PFAS in Aerosols Released During Bathroom Showering

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A Master's technical report submitted to the faculty of the University of North Carolina at Chapel Hill in partial fulfillment of the requirements for the degree of Master of Science in Environmental Engineering in the department of Environmental Science and Engineering in the Gillings School of Public Health.

Chapel Hill 2021

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ABSTRACT

Tina Wen: PFAS in Aerosols Released During Bathroom Showering (Under the direction of Karsten Baumann & Barbara Turpin)

Poly- and Perfluoroalkyl substances (PFAS) are characterized by strong bonds between carbon and fluorine atoms giving them long environmental lifetimes and the ability to bioaccumulate in humans, animals and plants. PFAS compounds have been detected in ground water, surface water bodies and municipal waters. They are widely used in personal care products as surfactants which provides pathways for human exposure. To my knowledge, human exposure to PFAS during showering has not been studied. The goal of this project is to measure the amount of PFAS that humans are exposed to while showering with or without the use of personal care products. PFAS concentrations were measured in scenarios background, water only, and a full shower with personal care product use. Results suggest that shower activities might contribute to bathroom PFNA, PFOA, PFHxA exposures; however the dataset is limited in size, findings are not statistically significant, and thus more measurements are warranted.

ACKNOWLEDGEMENTS

I have to thank my advisor and co-advisor, Dr. Karsten Baumann and Dr. Barbara Turpin who read my numerous revisions and helped make some sense of the confusion. Without their assistance and dedicated involvement in every step throughout the process, this paper would have never been accomplished. I would like to thank you very much for your support and understanding over the past two years. I would also like to show gratitude to another one of my committee , Dr. Jason Surratt for providing me insightful suggestion to improve my project. I would also like to thank Naomi Chang for extracting filters and operating ultra-high performance liquid chromatography-electrospray ionization tandem mass spectrometer (UHPLC/ESI-MS/MS) to provide analysis results. I would like to thank Dr.Karsten Baumann for instructing and Daniel Amparo for participating in filter sample collections. I would like to thank Dr. Glenn Morrison for Air Exchange Rate calculation method suggestions. Finally, I would like to thank my friends, lab mates for a cherished time spent together in the lab, and in social settings. My appreciation also goes out to my family and friends for their encouragement and support all through my studies.

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ABBREVIATIONS

- PFAS- Per- and polyfluoroalkyl substances
- PFOS- Perfluorooctanesulfonic acid
- PFOA- Perfluorooctanoic acid
- PFAA- Perfluoroalkyl acid
- ADHD- Attention deficit hyperactivity disorder
- pDR- MIE personal DataRAM nephelometer from Thermo Fisher Scientific Inc.
- PM_{2.5} Particulate Matter smaller than 2.5 micrometers in aerodynamic diameter
- UHPLC/ESI-MS/MS- Ultra-high performance liquid chromatography-electrospray ionization
- tandem mass spectrometry
- CO2- Carbon dioxide
- AER- Air Exchange Rate
- OWASA- Orange Water and Sewer Authority
- PFBA- Perfluorobutanoic acid
- PFNA- Perfluorononanoic acid
- PFHxA- Perfluorohexanoic acid
- PFHpS- Perfluoroheptanesulfonic acid
- PFDS- Perfluorodecane sulfonic acid
- PFDA- Perfluorodecanoic acid
- PFHxDA- Perfluorohexadecanoic acid
- H₃PO₄- Phosphoric acid

CHAPTER I: INTRODUCTION

1.1 Background

Poly- and Perfluoroalkyl substances (PFAS) are fluorinated aliphatic compounds. Due to their low polarizability, high thermal and chemical stability properties, PFAS are widely used in products such as non-stick cookware, water-resistant clothing, personal care products as surfactants, and surface protector. (Kissa, 2001) More than 4000 PFAS have been manufactured for product application, the direct use of these products provides pathways for human exposure to PFAS (OECD, 2018; 3M Company, 1999). PFOA exposure is associated with high cholesterol, thyroid disease, pregnancy-induced hypertension, ulcerative colitis, and kidney and testicular cancer (Barry & Winguist, 2013; Lopez-Espinosa, Mondal, Armstrong, Bloom, & Fletcher, 2012; Steenland, Zhao, Winquist, & Parks, 2013; Darrow, Stein, & Steenland, 2013). Also, there is statistically significant evidence showing the association of PFAS exposure with immunosuppression, dyslipidemia, neurodevelopmental effects leading to attention-deficit/ hyperactivity disorder (ADHD), behaviors in childhood and neuropsychological functions such as IQ and other scales or scores. (Sunderland, et al., 2019). Though human exposure to Perfluorooctanoic acid (PFOA) and perfluorooctanesulfonate (PFOS), which initially raised health effect concerns, has been declining (Gomis MI, 2017), new shorter chain length PFAS that are difficult to detect with standard methods are reported as having been replacing PFOS and PFOA (Wang, DeWitt, Higgins, & Cousins, 2017). Nonetheless, alternative PFAS can be as potent as their predecessors (Gomis, Vestergren, Borg, & Cousins, 2018).

Potential human exposures to PFAS start with the release of PFAS into the environment during manufacturing through ambient air, wastewater, and sludge via controlled or uncontrolled (fugitive) emissions. PFAS can also be released during product use by heating, volatilization, abrasion and using of packaging materials. On average, people in the U.S. spend approximately 90% of their time indoors, including at home (U.S. Environmental Protection Agency, 1989). Therefore, it is important to study indoor residential PFAS sources. Indoor air, drinking water, soil and house dust are media contributing to residential PFAS exposures (DeLuca, Angrish, Wilkins, Thayer, & Hubal, 2021).

While we know that PFAS is contained in water and personal care products, we are curious whether bathroom showering activities could be a meaningful contributor to PFAS inhalation exposures and how different the PFAS composition in shower droplet aerosol is from the PFAS composition in the water supply. Running hot water from shower heads generates PM₁₀ aerosols with concentration 300µg/m³ to 14000µg/m³ in the first 5 minutes. Hot water shower particle size distribution shows that the majority aerosol is deposited in the upper respiratory tract and thoracic region (Zhou, Benson, Irvin, Irshad, & Cheng, 2007). In this study, we conducted an initial investigation of the PFAS content in shower aerosols generated under realistic conditions.

1.2 Objectives

- Estimate the emission rates of PFAS in PM_{2.5} during active showering based on annual water quality reports.
- Conduct a pilot study to measure PM_{2.5} and PFAS concentrations in bathroom fine aerosol (PM_{2.5}) during showering.
- Compare concentrations without shower, with shower only, and with person showering.
- Provide advice on the design of a future study.

1.3 Hypothesis

We speculate that showering poses long-term inhalation exposure risk for PFAS compounds. Thus, we wish to test the following hypotheses: 1) PFASs contained in supply water are released into the air during showering. 2) PFASs contained in shower-associated personal care products are released into the air during showering. However, because the measurements to test these hypotheses have not previously been made, the goal of this project is to conduct a pilot study and use the results to provide a refined study design to test these hypotheses.

CHAPTER II: EXPERIMENTAL DETAILS AND METHODS

2.1 Sampling Procedure and Method

In this pilot project, PFAS analyses were conducted on PM_{2.5} filter samples, and real-time PM_{2.5} concentrations were measured in 3 bathrooms in occupied homes without restrictions on other personal activities, for the following test conditions: 1) no showering (background), 2) showering without a person, and 3) a full personal shower with personal care product use (Figure 1; Table 1). For each test condition each filter sample was collected for 1 h; for test cases 2 and 3, the shower was run for 10 min at the beginning of each filter-collection hour. Air exchange rates were estimated by measuring CO₂ decay when the occupant left the room. For each test condition in order to exceed PFAS detection limits, after a filter was loaded into the sampler, it remained in the sampler for 10-14 days and air was pulled through it only 1 h per day, during the test condition period, resulting in 6 sets of filters with 10-14 h of sampling per filter (10 L min⁻¹). Further, for initial analyses, some filters were composited, so that this pilot project has 4 complete sets of PFAS extracts from the 3 test conditions. Detailed methods are presented below.

Quartz filters were installed in MSP inlet heads to collect PM_{2.5} air samples for later lab extraction and analysis to determine particle-phase PFAS concentrations in the air. At the same time, nephelometry (880 nm laser light scattering) was used for real-time measurement of the PM_{2.5} mass concentration (MIE pDR-1500, Thermo Fisher Scientific, Franklin MA) and NDIR absorption was used for real-time measurement of the CO₂ mixing ratio (less reliable SD800, Extech Instruments, Melrose MA, was later replaced by Q-Trak model 7575, TSI Inc., Shoreview MN); both sensors also measured sample pressure, temperature and relative humidity. The raw

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data acquisition rate of both CO_2 and $PM_{2.5}$ sensors was synchronized to 30s intervals with corresponding time averages being recorded. We assume a certain fraction of the $PM_{2.5}$ mass is contributed by PFAS, therefore, real-time $PM_{2.5}$ mass logging data was helpful in estimating PFAS mass collected on the filters before the analytical results of the filter extractions were available. CO_2 concentration changes were used to calculate the air exchange rate (AER) of the room, which was used to estimate PFAS emission rates as described later. AER was calculated from the observed exponential decay of CO_2 after removing all CO_2 sources from the room.

The sequence of activities being monitored is illustrated in Fig.1.



Figure 1. 1 Sampling Scenario Order being sequentially followed in all sample collections

Table 1. 1 Number of days with executed sampling sequence, time period of sample collection, number of QF field and dynamic blanks as well as integrated Background, Water Only and Full Shower QF samples. ¹²

| SAMPLE SET | DAYS | PERIOD | FIELD BLANKS | DYNAMIC | BACK | WATER | FULL |
|------------|------|------------------------------|--------------|---------|--------|-------|--------|
| LABEL | | | | BLANKS | GROUND | ONLY | SHOWER |
| HOME A1 | 10 | Mar 13-22, 2020 | 1 | 0 | 1 | 1 | 1 |
| HOME A2 | 10 | May 25 – Jun 4, 2020 | 1 | 0 | 1 | 1 | 1 |
| HOME B1 | 14 | Mar 26 – Apr 14, 2020 | 1 | 0 | 1 | 1 | 1 |
| HOME B2 | 14 | Apr 16 – May 13, 2020 | 1 | 0 | 1 | 1 | 1 |
| HOME B3 | 14 | Dec 22,2020 – Jan 6, 2021 | 1 | 3 | 1 | 1 | 1 |
| HOME C | 14 | Jan 12 – 25, 2021 | 3 | 3 | 1 | 1 | 1 |

2.1.1 Air Sample Collection

For air samples collection, 3 omnidirectional PM_{2.5} impactor sample inlet heads (model M400 Micro-Environmental Monitor (MEM), MSP Corp. under TSI Inc., Shoreview MN, USA) loaded with pre-baked (12h at 550C) 37 mm Quartz fiber filters (Pallflex Tissuquartz 2500 QAT-UP, Pall Laboratory, Port Washington NY) were installed in the bathroom where the collection took place. Each MSP inlet head was connected to a pump with flow rate 10 L min⁻¹ and a dry gas meter venting to ambient air (Actaris Gallus 2000 G1.6, Owenton, KY, US) during active sampling time periods. Samples were taken in sequential order for approximately one hour under

¹ Filters collected in HOME A1 are composited with filters from HOME A2.

