered masses were below the limit of detection for the GC-MS. Since

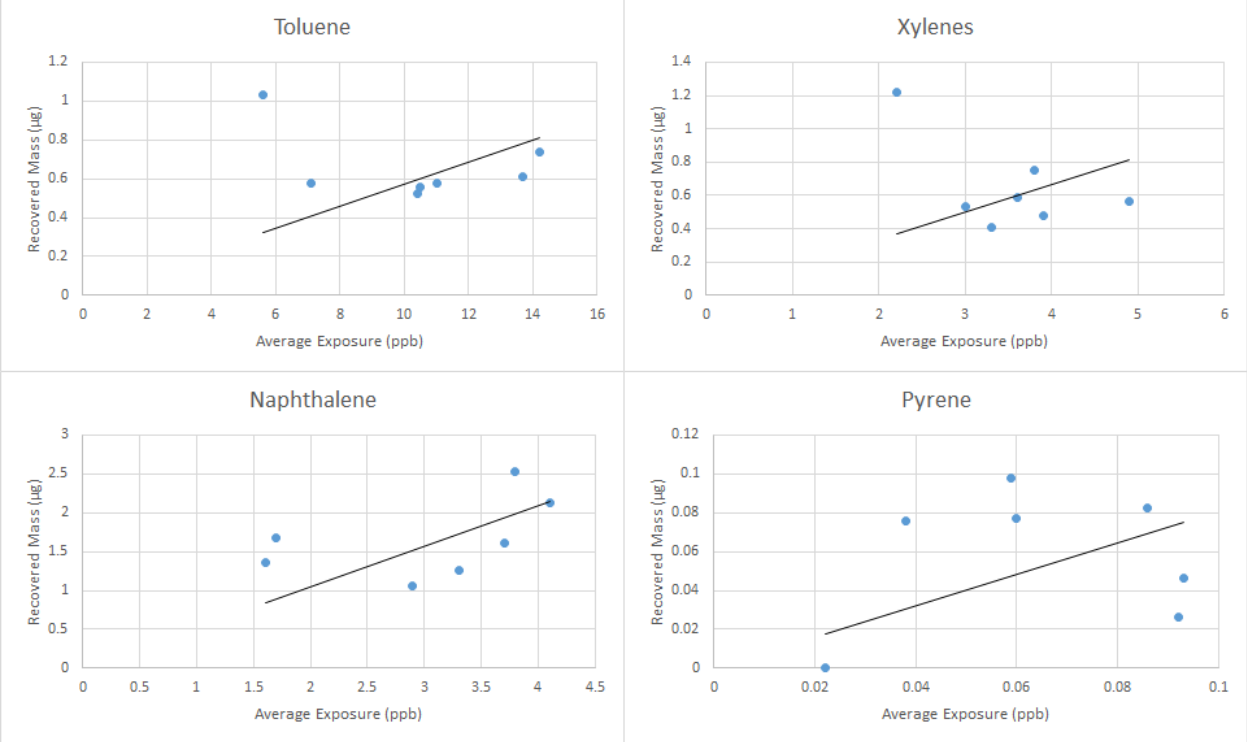
only trace amounts of the two compounds were present in the exposure chamber (see Figures A1-A4 and Tables A1-A4, Appendix A), this is not entirely unsurprising.

Correlations were forced through the point (0,0) because, as expected, the wristbands exposed to only fresh air, no smoke, showed no recovery of the analytes of interest. No exposure outputs no recovery.

R-Square values	*Total expos.*	*Avg. expos.*	*30min*	*25min*	*20min*	*15min*	*10min*	*5min*
Toluene	0.725	0.821	0.726	0.682	0.616	0.556	0.511	0.501
Xylenes	0.573	0.746	0.715	0.683	0.640	0.609	0.592	0.590
Naphthalene	0.885	0.917	0.877	0.871	0.864	0.854	0.838	0.821
Pyrene	0.703	0.709	0.706	0.705	0.705	0.698	0.691	0.708

Table 5: R-Square values for linear regressions between PTR-MS measurements of exposures and recovered masses of analytes.

