

**ANALYSIS OF BLACK CARBON IN TWO COOKSTOVE STUDIES IN RURAL AND
URBAN PERU**

by

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(Under the Direction of Luke P. Naehler)

ABSTRACT

Cookstoves emit harmful household air pollution (HAP), such as particulate matter (PM) and black carbon (BC). Interventions to decrease HAP in developing nations have ranges of effectiveness in reducing kitchen and personal exposure to HAP. Archived filters from two cookstove studies in Peru were analyzed for black carbon, where PM_{2.5} was significantly lower for intervention stoves or gas use. In rural Santiago de Chuco, traditional stoves had kitchen BC concentrations of 7.9 µg/m³ (N = 45, SE 1.37) while intervention brick stoves with chimneys had 5.1 µg/m³ (N = 45, SE 1.10). The observational study in urban Trujillo had kitchen non-gas BC concentrations of 4.0 µg/m³ (N = 63, SE 0.37), and gas stoves had 2.4 µg/m³ (N = 31, SE 0.24). Clean stoves lower kitchen and personal PM_{2.5} and BC concentrations, but the effect is greater for PM_{2.5}. These findings have implications for HAP-related health and climate research.

INDEX WORDS: Black carbon, Particulate matter, PM_{2.5}, Urban air pollution, Rural air pollution, Intervention cookstove, Improved cookstove, Wood burning, LPG, SootScan, Elemental carbon ratio, BC/PM, Health outcomes.

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A Thesis Submitted to the Graduate Faculty of The University of Georgia in Partial Fulfillment
of the Requirements for the Degree

MASTER OF SCIENCE

ATHENS, GEORGIA

2019

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December 2019

ACKNOWLEDGEMENTS

I would like to acknowledge Tony Hansen from Magee Scientific for his help with the SootScan. I thank the Household Air Pollution Intervention Network community for providing supplies for the diffusers. I thank Christopher Fitzgerald and Gideon St. Helen for access to their information and data for the filters.

I thank Olorunfemi Adetona and Adwoa Commodore for providing information about cookstove studies. I thank Jacob Kremer, Devan Campbell, Katherine Kearns, Abby Droese, Meghan Hardison, and Kayla Valentine for being great lab mates and providing feedback on my thesis. I thank Luke P. Naeher for serving as my major professor and taking me in during the middle of my program. I thank J.S. Wang, Stephen Rathbun, and John Yu who served as my committee members. The University of Georgia Interdisciplinary Toxicology Program has been invaluable for their support, with extra acknowledgements for Brian Cummings, John Wagner, Nikolay Filipov, Joanne Mauro, and Wanda Darden. I thank the UGA Science Library Makerspace for training me on 3D printing and modeling. I thank the organizers of ComSciCon ATL for teaching me about science communication and providing new opportunities to learn.

I am thankful for my mom, dad, and brother for their support throughout my academic career. I thank Angel Flores, Steven Weaver, and Craig Roubos for being spiritual and academic support during my program. I especially thank my wife Ruthanna Reardon for the priceless support and encouragement throughout my program and long hours of work. I am most thankful for God's help to provide me the mind and strength to make it through.

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CHAPTER 1

INTRODUCTION

Chapter 1 provides the layout for the chapters of the thesis. Chapter 2 is the literature review of cookstove studies, air pollution, and black carbon. The chapter also states the objective of the thesis. Chapter 3 is the methods of using the SootScan for black carbon analysis. Chapter 4 is a manuscript titled “Analysis of Black Carbon in Two Cookstove Studies in Rural and Urban Peru”, which will be submitted for publication into The Journal of Environmental Health. Chapter 5 is the discussion and conclusions of the thesis and manuscript.

CHAPTER 2

LITERATURE REVIEW

Cookstove Studies and Particulate Matter Background

The importance of studying household air pollution (HAP) can be seen in the number of lives that are impacted by it, where over 3 billion people rely on solid fuels for cooking and heating (Bruce, Perez-Padilla, & Albalak, 2000). Global observations of deaths attributable to household air pollution from solid fuels have estimates of 1.6 million in the year 2017 (Health Effects Institute, 2019; Institute for Health Metrics and Evaluation (IHME), 2017). Household air pollution is also responsible for an estimated 4% decrease of disability-adjusted life years (Bruce et al., 2000). A common research area for household air pollution is on the health impacts on children and women who tend to have the highest exposures to household air pollution. Exposure in women and children is higher because of the traditional role of women in cooking in the homes of developing nations, while men are typically not in the home during the day. It is also common for infants to be attached to the backs of their mothers while cooking. The amount of exposure to HAP that these individuals experience may vary drastically depending on the time of year, type of stove used, and purpose for stove use. All traditional wood-burning stoves produce incomplete combustion emissions because of the reduced oxygen to carbon ratio. This ratio can be improved with new stove designs that better circulate air across the fuel source (Watson, Crow, Lowenthal, & Merrifield, 2001). A key component of household air pollution is the emission of particulate matter (PM), especially PM that is 2.5 μ m in diameter or smaller (PM_{2.5}). The source of PM of concern is from incomplete combustion, but PM can

also have crustal and biological sources. Particulate matter is made of multiple chemical components and is a heterogeneous mixture. The World Health Organization (WHO) guidelines place an average exposure limit of $25 \mu\text{g}/\text{m}^3$ for 24-hour exposure and $10 \mu\text{g}/\text{m}^3$ for a yearly average exposure limit (WHO, 2014). One of the critical components of $\text{PM}_{2.5}$ is black carbon, a fraction of $\text{PM}_{2.5}$ that is the most light-absorbent (Fierce, Bond, Bauer, Mena, & Riemer, 2016). The importance of measuring black carbon is reflected in the potential health and climate impacts from black carbon (Garland et al., 2017; Janssen Nicole et al., 2011).

Not only is cooking a major source of total household air pollution related toxicity but also heating, lighting, pest control, tobacco smoke, and environmental factors. Proximity to a highway and vehicle use produce additional household exposures (Baumgartner et al., 2014). Accounting for the contribution of outside and ambient sources of air pollution is needed when examining the concentrations of pollutants inside of the home. The addition of PM from cookstoves and ambient sources will add to the total HAP exposures of an individual. Additionally, each source of PM will have its own heterogeneous mixtures of PM components.

Measurements into household air pollution exposure are done through personal or area monitoring. A typical measurement is the concentration of PM in $\mu\text{g}/\text{m}^3$. These measurements are then compiled to characterize the HAP produced by cookstoves in the home. PM_{10} levels in homes range from $300\text{-}3000 \mu\text{g}/\text{m}^3$ for a 24-hour average, with some peaks reaching up to $30000 \mu\text{g}/\text{m}^3$. This is much higher than the EPA's standard of $150 \mu\text{g}/\text{m}^3$ for the 24-hour average for PM_{10} (Bruce et al., 2000). The 24-hour EPA standard for $\text{PM}_{2.5}$ is $35 \mu\text{g}/\text{m}^3$ as of 2012 (EPA, 2012). Although using clean cookstoves lowers the concentrations of particulate matter, the standards are not always met. A clean cookstove may still produce enough particulate matter to surpass the standard if it is not properly maintained or used for heating in the home, which would

still lead to an increase in adverse health outcomes. Other measurements of air pollution that are measured are various PM sizes and distributions, carbon monoxide, black carbon, nitrous and sulfur oxides, and a variety of carcinogens. This mixture of pollutants can change depending on region and fuel types used such as coal, wood, and kerosene (Bruce et al., 2000; Johnson & Chiang, 2015).

The quality of fuel and stove used is often correlated with the socioeconomic status of the family (SES). The SES will contribute to a plethora of other health benefits such as access to medicine and vaccines, which makes characterizing the impacts of clean fuels even more challenging. Cost of the cleaner fuels and the specialized stoves may be unobtainable for some populations. Additionally, individuals may use both the traditional and improved stoves at the same time. This creates an obstacle for clean fuel use for impoverished populations. Culturally, the preparation of certain foods may still be preferred using traditional stoves (Bonjour et al., 2013). Despite the challenges to adoption of cleaner fuels and stoves, the rate of deaths attributable to solid fuel use has decreased globally since 1990 to the rate of 21 per 100,000 individuals as seen in Figure 2. 1 (Institute for Health Metrics and Evaluation (IHME), 2017). The decrease may be due to the effectiveness of interventions that have been implemented in recent decades such as improved stove designs provided by the Peruvian government in 2011 (Fitzgerald et al., 2012).

A surprising finding from the research is that the health effects of household air pollution were not a focus until after the year 2000. Instead, the focus had been on decreasing the amount of fuel consumption in homes. The shift towards exposure and health can be seen much more clearly now, but there are still many unanswered questions. Specific areas of focus are with respiratory illnesses and cardiovascular disease. This is especially important in children, as

respiratory infection is the leading cause of death worldwide in children under five years old. Studies show a strong odds ratio for household air pollution exposure and respiratory illness (Clark et al., 2011). Baumgartner and colleagues did a study of women in rural China that showed an increase of 2.2 mm Hg systolic blood pressure and 0.5 mm Hg diastolic blood pressure with an increase of 1-log- $\mu\text{g}/\text{m}^3$ of $\text{PM}_{2.5}$ (Baumgartner et al., 2011). An additional factor to consider is the impact of early childhood exposure to smoke pollution and its impacts on developmental diseases. Some of these exposures may occur as early as pregnancy and will not develop until the child reaches adulthood. It then becomes difficult to determine if the disease came from early exposure or from current exposure (Smith et al., 2011). One of the benefits of researching HAP and its health impacts are understanding how individual components of HAP can correlate to separate health outcomes.

Other health concerns from exposure to household air pollution and solid fuel use include higher cancer rates, increased tuberculosis infections, and infant mortality. Estimations into household air pollution's contribution into deaths by disease are 3.6% for cardiovascular disease, 9.2% for respiratory diseases, 12.2% for respiratory infections, and 0.9% for cancer (Institute for Health Metrics and Evaluation (IHME), 2017). An increase of cancer from household air pollutants is typically associated with tobacco smoke exposure, with less certainty from solid fuel use. This association is expected to be found and supported at some point, as several emissions from cookstoves are common among tobacco smoke emissions. The exposure to HAP may also lead to secondary causes of cancer, such as increased inflammation and a more susceptible immune system. Tuberculosis infection is also increased from solid fuel use, which is compounded by other low SES factors such as malnutrition (Bruce et al., 2000). However, diagnosing health outcomes is challenging in the developing world, as many of the individuals

who are exposed to the highest HAP do not have easy access to medical facilities. Due to the lack of medical access, some HAP studies combine exposure and health outcomes together. As measures of HAP exposure are taken, health checkups and collections for biomarkers are performed.