² Filters collected in HOME B1 are composited with filters from HOME B2.

i) background conditions, ii) water only conditions, and iii) full personal shower conditions, in order labeled as inlet 1, inlet 2, inlet 3.



Figure 2. 1 Background air sampling.



Figure 2. 1 Air sampling during shower water without person. The water runs for approximately 10 minutes.



Figure 2. 2 Air sampling during full shower activity. The shower run time is roughly 10 minutes.

The bathroom is well ventilated with door open between each sample. During sampling, the door was closed and the fan remained off. Filters remained in the samplers for 10-14 days and the activities were repeated each day, so that each filter sampled a composited 10-14 hours for one distinct test case. This strategy was adopted to overcome PFAS detection limits. This resulted in 6 sets of samples for PFAS analysis. Note that for initial PFAS analysis, some extracts were composited, reducing the number of PFAS measurements to 4 samples for each of the three test cases: i) background conditions, ii) water only conditions, and iii) full personal shower conditions. The filters are stored in petri-dishes covered with aluminum foil round pieces, they should all be remain in freezers when they are not installed in MSP inlet heads. During transferring, home freezers are fine, for longer terms of storage, the filters should be kept in the freezers in labs with temperature around -20°C.

Before starting each round of collection, field blanks and dynamic blanks, in which air was pumped through designated filters for 10 seconds, were collected and stored in Al-lined petrislides.

At the same time, we had Personal DataRAM (pDR) and Q-Trak for $PM_{2.5}$ mass concentration and CO_2 mixing ratio data recording, respectively. Each round of air samples collection took between 10 and 14 days, resulting in 10-14 sets of real-time $PM_{2.5}$ samples for each round; as summarized in Table 1.

2.1.2 Water Sample Collection

To understand the ratio of PFAS transferred from water to aerosols and particles, we need to compare the PFAS composition (profile) of the air samples with that of the water samples. In order to determine the PFAS profile in the supply water, 1 L polypropylene (PP) bottles were used to collect water samples from each sampling day in an aggregated manner. A total of 60 ml of water was collected directly from shower heads before and after each shower into graduated PP vials prepared with 60 mg ammonium acetate for sample conservation. After collection of 60 ml of shower water, the content was split equally into two 1L PP bottles for duplicate analysis and data quality assurance. Thus, as illustrated in Fig. 3, for a 14-day collection round, we would end up with 2 PP bottles each filled with 420 ml (14 x 30ml) of aggregated water sampled "before" and 2 other PP bottles with same amount of aggregate water collected "after" showering. This approach allows to probe for systematic differences in the supply water's PFAS profile before and after showering, whereby the water sat in the supply pipes for at least 24h ("before") compared to well-flushed supply system in the "after" samples. In addition, pre-acidified (H_3PO_4) 40 ml vials were used during the 14 DA sample collections (see Table 1) to determine the supply water's dissolved organic carbon (DOC) content in each of the before and after shower water samples. After collection, the water samples are stored in refridgerator at around 4°C.

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Figure 3. 1 Water Sampling Procedure. Collect 60 ml water from the shower head before shower and repeat it again after shower. After collection of 60ml shower water preserved with 60 mg ammonium acetate, split content equally into two 1L bottles for QA purposes.

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2.2 Extraction and Analysis

All the sample filters and field blanks collected in bathrooms are pre-baked 37 mm quartz fiber filters (Tissuquartz 2500 QAT-UP, Pall Laboratory, pre-baked at 550C for 12h). We followed the extraction and analytical methods developed by J. Zhou published in 2021. Briefly, the filters were spiked with internal standards and extracted 3 times with methanol, then evaporated to 5 mL. The solution was filtered through syringe filters and further evaporated to 300 μ L. The filtrate was transferred to vials and filled up with Milli-Q water and methanol to make a final volume of 100 μ L with 75:25 (v/v) solvent. The instrument used for analysis was an ultra-high performance liquid chromatography-electrospray ionization tandem mass spectrometer (UHPLC/ESI-MS/MS). (Zhou, et al., 2021)

2.3 Air Exchange Rate (AER)



Figure 4. 1 Air Flow Schematic Diagram in Bathroom

For ultimate determination of the PFAS emission rate from bathroom showering, the air exchange rate (AER) of the bathroom location is needed. The AER is assessed following the mass balance approach assuming that CO₂ is non-reactive.

$$\frac{d(CV)}{dt} = C_B IV - CIV + S - kCV \tag{1}$$

 C_B is the background CO₂ concentration in units of ppm, which is measured before sampling activities start, and we consider it to be a constant during measurement periods. C_B is retrieved for each sample collection event, with units of ppm. *I is air exchange rate (AER; hr⁻¹)*, which we are aimed to calculate. *V (m³)* is the volume of the space (bathroom) being measured for air exchange rates. *C (ppm)* is the concentration of CO₂ and is a variable that changes with time, C_0 is C at time zero in units of ppm; we have these data recorded by Q-Trak 7565 Indoor Air Quality Monitor, in units of ppm. *S (mass/hr)* is the source's emission rate of CO₂ into the room, with the only source being the person taking the shower in our case. We measure AER by examining the drop in CO₂ concentration after the person leaves the room. At that time, the source term *S* turns zero and remains zero as long as the person does not return. *k (1/hr)* stands for deposition rate and is also assumed to be zero for CO₂. When the AER is estimated, bathrooms are the spaces being monitored and only in flow and out flow are considered factors that contribute to CO₂ concentration change in the bathrooms being monitored. Therefore, when people leave the room (S=0), Equation (1) becomes the following for the CO_2 concentration in the room.

$$\frac{d(CV)}{dt} = C_B IV - CIV \tag{2}$$

After integration, we obtain the following equation:

$$\ln\left(\frac{C-C_B}{CO-C_B}\right) = -I \times t \tag{3}$$

where t is time, expressed in hours. Hence, the unit of air exchange rate (1) is $\frac{1}{hour}$.



Figure 5. 1 AER Calculation Plot

By plotting $\ln\left(\frac{c-c_B}{c_0-c_B}\right)$ vs time, the slope is -*I* (the air exchange rate). As shown in this chart, there is a linear relation between $\ln\left(\frac{c-c_B}{c_0-c_B}\right)$ and time. By generating a Pearson's regression line and its equation we get 7.2042 as the slope and an air exchange rate (I) of 7.2 for this example data set.

The following chapter describes the selection process for periods for which the average AER was calculated for each of the 3 bathroom collection locations TW, KB and DA. It also presents and discusses the PM_{2.5} concentrations measured by the real-time pDR sensors, and compares differences in average concentrations observed during the three different sampling conditions (Background, Water Only, Full Shower). Based on these average PM_{2.5} concentrations and

assumptions in respective municipal water quality reports, we estimate lower and upper bounds in expected PFAS concentrations in our filter samples. These estimates are then compared with measured PFAS concentrations from the UHPLC/ESI-MS/MS analyses.

CHAPTER III: RESULTS AND DISCUSSION

3.1 Measurement Results

3.1.1 Air Exchange Rate (AER) Calculation Results

AER is estimated in each sampling location from the measured decrease of CO₂ after reaching its peak mixing ratio, which occured when the study personnel left the room. We got 8 peaks from KB1 and and none from KB2, 9 peaks from TW1 and none from TW2 due to sensor malfunction, 13 peaks from TW3 and also 13 peaks from DA. The unreliable performance of the Extech SD800 used in KB1+2 and TW 1+2 prompted its replacement with the Q-Trak sensor used in TW3 and DA sampling rounds. The data selected for air exchange rate calculation is illustrated in the following table.

| Table of Data Selection for AER Calculation | | | | | | |
|---|--------------|----------------------|--------------|----------------------|--------------|--------------|
| Day | KB1 | KB2 | TW1 | TW2 | TW3 | DA |
| 1 | V | Cannot Identify peak | V | Cannot Identify peak | V | V |
| 2 | V | Cannot Identify peak | V | Cannot Identify peak | V | V |
| 3 | V | Cannot Identify peak | V | Cannot Identify peak | V | V |
| 4 | V | Cannot Identify peak | V | Cannot Identify peak | V | V |
| 5 | V | Cannot Identify peak | V | Cannot Identify peak | V | V |
| 6 | V | Cannot Identify peak | V | Cannot Identify peak | V | V |
| 7 | V | Cannot Identify peak | V | Cannot Identify peak | V | V |
| 8 | Not selected | Cannot Identify peak | V | Cannot Identify peak | V | V |
| 9 | V | - | V | Cannot Identify peak | Not selected | V |
| 10 | - | - | Not selected | Cannot Identify peak | V | V |
| 11 | - | - | Not selected | Cannot Identify peak | V | V |
| 12 | - | - | Not selected | - | V | Not selected |
| 13 | - | - | Not selected | - | V | V |
| 14 | - | - | - | - | V | V |

|--|

In this table, "-" means the data was not collected. "V" are the data sets that have been selected for AER calculation. "Cannot Identify peak" happened after applying hair spray in the bathroom and cause the signal to be unstable in TW2, the hair spray residue also impacted KB2 detection results. The detected values were fluctuating extremely, peaks cannot be identified, for the raw data, please see supplementary document. "Not selected" is when the peak is identifiable, but some other activities interrupted and cause a disturbance to the descending curve. To have more consistent curve for regression analysis, these peaks were excluded. An example of CO₂ data is shown below in Figure 6. The time period selected for AER calculation is based on the following criteria, we divided the data into mixing data, selected data and cut off data. Decay near the peak is usually associated with "mixing" rather than air exchange. Data near the baseline is more sensitive to introduced CO₂ from other sources, therefore we want to cut off the tail from the point which it is about 100 ppm higher than the baseline. However, the are few peaks decaying too fast and left fewer data points for calculation, in those cases, we cut off the tail at the point which is only 50 ppm higher than the baseline.



Figure 6. 1 AER Decending Data Selection

Table 3. 1 Air Exchange Rate of the 9 Collections selected in KB1.