For each analyte, the strongest correlation was found between the extracted analytes and the average exposure (although correlations to each measurement of pyrene exposure were approximately equivalent). The best of these correlations was naphthalene's, where 91.7% of the



variance between extracted naphthalene and average measured naphthalene can be accounted for by correlation (Figure 7). The weakest average correlation was between pyrene measured and pyrene extracted, where 70.9% of the variance can be accounted for by correlation. However, in every average correlation, the p-value of the linear regressions were less than the significance level of the regression's F-test, so the correlations can be considered significant.

Although the correlations of total exposure and the correlations of average exposure are related and therefore naturally close to each other, correlations between analytes and either total exposure or the last few minutes of exposure were weaker than average correlations. The most likely explanation is that the analytes of interest were absorbed and volatilized off of the wristbands in an equilibrium. If the equilibria were fairly fast, we might expect to see a strong correlation between the mass of analytes extracted and the mass of analyte each wristband was exposed to in the last five, fifteen, or thirty minutes of exposure, but for each analyte, the correlations are weaker in the last few minutes of exposure, not stronger. The adsorption-desorption kinetics must be relatively slow.

The plots shown in Figure 7 introduce some interesting ideas. For toluene and xylenes in particular, it's clear why a correlation appeared, as most of the points fall along a fairly linear path. Less clear is the point farthest to the left on these plots, both of which correspond to the two-hour portion of Trial 3 (see Appendix B for all recovered masses). Although this point does not appear out of trend on the plots for naphthalene and pyrene, toluene and xylenes are chemically similar enough that a difference in the evaporation process could affect them but not naphthalene and pyrene. Alternatively, this pattern could be reflective of the pattern identified in Chapter Three, where smaller masses of toluene and xylenes return with higher recoveries. Limited by the number of trials, it's difficult to say for certain.

Naphthalene shows the strongest correlation both mathematically and visually. This is hardly surprising, given our internal standard is naphthalene d-10, and serves to underline that in future studies best practice would involve deuterated internal standards for all analytes of interest. Pyrene gives the weakest correlation. This is also unsurprising, given that the average correlation is only the "best" by a slim margin, but despite the potential for error, we may yet find this correlation useful.

Using these data, we can predict with some measure of certainty the amount of these analytes a wristband was exposed to. The potential for error is relatively high, but an approximation is possible. The regression equations were used to calculate estimated average exposure levels for the exposure trials for which the PTR-MS was not used. Error was propagated from each correlation's standard uncertainty. The results are presented in Table 6.

Approx. Exposure	Toluene (average ppb)	Xylenes (average ppb)	Naphthalene (average ppb)	Pyrene (average ppb)
Trial 5 2hr 1	8.31 ± 6.23	3.01 ± 2.62	2.17 ± 1.17	0.0499 ± 0.0534
Trial 5 2hr 2	12.5 ± 5.85	3.07 ± 2.60	2.73 ± 1.11	0.0619 ± 0.0517
Trial 6 2hr	27.5 ± 12.7	8.52 ± 5.69	2.43 ± 1.14	0.0437 ± 0.0549
Trial 6 4hr	42.1 ± 22.3	10.7 ± 7.98	0.496 ± 1.56	0.0873 ± 0.0524
Trial 7 2hr	21.2 ± 8.93	7.13 ± 4.34	1.29 ± 1.35	0.0154 ± 0.0649
Trial 7 4hr	16.0 ± 6.60	4.50 ± 2.52	1.67 ± 1.26	0.0709 ± 0.0512

Table 6: Predicted wristband exposures based on the mass recovered from the wristbands.

These results suggest several things. First of all, note that the first two results are two iterations of the same trial, taken from two different wristbands. For the xylenes, naphthalene, and pyrene, the predicted exposures are relatively similar, showing no statistically significant difference, but the toluene results do differ by about 30%. Likely toluene's volatility is the culprit; inconsistencies in the evaporation step for the two wristbands could cause the toluene to volatilize at different rates in different evaporants.