Exposure assessment also runs into the problem of social and community exposures. Individuals do not spend all their time just inside their home. Ambient exposures from outside such as vehicle exhaust and emissions from neighboring homes will change the exposure amount. The change in location and exposure to PM_{2.5} and BC was demonstrated by Quinn et al. by including GPS tracking with an automated microenvironmental aerosol sampler (Quinn et al., 2018). Seeing the stove or the pollution sources in homes may interfere with the assessment that fieldworkers and other individuals make. Collecting samples before and after interventions also adds to the time and resource requirement for studies. The inconsistent styles of stoves and housing produces a wide range of exposures for the individuals in the home. Interventions would then have widely ranging impacts.

As research into HAP from cookstoves advances, need for knowledge into the components of HAP has grown. Improvements in monitoring technology and methods for determining the components of HAP provide extra insights into the exposures that individuals have from different cookstoves. Black carbon is one of the components of PM_{2.5} that can be measured using multiple methods and can be measured from samples collected years earlier.

Black Carbon Background

Particulate matter is a heterogeneous mixture of substances that have different ratios of components based on the source of the particulate matter. Black carbon is one of many components of PM_{2.5} that is of major concern for human health due to its links to asthma, lower

birth weights, and cardiovascular disease (Nicole AH Janssen, 2012). Determining the exact amount of black carbon in PM_{2.5} can be challenging, since it shares overlapping characteristics with elemental carbon. Thus, elemental carbon from thermal optical analysis is often used as a surrogate for BC from light transmission, which is referred to as “Equivalent black carbon” (Briggs & Long, 2016). They both are carbonaceous particles that develop from the incomplete combustion of carbon-based fuels and are light absorbing. A consideration for black carbon is a lack of water solubility, which impacts the aging and coating of BC exposed to the atmosphere (Briggs & Long, 2016). These characteristics help BC and EC to stand out from the other components of PM_{2.5} created during incomplete biomass combustion, such as organic carbon (Petzold et al., 2013).

Black carbon will typically be in the form of an aggregate, being made up of smaller parts that are 20-60 nm in diameter. These aggregates will form to be in two main shapes, either spread out and branched, or more compact and spherical (Liu, 2019). The total size of these aggregates will vary by source and environmental factors. Some examples of sizes range from 30-100 nm for diesel exhaust and 130-160 for wood stoves (Drinovec et al., 2017).

PM_{2.5} alone does not provide as strong of a correlation to health outcomes as analyzing the components of PM_{2.5} (Grahame, Klemm, & Schlesinger, 2014). For individuals admitted to a Boston health center due to ischemic stroke, black carbon had the highest incidence rate ratio (1.2, 95% CI 0.94, 1.54) out of 18 constituents of PM_{2.5} (Mostofsky et al., 2012). Additionally, BC has showed ranges of increased all-cause mortality compared to only PM₁₀ for vehicle heavy emissions (Janssen Nicole et al., 2011). Some biomarkers of exposure may also be used to estimate the impact of BC exposure, such as markers of inflammation like nitric oxide, IL-1 β , and 8-isoprostane (De Prins et al., 2014). By attributing direct health impacts from BC,

interventions can be designed in ways that decrease the components of PM_{2.5} that are strongly associated with harmful health outcomes.

A quarter of the global emissions of black carbon is expected to come from uses in homes, such as cooking and heating (Wathore, Mortimer, & Grieshop, 2017). A large amount of the focus on black carbon has been on ambient and environmental concentrations, or with the source apportionment of diesel exhaust. This focus on vehicle emissions may be based on developed nations instead of the developing world. The estimated BC emissions of the United States had 40 Gg/yr (1Gg=1100 tons) from residential sources and 216 Gg/yr from transportation. South America had emissions of 71 Gg/yr from residential and 169 Gg/yr from transportation (Grahame et al., 2014). Total BC emissions from the residential sector grew from 1960 until 2006 but has leveled off. This increase is mainly tied to population increases in developing nations (Wang et al., 2014). Research into HAP and BC emissions has many challenges, with one of the biggest hurdles being the heterogeneity of the cookstoves and the homes where they are used.

One of standards for measuring black carbon is the thermal optical analysis (TOA). This method directly measures EC through destructive methods, which is then used as a surrogate measure of BC. A nondestructive method that can measure BC is to use the transmission or absorbance of light through an exposed filter. The SootScan OT21 Transmissometer (Magee Scientific Corporation, Berkeley, CA) measures the concentration of black carbon on the surface of a filter through the transmission of 880 nm light through the filter, which is the wavelength of light that BC strongly absorbs. Use of the SootScan for BC analysis has been tested in multiple studies, with work done by Presler-Jur et al. in 2017 being an example. Samples collected on

5393 Teflon filters were analyzed using the SootScan in comparison to TOA (Presler-Jur, Doraiswamy, Hammond, & Rice, 2017).

An applicable and recent study correlating stove use to black carbon was done with 19 different stoves that are commonly used in the developing world (Garland et al., 2017). In the study, the results from TOA were compared to the results of using the SootScan. Linear regression compared the results of the two different instruments/methods. TOA produces data in $\mu\text{g}/\text{m}^3$, and the SootScan produces data in optical transmittance, which converts into light attenuation (ATN). These two results were used to create the slope of linear regression to produce the attenuation cross-section, also known as sigma. The sigma value is then used to convert ATN into μg of BC found on a sample filter. The sigma value is not consistent among all conversions, depending on filter material and BC source. For example, Teflon FRM filters has a sigma of $4.2 \text{ cm}^2/\mu\text{g}$ for environmental sampling with unspecified sources (Hansen, 2015; Neil Frank, 2009). The sigma found in the traditional cookstove experiment was $13.7 \text{ cm}^2/\mu\text{g}$. A representative sigma value can be used when comparing similar studies, but a more accurate value could be determined using TOA. The μg of BC on the filter can be used to calculate the BC concentration, which is described in the methods chapter. Gravimetric data can be compared to the μg of BC to produce a ratio of BC to $\text{PM}_{2.5}$. Of the 19 different types of traditional cookstoves tested by Garland, the BC/ $\text{PM}_{2.5}$ ratio ranged from 0.003 to 0.38 (Garland et al., 2017). Additional considerations with BC concentrations are the influence of ambient BC compared to indoor BC. A study of homes that used biomass stoves in West Africa showed that indoor concentrations of BC were higher ($2\text{-}14 \mu\text{g}/\text{m}^3$) than ambient concentrations ($2\text{-}11 \mu\text{g}/\text{m}^3$). This suggest that in regions that rely heavily on solid fuel, that the main contributor of BC emissions are cookstoves (Zhou et al., 2014).

Use of the SootScan OT21 has typically been applied to studies on environmental pollution or from diesel fuel. These studies also have been done in a manner where banked samples were used, but no pre-exposure scan was performed. Instead, a representative blank filter is used, but this may be inaccurate due to the variation of every Teflon filter (Presler-Jur et al., 2017). Additional considerations when using the OT21 include the use of a diffuse filter to dampen the light transmitted, such as used by Quinn et al. (Quinn et al., 2018).

Scope of Thesis

The use of the SootScan allows for retrospective BC analysis of archived samples. The SootScan has already been used on archived filters exposed to woodsmoke and non-woodsmoke sources (Neil Frank, 2009). Applying the same concept to previous studies of cookstove emissions will provide insight into future work in the developing world. Teflon filters from two previous cookstove studies were used for the purpose of analyzing their BC concentrations in relation to PM_{2.5} concentration for use in this research. The new analysis was done using the SootScan and the archived filters, where the concentrations of PM_{2.5} and BC of the stove types and fuel types were compared in the studies. The two studies were both located in Peru: Santiago de Chuco in 2008 by Fitzgerald et al. (Fitzgerald et al., 2012), and Trujillo in 2004 by St. Helen et al. (Helen et al., 2015). Both studies used gravimetric analysis for PM_{2.5} in $\mu\text{g}/\text{m}^3$. Both studies focused on stove and fuel types, with Santiago de Chuco being connected to the provision of an improved cookstove for the home. The study in Trujillo was cross-sectional. Additional details of the instruments and sampling protocols for both studies will be included in the methods section.

Although the two studies have a component of a traditional stove and improved stove, they are not directly comparable due to differences in altitudes, home conditions, the type of

traditional or improved cookstove, and fuel sources. Addition of central site sampling from Trujillo provides insights into ambient BC concentrations. The impact of being in a rural, peri-urban, or urban location would contribute to different baseline ambient concentrations of PM_{2.5} and BC.

The BC concentration will be used in multiple ways for each study. Total BC concentrations can be measured for each stove type to compare their BC emissions. The concentrations of BC and PM_{2.5} will be used to determine how closely they correlate. The ratio of BC to PM_{2.5} will also be used to represent the proportion of mass that BC makes up of the PM_{2.5}. A secondary use for the ratio is the focus of the efforts to mitigate climate change (Garland et al., 2017). The role of BC as a component of PM_{2.5} will help to influence policy and interventions in human health and environmental protection. This research will also provide additional information on study design for using the SootScan for black carbon studies, and address some of the shortfalls of exclusively using archived samples.