Location KB1

| Peak | AER(1/hr) |
|---------|-----------|
| DAY1 | 0.9 |
| DAY2 | 1.6 |
| DAY3 | 2.3 |
| DAY4 | 3.7 |
| DAY5 | 2.1 |
| DAY6 | 2.3 |
| DAY7 | 0.7 |
| DAY9 | 0.6 |
| Average | 1.8 |
| STDEV | 1.1 |

Table 3. 2 Air Exchange Rate of the 9 Collections selected in TW1 and TW2.

| Location | TW1 |
|----------|-----------|
| Peak | AER(1/hr) |
| DAY1 | 22.3 |
| DAY2 | 22.3 |
| DAY3 | 102.3 |
| DAY4 | 9.6 |
| DAY5 | 22.2 |
| DAY6 | 21.2 |
| DAY7 | 14.3 |

| DAY8 | 19.1 |
|---------|------|
| DAY9 | 8.2 |
| Average | 26.8 |
| STDEV | 28.8 |

Table 3. 3 Air Exchange Rate of the 14 Collections selected in TW3.

| Location | TW3 |
|----------|-----------|
| Peak | AER(1/hr) |
| DAY1 | 7.3 |
| DAY2 | 6.5 |
| DAY3 | 7.1 |
| DAY4 | 7.4 |
| DAY5 | 10.6 |
| DAY6 | 8.8 |
| DAY7 | 11.3 |
| DAY8 | 9.3 |
| DAY10 | 9.2 |
| DAY11 | 12.1 |
| DAY12 | 7.6 |
| DAY13 | 11.2 |
| DAY14 | 6.5 |
| Average | 8.8 |

| STDEV | 2.0 |
|-------|-----|
| | |

Table 3. 4 Air Exchange Rate of the 14 Collections selected in DA.

| Location | DA |
|----------|-----------|
| Peak | AER(1/hr) |
| DAY1 | 0.037 |
| DAY2 | 0.044 |
| DAY3 | 0.050 |
| DAY4 | 0.040 |
| DAY5 | 0.037 |
| DAY6 | 0.046 |
| DAY7 | 0.036 |
| DAY8 | 0.033 |
| DAY9 | 0.036 |
| DAY10 | 0.062 |
| DAY11 | 0.037 |
| DAY13 | 0.043 |
| DAY14 | 0.044 |
| Average | 0.042 |
| STDEV | 0.008 |

The air exchange rate in each sampling location varies a lot. Air exchange rate could vary due to the size of the room and ventilation condition of the room as discussed later in section 3.3.

3.1.2 Real-Time Aerosol Results

The real time $PM_{2.5}$ concentration was measured at the same time that filter samples were being collected. Below we compare the $PM_{2.5}$ concentration recorded by nephelometer under 1) background conditions, 2) water only conditions, and 3) full personal shower conditions. Those conditions are in order labeled as Inlet 1, Inlet 2 and Inlet 3. The results from real time $PM_{2.5}$ concentration are provided in Tables 4(a) – 4(f), where "avg" is the average of measured $PM_{2.5}$ concentration within the collection time for the certain scenario. "Volume" is recorded by DGM, the air volume flowing through each inlet head is slightly different but very close to one another. "Sum" is the accumulated mass of $PM_{2.5}$ collected, it is calculated by multiplying the average concentration with volume. "Max" is the overall maximum concentration detected in one location for one inlet head. "STD" stands for overall standard deviation of the 10~14 days data. Table 4(a)-4(f) present real-time $PM_{2.5}$ concentrations separately by location. The data plotted as Figure 6(a)-6(f) are averages of the recorded 30s measurements within the one hour collection time period for each sequence.

| Real time PM _{2.5} conc. in KB1 | | | |
|--|---------|---------|---------|
| | inlet 1 | inlet 2 | inlet 3 |
| avg(µg/m³) | 5.7 | 10.7 | 13.6 |
| Total Volume (m ³) | 6.6 | 8.3 | 9.9 |
| sum mass PM _{2.5} (μg) | 37.6 | 88.8 | 134.0 |
| std(µg/m³) | 3.5 | 5.4 | 6.2 |
| max(µg/m³) | 14.6 | 26.5 | 65.3 |

| Real time PM _{2.5} conc. in KB2 | | | |
|--|---------|---------|---------|
| | inlet 1 | inlet 2 | inlet 3 |
| avg(µg/m³) | 3.8 | 6.5 | 14.6 |
| Total Volume (m ³) | 8.1 | 8.9 | 8.8 |
| sum mass PM _{2.5} (μg) | 30.3 | 58.0 | 128.9 |
| std(µg/m³) | 0.4 | 3.5 | 6.3 |
| max(µg/m³) | 6.1 | 20.1 | 53.8 |

Table 4. 2 Summary Table of Real Time PM_{2.5} Concentration Monitored by pDR in Location KB2

Table 4. 3 Summary Table of Real Time PM_{2.5} Concentration Monitored by pDR in Location TW1

| Real time PM _{2.5} conc. in TW1 | | | |
|--|---------|---------|---------|
| | inlet 1 | inlet 2 | inlet 3 |
| avg(µg/m³) | 5.9 | 57.0 | 28.3 |
| Total Volume (m ³) | 13.6 | 8.9 | 10.1 |
| sum mass PM _{2.5} (μg) | 79.7 | 508.2 | 286.8 |
| std(µg/m³) | 4.4 | 111.5 | 39.6 |
| max(µg/m³) | 36.2 | 983.9 | 661.0 |

Table 4. 4 Summary Table of Real Time PM_{2.5} Concentration Monitored by pDR in Location TW2

| Real time PM _{2.5} conc. in TW2 | | | |
|--|---------|---------|---------|
| | inlet 1 | inlet 2 | inlet 3 |

| avg(µg/m³) | 19.6 | 24.8 | 22.8 |
|---------------------------------|-------|-------|-------|
| Total Volume (m ³) | 9.4 | 9.0 | 10.9 |
| sum mass PM _{2.5} (μg) | 184.3 | 224.3 | 247.5 |
| std(µg/ m³) | 26.6 | 35.6 | 32.5 |
| max(µg/ m³) | 117.1 | 283.5 | 235.2 |

Table 4. 5 Summary Table of Real Time PM_{2.5} Concentration Monitored by pDR in Location TW3

| Real time PM _{2.5} conc. in TW3 | | | |
|--|---------|---------|---------|
| | inlet 1 | inlet 2 | inlet 3 |
| avg(µg/m³) | 2.1 | 3.1 | 5.7 |
| Total Volume (m ³) | 9.6 | 9.0 | 8.4 |
| sum mass PM _{2.5} (μg) | 20.2 | 28.0 | 48.2 |
| std(µg/m³) | 1.7 | 3.1 | 5.7 |
| max(µg/m³) | 8.1 | 23.1 | 28.3 |

Table 4. 6 Summary Table of Real Time PM_{2.5} Concentration Monitored by pDR in Location DA

| Real time PM _{2.5} conc. in DA | | | |
|---|---------|---------|---------|
| | inlet 1 | inlet 2 | inlet 3 |
| avg(µg/m³) | 31.7 | 12.1 | 13.6 |
| Total Volume (m ³) | 9.9 | 10.0 | 9.6 |
| sum mass PM _{2.5} 5 (μg) | 312.4 | 120.5 | 130.6 |
| std(µg/m³) | 64.6 | 20.4 | 14.0 |
| max(µg/m³) | 269.1 | 211.2 | 86.0 |



Figure 7. 1 One hour average PM_{2.5} Concentration for Each Inlet Head (1: Background, 2: Water Only, 3: Full Shower) in KB1 by Day.



Figure 7. 2 One hour average PM_{2.5} Concentration for Each Inlet Head (1: Background, 2: Water Only, 3: Full Shower) in KB2 by Day.



Figure 7. 3 One hour average PM_{2.5} Concentration for Each Inlet Head (1: Background, 2: Water Only, 3: Full Shower) in TW1 by Day.



Figure 7. 4 Estimated Average PM_{2.5} Concentration of Each Inlet Head in TW2 Day by Day

Comparison Chart.


Figure 7. 5 One hour average PM_{2.5} Concentration for Each Inlet Head (1: Background, 2: Water

Only, 3: Full Shower) in TW3 by Day.



Figure 7. 6 One hour average PM_{2.5} Concentration for Each Inlet Head (1: Background, 2: Water Only, 3: Full Shower) in DA by Day.



Figure 7. 7 One hour average PM_{2.5} Concentration for Each Inlet Head (1: Background, 2: Water Only, 3: Full Shower) in DA from Day 5 to Day 14.



Figure 8. 1 Average PM_{2.5} Concentration for Each Sample Set and Standard Deviation of the 1 h Measurements.

The PM_{2.5} concentration average displayed in Fig. 7 is the average of all 1-h averages measured in real-time (30s resolution) during each inlet's collection period, with the number of periods ranging from 10 (KB) to 14 (TW and DA) among the 6 sets. 3 out of these 6 collection sets showed that the PM_{2.5} concentration increases as more activities are involved. It turned out Inlet 3> Inlet 2> Inlet 1, which supports our assumption that running shower water generates particles, and there could be more particles generated during human showering processes. For all but 1, Inlet 2 was higher than inlet 1. For those that did not match with our hypotheses, we observed extremely high standard deviation and maximum PM_{2.5} concentration.

To test whether the PM_{2.5} concentration was significantly different with the shower running (inlet 2), compared to without the shower running (inlet 1), with a person showering (inlet 3) compared to with the shower running (inlet 2), and with a person showering (inlet 3) compared to without the shower running (inlet 1), I conducted t-tests with 95% confidence ($\alpha = 0.05$) on data from inlet 2 vs 1, inlet 3 vs 2, and inlet 3 vs 1, respectively. We found that the results in TW1 shows that inlet 2 (p-value=0.01198) and inlet 3 (p-value=0.0003279) concentrations are higher than inlet 1 concentration. TW2 shows no significant difference in PM_{2.5} concentration among the three inlets. TW3 shows both inlet 2 (p-value=0.003605) and inlet 3 (p-value=0.0005918) are higher than inlet 1, while inlet 3 is also significantly higher than inlet 2 (p-value=0.003244). In KB1, inlet 3 (p-value=7.74e-05) is found significantly higher than inlet 1, however, the evidence is not sufficient to conclude that inlet 3 is higher than inlet 2 or inlet 2 higher than inlet 1 at the 95% CI. In KB2, the difference between inlet 1 and 2 is not significant but inlet 3 is found to be higher than both inlet 2 (p-value=0.003648) and inlet 1 (p-value=1.802e-05). In DA, all inlets were found no significant difference among them.