Secondly it should not be ignored that the error on every result is fairly large, to be expected with correlations that, while evident, are relatively weak. Despite this, however, these predictions are not out of the realm of probability. To check, correlations were also drawn between average $PM_{2.5}$ concentration and average concentration of each analyte measured by the PTR-MS in trials 1-4.

R-Square values	Toluene avg. conc. (ppb)	Xylenes avg. conc. (ppb)	Naphthalene avg. conc. (ppb)	Pyrene avg. conc. (ppb)
$PM_{2.5}$ avg. conc. (mg/m^3)	0.957	0.956	0.980	0.720

Table 7: R-Square values of the correlations between average PM concentration and average analyte concentration from trials 1-4.

Because these correlations are fairly strong (with the exception of Pyrene, which appeared in very low concentrations at any given point during the trials), we can predict the average concentrations of each analyte present in trials 5-7 from the measured $PM_{2.5}$ for those trials.

	Avg. $PM_{2.5}$ (mg/m^3)	**Predicted Toluene (avg. ppb)**	**Predicted Xylenes (avg. ppb)**	**Predicted Naphthalene (avg. ppb)**	**Predicted Pyrene (avg. ppb)**
Trial 5 2hr	3.14	9.23 ± 4.04	3.10 ± 0.910	2.67 ± 0.521	0.0684 ± 0.0498
Trial 6 2hr	1.57	4.61 ± 15.8	1.55 ± 1.09	1.34 ± 0.581	0.0342 ± 0.0498
Trial 6 4hr	1.54	4.53 ± 16.1	1.52 ± 1.10	1.31 ± 0.583	0.0336 ± 0.0498
Trial 7 2hr	0.87	2.56 ± 21.4	0.859 ± 1.23	0.741 ± 0.628	0.0190 ± 0.0498
Trial 7 4hr	0.83	2.44 ± 21.7	0.820 ± 1.24	0.707 ± 0.631	0.0181 ± 0.0498

Table 8: Predicted average concentrations of analytes based on average $PM_{2.5}$ concentrations.

Because the correlations between average $PM_{2.5}$ concentration and average concentrations of the analytes were not calibrated to very low concentrations, as $PM_{2.5}$ drops below $1mg/m^3$ (or $2mg/m^3$ in the case of toluene and pyrene), the errors get large and unwieldy. That having been said, in most cases, no statistically significant differences are observed between the average values calculated from $PM_{2.5}$ and those calculated from wristband

extractions. Whether the recoveries predicted by the wristbands are specific enough to be useful, even with these correlations, will be discussed in the next chapter.

Chapter Five: Discussion of Results

Are Wristbands a Valid Source of Quantitative Data?

Silicone wristbands have been used for qualitative exposure data in a variety of situations, but this study aimed to determine whether they would make a useful tool for collecting quantitative data from wood smoke exposure. Having optimized the extraction method to the best of our ability and worked around equipment limitations on the evaporation front, this research suggests that the answer is yes, with some caveats.

The first caveat comes from the limitations introduced by the uncertainty in the evaporation step. Uneven and unpredictable patterns of evaporation of these volatile and semivolatile analytes can be worked around by an internal standard, but even the internal standard does not ensure certainty in controlling for the temperature and air flow of evaporation. This does not mean this method is without its uses, however. Evaporation may be better controlled with equipment that is a little more sophisticated than a hose attached to an air filter. We might remove that uncertainty with a more controlled evaporator, or perhaps eschewing evaporation entirely in favor of headspace analysis. One of these steps, especially the latter, would go far in increasing retention of the more volatile compounds. Headspace analysis would also enable quantification of compounds that otherwise volatilize away completely, such as benzene.

The second caveat comes from the uncertainty in predicting actual exposure from wristband recoveries. As recovery improves, so should correlations between recovery and exposure, but in the case that they do not, more data is required to fill out the best correlations and remove uncertainty. Further tests should be run to see if average exposure over time is in fact the best measurement of exposure.