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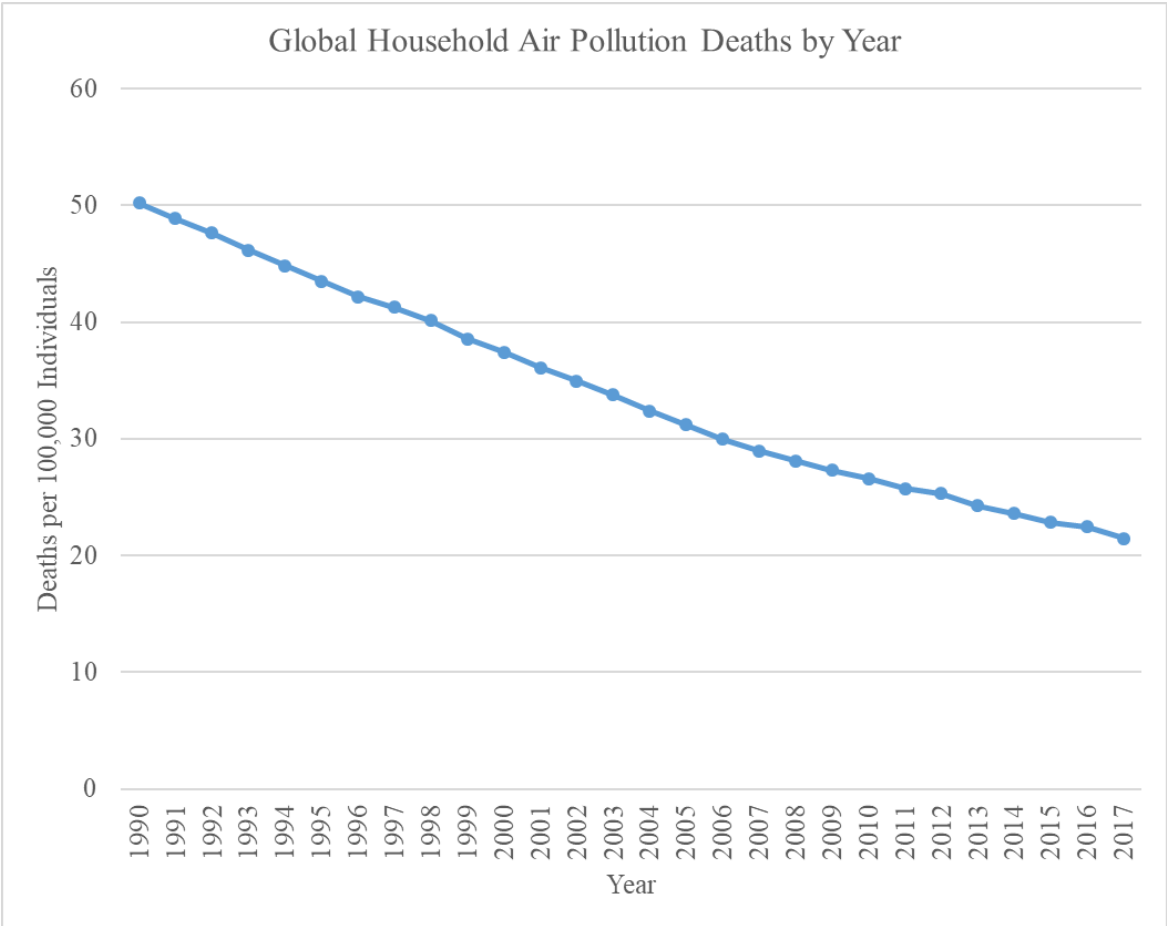


Figure 2. 1 Global deaths from HAP solid fuel use from 1990-2017 per 100,000 individuals. The rate of deaths attributable from household air pollution (HAP) with solid fuel sources have decreased since 1990.

(Institute for Health Metrics and Evaluation (IHME), 2017)

Developed from Global Burden of Disease Study 2017, under Open Data Commons Attribution License, accessible at <https://vizhub.healthdata.org/gbd-compare/>.

CHAPTER 3

METHODS AND MATERIALS

Black Carbon Analysis by Optical Transmission

Particulate matter from biomass and fossil fuels gathered on filters contain a heterogeneous mixture of components, with black carbon being one of the main components. In order to determine the mass of black carbon on a filter, destructive or nondestructive methods can be used. One of the nondestructive methods is the optical transmission of light through the filter, which can be accomplished with the Magee Scientific SootScan Model OT21 Transmissometer (Magee Scientific Corporation, Berkeley, CA), as seen in Figure 3. 1. The SootScan is the main instrument that was used in the analysis of filters from cookstove studies for black carbon from Santiago de Chuco (Fitzgerald et al., 2012) and Trujillo (Helen et al., 2015), Peru. Procedure for the SootScan was followed according to the manual provided by Magee Scientific, with the additional use of a diffuse filter (Magee Scientific, 2016). Examples of exposed filters can be seen in Figure 3. 2.

The SootScan measures black carbon by comparing the 880 nm infrared (IR) light absorbance between a blank and sample filter. The IR light that passes through the filters gives a reading of transmitted light intensity. The blank filter will give one reading, while the sample filter will give a second reading. These two transmitted intensities will then be used to provide the IR attenuation using

$$ATN = 100 * \ln(IRB/IR)$$

where IRB is the blank transmission and IR is the sample transmission. An example of an ATN value of a visibly light filter would be

$$\text{ATN} = 100 * \ln(236227/207641) = 12.9$$

to get the attenuation. An example of an ATN value for a visibly dark filter would be

$$\text{ATN} = 100 * \ln(239349/9131) = 326.62$$

to get the attenuation.

The attenuation of a sample is ultimately only a measure of how much 880 nm light that passes through the filter. The accuracy of the ATN from the SootScan can be checked by measuring neutral density filters. The SootScan for use in this research was validated at time of the manufacturing certification (Magee Scientific, 2014).

Three additional variables are important for calculating BC concentration from the ATN. They are the BC attenuation cross-section (also known as sigma), area of sample on the filter, and the volume of air passed through the filter. The area of sample on the filter is dependent on the instrument collecting the sample and the filter size. Most instruments deposit PM_{2.5} across the complete area of the filter, minus any area taken up by the protective plastic ring. Some instruments will only deposit over a smaller area of the sample and not use the entire filter, such with use of the MicroPEM aerosol real time monitor (RTI International, Research Triangle Park, NC), which has 10mm of exposure on a 25mm filter. 37mm filters have exposure diameters of 29.5mm to account for the protective ring, which allows for 6.8cm² of area for exposure. The volume is a product of the average flow rate by sampling the time. Each instrument has its own ideal flow rate, and each study uses its own sampling time. The instruments produce an output of average flow and total time for collection. These variables are multiplied for each individual sample to give a total volume of air passed through the same filter in m³.

The BC attenuation cross-section or mass absorption cross-section (MAC, sigma, or σ) is a variable that changes according to fuel type, stove use, filter type, and other variables (Lioussé, Cachier, & Jennings, 1993). This variable is vital in converting ATN into mass of BC, as the ATN does not directly reflect the amount of BC on a filter. Particulate matter such as dust and brown carbon may change the transmission of 880 nm light through the filter. In order to determine how the ATN relates to BC, the ATN needs to be compared to a known amount of BC through other methods such as thermal optical analysis (TOA). TOA a destructive method that directly measures elemental carbon, which is used as a surrogate for BC. In order to produce data from the SootScan and TOA, duplicate filters need to be used for representative sites, controls, and interventions. The possibility of calculating sigma from previous studies is not always possible, so representative values for sigma need to be used (Garland et al., 2017).

The IR attenuation can be used to get the concentration of black carbon using

$$BC = ((\text{Filter area}/\text{Sample volume}) * \text{ATN} * 10^4) / \sigma$$

where the results will be in $\mu\text{g}/\text{m}^3$ (Presler-Jur, Doraiswamy, Hammond, & Rice, 2017). Using this formula with modified values allows for an ATN to be converted into BC concentration. The sigma value that will be used is $13.7 \text{ cm}^2/\mu\text{g}$, as this value was calculated from the use of traditional cookstoves with wood as fuel using a Teflon filter. This value was determined by Garland and colleagues from comparing the ATN from the SootScan to the results of thermal optical analysis (Garland et al., 2017). The accuracy of this sigma value for use in Peru household air pollution samples may be questionable, as the original value was calculated using Cambodian household air pollution samples. An additional unknown is if the filters being stored in the freezer at the University of Georgia (UGA) for more than ten years impacted the reading from the SootScan.

Diffuser Material Selection and Description

The use of diffusers with the SootScan may be a requirement based on the filter material. Teflon filters allow for an excessive amount of light to pass through. The solution to this is to add in a diffuser to decrease the total amount of light to be transmitted past the filter. The decrease of light prevents an error of the SootScan to receive too light of a reading.

Two different diffuser materials were tested for use as diffusers for 37mm filters: Tissuquartz (2500QAT-UP, Pall Life Sciences, Ann Arbor, MI) and Emfab (TX40H120-WW, Pall Life Sciences, Ann Arbor, MI). Diffuser selection was done by testing different materials for their quality of scan and protection of the filter. An ideal diffuser material would produce a consistent IR ATN when switching between each diffuser of the same type. This is important in comparing the blank scan and the sample scan, as both the blank filter and sample filter need a diffuser.

A test was done to compare the use of Tissuquartz and Emfab as a diffuser for the SootScan. This test was done on three 15mm Teflon filters from the pilot phase of a cookstove study (Household Air Pollution Intervention Network). The filters were selected based on their visual filter loading of a light, medium, and dark appearance, with the assumption that the darker the filter, the higher the IR ATN would be. Two Tissuquartz and two Emfab filters were cut to fit the 15mm cartridge of the SootScan and placed in as diffusers. Each of the three filters were then scanned for 6 sets of 25 scans for each diffuser. Each set had a rescan of the blank filter and diffuser. The difference of the maximum and minimum IR ATN for each set of 25 scans and the total of 150 scans were compared, along with the standard deviation of the sets and the total 150 scans. Results showing the minimum ATN, maximum ATN, and averages, are shown in Table 3. 1. Both diffuser types produced similar IR ATN averages for all three filters. The difference

between the averages are within typical variation seen between scanning sessions when the blank filter is rescanned.

The IR ATN values between the Emfab and Tissuquartz diffusers did not produce a noticeable difference. The durability and physical integrity each diffuser were the characteristics that determined which one would be used for the study. Some diffusers can leave fibers or grains on the filters or may lead to tearing when the filter and diffuser is secured in the SootScan. The Tissuquartz diffuser would start to deteriorate around 200 scans due to contact with the tweezers and the clamp of the SootScan cartridge. As it deteriorated, some of the Tissuquartz material would stick to the sample filters. The Emfab diffuser would last for around 500 scans before deteriorating. The Emfab diffusers have two different sides, one side is a tissue-like material and the other side is a weaved glass fiber material. These are used with the glass fiber facing downwards. The Emfab diffusers were selected to be used, as they are sturdier and less likely to tear. A drawback is that the edges of the diffuser tends to tear over time. This was corrected for by taping the outer edge of the Emfab diffuser. All 37mm filters for this study were scanned using an Emfab diffuser.

Limitations

The SootScan has a limit to the accuracy and range when samples are too dense with BC. When ATN levels are too high, the SootScan gives an Error 60, which is when the sample is too dark to read. This leaves the sample with a BC level that cannot be determined, but it can be assumed that it is higher than the max ATN (approximately 500) that the SootScan will give. In addition to a maximum limit, the ATN reading loses a linear prediction of actual BC as the levels are higher. Readings above 125 ATN no longer follow the linear prediction.