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3.1.3 PFAS Mass Estimation Based on Real-Time Data

The real time PM_{2.5} results in Water Only condition (inlet 2) were used to estimate the total PFAS mass released from shower water and collected by filter, making several assumptions. The estimation assists with making decision on the sampling time length and is later compared with PFAS mass extracted from the filters and actually measured by UHPLC-ESI-MS/MS. The estimated PFAS mass is calculated as follow equation.

 $\frac{Sufate Mass in water report}{PFAS Mass in water report} = \frac{Sulfate Mass on QF}{Estimated PFAS Mass on QF}$

$$\frac{Sufate Mass in water report (ug/g) \times 10^{6} (\frac{pg}{ug})}{PFAS Mass in water report (\frac{pg}{g})} = \frac{Sulfate Mass in aerosol (ug) \times 10^{6} (\frac{pg}{ug})}{Estimated PFAS Mass in aerosol (pg)}$$

To calculate the estimation, we need sulfate mass from water report, PFAS mass from water report, and sulfate mass on filter. We did not measure sulfate, to fill in the sulfate mass for calculation, we assume 33% of PM_{2.5} mass is sulfate, which is a reasonable assumption for ambient aerosol (Frank, 2006), which means 0.33 times the measured real-time PM_{2.5} concentration is the concentration of sulfate being collected. We use sulfate as a conservative tracer. (Ideally, we would have an estimate of the ratio of sulfate to $PM_{2.5}$ from shower aerosol. We have not found that reported in the literature, and one recommendation we will make is that sulfate is measured in the source water and in aerosol in future shower studies.) Then, we use the ratio of sulfate to PFAS concentration in water from the annual municipal water reports. Due to lack of any sources other than the municipal shower water, we assume the sulfate: PFAS ratio in water is maintained in the collected bathroom aerosol, hence we apply the same ratio to the total PM2.5 mass from Tables 4 (above) to calculate the particulate PFAS mass estimate. For locations TW and DA, the water supply is from Orange Water and Sewer Authority (OWASA). For location KB, the water supply is from Cary/Apex Water Treatment Facility. One additional source of uncertainty is that the water reports do not take into consideration daily fluxuations in PFAS in the source water. Mass is converted to concentration by dividing by the total sample volume

(Table 5.2). Figure 9.1 shows the estimated particulate PFAS concentration released from shower water based on the approach above for individual compounds and the sum, using each municipality's water quality report (Cary 5/12/2020 & OWASA 2020) in estimates.



Figure 9. 1 Estimated particulate PFAS concentrations in air released from shower water based on water reports and assumptions. Shown are individual PFAS.

The sum of PFAS estimates may be an upperbound, because we did not subtract the background aerosol from the shower aerosol. The high concentration estimation in TW1, TW2 and DA could be caused by other factors (e.g. such as high background PM_{2.5} levels unrelated to showering, which were not subtracted in this exercise). However, in KB1, KB2 and TW3, where the background aerosol concentrations are considerably lower, we still estimate a considerable PFAS contribution from the shower water supply. Quite a few types of PFAS are expected to be detected on filter samples.

3.2 PFAS Measurement Results

3.2.1 Filter PFAS Analysis Results

To date, two sets of filters and field blanks have been analyzed for PFAS compounds. KB1 and KB2 filters were extracted and extracts were composited for analysis, so that more species would be above the field measurement detection limits. Likewise, extracts for TW1 and TW2, and separately the associated field blanks, were composited. Therefore, the total mass of PFAS detected reflects 2 rounds of collection in KB and TW location. The results are shown for i) background conditions, ii) water only conditions, and iii) full personal shower conditions. They are in order labeled as Inlet 1, Inlet 2 and Inlet 3 in Table 5.

Table 5. 1 PFAS Concentration in Filter Extracts in units of ng PFAS compound per mL of extract. <DL (Detection Limit) indicates the measurement was below the instrument (analytical) detection limit. Note, with only 2 field blank measurements, it is not possible to define the field measurement detection limit.

| | TW1+2_Inlet 1 | TW1+2_Inlet 2 | TW1+2_Inlet 3 | KB1+2_Inlet 1 | KB1+2_Inlet 2 | KB1+2_Inlet 3 | TW Blk | KB Blk |
|-------------------|---|---|---|---|---|---|---|-------------------|
| Component Name | Conc (ng/mL) | Conc (ng/mL) | Conc (ng/mL) | Conc (ng/mL) | Conc (ng/mL) | Conc (ng/mL) | Conc (ng/mL) | Conc (ng/mL) |
| PFMOAA | <dl< td=""><td><dl< td=""><td>0.8</td><td><dl< td=""><td>0.1</td><td>0.2</td><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<> | <dl< td=""><td>0.8</td><td><dl< td=""><td>0.1</td><td>0.2</td><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<> | 0.8 | <dl< td=""><td>0.1</td><td>0.2</td><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<> | 0.1 | 0.2 | <dl< td=""><td><dl< td=""></dl<></td></dl<> | <dl< td=""></dl<> |
| PFBA | 11.6 | 7.6 | 7.2 | 6.9 | 6.8 | 11.8 | 1.5970 | 1.8680 |
| PFHxA 2 | 0.4 | 1.6 | 0.6 | 0.2 | 1.2 | 1.2 | 0.0151 | 0.5994 |
| GenX | <dl< td=""><td>1.5</td><td><dl< td=""><td><dl< td=""><td>0.7</td><td><dl< td=""><td>1.7970</td><td>2.1960</td></dl<></td></dl<></td></dl<></td></dl<> | 1.5 | <dl< td=""><td><dl< td=""><td>0.7</td><td><dl< td=""><td>1.7970</td><td>2.1960</td></dl<></td></dl<></td></dl<> | <dl< td=""><td>0.7</td><td><dl< td=""><td>1.7970</td><td>2.1960</td></dl<></td></dl<> | 0.7 | <dl< td=""><td>1.7970</td><td>2.1960</td></dl<> | 1.7970 | 2.1960 |
| PFPeS 1 | <dl< td=""><td>1.1</td><td>0.4</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<> | 1.1 | 0.4 | <dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""></dl<></td></dl<> | <dl< td=""></dl<> |
| PFHpA 2 | 0.2 | 3.1 | 0.3 | <dl< td=""><td>0.6</td><td>0.5</td><td>0.3199</td><td>0.3145</td></dl<> | 0.6 | 0.5 | 0.3199 | 0.3145 |
| PFHxS 2 | <dl< td=""><td>7.9</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<> | 7.9 | <dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""></dl<></td></dl<> | <dl< td=""></dl<> |
| PFOA 2 | 5.9 | 57.4 | 15.1 | 0.5 | 3.3 | 10.3 | 0.0180 | 0.3568 |
| PFHpS 1 | <dl< td=""><td><dl< td=""><td>0.8</td><td>2.5</td><td>3.4</td><td>2.0</td><td>3.0770</td><td>1.1990</td></dl<></td></dl<> | <dl< td=""><td>0.8</td><td>2.5</td><td>3.4</td><td>2.0</td><td>3.0770</td><td>1.1990</td></dl<> | 0.8 | 2.5 | 3.4 | 2.0 | 3.0770 | 1.1990 |
| PFNA 2 | 0.5 | 2.0 | 1.2 | 0.1 | 0.3 | 0.2 | 0.0387 | <dl< td=""></dl<> |
| PFOS 1 | 12.9 | 55.0 | 16.1 | <dl< td=""><td>2.8</td><td>1.1</td><td>0.0747</td><td><dl< td=""></dl<></td></dl<> | 2.8 | 1.1 | 0.0747 | <dl< td=""></dl<> |
| PFDA 2 | <dl< td=""><td><dl< td=""><td><dl< td=""><td>0.1</td><td>0.3</td><td>0.2</td><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""><td>0.1</td><td>0.3</td><td>0.2</td><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<> | <dl< td=""><td>0.1</td><td>0.3</td><td>0.2</td><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<> | 0.1 | 0.3 | 0.2 | <dl< td=""><td><dl< td=""></dl<></td></dl<> | <dl< td=""></dl<> |
| PFNS 1 | 1.4 | <dl< td=""><td>1.2</td><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<> | 1.2 | <dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""></dl<></td></dl<> | <dl< td=""></dl<> |
| PFDS 1 | 0.6 | <dl< td=""><td><dl< td=""><td>1.2</td><td>4.1</td><td>17.7</td><td>0.3512</td><td>0.2821</td></dl<></td></dl<> | <dl< td=""><td>1.2</td><td>4.1</td><td>17.7</td><td>0.3512</td><td>0.2821</td></dl<> | 1.2 | 4.1 | 17.7 | 0.3512 | 0.2821 |
| PFTA 2 | 0.4 | <dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>0.3190</td><td>0.4933</td></dl<></td></dl<></td></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td>0.3190</td><td>0.4933</td></dl<></td></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""><td><dl< td=""><td>0.3190</td><td>0.4933</td></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""><td>0.3190</td><td>0.4933</td></dl<></td></dl<> | <dl< td=""><td>0.3190</td><td>0.4933</td></dl<> | 0.3190 | 0.4933 |
| PFHxDA | <dl< td=""><td><dl< td=""><td>9.0</td><td><dl< td=""><td><dl< td=""><td>3.6</td><td>1.9060</td><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<> | <dl< td=""><td>9.0</td><td><dl< td=""><td><dl< td=""><td>3.6</td><td>1.9060</td><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<> | 9.0 | <dl< td=""><td><dl< td=""><td>3.6</td><td>1.9060</td><td><dl< td=""></dl<></td></dl<></td></dl<> | <dl< td=""><td>3.6</td><td>1.9060</td><td><dl< td=""></dl<></td></dl<> | 3.6 | 1.9060 | <dl< td=""></dl<> |

The value is shown in ng/mL, which is the concentration of PFAS in the 100uL extraction solution.

Table 5b shows the PFAS concentration in air with units of pg/m^3 . To convert unit from ng/mL to pg/m^3 , we multiplied the value by 100μ L (0.1 mL) and divided by the air sample volume recorded.