Even with those caveats, however, the potential of silicone wristbands is unmistakable. This research does present definite trends and relationships that, while inexact and limited by the relatively small number of studies, are quantitative. This is a tool with potential, not just for wood smoke exposure, but for any other analyte that can be absorbed by and extracted from the wristbands.

What Circumstances Are the Wristbands Useful For?

In the case of wood smoke, the data suggests a few best practices for the use of silicone wristbands as quantitative passive receptors.

First, the wristbands ought to be used in areas of high wood smoke concentration, ideally higher than 1-2mg/m^3 $PM_{2.5}$ This is 2-4 times higher than the highest point marked by the Environmental Protection Agency's Air Quality Index[31], so the use of this wristband for residential use—e.g. in neighborhoods affected by wildfires or homes with a wood stove or cooking fire—is limited to very extreme cases, unless the predicted values of analytes can be calibrated to lower concentrations of $PM_{2.5}$. The wristbands would be useful in a firefighting context, however. They might even be useful for individuals to use in pairs, one inside protective clothing and one outside, to test how proof protective clothing is against these small VOCs and PAHs.

Second, the wristbands ought to be used to find average exposures over multiple hours. The upper limit of time the wristbands will be useful remains to be discovered, but at least two hours seem to be necessary to establish an equilibrium that accurately reflects the concentration of exposure. Wristbands are not for very short exposures, but the data they give about average exposure might be very useful indeed for understanding cancer risk for firefighting personnel,

especially from an epidemiological perspective. To that end, the third best practice, especially until the uncertainty in the method is dispelled, would be to deploy multiple wristbands in a study, for the fullest understanding of each individual's exposure and the best idea of a group's average exposure.

Future Directions

This research can and should be built upon. Improving the extraction method and analysis is a matter of controlling or eliminating the evaporation step, the source of the most uncertainty. This could be accomplished, as previously mentioned, through a more sophisticated evaporation apparatus or through headspace analysis. Becoming surer of recovery from the wristbands ensures more certainty in every other step of quantifying exposure data.

More studies should also be done comparing recoveries from the wristbands to actual ambient exposure. If they are both amenable to the idea, this researcher recommends further collaboration between the Lu Hu group and Center for Environmental Health Sciences. The more exact data collected, the better our correlations between wristband recovery and exposure will be.

More questions remain about the properties of the wristbands as well. What other wood smoke markers could they absorb that would be useful for calculating exposure? Is there an upper limit to the time it is useful to wear them? How long exactly is needed to establish equilibria that provide useful correlation data? As is always the case, more research is required.

Acknowledgements

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The author also offers personal thanks to Dr. Brittany Busby, without whom finishing this research would have been impossible, to her friends far away but close to her heart, who kept her sane, and to her family, who remain supportive of all endeavors scientific and otherwise.

Finally, thanks be to God. May the words of my mouth and the meditations of my heart be pleasing in your sight, O Lord, my Rock and my Redeemer.

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Appendix A: Exposure Trial PTR-MS Plots and Integrations