While many of the studies that used the SootScan recommended measuring the filters before use, very few were able to do so. Alternatively, it may be best to do a premeasurement of the filters to gather the IR transmitted intensity as the blank, and then use the premeasurement in the calculation of ATN, such that

$$\text{ATN}=100*\ln(\text{pre-IR}/\text{post-IR})$$

where the pre-IR is the transmission value before exposure, and the post-IR is the transmission value after exposure. For the sake of this study, this method was unavailable, as all samples have come from previously completed studies. In order to better account for the lack for premeasurements, multiple blank filters were scanned. The blank filter that had the median ATN was chosen to be the blank filter used for the studies. This selection of a median blank would prevent attenuations from being too high or too low. Additionally, the SootScan was not in a climate-controlled room or vent hood. However, the SootScan was only used when the humidity and temperature was within operating parameters according to Magee Scientific (Magee Scientific, 2016).

Multiple sigma values have been previously calculated for the SootScan BC conversion. Due to the variability of the samples, each type of stove and fuel combination will need its own sigma value. This is important even for similar stove and fuel use in different altitudes and humidity. Additionally, the material of the filter changes how the PM_{2.5} is accumulated on the filter as well as having its own optical properties. Many of the sigma values have been calculated from ambient measurements. Comparing an ambient sigma calculated in the OT21 Transmissometer Analysis Worksheet template 2.4 (Hansen, 2015), which used Teflon filters gave a sigma of 4.2 cm²/μg from “EPA empirical EC relation for TEFLON FRM filters”. An additional study that used a sigma was from Chow et al. The study used samples from Mexico

City from the IMPROVE (n=260) samples, and a sigma of $11.6 \text{ cm}^2/\mu\text{g}$ was used. Although this study had more similarities to the two Peru studies, the measurements were not taken with the SootScan, but a Teflon filter was still used (Chow, Watson, Edgerton, & Vega, 2002).

A comparable study to estimate the sigma value is from Garland et al. (Garland et al., 2017), where a SootScan OT21 was used along with Teflon filters exposed to HAP from cookstoves. Measurements from the SootScan were compared directly with thermal optical analysis (TOA) from quartz filters. Filters from Cambodia (N = 44) had concurrent sample collection with quartz and Teflon filters. The quartz filters were used for TOA with NIOSH Method 5040, which used an OC-EC Aerosol Analyzer. The Teflon filters were used for BC attenuation from the SootScan. The linear relationship between TOA and the attenuation from this study gave a sigma of $13.7 \text{ cm}^2/\mu\text{g}$ from the Cambodian samples.

Customized SootScan Cartridge for Filters Exposed with the MicroPEM

The SootScan typically comes with different cartridges that can fit 47mm, 37mm, and 25mm filters. These cartridges have an opening or aperture that is 15mm in diameter that allows for the transmitted light to pass through. This opening is suitable for filters that have the entire or most of the filter having been exposed. However, some instruments do not deposit $\text{PM}_{2.5}$ evenly across the filter, such as the MicroPEM. The MicroPEM deposits $\text{PM}_{2.5}$ on a 10mm diameter area of a 25mm filter. Using the standard 25mm cartridge of the SootScan will then have areas scanned that have not been exposed to $\text{PM}_{2.5}$. This would be expected to underestimate the BC reading, especially at higher concentrations. Light would be free to pass through 56% of the area that is scanned, with only the blank area of the filter and diffuser to block transmission. The change in reading should have no impact on the blank filter, but any exposed filter would not have an accurate scan. In order to account for this problem, a custom

25mm cartridge with a 10mm exposure hole had to be made. A 3D object file was created in Tinkercad (©2019 Autodesk), with the overall design based on the standard 25mm cartridge. The exposure hole was modified to be 10mm in diameter. The object was then 3D printed using PLA plastic with the MakerBot Replicator 5th Gen. (MakerBot Industries, LLC., Brooklyn, NY), located at the University of Georgia Science Library Makerspace. Figure 3. 3 shows the printed cartridge along with the base schematic.

The smaller diameter of the exposure hole will ultimately block more of the transmitted light, but two factors negate the smaller transmission. The SootScan adjusts the amount of light emitted from the LED to the point that enough light is transmitted to the detector. This adjustment was confirmed with a representative from Magee Scientific. The second factor is that the sample and blank are both impacted in the same way from the cartridge. The transmitted IR light of the blank and sample filter will be used in the ATN calculation. A test was performed with a blank filter and a filter with 10mm of exposure verify the cartridge. The blank filter had an IR ATN of 0.27 for the original cartridge, and 0.21 for the 3D printed cartridge. These two values are within range of what would be typically seen by rescanning the same filter. The filter with 10mm of PM_{2.5} exposure had an IR ATN of 35.08 for the original cartridge and 38.64 with the 3D printed cartridge. This 10% increase in IR ATN supports the need for having the smaller opening for a more accurate BC measurement. The use of 3D printed cartridges for the SootScan allows for prototypes to be quickly tested and for implementation of modifications. This should also be considered for the addition of semi-permanent diffusers.

Methods Synthesis

Use of the SootScan allows for a nondestructive and efficient method of adding additional black carbon data for previous and current air pollution studies. The collection methods, type of filter, and source of particulate matter need to be accounted for when extrapolating BC concentration from the ATN given by the SootScan. Modifications such as diffusers and custom cartridges for filters allow the SootScan to be adaptable for a variety of sampling methods.

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Table 3. 1 Diffuser test results from three exposed 15mm filters.

Emfab Diffuser			
Filter Loading	Minimum ATN	Maximum ATN	Mean ATN
Light	13.17	20.89	17.23
Medium	58.38	64.47	61.62
Dark	134.69	140.11	137.81

Tissuquartz Diffuser			
Filter Loading	Minimum ATN	Maximum ATN	Mean ATN
Light	14.99	20.51	18.16
Medium	58.6	63.96	61.74
Dark	134.46	138.12	136.23

Each of the three filters were scanned 150 times for both the Emfab and Tissuquartz diffusers. The results of all 150 scans show mean, minimum and maximum optical attenuation (ATN) values. The mean ATN between the two filters is similar enough for either to be used as a diffuser for the SootScan.



Figure 3. 1 Image of the SootScan OT 21 Transmissometer.
The image is of the SootScan that was used at UGA. The cartridge slots are pulled out so that the blank filter can be scanned. The image shows the 15mm cartridge with a filter in place.

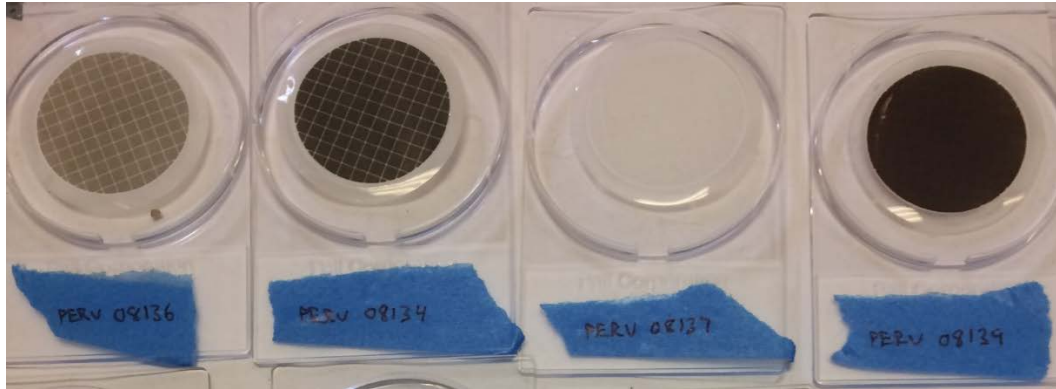


Figure 3. 2 Filters exposed to PM_{2.5} and BC emissions from household cookstoves. The filters were stored in the freezers at UGA. The image contains filters from the study in Santiago de Chuco by Fitzgerald et al. in 2008 (Fitzgerald et al., 2012). The loading of particulate matter 2.5 μ m (PM_{2.5}) and black carbon (BC) are visible on the Teflon filters.

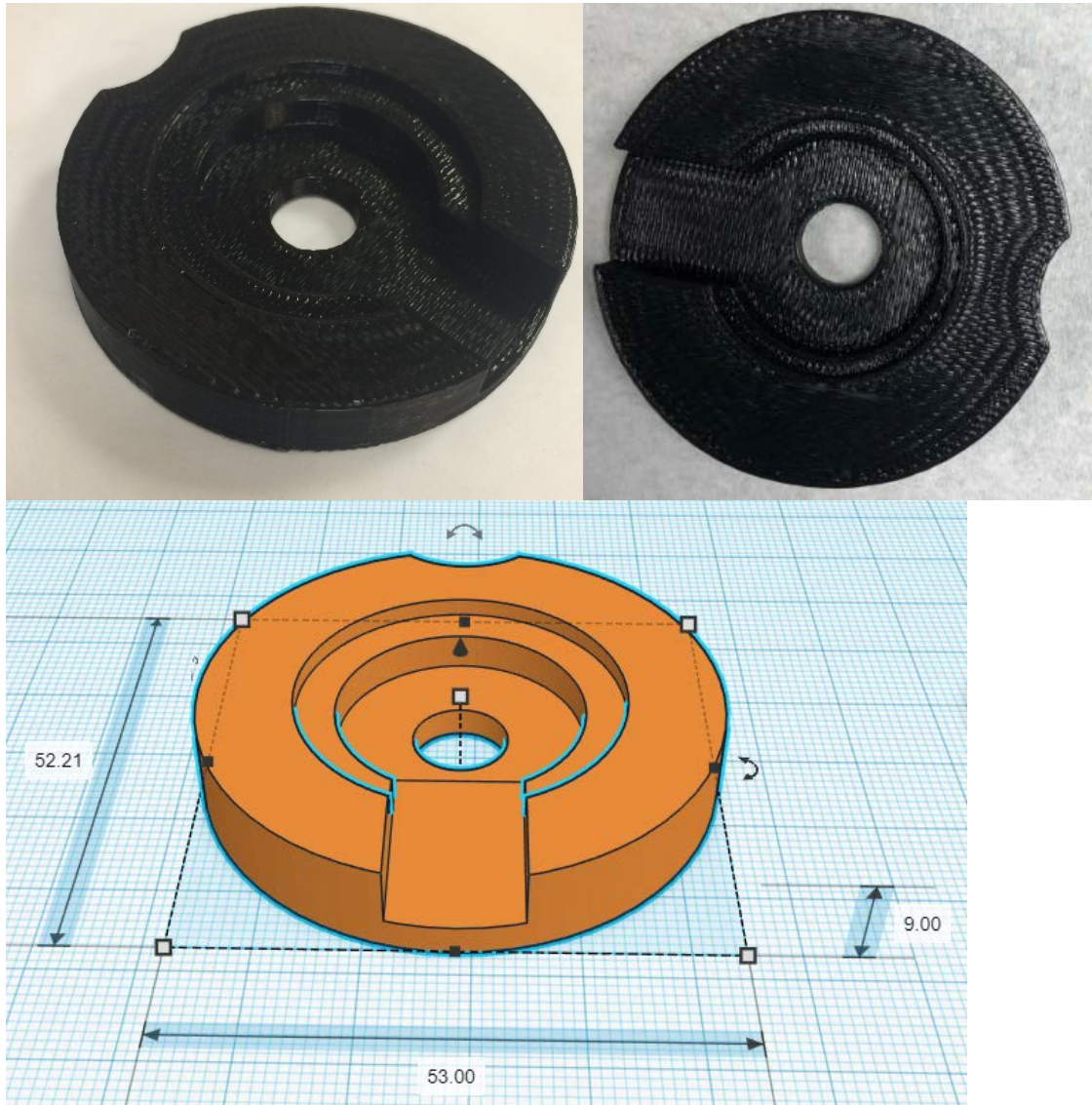


Figure 3.3 25mm Custom Cartridge Schematic.