Table 5. 2 Filter Analysis Results (Concentration of PFAS in Air, Field blanks subtracted). Note, with only 2 field blank measurements, it is not possible to define the field measurement detection limit. Thus, until further analyses are complete, we cannot confirm whether the measurements reported here are detectable.

| | TW1+2_Inlet 1 | TW1+2_Inlet 2 | TW1+2_Inlet 3 | KB1+2_Inlet 1 | KB1+2_Inlet 2 | KB1+2_Inlet 3 |
|-------------------|---|---|---|---|---|-------------------------------|
| Component Name | Air Concentration (pg/m^3) | Air Concentration (pg/m^3) | Air Concentration (pg/m^3) | Air Concentration (pg/m^3) | Air Concentration (pg/m^3) | Air Concentration (pg/m^3) |
| PFMOAA | <dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""></dl<></td></dl<> | <dl< td=""></dl<> |
| PFBA | 43.6 | 33.2 | 26.5 | 34.1 | 28.6 | 52.9 |
| PFHxA 2 | 1.5 | 9.0 | 2.6 | 0.0 | 3.2 | 3.4 |
| GenX | <dl< td=""><td>0.0</td><td><dl< td=""><td><dl< td=""><td>0.0</td><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<> | 0.0 | <dl< td=""><td><dl< td=""><td>0.0</td><td><dl< td=""></dl<></td></dl<></td></dl<> | <dl< td=""><td>0.0</td><td><dl< td=""></dl<></td></dl<> | 0.0 | <dl< td=""></dl<> |
| PFPeS 1 | <dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""></dl<></td></dl<> | <dl< td=""></dl<> |
| PFHpA 2 | 0.0 | 15.4 | 0.0 | <dl< td=""><td>1.4</td><td>1.1</td></dl<> | 1.4 | 1.1 |
| PFHxS 2 | <dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""></dl<></td></dl<> | <dl< td=""></dl<> |
| PFOA 2 | 25.6 | 319.6 | 72.1 | 0.6 | 17.1 | 53.0 |
| PFHpS 1 | <dl< td=""><td><dl< td=""><td>0.0</td><td>8.9</td><td>12.5</td><td>4.3</td></dl<></td></dl<> | <dl< td=""><td>0.0</td><td>8.9</td><td>12.5</td><td>4.3</td></dl<> | 0.0 | 8.9 | 12.5 | 4.3 |
| PFNA 2 | 2.0 | 11.0 | 5.5 | <dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""></dl<></td></dl<> | <dl< td=""></dl<> |
| PFOS 1 | 56.0 | 306.0 | 76.6 | <dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""></dl<></td></dl<> | <dl< td=""></dl<> |
| PFDA 2 | <dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""></dl<></td></dl<> | <dl< td=""></dl<> |
| PFNS 1 | <dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""></dl<></td></dl<> | <dl< td=""></dl<> |
| PFDS 1 | 1.0 | <dl< td=""><td><dl< td=""><td>6.1</td><td>22.0</td><td>93.0</td></dl<></td></dl<> | <dl< td=""><td>6.1</td><td>22.0</td><td>93.0</td></dl<> | 6.1 | 22.0 | 93.0 |
| PFTA 2 | 0.4 | <dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""></dl<></td></dl<> | <dl< td=""></dl<> |
| PFHxDA | <dl< td=""><td><dl< td=""><td>34.0</td><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<></td></dl<> | <dl< td=""><td>34.0</td><td><dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<></td></dl<> | 34.0 | <dl< td=""><td><dl< td=""><td><dl< td=""></dl<></td></dl<></td></dl<> | <dl< td=""><td><dl< td=""></dl<></td></dl<> | <dl< td=""></dl<> |
| | | | | | | |

Air Concentration $\left(\frac{pg}{m^3}\right) = Solution Concentration \left(\frac{ng}{ml}\right) \times 100\mu l \times \frac{1ml}{1000\mu l} \times \frac{10^3 pg}{1ng}$

 \div Air Sample Volume (m^3)



Figure 10. 1 Measured PFAS on Filters (Not Blank Subtracted) and the Values of the Blanks, for Compounds where the Detected Value in Inlet 2,3 are Higher Than Field Blanks (Red Line: KB Field Blank; Blue Line: TW Field Blank) in Both Locations. Note, It Will Not Be Possible to Compute the Field Measurement Detection Limit until More Samples and Blanks Have Been Analyzed, So while Inlet 2 and 3 Concentrations Shown Here Are Higher Than the Blank, They May or May Not Be above Field Measurement Detection Limits. Nevertheless, These Results Suggest Some PFAS Will Be Detected with this Measurement Scheme.



Figure 10. 2 Measured PFAS on Filters (Not Blank Subtracted) and the Value of the Blank, for Compounds where the Detected Values in Inlet Head 1,2,3 are Higher Than Field Blank Blank (Red Line: KB Field Blank; Blue Line: TW Field Blank) - In At Least One of the Location



Figure 10. 3 Measured PFAS on Filters (Not Blank Subtracted) and the Value of the Blank, for Compounds where the Detected Values only appear Inlet 3

3.2.2 Estimated PFAS Concentration and Analysis Results Comparison

The estimated concentrations are obtained by dividing the estimated masses with accumulated air sample volume through inlet head 2. The estimated masses are obtained from the real-time PM_{2.5} measurements and water report (Cary 5/12/2020 & OWASA 2020) PFAS content, assuming the water report's sulfate:PFAS ratio is maintained. The analytical results from the UHPLC-ESI-MS/MS detection yield concentration of PFAS in 100µL extract solution. To convert the units into mass (pg), we multiply the unit ng/mL by 0.1 mL, and then 1000 to yield pg. The comparison of estimated (from section 3.1.3) and measured (from section 3.2.1) PFAS concentrations in aerosols are shown in Figure 10.



Figure 11. 1 Estimated and Detected PFAS Concentration Comparison in Location KB.



Figure 11. 2 Estimated and Detected PFAS Concentration Comparison in Location TW.

The analytical results shown are background (Inlet 1) subtracted.

3.2.3 PFAS Composition in Water and Air

The water supply in location TWs is from Orange Water and Sewer Authority (OWASA), and water supply in location KB is from Cary/Apex Water Treatment Facility and distribution system (Cary). We compare the PFAS composition given in the OWASA and Cary water reports in 2019 with the Inlet 2 filter (shower running but no person showering) analysis results. The charts are as follow: Did you use the data from the Cary Water sample collected on 5/12/2020 see at https://www.townofcary.org/home/showpublisheddocument?id=25025 page 5 Filter Effluent?





KB.



Figure 12. 2 PFAS Component Composition in OWASA Water vs. Air Sample PFAS Composition in TW.

It is interesting that PFOS and PFOA are enhanced in the aerosol samples in both cases, relative to the water report. They both contributed about the same percentage to the air samples of both location. PFBA remains the same percentage during the process of transferring from water to aerosols. PFHxA and PFHpA decrease greatly. In TW results, PFHxS also remained the same percentage. And note that some components were recorded "ND"-Not detected in Cary Water Report, for example, PFOA and PFOS.

3.3 Discussion

3.3.1 Air Exchange Rate (AER) & PM_{2.5} Concentration

The AER in each location varies a lot. The bathroom location for KB1 and KB2 samples was the upper floor in a single-family house, while TW1,TW2, TW3 and DA were collected in single-floor apartments. The AER in TW is extremely high, which could possibly be attributed to some factors, such as small room, large gap under the door and the HVAC system being on during the whole day. The high CO₂ concentration background level in TW1, TW2 and DA also caused diffculty in selecting data points for AER calculation since the descending curve is steep and fewer data points are on the descending curve. Also, not keeping the whole apartment well

ventilated would cause CO₂ to accumulate; the elevated background CO₂ concentration increases uncertainty in the AER calculation.

According to t-test results on PFAS as described in section 3.1.2, we have 2 sets of samples out of 6 showing that inlet 2 have higher values than inlet 1, the results from these 2 sets support the hypothesis that shower water running is an activity that could release aerosols and particles. Three out of 6 sets of sample supported the hypothesis assuming actual shower activity using personal care products release more aersols than shower water running without person attending. In TW1, TW2, and DA, we found that the background level concentration is high, the unexpected results may be possibly caused by other variable sources contributing to the realtime measurement. Since TWs and DA sites are in apartments, where the kitchens are close to the bathrooms, and according to records, where cooking activities were going on before or during the sample collection times. To improve this issue in the next sampling campaign, it is suggested that i) cooking should be avoided before conducting sample collections, ii) the background PM_{2.5} level should be monitored continuously in another room, iii) the house or apartment should be well ventilated before collection, and iv) the collection should only start after the background concentration level has returned to the ambient CO₂ level. Furthermore, the HVAC system setting should be consistently kept either "Off" or "On", and the window outside the room should be constantly open to avoid CO2 concentration accumulating in the whole apartment or house.

3.3.2 PFAS Composition

During transformation from water to air, the compositional fractions of PFOA and PFOS increase, while the percentage of PFBA remains the same and PFHxA decreases relative to total measured or estimated PFAS.

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| Property | CAS | Water solubility (mg/L) | Mp/Bp (°C) | Vapour pressure (Pa) | Log Pow | Log Koc |
|--|------------|--|---------------|----------------------------|---|------------|
| PFOS, perfluorooctane sulfonic acid | 1763-23-1 | 519-570 ³ | | 3.31x10-43 | 5.5-7.034 | 2.57-3.34 |
| PFOA, perfluorooctanoic acid | 335-67-1 | 3400 5 | | 12.1^{5} | 3.62 | 2.11 5 |
| PFHxS, perfluorohexane sulfonic acid | 355-46-4 | 243.41 | 190/4521 | 1.08x10-61 | 2.21 | 3.36/2.141 |
| PFHxA, perfluorohexanoic acid | 307-24-4 | 29.5 ⁵ <<29 ⁶ | | 121 ⁵ | 2.51 ² 3.12-3.26 ⁶ | |
| PFHxA, perfluorohexanoate, sodium salt | 2923-26-4 | 29.56 | | ~ 0 6 | 0.706 | |
| PFPeS, perfluoropentane sulfonic acid | 2706-91-4 | | | | | |
| PFPeA, perfluoropentanoic acid | 2706-90-3 | 120 5 | | | 1.98° | |
| PFBS, perfluorobutane sulfonate, potas- sium salt | 29420-49-3 | 4340 ¹ | 188/4471 | 1.49x10-61 | 0.261 | 2.25/1.071 |
| PFBA, perfluorobutanoic acid | 375-22-4 | 447 ⁵ | | | 1.43 ² | |
| 8:2 FTOH, fluorotelomer alcohol | 678-39-7 | 0.2 - 0.3 5 | | 1.64 5 | 5.58 5 | 4.13 5 |
| 6:2 FTOH, fluorotelomer alcohol | 647-42-7 | 19 ³ | | 22.1 5 | 4.54 5 | 2.43 5 |
| 4:2 FTOH, fluorotelomer alcohol | 2043-47-2 | 97 ¹ | -44/1131 | 1330 ¹ | 3.07/3.301 | 2.34/2.831 |
| 6:2 FTS, fluorotelomer sulfonamide | 27619-97-2 | | | | 3.47-3.984 | |
| 6:2 FTAC, fluorotelomer acrylate | 17527-29-6 | 0.386 | | 44-3 ⁶ | 5.26 | |