Plots of Analyte Concentrations Over Time

Figure A1: Trial 1

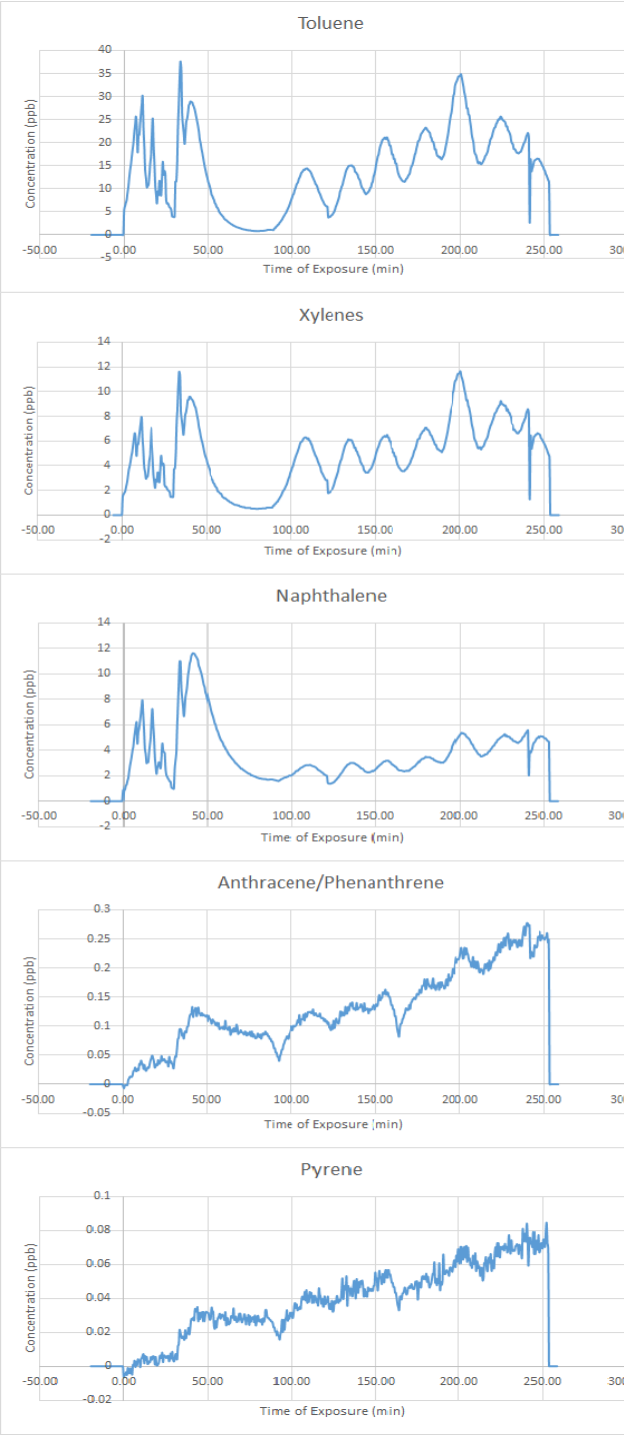