(Top) The printed 25mm cartridge with a 10mm opening using black PLA plastic. (Bottom) The schematic created in Tinkercad with mm measurements.

Cartridges were printed at the UGA Science Library Makerspace using the MakerBot Replicator.

CHAPTER 4
ANALYSIS OF BLACK CARBON IN TWO COOKSTOVE STUDIES IN RURAL AND
URBAN PERU¹

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To be submitted to The Journal of Environmental
Health

Analysis of Black Carbon in Two Cookstove Studies in Rural and Urban Peru

Abstract

Cookstoves emit harmful household air pollution (HAP), such as particulate matter (PM) and black carbon (BC). Interventions to decrease HAP in developing nations have ranges of effectiveness in reducing kitchen and personal exposure to HAP. Archived filters from two cookstove studies in Peru were analyzed for black carbon, where $PM_{2.5}$ was significantly lower for intervention stoves or gas use. In rural Santiago de Chuco, traditional stoves had kitchen BC concentrations of $7.9 \mu\text{g}/\text{m}^3$ (N = 45, SE 1.37) while intervention brick stoves with chimneys had $5.1 \mu\text{g}/\text{m}^3$ (N = 45, SE 1.10). The observational study in urban Trujillo had kitchen non-gas BC concentrations of $4.0 \mu\text{g}/\text{m}^3$ (N = 63, SE 0.37), and gas stoves had $2.4 \mu\text{g}/\text{m}^3$ (N = 31, SE 0.24). Clean stoves lower kitchen and personal $PM_{2.5}$ and BC concentrations, but the effect is greater for $PM_{2.5}$. These findings have implications for HAP-related health and climate research.

Introduction

The importance of studying household air pollution (HAP) can be seen in the number of lives that are impacted by it, where over 3 billion people rely on solid fuels for cooking and heating (Bruce, Perez-Padilla, & Albalak, 2000). Global observations of deaths attributable to household air pollution from solid fuels reached 1.6 million in the year 2017 (Health Effects Institute, 2019; Institute for Health Metrics and Evaluation (IHME), 2017). Household air pollution is also responsible for an estimated 4% decrease of disability-adjusted life years (Bruce et al., 2000). A common research area for household air pollution is on the health impacts on children and women, who tend to have the highest exposures to household air pollution.

Exposure in women and children is higher because of the traditional role of women in cooking in the homes of developing nations, while men are typically not in the home during the day. The amount of exposure to air pollution that these individuals experience may vary drastically depending on the time of year, type of stove used, and purpose for stove use. All traditional wood-burning stoves produce incomplete combustion emissions because of the reduced oxygen to carbon ratio. This ratio can be improved with new stove designs that better circulate air across the fuel source (Watson, Crow, Lowenthal, & Merrifield, 2001). A key component of household air pollution is the emission of particulate matter (PM), especially PM that is $2.5\mu\text{m}$ in diameter or smaller ($\text{PM}_{2.5}$). The source of $\text{PM}_{2.5}$ of concern is from incomplete combustion, but $\text{PM}_{2.5}$ can also have crustal and biological sources. Particulate matter is made of multiple chemical components and is a heterogeneous mixture. The World Health Organization (WHO) guidelines place an average exposure limit of $25\ \mu\text{g}/\text{m}^3$ for 24-hour exposure and $10\ \mu\text{g}/\text{m}^3$ for a yearly average exposure limit (WHO, 2014). Particulate matter has different ratios of components based on the source of the $\text{PM}_{2.5}$. Black carbon, the most light-absorbent fraction of $\text{PM}_{2.5}$ (Fierce, Bond, Bauer, Mena, & Riemer, 2016), is of major concern for human health due to its links to cardiovascular disease, lower birth weights, and asthma (Nicole AH Janssen, 2012).

Adoption of improved cookstoves and cleaner fuels can be challenging because of increased cost, cultural embeddedness, and preference in traditional cooking methods. Cost of the cleaner fuels and the specialized stoves may be unobtainable for some populations. Additionally, individuals may use both the traditional and improved stoves at the same time. This creates an obstacle for exclusive clean fuel use for impoverished populations (Bonjour et al., 2013). Despite the challenges to adoption of cleaner fuels and stoves, the rate of deaths attributable to solid fuel use has decreased globally since 1990 to the rate of 21 per 100,000

individuals (Institute for Health Metrics and Evaluation (IHME), 2017). The decrease may be due to the effectiveness of interventions that have been implemented in recent decades such as improved stove designs provided by the Peruvian government in 2011 (Fitzgerald et al., 2012).

Determining the exact amount of black carbon in $PM_{2.5}$ can be challenging, since it shares overlapping characteristics with elemental carbon. Thus, elemental carbon from thermal optical analysis is often used as a surrogate for BC from light transmission, which is referred to as “Equivalent black carbon”. (Briggs & Long, 2016). They both are carbonaceous particles that develop from the incomplete combustion of carbon-based fuels and are light absorbing. A consideration for black carbon is a lack of water solubility, which impacts the aging and coating of BC exposed to the atmosphere (Briggs & Long, 2016). These characteristics help BC and EC to stand out from the other components of $PM_{2.5}$ created during incomplete biomass combustion, such as organic carbon (Petzold et al., 2013). While TOA measures elemental carbon through destructive methods, which is then used as a surrogate measure for BC, a nondestructive method that is able to measure BC is to use the transmission or absorbance of light through an exposed filter. The SootScan OT21 Transmissometer (Magee Scientific Corporation, Berkeley, CA) measures the concentration of black carbon on the surface of a filter through the transmission of 880 nm light through the filter, which is the wavelength of light that BC strongly absorbs. Use of the SootScan for BC analysis has been tested in multiple studies, with work done by Presler-Jur et al. in 2017 being an example. Samples collected on 5393 Teflon filters were analyzed using the SootScan in comparison to TOA (Presler-Jur, Doraiswamy, Hammond, & Rice, 2017).

Epidemiological studies have provided evidence for potential health impacts that can be directly attributed to BC (Garland et al., 2017; Janssen Nicole et al., 2011). $PM_{2.5}$ alone does not provide as strong of a correlation to health outcomes as analyzing the components of $PM_{2.5}$

(Grahame, Klemm, & Schlesinger, 2014). For individuals admitted to a Boston health center due to ischemic stroke, black carbon had the highest incidence rate ratio (1.2, 95%CI 0.94, 1.54) out of 18 constituents of PM_{2.5} (Mostofsky et al., 2012). Additionally, BC has showed ranges of increased all-cause mortality compared to only PM₁₀ for vehicle heavy emissions (Janssen Nicole et al., 2011). Some biomarkers of BC exposure that increase are markers of inflammation like nitric oxide, IL-1 β , and 8-isoprostane (De Prins et al., 2014). By attributing direct health impacts from BC, interventions can be designed in ways that decrease the components of PM_{2.5} that are most harmful to human health.

A quarter of the global emissions of black carbon is expected to come from uses in homes, such as cooking and heating (Wathore, Mortimer, & Grieshop, 2017). A large amount of the focus on black carbon has been on ambient and environmental concentrations, or with the source apportionment of diesel exhaust. This focus may be based on developed nations instead of the developing world (Wang et al., 2014). Research into HAP has many challenges, with one of the biggest hurdles being the heterogeneity of the cookstoves and the homes where they are used. The differences in stove designs and fuel sources leads to a variety of HAP exposures, as well as changes in the content of BC from the stove emissions.

One of the most applicable and recent studies correlating stove use to black carbon was done with 19 different stoves that are commonly used in the developing world by Garland and colleagues (Garland et al., 2017). In the study, the results from TOA were compared to the results of using the SootScan. Linear regression compared the results of the two different instruments and methods. TOA produces data in $\mu\text{g}/\text{m}^3$, and the SootScan produces data in optical transmittance, which converts into light attenuation (ATN). These two results were used to create the slope of linear regression to produce the attenuation cross-section, also known as

sigma. The sigma value is then used to convert ATN into μg of BC found on a sample filter. The sigma value is not consistent among all conversions, depending on filter material and BC source. For example, Teflon FRM filters have a sigma of $4.2 \text{ cm}^2/\mu\text{g}$ that is suitable for environmental sampling with unspecified sources (Hansen, 2015; Neil Frank, 2009). The sigma found in the traditional cookstove experiment was $13.7 \text{ cm}^2/\mu\text{g}$. A representative sigma value can be used when comparing similar studies, but a more accurate value could be determined using TOA. The sigma can then be used to calculate the μg of BC on the filter, which is described in the methods section. Gravimetric data can then be compared to the μg of BC to produce a ratio of BC to $\text{PM}_{2.5}$. Of the 19 different types of traditional cookstoves tested by Garland, the BC/ $\text{PM}_{2.5}$ ratio ranged from 0.003 to 0.38 (Garland et al., 2017). Additional considerations with BC concentrations are the influence of ambient BC compared to indoor BC. A study of homes that used biomass stoves in West Africa showed that indoor concentrations of BC were higher ($2\text{-}14 \mu\text{g}/\text{m}^3$) than ambient concentrations ($2\text{-}11 \mu\text{g}/\text{m}^3$). This suggests that in regions that rely heavily on solid fuel, the main contributor of BC emissions is cookstoves (Zhou et al., 2014).