Table 6. 1 Physico-Chemical Properties of Selected Short-Chain PFAS (And PFOS, PFOA and8:2 FTOH) (The Danish Environmental Protection Agency, 2015)

Long-chain PFAS components are more likely to transfer to air during water drop spraying. (Margot Reth, 2011) Water solubility of each component could also be affect by its polarity. (The Danish Environmental Protection Agency, 2015) According to the table above, PFOA has high water solubility, which indicates that there is less percentage of PFOA being transferred to aerosols during shower. However, we see high percentage of PFOA in the aerosol composition, possibly due to its surfactant-like property of staying in the condensed phase as droplets evaporate. Another reason for this result could possibily be that PFOA exist in ambient environment (e.g. in dust on various surfaces) . PFOA concentration in home dust can be significant, as shown in following table. (The Danish Environmental Protection Agency, 2015)

| PFAS | LOQ | Of % detect | fice dust (n GM ng/g | =31) Range | Ho: % detect | me dust (n GM ng/g | =30) Range | Veh % detect | icle dust (GM ng/g | (n=13) Range |
|-------------|-----|----------------|-------------------------|---------------|-----------------|-----------------------|---------------|-----------------|------------------------|-----------------|
| PFOA | 5 | 74 | 32.0 | 15-336 | 77 | 23.7 | 5-894 | 54 | 11.4 | 21-58 |
| PFHxA | 5 | 68 | 10.8 | 5-102 | 57 | 8.7 | 5-1380 | 54 | 5.9 | 5-18 |
| PFPA | 5 | 39 | nr | 5-28 | 33 | nr | 5-249 | 23 | nr | 7-18 |
| PFBA | 5 | 48 | nr | 5-148 | 90 | 13.9 | 5-999 | 85 | 11.5 | 5-240 |
| PFOS | 7 | 55 | 14.6 | 7-98 | 73 | 26.9 | 14-280 | 54 | 15.8 | 10-280 |
| PFHxS | 5 | 23 | nr | 5-19 | 40 | nr | 6-430 | 46 | nr | 5-108 |
| PFBS | 5 | 10 | nr | 8-12 | 3 | nr | 5-5 | nr | - report | <5 |
| 6:2 FTOH | 50 | 35 | nr | 90- 2390 | 0 | nr | <50 | 8 | nr | 2-243 |
| 8:2 FTOH | 5 | 100 | 309 | 15- 3390 | 57 | 10.8 | 9-136 | 69 | 11.3 | 8-82 |

Table 7. 1 PFAS In Office, Home and Vehicle Dust (Fraser AJ, 2013)

CHAPTER IV: CONCLUSIONS AND RECOMMENDATIONS

We measured filter collected PFAS concentration, PM2.5 real-time data, and CO2 realtime data. We expect that there are aerosols released when the shower is running (Inlet 2), and more aerosols are released from a shower with an actual person taking it (Inlet 3), alhough only 3 (KB1, KB2, TW3) out of 6 sets of samples matched with our expectation that most aerosols are generated in the full shower scenario (Inlet 3), and the least in the background scenario (Inlet 1). We suspect that the background PM2.5 concentration in the homes is high and variable. We expect that there are other (variable) sources of indoor PM2.5 and PFAS, and the measurements, perhaps particularly the other 3 sets, could be substantially influenced by other sources, such as cooking and dish washing. Therefore, recommendations below for conducting a followup study aim to reduce such interferences. Filter analysis results are suggestive that PFAS concentrations increase when there is activity such as showering, use of personal care products and hair drying in the bathroom, especially for PFNA, PFOA, PFHxA. The PFBA background levels are high at both locations, and thus we are uncertain if shower activities generate PFBA, but our preliminary results suggest that humans might be exposed to PFBA during showering. PFOS, PFHpS, PFDS, PFDA were found at elevated levels during activities in one of the locations. These components are potentially released from showering, but we need more evidence to confirm. Last but not least, PFHxDA is only found in full shower scenario, so it is possible that PFHxDA is contained in personal care products we used for showering (Shampoo, Conditioner, Body wash). It is important to note that we only have PFAS measurements for a small number of samples and only two field blanks. We do not have enough field blank measurements to calcuate field measurement

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detection limits for each measured PFAS. Thus, we cannot know for sure whether the PFAS concentrations reported are detectable (> field measurement detection limits).

For further studies, if we want to design it in another way, it is recommended that the sample collections should be conducted in a more isolated space, for example, a room with shower place in the lab building, which is not used for any other purposes. The air exchange rate could be calculated by measuring CO₂ concentration released into the space from a tank instead of depending on CO₂ produced by occupants, since occupants and the activities they conduct provide more uncertainties. The collection could be operated continuosly for 10~14 hours for each inlet heads/ scenarios. It makes it easier for Inlet 1 (background) and Inlet 2 (water only) collection. For Inlet 3 (full shower), we could have one person enter the room every one hour to foam up shampoo and bodywash with tools like bath loofahs, then rinse it off and leave the room. At the same time, we want to keep monitoring PM_{2.5} and CO₂ concentration outside the room to make sure we keep track of sources outside the room. For each scenario, 3 field blanks should be collected before starting the sampling.

APPENDIX A: REAL-TIME CO2 DATA & AIR EXCHANGE RATE CALCULATION



PLOTS LISTING

Real-Time CO₂ Plots in KB1:



Air Exchange Rate Calculation Plots in KB1:

Time (hr)

-1.4

-1.6 -1.8



-0.25

-0.3

-0.35

y = -2.3094x + 0.1145

 $R^2 = 0.8517$

Time (hr)



Real-Time CO₂ Plots in TW1:















Air Exchange Rate Calculation Plots in TW1:











Real-Time CO₂ Plots in TW3:













Air Exchange Rate Calculation Plots in TW3:













Real-Time CO₂ Plots in DA:











Air Exchange Rate Calculation Plots in DA:



















APPENDIX B: PFAS RESULTS T-TEST R CODES & ANALYSIS RESULTS

> #PFMOAA

> t.test(PFMOAA_inlet1, PFMOAA_inlet2, paired = TRUE, alternative = "two.sided")

Paired t-test

data: PFMOAA_inlet1 and PFMOAA_inlet2

t = -1, df = 1, p-value = 0.5

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

-3.58822 3.06463

sample estimates:

mean of the differences

-0.2617953

> t.test(PFMOAA_inlet1, PFMOAA_inlet3, paired = TRUE, alternative = "two.sided")

Paired t-test

data: PFMOAA_inlet1 and PFMOAA_inlet3

t = -1.8087, df = 1, p-value = 0.3215

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

-19.20767 14.42076

sample estimates:

mean of the differences

-2.393456

> t.test(PFMOAA_inlet2, PFMOAA_inlet3, paired = TRUE, alternative = "two.sided")

Paired t-test

data: PFMOAA_inlet2 and PFMOAA_inlet3

t = -1.3448, df = 1, p-value = 0.407

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

-22.27230 18.00898

sample estimates:

mean of the differences

-2.131661

>

>

> #PFBA

> t.test(PFBA_inlet1, PFBA_inlet2, paired = TRUE, alternative = "two.sided")

Paired t-test

data: PFBA_inlet1 and PFBA_inlet2

t = 3.2326, df = 1, p-value = 0.191

alternative hypothesis: true difference in means is not equal to 0 95 percent confidence interval: -23.31907 39.23297 sample estimates:

mean of the differences

7.956949

> t.test(PFBA_inlet1, PFBA_inlet3, paired = TRUE, alternative = "two.sided")

Paired t-test

data: PFBA_inlet1 and PFBA_inlet3

t = -0.046994, df = 1, p-value = 0.9701

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

-228.9920 227.3044

sample estimates:

mean of the differences

-0.843815

> t.test(PFBA_inlet2, PFBA_inlet3, paired = TRUE, alternative = "two.sided")

Paired t-test

data: PFBA_inlet2 and PFBA_inlet3

t = -0.568, df = 1, p-value = 0.6711

alternative hypothesis: true difference in means is not equal to 0 95 percent confidence interval: -205.6729 188.0714 sample estimates: mean of the differences

-8.800764

>

```
> #PFHxA
```

> t.test(PFHxA_inlet1,PFHxA_inlet2, paired = TRUE, alternative = "two.sided")

Paired t-test

data: PFHxA_inlet1 and PFHxA_inlet2

t = -2.5094, df = 1, p-value = 0.2414

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

-32.28854 21.63830

sample estimates:

mean of the differences

-5.325121

> t.test(PFHxA_inlet1, PFHxA_inlet3, paired = TRUE, alternative = "two.sided")

Paired t-test

data: PFHxA_inlet1 and PFHxA_inlet3
t = -1.9061, df = 1, p-value = 0.3076
alternative hypothesis: true difference in means is not equal to 0
95 percent confidence interval:
-16.96517 12.53914
sample estimates:
mean of the differences
-2.213012

> t.test(PFHxA_inlet2, PFHxA_inlet3, paired = TRUE, alternative = "two.sided")

Paired t-test

data: PFHxA_inlet2 and PFHxA_inlet3

t = 0.94792, df = 1, p-value = 0.517

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

-38.60347 44.82768

sample estimates:

mean of the differences

3.112108

>

> #GenX

> t.test(GenX_inlet1,GenX_inlet2, paired = TRUE, alternative = "two.sided")

Paired t-test

data: GenX_inlet1 and GenX_inlet2

t = NaN, df = 1, p-value = NA

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

NaN NaN

sample estimates:

mean of the differences

0

> t.test(GenX_inlet1, GenX_inlet3, paired = TRUE, alternative = "two.sided")

Paired t-test

data: GenX_inlet1 and GenX_inlet3

t = NaN, df = 1, p-value = NA

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

NaN NaN

sample estimates:

mean of the differences

0

> t.test(GenX_inlet2, GenX_inlet3, paired = TRUE, alternative = "two.sided")
Paired t-test

data: GenX_inlet2 and GenX_inlet3

t = NaN, df = 1, p-value = NA

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

NaN NaN

sample estimates:

mean of the differences

0

>

> #PFPeS

> t.test(PFPeS_inlet1,PFPeS_inlet2, paired = TRUE, alternative = "two.sided")

Paired t-test

data: PFPeS_inlet1 and PFPeS_inlet2

t = -1, df = 1, p-value = 0.5

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

-41.97334 35.84862

sample estimates:

mean of the differences

-3.062361

> t.test(PFPeS_inlet1, PFPeS_inlet3, paired = TRUE, alternative = "two.sided")

Paired t-test

data: PFPeS_inlet1 and PFPeS_inlet3

t = -1, df = 1, p-value = 0.5

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

-12.08257 10.31949

sample estimates:

mean of the differences

-0.8815401

> t.test(PFPeS_inlet2, PFPeS_inlet3, paired = TRUE, alternative = "two.sided")