Figure A2: Trial 2

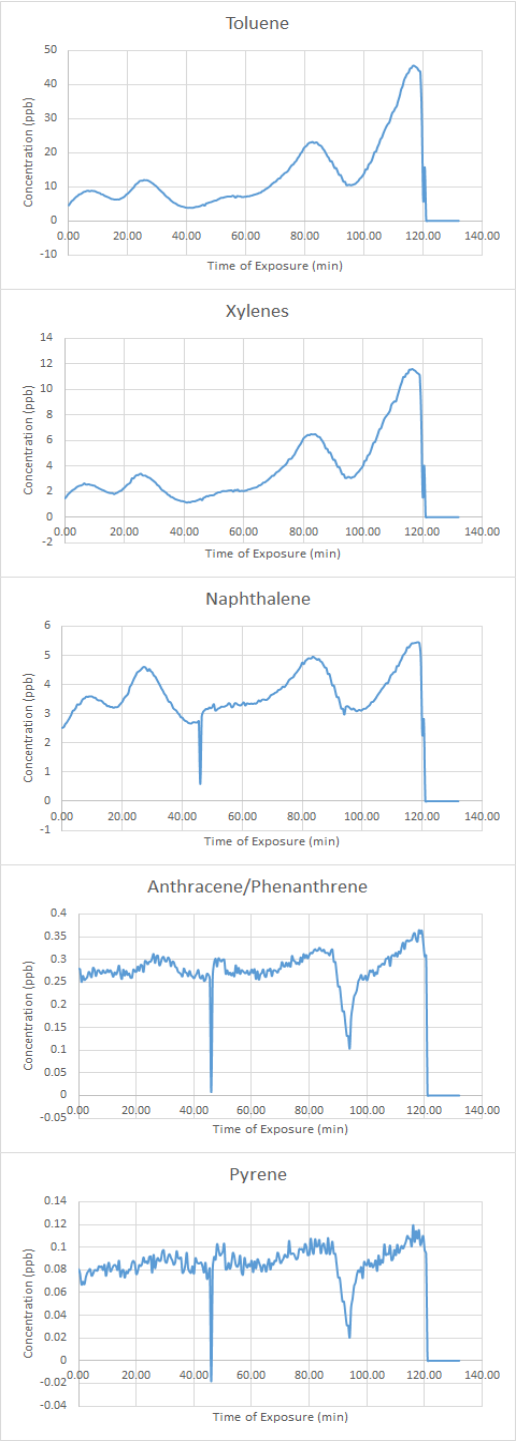


Figure A3: Trial 3