The use of the SootScan allows for retrospective BC analysis of archived samples. The SootScan has already been used on archived filters exposed to woodsmoke and non-woodsmoke sources (Neil Frank, 2009). Applying the same concept to previous studies of cookstove emissions will provide insight into future work in the developing world. Teflon filters from two previous cookstove studies were used for analyzing their BC concentrations in relation to $\text{PM}_{2.5}$ concentrations. The two studies were both located in Peru: Santiago de Chuco in 2008, and Trujillo in 2004. Each of these studies used gravimetric analysis for $\text{PM}_{2.5}$ in $\mu\text{g}/\text{m}^3$. Both

studies focused on stove and fuel types, with Santiago de Chuco being connected to the provision of an improved cookstove for the home.

Although the two studies have a component of a traditional stove and improved stove, they are not directly comparable due to differences in altitudes, home conditions, the type of traditional or improved cookstove, and fuel sources. Addition of central site sampling from Trujillo provides insights into ambient BC concentrations. The impact of being in a rural, peri-urban, or urban location would contribute to different baseline ambient concentrations of PM_{2.5} and BC.

The BC concentration will be used in multiple ways for each study. Total BC concentrations are measured for each stove type to compare their BC emissions. The concentrations of BC and PM_{2.5} will be used to determine how closely they correlate. The ratio of BC to PM_{2.5} will also be used to represent the proportion of mass that BC makes up of the PM_{2.5}. A secondary use for the ratio is the focus of the efforts to mitigate climate change (Garland et al., 2017). The role of BC as a component of PM_{2.5} will help to influence policy and interventions in human health and environmental protection. This research will also provide additional information on study design for using the SootScan for black carbon studies, and address some of the shortfalls of exclusively using archived samples.

Santiago de Chuco Study

The province of Santiago de Chuco had a population of 6400 at the time of the sample collection in winter season of 2008. The altitude of the Andes Mountains in this region is from 3000m to 3400m.

The Santiago de Chuco study by Fitzgerald et al. has air samples for before and after the intervention. These air samples were collected for 48 hours for both the kitchen and personal

exposures. This provides for a stronger design than many other household air pollution studies, as many only have observational data. Each of the 64 homes started out with a traditional stove, typically using stones and an open fire. After the pre-intervention measurements were taken, improved brick stoves with a chimney were installed. There were two styles of intervention stoves used in three communities in Santiago de Chuco. Both intervention stoves were very similar in design, but were used in different communities (Fitzgerald et al., 2012).

Trujillo Study

The study in Trujillo by St. Helen et al. is in an urban setting, where a variety of fuel sources are available and used. The city is located west of the Andes Mountains, and has an elevation of 30m. The population of the city at that time was 757,266. The household air pollution samples were collected from May to July in 2004. The individuals recruited for the study were pregnant women in their first trimester.

The Trujillo study was an observational study, where homes predominantly used either a single fuel type, or a combination of fuels. The fuels types that were used were gas, kerosene, wood, and coal briquette. Homes that used gas plus an additional fuel were considered to be “Combination with gas”, and homes that used multiple fuels, but no gas were “Combination without gas”. In addition to the homes, sampling was done at the city hall in Trujillo as one of the central sites to provide for ambient PM_{2.5} concentrations (Helen et al., 2015). Trujillo includes 48 hour sampling of the kitchen and personal exposures, and includes a secondary sample from the home in a room that is not the kitchen.

Methods

Santiago de Chuco

Subjects were chosen for the study based on the requirement that the homes used an open fire for cooking, and that the woman of the household was 18 to 45 years old. All households had air monitoring before and after the improved stoves were installed, which included both personal sampling on the mothers and area sampling. The intervention involved the installation of two different designs of improved stoves. The stoves were similar in design as both had multiple holes for the stove, a chimney, and a tube connecting the stove to the chimney. The first stove design (Stove 1 or Huayatan) was provided by the Juntos National Program and was used in the Huayatan community. Stove 1 was constructed by the household after the materials were delivered. The second stove design (Stove 2 or Chaguin) was made by the Barrick Gold Corporation and was used in the Chaguin and Cachulla Baja communities. Stove 2 was constructed by a mason for the homes, as it was larger and more complex. The result of both stoves is the provision of a chimney to direct smoke outside of the home, and a chamber for the fuel to burn more efficiently. All stoves used eucalyptus wood as fuel, and the limited motor vehicle traffic in the area would provide a negligible amount of PM_{2.5} to the sampling.

Time-integrated measurements for PM_{2.5} were taken over 48 hours using 37 mm Teflon filters (Pall, East Hills, NY, Teflo 2.0 µm). Filters were loaded into Triplex Cyclones (BGI Inc., Waltham, MA, Model SCC 1.062) with SKC universal sampling pumps (SKC Inc, Eighty-Four, PA, Aircheck® XR5000 for personal and XR2000 for kitchen) running at 1.5L per minute. Kitchen (area) sampling units were placed near the stoves with piping that reached to the height of 1.5m. Personal sampling units were attached to a vest that the participants wore. All sampling was completed during the winter in 2008. After the completion of the sampling time, samples

were frozen and transported to the University of Georgia (Athens, GA) where they were weighed on a Cahn C-35 microbalance (Thermo Scientific, Waltham, MA, Orion 10935-01). After weighing, samples were placed in a -20°C freezer for long-term storage.

Trujillo

Air sampling was done in 100 homes, with air monitoring done in the kitchen, on personal monitors, and in a secondary room. The secondary room was where the individual spent the most time in besides the kitchen. Subjects were selected based on being in their first trimester of pregnancy. No stove or clean fuel intervention was performed. Samples for the kitchen, secondary room, personal, and city hall were collected for 48 hours. The kitchen and secondary samples were collected at the height of 2m. Personal sampling equipment was attached to a vest worn by the individual. Samples were collected on 37mm Teflon filters (Pall, 2.0 μm), that were loaded into a Triplex PM_{2.5} Cyclone (BGI, model SCC 1.062, Waltham, MA). The Cyclone had airflow from an AirChek 200 pump (SKC, Eighty Four, PA) that ran at 1.5 L/min. After sampling completion, the filters were frozen and followed the same protocol as with the Santiago de Chuco study.

Addition of Black Carbon Data

Analysis for black carbon was performed in the summer of 2018 on the original Teflon filters from the studies. This was done by using the SootScan Dual Wavelength Optical Transmissometer according to the manual provided by Magee Scientific (Magee Scientific, 2016). The only addition was the use of a diffuser filter to dampen the amount of light transmitted, as recommended for use with Teflon filters (Hansen, 2015). The SootScan provides a nondestructive method of measuring black carbon by transmission of infrared light (880 nm) through the filter, based on the Beer-Lambert law (Davy, Tremper, Nicolosi, Quincey, & Fuller,

2017). The transmission of a sample is compared to the transmission of a blank filter to provide the IR attenuation using

$$ATN = 100 * \ln(IRB/IR)$$

where IRB is the blank transmission and IR is the sample transmission. The attenuation can then be used to calculate the concentration of black carbon using

$$BC (\mu\text{g}/\text{m}^3) = ((\text{Filter area}/\text{Sample volume}) * ATN * 10^4) / \sigma$$

where sigma (σ) is also known as the attenuation cross-section or mass absorption cross-section (MAC). The value of sigma will vary based on the sample source, filter type, and instrument used (Liousse, Cachier, & Jennings, 1993). The filter area used for this study is 6.8 cm², considering a 29.5mm diameter of exposed material for the filter. The value of sigma used for this study was 13.7 cm²/μg, based on the work by Garland et al. (Garland et al., 2017), which also used a Teflon filter and traditional biomass cookstoves.

Filters were scanned twice, and the average of the ATN was used for the BC concentration calculation. Filters were scanned after they were exposed for the study, and no scans were done at baseline. The lack of scans of the filters before exposure means that the baseline ATN cannot be compared to the exposed ATN of the filter, and each Teflon filter has some variance. A representative unexposed filter was used for the blank scan.

Statistical Analysis

Data analysis was performed with SAS 9.4 (SAS Institute Inc., Cary, NC). Data from the original studies were used for PM_{2.5}, and only homes that were used in the original study were used for black carbon. Gravimetric data for PM_{2.5} was matched with the BC data. Black carbon concentrations were natural log transformed to account for the right skewed distribution of the data. Ratios of BC to PM_{2.5} concentration were calculated using the untransformed data.

A paired t-test was used to compare the pre-intervention and post-intervention concentration of BC and the BC/ PM_{2.5} ratio in Santiago de Chuco, combining both stove types. Analysis of variance was done for all six categories of fuel in Trujillo use to determine if there were significant differences in fuel types for kitchen, personal, and secondary sampling. The Trujillo data had some analysis that combined all non-gas samples together in order to provide contrast against gas using homes and to account for the low number of observations for some fuel types. The non-gas homes are a kerosene, wood, coal, combination without gas, and combination with gas. Combination with gas was not included in the gas home category in order to have an ideal group for lower emissions. Dunnett's t-test was used to compare gas vs. non-gas fuels use for concentration of BC. Means were used for the log-transformed data for BC and PM_{2.5} to compare the city hall data to gas homes. For both Santiago de Chuco and Trujillo, regressions between PM_{2.5} and BC were done with the log-transformed data, and geometric means were used for mean comparisons.

Samples excluded from Santiago de Chuco were two kitchen samples that could not be fully matched to the historic data set. Seven samples were excluded from Trujillo due to tears in the filters, a sample that could not be matched, or having a BC/ PM_{2.5} ratio above one. A BC/ PM_{2.5} ratio above one is impossible, since the BC that is being considered is a component of PM_{2.5}.

Results

Santiago de Chuco

Although 64 homes were used in the study, several homes were removed from the published paper from Fitzgerald et al. in 2012 (Fitzgerald et al., 2012), due to equipment failure, participant dropout, or illness. Additionally, some homes lacked PM_{2.5} data, which would also

leave out the BC data. The most reliable data to be used would be from the published paper. After accounting for any damaged filters, there are 43 homes matched for pre- and post- kitchen sets, and 45 homes matched for pre- and post- personal sets, and 40 homes had all measurements for home and kitchen. Some kitchen samples had duplicate filters, so the BC concentrations were averaged together for the two samples. Only samples that had both pre and post PM_{2.5} measurements were used in the analyses. All PM_{2.5} analyses for Santiago de Chuco were presented by Fitzgerald et al. in the original published paper. Any PM_{2.5} data presented in this paper is a subset from the original paper.

BC Distribution

The distribution of BC can be seen in Figure 4. 1 and the log-transformed distribution can be seen in Figure 4. 2. Characterization of the distribution data of BC is important for understanding exposure. This distribution is examined by stove type, location, and before/after intervention. The distribution is skewed to the right (Skewness = 2.06 for all BC measurements). The right skewed data means that most individuals are exposed to a lower range of BC, but some individuals have much higher exposures. The log-transformed data normalizes the BC distribution, and brings in some of the concentrations that are higher than the rest of the data.