Paired t-test

data: PFPeS_inlet2 and PFPeS_inlet3

t = 1, df = 1, p-value = 0.5

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

-25.52913 29.89078

sample estimates:

mean of the differences

2.180821

>

>

> #PFHpA

> t.test(PFHpA_inlet1,PFHpA_inlet2, paired = TRUE, alternative = "two.sided")

Paired t-test

data: PFHpA_inlet1 and PFHpA_inlet2

t = -1.205, df = 1, p-value = 0.441

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

-96.95841 80.16175

sample estimates:

mean of the differences

-8.398328

> t.test(PFHpA_inlet1, PFHpA_inlet3, paired = TRUE, alternative = "two.sided")

Paired t-test

data: PFHpA_inlet1 and PFHpA_inlet3

t = -1, df = 1, p-value = 0.5

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

-7.537153 6.437336

sample estimates:

mean of the differences

-0.5499081

> t.test(PFHpA_inlet2, PFHpA_inlet3, paired = TRUE, alternative = "two.sided")

Paired t-test

data: PFHpA_inlet2 and PFHpA_inlet3

t = 1.0437, df = 1, p-value = 0.4864

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

-87.6989 103.3957

sample estimates:

mean of the differences

7.84842

>

>

> #PFHxS

> t.test(PFHxS_inlet1,PFHxS_inlet2, paired = TRUE, alternative = "two.sided")

Paired t-test

data: PFHxS_inlet1 and PFHxS_inlet2

t = -1, df = 1, p-value = 0.5

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

-302.9712 258.7619

sample estimates:

mean of the differences

-22.10468

> t.test(PFHxS_inlet1, PFHxS_inlet3, paired = TRUE, alternative = "two.sided")

Paired t-test

data: PFHxS_inlet1 and PFHxS_inlet3

t = NaN, df = 1, p-value = NA

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

NaN NaN

sample estimates:

mean of the differences

0

> t.test(PFHxS_inlet2, PFHxS_inlet3, paired = TRUE, alternative = "two.sided")

Paired t-test

data: PFHxS_inlet2 and PFHxS_inlet3

t = 1, df = 1, p-value = 0.5

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

-258.7619 302.9712

sample estimates:

mean of the differences

22.10468

>

>

> #PFOA

> t.test(PFOA_inlet1,PFOA_inlet2, paired = TRUE, alternative = "two.sided")

Paired t-test

data: PFOA_inlet1 and PFOA_inlet2

t = -1.1188, df = 1, p-value = 0.4643

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

-1918.006 1607.562

sample estimates:

mean of the differences

-155.222

> t.test(PFOA_inlet1, PFOA_inlet3, paired = TRUE, alternative = "two.sided")

Paired t-test

data: PFOA_inlet1 and PFOA_inlet3

t = -16.76, df = 1, p-value = 0.03794

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

-86.86267 -11.95130

sample estimates:

mean of the differences

-49.40699

> t.test(PFOA_inlet2, PFOA_inlet3, paired = TRUE, alternative = "two.sided")

Paired t-test

data: PFOA_inlet2 and PFOA_inlet3

t = 0.74685, df = 1, p-value = 0.5916

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

-1694.425 1906.055

sample estimates:

mean of the differences

105.8151

>

>

> #PFHpS

> t.test(PFHpS_inlet1,PFHpS_inlet2, paired = TRUE, alternative = "two.sided")

Paired t-test

data: PFHpS_inlet1 and PFHpS_inlet2

t = -1, df = 1, p-value = 0.5

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

-24.57755 20.99121

sample estimates:

mean of the differences

-1.79317

> t.test(PFHpS_inlet1, PFHpS_inlet3, paired = TRUE, alternative = "two.sided")

Paired t-test

data: PFHpS_inlet1 and PFHpS_inlet3

t = 1, df = 1, p-value = 0.5

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

-27.16737 31.80890

sample estimates:

mean of the differences

2.320767

> t.test(PFHpS_inlet2, PFHpS_inlet3, paired = TRUE, alternative = "two.sided")

Paired t-test

data: PFHpS_inlet2 and PFHpS_inlet3

t = 1, df = 1, p-value = 0.5

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

-48.15859 56.38646

sample estimates:

mean of the differences

4.113937

>

>

>

```
> #PFNA
```

> t.test(PFNA_inlet1,PFNA_inlet2, paired = TRUE, alternative = "two.sided")

Paired t-test

data: PFNA_inlet1 and PFNA_inlet2

t = -1.2594, df = 1, p-value = 0.4272

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

-55.70439 45.65785

sample estimates:

mean of the differences

-5.023266

> t.test(PFNA_inlet1, PFNA_inlet3, paired = TRUE, alternative = "two.sided")

Paired t-test

data: PFNA_inlet1 and PFNA_inlet3

t = -1.0139, df = 1, p-value = 0.4956

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

-23.99378 20.44744

sample estimates:

mean of the differences

-1.773169

> t.test(PFNA_inlet2, PFNA_inlet3, paired = TRUE, alternative = "two.sided")

Paired t-test

data: PFNA_inlet2 and PFNA_inlet3

t = 1.451, df = 1, p-value = 0.3842

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

-25.21041 31.71060

sample estimates:

mean of the differences

3.250097

- >
- >
- >

> #PFNS

> t.test(PFNS_inlet1,PFNS_inlet2, paired = TRUE, alternative = "two.sided")

Paired t-test

data: PFNS_inlet1 and PFNS_inlet2

t = 1, df = 1, p-value = 0.5

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

-34.64279 40.56149

sample estimates:

mean of the differences

2.959352

> t.test(PFNS_inlet1, PFNS_inlet3, paired = TRUE, alternative = "two.sided")

Paired t-test

data: PFNS_inlet1 and PFNS_inlet3

t = 1, df = 1, p-value = 0.5

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

-1.174174 1.374781

sample estimates:

mean of the differences

0.1003035

> t.test(PFNS_inlet2, PFNS_inlet3, paired = TRUE, alternative = "two.sided")

Paired t-test

data: PFNS_inlet2 and PFNS_inlet3

t = -1, df = 1, p-value = 0.5

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

-39.18671 33.46861

sample estimates:

mean of the differences

-2.859049

>

>

> #PFDS

> t.test(PFDS_inlet1,PFDS_inlet2, paired = TRUE, alternative = "two.sided")

Paired t-test

data: PFDS_inlet1 and PFDS_inlet2

t = -0.87746, df = 1, p-value = 0.5415

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

-115.2005 100.3174

sample estimates:

mean of the differences

-7.441555

> t.test(PFDS_inlet1, PFDS_inlet3, paired = TRUE, alternative = "two.sided")

Paired t-test

data: PFDS_inlet1 and PFDS_inlet3

t = -0.97637, df = 1, p-value = 0.5076

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

-601.7802 515.8957

sample estimates:

mean of the differences

-42.94225

> t.test(PFDS_inlet2, PFDS_inlet3, paired = TRUE, alternative = "two.sided")

Paired t-test

data: PFDS_inlet2 and PFDS_inlet3

t = -1, df = 1, p-value = 0.5

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

-486.5797 415.5784

sample estimates:

mean of the differences

-35.50069

- >
- >

> #PFTA

> t.test(PFTA_inlet1,PFTA_inlet2, paired = TRUE, alternative = "two.sided")

Paired t-test

data: PFTA_inlet1 and PFTA_inlet2

t = 1, df = 1, p-value = 0.5

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

-2.572736 3.012287

sample estimates:

mean of the differences

0.2197754

> t.test(PFTA_inlet1, PFTA_inlet3, paired = TRUE, alternative = "two.sided")

Paired t-test

data: PFTA_inlet1 and PFTA_inlet3

t = 1, df = 1, p-value = 0.5

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

-2.572736 3.012287

sample estimates:

mean of the differences

0.2197754

> t.test(PFTA_inlet2, PFTA_inlet3, paired = TRUE, alternative = "two.sided")

Paired t-test

data: PFTA_inlet2 and PFTA_inlet3

t = NaN, df = 1, p-value = NA

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

NaN NaN

sample estimates:

mean of the differences

0

> #PFHxDA

> t.test(PFHxDA_inlet1,PFHxDA_inlet2, paired = TRUE, alternative = "two.sided")

Paired t-test

data: PFHxDA_inlet1 and PFHxDA_inlet2

t = NaN, df = 1, p-value = NA

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

NaN NaN

sample estimates:

mean of the differences

0

> t.test(PFHxDA_inlet1, PFHxDA_inlet3, paired = TRUE, alternative = "two.sided")

Paired t-test

data: PFHxDA_inlet1 and PFHxDA_inlet3

t = -3.5329, df = 1, p-value = 0.1756

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

-121.78454 68.79532

sample estimates:

mean of the differences

-26.49461

> t.test(PFHxDA_inlet2, PFHxDA_inlet3, paired = TRUE, alternative = "two.sided")

Paired t-test

data: PFHxDA_inlet2 and PFHxDA_inlet3

t = -3.5329, df = 1, p-value = 0.1756

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

-121.78454 68.79532

sample estimates:

mean of the differences

-26.49461

APPENDIX C: PM2.5 REAL-TIME RESULTS T-TEST R CODES & ANALYSIS RESULTS FOR EACH SAMPLE SET

#TW1

pDR_PFAS_TW_1_analysis <- read_excel("Library/Mobile Documents/com~apple~CloudDocs/Lab/Technical Report/Sample Results/Real time aerosol PDR+PFAS estimation/pDR_PFAS_TW_1 analysis.xlsx", + sheet = "t-test summary table")

Inlet1<-unlist(c(pDR_PFAS_TW_1_analysis[,1]))

Inlet2<-unlist(c(pDR_PFAS_TW_1_analysis[,2]))

Inlet3<-unlist(c(pDR_PFAS_TW_1_analysis[,3]))

t.test(Inlet1, Inlet2, paired = TRUE, alternative = "two.sided")

t.test(Inlet1, Inlet3, paired = TRUE, alternative = "two.sided")

t.test(Inlet2, Inlet3, paired = TRUE, alternative = "two.sided")

Paired t-test

data: Inlet1 and Inlet2
t = -3.1371, df = 9, p-value = 0.01198
alternative hypothesis: true difference in means is not equal to 0
95 percent confidence interval:
 -86.54187 -14.02385
sample estimates:
mean of the differences

> t.test(Inlet1, Inlet3, paired = TRUE, alternative = "two.sided")

Paired t-test

data: Inlet1 and Inlet3

t = -5.6151, df = 9, p-value = 0.0003279

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

-34.09438 -14.51234

sample estimates:

mean of the differences

-24.30336

> t.test(Inlet2, Inlet3, paired = TRUE, alternative = "two.sided")