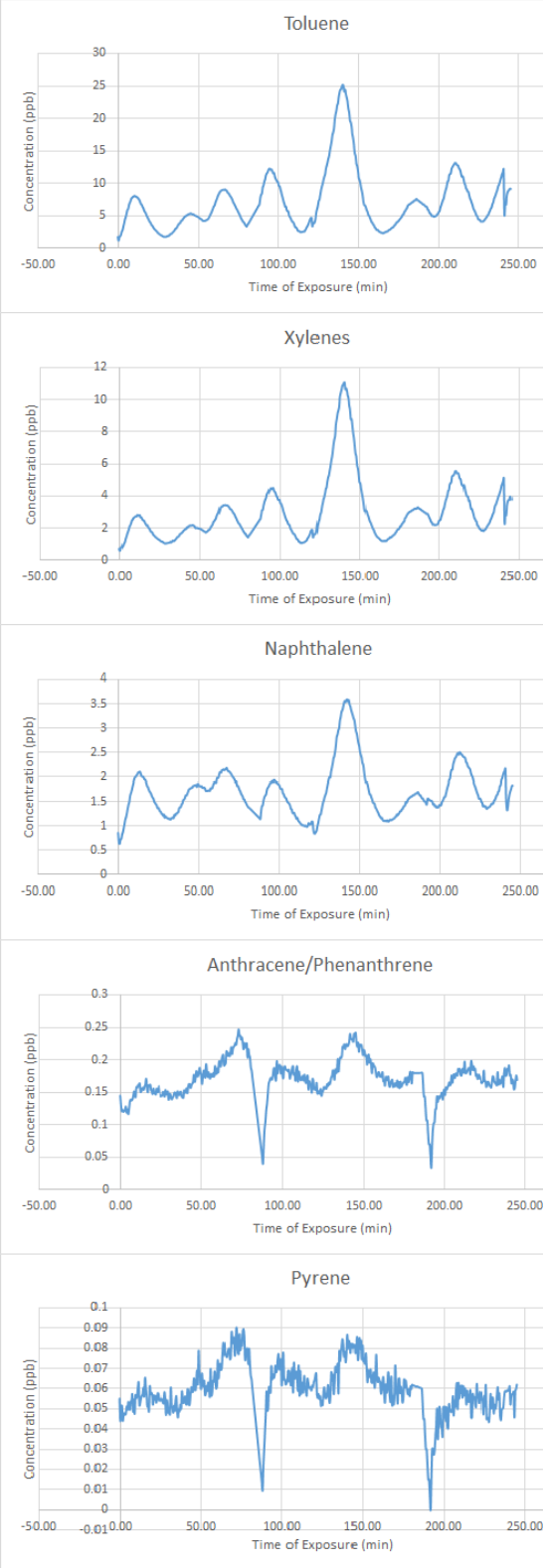
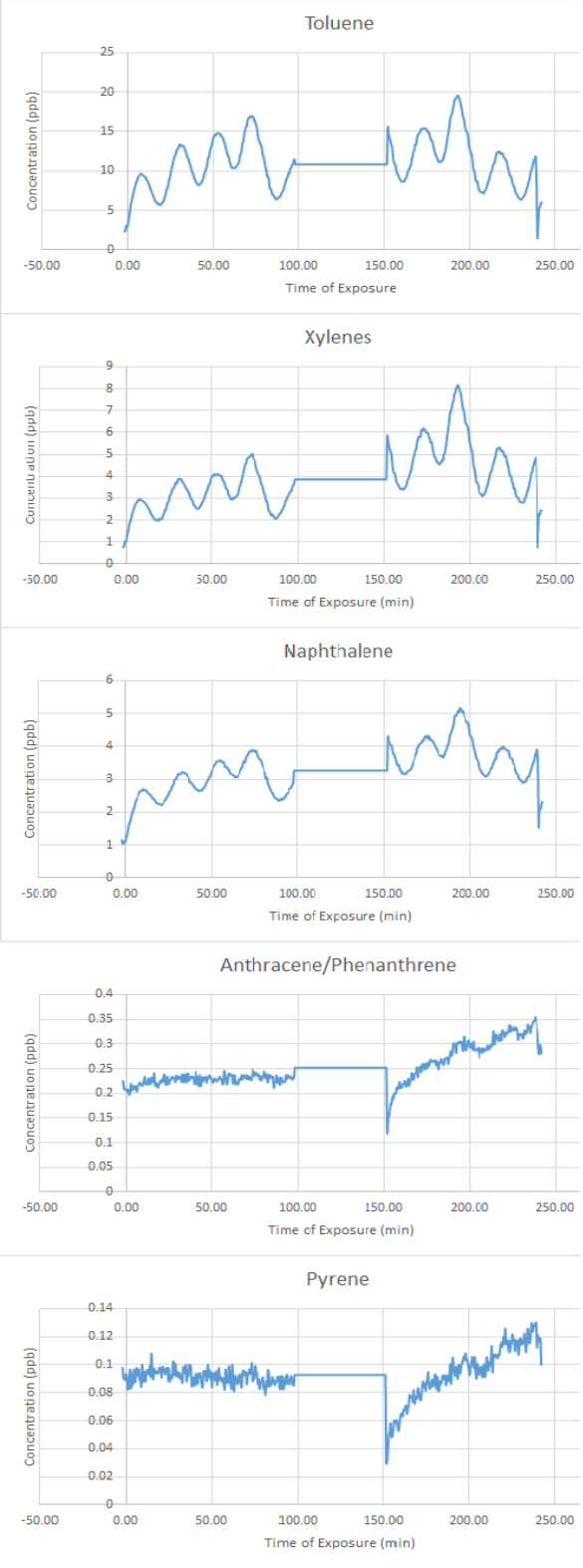