Mean Comparisons

The geometric mean of the two different stoves types and pre-/post-intervention for BC concentration can be compared to determine the effectiveness of the stoves. Table 4. 1 displays the geometric means and percentage reductions of both stove types for kitchen and personal PM_{2.5} and BC. A significant mean decrease of PM_{2.5} and BC occurs for the intervention stoves, but reductions were greater for PM_{2.5} than for BC. Reductions for PM_{2.5} were 64.5%, 41.2%, 59.97%, and 53.8% for Stove 1 kitchen and personal and Stove 2 kitchen and personal samples,

respectively. Reductions for BC were 31.7%, 25.6%, 36.3%, and 20.8% for Stove 1 kitchen and personal and Stove 2 kitchen and personal samples, respectively. Reductions of the concentrations are presented in Figure 4. 3.

The ratio of BC to PM_{2.5} in terms of concentration for both pollutants is an additional factor to consider when examining the efficiency of the stoves. This ratio of BC/ PM_{2.5} increased after the intervention stove was installed. Table 4. 2 shows the geometric means of the BC/ PM_{2.5} ratios before and after intervention. The geometric means of the ratios ranged from 3.37% to 4.68% before the intervention and 5.93% to 9.27% after the intervention. Stove 2 had two outliers for the intervention kitchen samples. These two samples had PM_{2.5} at 3.5 µg/m³ and 2.7 µg/m³ with BC at 1.2 µg/m³ and 0.7 µg/m³ respectively. The PM_{2.5} were among the lowest for the study and may have led to the high BC/ PM_{2.5} ratios for those two samples, especially considering the lack of baseline measurement error.

The BC/ PM_{2.5} ratio for the stoves is displayed in Figure 4. 4. The t-test of the ratio for kitchen and personal showed a significant increase for both personal and kitchen (P<.001 for kitchen and P=.0004 for personal).

A paired t-test showed a significant decrease in the concentration BC from pre to post-intervention of 2.63 µg/m³ (P=.0036, 95%CL 1.06, 4.20) for the kitchen samples and a significant decrease of 2.12 µg/m³ (P=.0236, 95%CL 0.86, 3.38) for the personal samples. This result is reflective of a significant decrease of PM_{2.5} concentration that was in the original published paper. The ratio of BC/ PM_{2.5} significantly increased after the intervention. This increase of the ratio was by 4.3% (P<.0001, 95%CL 2.6%, 5.8%) for the kitchen samples and an increase of the ratio by 1.7% (P=.0004, 95% CL 0.8%, 2.6%). Table 4. 3 displays the results of the paired t-test.

Correlation of BC and PM_{2.5}

Black carbon and particulate matter are predicted to be positively correlated with each other, as BC is a component of PM_{2.5}. Figure 4. 5 shows the correlation for the log transformed data for the kitchen and personal BC and PM_{2.5}. The top graph is for the traditional stove, and the right bottom graph is for the intervention stove. Both stoves show a strong correlation between BC and PM_{2.5} (Pre R²=.69, Post R²=.77). Strong correlations have been seen in other studies such where R² ranged from 0.49-0.99(Nicole AH Janssen, 2012).

Trujillo

All PM_{2.5} analyses for Trujillo were a subset of the data presented by St. Helen et al. in 2015 (Helen et al., 2015). Any PM_{2.5} data presented in this paper is from the original document, with the exception of any removed or added samples. A total of 100 homes were used in the original study cross-sectional study. Two homes were removed for fuel analysis for missing the fuel type or only having a single observation such as with one electrical stove home.

Kitchen BC Means Comparisons

Trujillo gas stoves generally all had low BC concentration, while some of the other stoves had very high variability. Counts for each stove type are in Table 4. 4. The geometric mean for gas was 2.43 µg/m³ with a standard error of 0.23. Non-gas stoves means ranged from 2.77-8.00 µg/m³ and standard errors ranged from 0.35-1.33. The higher standard error for the combination gas may be expected, as additional fuel types would produce a range of BC concentrations. As a comparison, a study by Underhill in 2015 had BC concentrations of 7.6 µg/m³ indoors and 8.1 µg/m³ outdoors in a peri-urban area outside of Lima (Underhill et al., 2015). It may need to be considered that most of the BC for some stove types comes from other sources. Using Dunnett's t-test with the gas stove as the comparison stove, only the wood stove

was significantly higher ($P < .05$) for the log transformed BC and $PM_{2.5}$ data, although consideration of low statistical power is needed. Figure 4. 6 and Table 4. 5 display the geometric means of BC for the kitchen samples. Figure 4. 7 and Table 4. 6 display the geometric means for $PM_{2.5}$ for the kitchen samples.

BC/ $PM_{2.5}$ Kitchen Ratios and Correlation

BC/ $PM_{2.5}$ ratios ranged from means of 4.6%-6.4%. Combination with gas had the highest mean and standard error of 0.012. The large range of the ratio for the combination with gas stove and only gas stove is an indicator that the BC may be coming from a source that is not the stove. Figure 4. 8 and Table 4. 7 show the geometric means for the BC/ $PM_{2.5}$ ratio for the kitchen samples.

Linear regressions of $PM_{2.5}$ and BC kitchen concentrations for the gas stove and wood stove are shown in Figure 4. 9. The BC and $PM_{2.5}$ for the gas stove shows no correlation at $R^2 = .02$, while the wood stove has a weak correlation at $R^2 = .78$.

ANOVA for Kitchen, Personal, and Secondary Data

Kitchen and secondary samples show significant differences ($P < 0.0001$, $P = 0.0485$), while the personal measurements do not show a significant difference ($P = 0.2834$) for the log transformed BC concentrations among the fuel types. The ANOVA did not determine which fuels were significantly different from one another. The results of the ANOVA's are in Figure 4. 10, Figure 4. 11, and Figure 4. 12.

City Hall Measurements, Gas, and Non-gas Results

Trujillo included sampling from two central sites for ambient measurements. One location was at an airport that was outside of the city, and the other location was at the city hall that is centrally located in the city. The city hall had a geometric mean BC concentration of 1.93

$\mu\text{g}/\text{m}^3$ (N=84). Gas stoves had a BC concentration of $0.92 \mu\text{g}/\text{m}^3$ higher than the city hall measurements on average. This was significant for the log transformed data (P=.0132).

Table 4. 8 displays the comparisons among the city hall, gas, and non-gas BC concentrations. Indoor concentrations of BC and $\text{PM}_{2.5}$ tend to be affected by ambient concentrations, so each kitchen sample would have some portion of BC coming from outside of the home.

Santiago de Chuco and Trujillo Results Comparison

The geometric means of the BC concentration of the Santiago de Chuco traditional stoves were $8.2 \mu\text{g}/\text{m}^3$, $7.4 \mu\text{g}/\text{m}^3$ for kitchen samples, $5.4 \mu\text{g}/\text{m}^3$, and $4.7 \mu\text{g}/\text{m}^3$ for personal samples. Intervention stoves had BC concentrations of $5.6 \mu\text{g}/\text{m}^3$ and $4.1 \mu\text{g}/\text{m}^3$ for kitchen samples and $4.1 \mu\text{g}/\text{m}^3$ and $3.7 \mu\text{g}/\text{m}^3$ for personal samples. Trujillo gas stoves had BC concentrations of $2.4 \mu\text{g}/\text{m}^3$ and $2.5 \mu\text{g}/\text{m}^3$ for kitchen and personal gas samples. Non-gas stoves had BC concentrations of $4.0 \mu\text{g}/\text{m}^3$ and $3.0 \mu\text{g}/\text{m}^3$ for kitchen and personal samples. An additional point of comparison for the two studies is the looking at the wood fuel homes in Trujillo, which had a kitchen geometric mean of $8.0 \mu\text{g}/\text{m}^3$, which falls between traditional stoves in Santiago de Chuco, but above the intervention stoves.

The mean reduction of BC concentration for the intervention stoves were $2.6 \mu\text{g}/\text{m}^3$ for the kitchen and $2.1 \mu\text{g}/\text{m}^3$ for personal samples in Santiago de Chuco. Trujillo had a reduction of $1.6 \mu\text{g}/\text{m}^3$ for the kitchen and $0.5 \mu\text{g}/\text{m}^3$ for personal samples. The percentage reduction was 40% for kitchen and 16% for personal samples.

Discussion

Santiago de Chuco Discussion

The implementation of improved cookstoves would be expected to help bring down the $\text{PM}_{2.5}$ concentrations, leading to a decrease of BC concentrations, for both area and personal

measurements. These lower concentrations of PM_{2.5} and BC are reflected in the intervention that was implemented for Santiago de Chuco. The intervention stoves were effective even within the homes using the same fuel type of wood and could be implemented in a wide ranging and cost-efficient manner. Reductions of BC concentration going from traditional to the improved cookstove are 30.6%, 35.3%, 25.6%, and 20.9% for Stove 1 area and personal and Stove 2 area and personal respectively. This was a smaller reduction than PM_{2.5}, which can partially explain the increase in the BC/ PM_{2.5} ratio when implementing an improved cookstove. The design of the improved cookstove had a chamber for the fuel that provided an environment where fuel can be burned at a hotter temperature and for a longer time (Just, Rogak, & Kandlikar, 2013). These two factors decrease the amount of organic carbon left from incomplete combustion that results in a higher BC/ PM_{2.5} ratio. Black carbon from outside of the homes could be considered as a reason that the BC reduction was not as great as the PM_{2.5} reduction. However, ambient samples only averaged 0.44 µg/m³ for BC in Santiago de Chuco.

Trujillo Discussion

The different fuel sources used in Trujillo provide a range of exposures to both particulate matter and black carbon. Benefits of using gas stoves were the strongest when comparing to wood stove use, but other fuel types were not as low in PM_{2.5} and BC concentrations as was initially expected. A major part of the study in Trujillo is that it is in an urban setting with emissions from motor vehicles and diesel engines. Diesel engines are known emitters of black carbon, especially in older engines that lack the proper filters or catalyzers. The ambient BC concentration of 1.93 µg/m³ is small compared to the range of emissions that can come from using biomass or coal for cooking. However, this ambient BC may be the main source of BC in homes that use LPG for cooking. This was also seen in a semi-urban area of

Lima, where indoor BC concentrations were at $7.6 \mu\text{g}/\text{m}^3$, which was slightly lower than outdoor BC concentrations of $8.1 \mu\text{g}/\text{m}^3$ (Underhill et al., 2015). Overall, wood tended to be the fuel source that had the highest $\text{PM}_{2.5}$ and BC emissions, and gas tended to have the lowest $\text{PM}_{2.5}$ and BC emissions. The differences in fuel source emissions were the strongest in the kitchen and secondary room, and weakest in personal samples. The large ranges of $\text{PM}_{2.5}$ and BC concentrations reflects the diverse fuel sources, and variety of homes in an urban setting.