Paired t-test

data: Inlet2 and Inlet3

t = 1.5545, df = 9, p-value = 0.1545

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

-11.82664 63.78565

sample estimates:

mean of the differences

#TW2

pDR_PFAS_TW_2_analysis <- read_excel("Library/Mobile Documents/com~apple~CloudDocs/Lab/Technical Report/Sample Results/Real time aerosol PDR+PFAS estimation/pDR_PFAS_TW_2 analysis.xlsx", + sheet = "t-test summary table")

Inlet1<-unlist(c(pDR_PFAS_TW_2_analysis[,1])) Inlet2<-unlist(c(pDR_PFAS_TW_2_analysis[,2])) Inlet3<-unlist(c(pDR_PFAS_TW_2_analysis[,3]))

t.test(Inlet1, Inlet2, paired = TRUE, alternative = "two.sided")
t.test(Inlet1, Inlet3, paired = TRUE, alternative = "two.sided")

t.test(Inlet2, Inlet3, paired = TRUE, alternative = "two.sided")

Paired t-test

data: Inlet1 and Inlet2
t = -0.35853, df = 4, p-value = 0.7381
alternative hypothesis: true difference in means is not equal to 0
95 percent confidence interval:
 -44.36621 34.21835
sample estimates:
mean of the differences
 -5.073928

> t.test(Inlet1, Inlet3, paired = TRUE, alternative = "two.sided")

Paired t-test

data: Inlet1 and Inlet3
t = -0.69108, df = 4, p-value = 0.5275
alternative hypothesis: true difference in means is not equal to 0
95 percent confidence interval:
 -35.62138 21.42261
sample estimates:
mean of the differences

-7.099382

> t.test(Inlet2, Inlet3, paired = TRUE, alternative = "two.sided")

Paired t-test

data: Inlet2 and Inlet3

t = -0.46309, df = 4, p-value = 0.6674

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

-14.16909 10.11818

sample estimates:

mean of the differences

-2.025454

#TW3

pDR_PFAS_TW_3_analysis <- read_excel("Library/Mobile Documents/com~apple~CloudDocs/Lab/Technical Report/Sample Results/Real time aerosol PDR+PFAS estimation/pDR_PFAS_TW_3 analysis.xlsx", + sheet = "t-test summary table")

Inlet1<-unlist(c(pDR_PFAS_TW_3_analysis[,1])) Inlet2<-unlist(c(pDR_PFAS_TW_3_analysis[,2])) Inlet3<-unlist(c(pDR_PFAS_TW_3_analysis[,3]))

t.test(Inlet1, Inlet2, paired = TRUE, alternative = "two.sided")

t.test(Inlet1, Inlet3, paired = TRUE, alternative = "two.sided")

t.test(Inlet2, Inlet3, paired = TRUE, alternative = "two.sided")

Paired t-test

data: Inlet1 and Inlet2 t = -3.5429, df = 13, p-value = 0.003605 alternative hypothesis: true difference in means is not equal to 0 95 percent confidence interval: -1.6451755 -0.3988063 sample estimates: mean of the differences -1.021991

> t.test(Inlet1, Inlet3, paired = TRUE, alternative = "two.sided")

Paired t-test

data: Inlet1 and Inlet3

t = -4.5051, df = 13, p-value = 0.0005918

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

-5.665803 -1.993048

sample estimates:

mean of the differences

-3.829426

> t.test(Inlet2, Inlet3, paired = TRUE, alternative = "two.sided")

Paired t-test

data: Inlet2 and Inlet3

t = -3.598, df = 13, p-value = 0.003244

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

-4.493104 -1.121766

sample estimates:

mean of the differences

-2.807435

#KB1

pDR_PFAS_KB_1_analysis <- read_excel("Library/Mobile Documents/com~apple~CloudDocs/Lab/Technical Report/Sample Results/Real time aerosol PDR+PFAS estimation/pDR_PFAS_KB_1 analysis.xlsx", + sheet = "t-test summary table")

Inlet1<-unlist(c(pDR_PFAS_KB_1_analysis[,1])) Inlet2<-unlist(c(pDR_PFAS_KB_1_analysis[,2])) Inlet3<-unlist(c(pDR_PFAS_KB_1_analysis[,3]))

t.test(Inlet1, Inlet2, paired = TRUE, alternative = "two.sided")
t.test(Inlet1, Inlet3, paired = TRUE, alternative = "two.sided")
t.test(Inlet2, Inlet3, paired = TRUE, alternative = "two.sided")

> t.test(Inlet1, Inlet2, paired = TRUE, alternative = "two.sided")

Paired t-test

data: Inlet1 and Inlet2

t = -1.6815, df = 8, p-value = 0.1312

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

-9.836896 1.540515

sample estimates:

mean of the differences

-4.148191

> t.test(Inlet1, Inlet3, paired = TRUE, alternative = "two.sided")

Paired t-test

data: Inlet1 and Inlet3

t = -6.8188, df = 9, p-value = 7.74e-05

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

-10.228168 -5.132285

sample estimates:

mean of the differences

-7.680226

> t.test(Inlet2, Inlet3, paired = TRUE, alternative = "two.sided")

Paired t-test

data: Inlet2 and Inlet3

t = -1.3042, df = 8, p-value = 0.2284

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

-8.779751 2.436194

sample estimates:

mean of the differences

-3.171779

#KB2

pDR_PFAS_KB_2_analysis <- read_excel("Library/Mobile Documents/com~apple~CloudDocs/Lab/Technical Report/Sample Results/Real time aerosol PDR+PFAS estimation/pDR PFAS KB 2 analysis.xlsx", + sheet = "t-test summary table")

Inlet1<-unlist(c(pDR_PFAS_KB_2_analysis[,1])) Inlet2<-unlist(c(pDR_PFAS_KB_2_analysis[,2])) Inlet3<-unlist(c(pDR_PFAS_KB_2_analysis[,3]))

t.test(Inlet1, Inlet2, paired = TRUE, alternative = "two.sided")
t.test(Inlet1, Inlet3, paired = TRUE, alternative = "two.sided")
t.test(Inlet2, Inlet3, paired = TRUE, alternative = "two.sided")

> t.test(Inlet1, Inlet2, paired = TRUE, alternative = "two.sided")

Paired t-test

data: Inlet1 and Inlet2

t = -1.8802, df = 7, p-value = 0.1021

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

-6.1796366 0.7052916

sample estimates:

mean of the differences

-2.737172

> t.test(Inlet1, Inlet3, paired = TRUE, alternative = "two.sided")

Paired t-test

data: Inlet1 and Inlet3

t = -10.264, df = 7, p-value = 1.802e-05

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

-12.98180 -8.12019

sample estimates:

mean of the differences

-10.551

> t.test(Inlet2, Inlet3, paired = TRUE, alternative = "two.sided")

Paired t-test

data: Inlet2 and Inlet3

t = -4.2817, df = 7, p-value = 0.003648

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

-12.129085 -3.498563

sample estimates:

mean of the differences

-7.813824

#DA

pDR_PFAS_DA_analysis <- read_excel("Library/Mobile Documents/com~apple~CloudDocs/Lab/Technical Report/Sample Results/Real time aerosol PDR+PFAS estimation/pDR PFAS DA analysis.xlsx", + sheet = "t-test summary table")

Inlet1<-unlist(c(pDR_PFAS_DA_analysis[,1])) Inlet2<-unlist(c(pDR_PFAS_DA_analysis[,2])) Inlet3<-unlist(c(pDR_PFAS_DA_analysis[,3]))

t.test(Inlet1, Inlet2, paired = TRUE, alternative = "two.sided")
t.test(Inlet1, Inlet3, paired = TRUE, alternative = "two.sided")
t.test(Inlet2, Inlet3, paired = TRUE, alternative = "two.sided")

> t.test(Inlet1, Inlet2, paired = TRUE, alternative = "two.sided")

Paired t-test

data: Inlet1 and Inlet2

t = 1.5213, df = 13, p-value = 0.1521

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

-8.67392 49.97007

sample estimates:

mean of the differences

20.64808

> t.test(Inlet1, Inlet3, paired = TRUE, alternative = "two.sided")

Paired t-test

data: Inlet1 and Inlet3

t = 1.2312, df = 13, p-value = 0.2401

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

-14.62278 53.37524

sample estimates:

mean of the differences

19.37623

> t.test(Inlet2, Inlet3, paired = TRUE, alternative = "two.sided")

Paired t-test

data: Inlet2 and Inlet3

t = -0.50575, df = 13, p-value = 0.6215

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

-6.704684 4.160986

sample estimates:

mean of the differences

-1.271849

APPENDIX D: PM2.5 REAL-TIME RESULTS T-TEST R CODES & ANALYSIS RESULTS FOR EACH INLETS

library(readxl)

Average_PM2_5_in_each_location_Summary_Chart <- read_excel("~/Library/Mobile Documents/com~apple~CloudDocs/Lab/Technical Report/Sample Results/Average PM_{2.5} in each location Summary Chart.xlsx", + sheet = "t-test")

Inlet1<-unlist(c(Average_PM2_5_in_each_location_Summary_Chart[,2])) Inlet2<-unlist(c(Average_PM2_5_in_each_location_Summary_Chart[,3])) Inlet3<-unlist(c(Average_PM2_5_in_each_location_Summary_Chart[,4]))

t.test(Inlet1, Inlet2, paired = TRUE, alternative = "two.sided")
t.test(Inlet1, Inlet3, paired = TRUE, alternative = "two.sided")
t.test(Inlet2, Inlet3, paired = TRUE, alternative = "two.sided")

> t.test(Inlet1, Inlet2, paired = TRUE, alternative = "two.sided")

Paired t-test

data: Inlet1 and Inlet2
t = -0.79822, df = 5, p-value = 0.461
alternative hypothesis: true difference in means is not equal to 0
95 percent confidence interval:
-32.03948 16.85637

sample estimates:

mean of the differences

-7.591555

> t.test(Inlet1, Inlet3, paired = TRUE, alternative = "two.sided")

Paired t-test

data: Inlet1 and Inlet3

t = -0.91771, df = 5, p-value = 0.4009

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

-18.95884 8.98335

sample estimates:

mean of the differences

-4.987746

> t.test(Inlet2, Inlet3, paired = TRUE, alternative = "two.sided")

Paired t-test

data: Inlet2 and Inlet3

t = 0.48369, df = 5, p-value = 0.649

alternative hypothesis: true difference in means is not equal to 0

95 percent confidence interval:

-11.23430 16.44191

sample estimates:

mean of the differences

2.603808

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