Figure A4: Trial 4



Tables of Integrated Values Over Time

Integrations were taken using Matlab, by finding the area under the curves from the plots above. "Total" exposure integrations were taken from minute 0 to minute 120 or 240, as appropriate for the time of exposure. Tables of all points along the curve are available on request.

Table A1: Trial 1

Trial 1	**Exposure time (min)**	**total**	**last 30 min**	**last 25 min**	**last 20 min**	**last 15 min**	**last 10 min**	**last 5 min**
toluene	120	2491.2	529.9	503.3	444.7	338.7	198.4	74.8
	240	6796.1	1199.6	1040.7	843.6	598.3	361.8	172.9
xylenes	120	863.3	234.4	222	195.7	149.3	88	33.7
	240	2334.1	433.7	378.2	308.7	221.7	136	65.8
naph	120	1070.6	135.2	118.6	99.4	76.1	48.5	21
	240	1799.2	266	229.6	190.3	143	91.7	44
phen/ anth	120	18.9	5.8	5.3	4.4	3.4	2.3	1
	240	59.9	13.5	11.5	9.5	7.2	4.7	2.3
pyrene	120	5.3	2	1.8	1.5	1.2	0.8	0.4
	240	18.2	3.9	3.3	2.7	2.1	1.3	0.6

Table A2: Trial 2

Trial 2	**Exposure time (min)**	**total**	**last 30 min**	**last 25 min**	**last 20 min**	**last 15 min**	**last 10 min**	**last 5 min**
toluene	120	3260.5	1477.4	1350.8	1234.2	1053.2	777.6	396
xylenes	120	916.2	403.8	366.8	332.8	280.4	202.8	101.1
naphthalene	120	887.4	235.3	200.8	169.3	135.9	96.1	48.3
phen/anth	120	66.9	16.4	14.6	12.2	9.4	6.4	3.2
pyrene	120	20.6	5	4.6	3.8	2.9	2	1

Table A3: Trial 3

Trial 3	Exposure time (min)	total	last 30 min	last 25 min	last 20 min	last 15 min	last 10 min	last 5 min
toluenes	120	1329.6	404.7	292.4	181.4	103.2	56.5	28.7
	240	3422.3	462.7	340.2	248.9	191.4	148.1	86.2
xylenes	120	524.9	153.3	112.2	71.7	42.4	23.9	12.1
	240	1437.6	197.7	146	107.3	82.3	63.1	36.4
naphthalene	120	376.2	86.4	68.9	50	33.4	20	9.1
	240	815.4	109.4	84.8	62.8	45.5	31.3	16.5
phen/anth	120	39.8	10.3	8.7	6.8	5	3.2	1.5
	240	81.3	10.3	8.4	6.6	4.9	3.3	1.6
pyrene	120	14.4	3.8	3.2	2.5	1.8	1.2	0.6
	240	28.3	3.2	2.6	2.1	1.5	1	0.5

Table A4: Trial 4

Trial 4	Exposure time (min)	total	last 30 min	last 25 min	last 20 min	last 15 min	last 10 min	last 5 min
toluenes	120	2518.3	618.9	531.9	423	314.5	206.1	97.6
	240	5264.2	559.5	460.8	338.6	236.1	164.6	90.3
xylenes	120	780.9	214.6	186.7	150.4	111.8	73.3	34.7
	240	1870	237.9	196.1	144.3	100.5	69.4	37.7
naphthalene	120	705.1	182.2	157.3	127.3	94.7	62	29.4
	240	1580.8	203.1	169.5	130.6	93.1	61.3	31.2
phen/anth	120	55.4	14.5	12.2	9.8	7.3	4.8	2.3
	240	120.5	19	16	12.8	9.6	6.3	3.1
pyrene	120	21.9	5.4	4.5	3.6	2.7	1.8	0.8
	240	44.3	6.7	5.7	4.6	3.4	2.3	1.1

Appendix B: Total Masses of Each Analyte Recovered from Exposed Wristbands

As outlined above, masses were calculated from calibration curves between the relative areas of the analyte and naphthalene d-10 and mass present in a spike. Phenanthrene and Anthracene were not included because recovered masses were below the limit of detection for the GC-MS.

Table B1: Recovered masses from exposed wristbands.

Trial #	**Time of exposure (min)**	**Toluene (µg)**	**Xylenes (µg)**	**Naphthalene (µg)**	**Pyrene (µg)**
1	120	0.522793	0.585508	2.124793	0
1	240	0.738625	0.56336	2.532728	0.07602
2	120	0.608985	0.75238	1.605224	0.082563
3	120	1.030217	1.223987	1.353112	0.077318
3	240	0.5765	0.532136	1.685152	0.098078
4	120	0.559719	0.409323	1.051695	0.026195
4	240	0.575341	0.477654	1.264606	0.046637
5 (1)	120	0.475229	0.502179	1.13855	0.040469
5 (2)	120	0.715211	0.511653	1.432552	0.050181
6	120	1.574608	1.421163	1.275962	0.035328
6	240	2.407165	1.789335	0.260185	0.070755
7	120	1.209683	1.188086	0.67742	0.012509
7	240	0.914098	0.750719	0.876688	0.05742