One weakness of the Trujillo BC analysis is the parent data set that was used for this study only used the complete sample set applicable for BC. This led to some filters being used that were excluded from the original data set. The difference in samples used creates a variation in the sample size and related results of $\text{PM}_{2.5}$, but are only minor differences. In addition, three of the wood users were recoded as kerosene. The change leads to three fewer wood users and three more kerosene users compared to the original study by St. Helen et al. (Helen et al., 2015).

Santiago de Chuco and Trujillo Discussion

A goal of providing cleaner stoves is to lower the concentration of $\text{PM}_{2.5}$ exposure to provide better health outcomes. The components of $\text{PM}_{2.5}$ have different toxicities, with BC being a major component of interest for health. Although the total concentrations of BC were lower, the ratio of BC to $\text{PM}_{2.5}$ was higher after the intervention stove was installed. The kitchen ratios of BC/ $\text{PM}_{2.5}$ averaged 4.1% for the traditional stove, and 8.5% for the intervention stove in the Santiago de Chuco study. This increased ratio brings up the concern that intervention stoves may not provide as much of a health benefit as expected, but the overall decrease of BC concentration would still provide a substantial benefit. Janssen estimated that a decrease of $0.55 \mu\text{g}/\text{m}^3$ of elemental carbon would lead to an increased life expectancy of 3.6 months. Although elemental carbon and black carbon are not always at a 1:1 ratio, they have very high correlations

(Janssen Nicole et al., 2011). The decrease of BC by $2.63 \mu\text{g}/\text{m}^3$ for the improved stove in Santiago de Chuco and $1.41 \mu\text{g}/\text{m}^3$ lower of BC comparing gas to all other stoves in Trujillo would more than meet what is needed to increase life expectancy. However, the increase in life expectancy is based on decreased exposure to traffic emissions. The lack of research into the health impact of BC exposure due to cookstoves was noted by Downward and colleagues. A majority of the studies focused on BC from traffic and not cookstoves, likely due to a focus on urban areas in developed nations (Downward et al., 2016).

The other concern is with the climate impact of BC, since organic carbon tends to have a cooling effect. A higher BC to organic carbon ratio may outweigh the climate impact benefit of decreasing overall emissions. Despite this increased ratio, some studies have shown that cleaner fuels and stoves tend to have a smaller climate impact. When accounting for the balance of organic carbon and black carbon on warming or cooling of the climate, intervention stoves tended to have a lower warming effect than traditional stoves (Garland et al., 2017). Additionally, black carbon only stays in the atmosphere for a range of 3 to 11 days (Bond et al., 2013), which would provide an expected decrease in local temperatures by lowering the direct radiative forcing from BC. Stoves that can decrease illness as well as decrease climate impacts would have a strong support for funding and policy.

There are several challenges when comparing black carbon concentrations among different studies, as the emission of BC is impacted by a variety of factors. Altitude, fuel type, ambient temperature, humidity, and fire temperature all change the amount and properties of black carbon emitted. Sample collection also requires going into homes for multiple visits, and compliance of the participants in the study. The challenge is compounded by differences in study design and measurement techniques. Santiago de Chuco was in a rural community with

pre-intervention and post-intervention stoves that only uses wood for fuel, while Trujillo is an observational study in an urban setting that focuses on a variety of fuel types. The properties of BC may even be different, as a high portion of BC in Trujillo may be from diesel fuel emissions. This would lead to several of the filters from Trujillo to contain black carbon particles from both diesel and biomass burning, which would create a heterogeneous mixture of BC. Each BC particle would have different aggregate properties and coatings, changing what the ideal sigma value would be for the study (Drinovec et al., 2017).

The original study and intervention sought to measure the changes in CO and PM_{2.5} using an intervention stove, with the ultimate goal of improving health outcomes. Due to this, the stoves may have been designed in a way that would limit the PM_{2.5} and CO, but not have been designed specifically for BC. However, they still managed to lower BC concentrations.

Several limitations come from the approach of using archived filters with the SootScan for measuring equivalent black carbon. The main limitation is the lack of scans for infrared (IR) attenuation before exposure. This scan would have provided a baseline IR transmission for each filter and could be used as a blank value in the ATN calculation. The baseline is needed, since Teflon filters have slightly different base values before exposure. This correction would work on an individual sample basis and could lead to a decrease or increase in BC concentration. Additionally, the sigma of 13.7 cm²/μg used in calculations is assumed from a comparable study (Garland et al., 2017), but a known difference is that the scans for the studies used an Emfab filter as an optical diffuser, which may impact what the actual sigma value should be for the BC concentration calculations. Measurements from the SootScan were compared directly with thermal optical analysis (TOA) from quartz filters. Filters from Cambodia (N = 44) had concurrent sample collection with quartz and Teflon filters. The quartz filters were used for

TOA with NIOSH Method 5040, which used an OC-EC Aerosol Analyzer. The Teflon filters were used for BC attenuation from the SootScan. The linear relationship between TOA and the attenuation from this study gave a sigma of $13.7 \text{ cm}^2/\mu\text{g}$ from the Cambodian samples. The accuracy of this sigma value for use in Peru household air pollution samples may be questionable, as the original value was calculated using Cambodian household air pollution samples. An additional unknown is if the filters being frozen for more than ten years affected the reading from the SootScan.

An additional change that was not done was using a filter loading correction. This would have the biggest impact on filters that have an ATN above 125. Depending on how saturated a filter is, the BC concentration can be 50% higher, based on a sample correction from Janssen (Janssen Nicole et al., 2011). Santiago de Chuco had 22 filters and Trujillo had 12 filters that had attenuations above 125. This may have led to an underestimation of BC, as the correction factor accounts for overloading of filters. The correction was not done due to the current uncertainty of the value of the correction factor for BC originating from cookstoves. A counter to the underestimation is that using optical methods of measuring equivalent BC often is biased towards over estimating BC (Bond et al., 2013).

Black carbon emissions gathered within close proximity to cookstoves would be expected to have different properties than atmospheric black carbon. BC goes through an aging process in the atmosphere. BC gathered at the source would not have the same aging impacts if they were properly stored and away from UV exposure (Bond et al., 2013). The kitchen BC from Santiago de Chuco and Trujillo would not have had time to mix with other components in the atmosphere, due to the sample being taken at the source of the emissions. This needs to be considered when deciding on sigma values to use. This would also mean that the central site data for Trujillo

needs its own sigma if the BC from the central site would have more BC that has aged in the atmosphere compared to kitchen samples. Black carbon that has aged typically has a higher sigma value, which would lead to a lower calculated BC concentration (Bond et al., 2013).

The total reduction of BC in Santiago de Chuco was greater than in Trujillo, but even non-gas homes in Trujillo had less BC than intervention homes in Santiago de Chuco. The amount of BC reduction is important for making intervention choices and strategies. Some individuals will already be exposed to a high BC concentration, and even after intervention stoves are implemented, they would be above recommended limits of BC. Other interventions easily produce a high reduction, but the starting BC concentration would already be low enough not to warrant health concerns. It will also be important to consider whether an improved cookstove intervention that still uses wood is valid, or if the intervention should provide cleaner fuels such as LPG. Additionally, if the main source of BC is not from the cookstove, then separate interventions are needed. Determining an effective intervention may change depending on measurement of the BC concentration decrease. The percentage reduction, total $\mu\text{g}/\text{m}^3$ reduction, or a set concentration should all be considered. A reminder is that many individuals who receive interventions still have exposures above the $10 \mu\text{g}/\text{m}^3$ yearly average for $\text{PM}_{2.5}$, which is above WHO guidelines (WHO, 2014). If interventions reflect the smaller decrease of BC compared to $\text{PM}_{2.5}$, then some interventions that meet the $\text{PM}_{2.5}$ guideline may not meet a potential BC guideline.

BC concentrations were only measured with a 48-hour time integrated sample, which provides a basis for daily and long-term exposure assessment. However, peak concentrations during stove use can reach into the hundreds of $\mu\text{g}/\text{m}^3$, such as in a study by Kar and colleagues which had a mean of $335 \mu\text{g}/\text{m}^3$ for the traditional stove, $224 \mu\text{g}/\text{m}^3$ for a natural draft stove, and

78 $\mu\text{g}/\text{m}^3$ for a forced draft stove (Kar et al., 2012). Santiago de Chuco had real time $\text{PM}_{2.5}$ measurements for some of the homes, so an extrapolation of BC concentration could be made. The challenge to this extrapolation is that the BC content changes throughout the burning of biomass, as the temperature and flow of air changes while burning. Not all improved stoves will decrease BC concentrations, such as with a natural draft stove design in India, where a traditional mud stove and natural draft stove had no significant difference in BC concentration during cooking time (Kar et al., 2012).

Conclusions

Use of the SootScan can provide an efficient method of gathering black carbon data from archived filters collected from cookstove studies. Although a lack of data from unexposed filters will lead to less accurate data, a representative blank filter can still be used to provide insights into black carbon concentrations for archived filters. As more data sets become available and further analysis on black carbon concentrations from cookstoves are completed, improved sigma values and correction factors can be used.

The comparison of the stoves of Santiago de Chuco and Trujillo show that significant decreases of black carbon concentrations are obtainable for cookstoves in both rural and urban environments. Switching fuels to LPG appears to be the most effective for lowering BC exposure, but substantial benefits can still be obtained with an intervention stove that still uses wood. New designs of intervention stoves should still be considered that decrease both the concentration of black carbon and the BC/ $\text{PM}_{2.5}$ ratio. The decrease of BC exposure that was measured from the studies in Santiago de Chuco and Trujillo are potentially enough to provide health benefits to the affected individuals.

Acknowledgements

The authors would like to acknowledge Tony Hansen from Magee Scientific for his help with the SootScan. We thank the Household Air Pollution Intervention Network community for providing supplies for the diffusers. We thank Christopher Fitzgerald and Gideon St. Helen for access to their information and data for the filters.

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Table 4. 1 Santiago de Chuco reduction of the concentrations of PM_{2.5} and BC from the use of the intervention stoves.

PM _{2.5} µg/m ³						
Stove 1	Kitchen N = 24			Personal N = 27		
	Pre	Post	%Red	Pre	Post	%Red
Geomean	243.9	86.5	64.5	116.4	68.4	41.2
95% CI	(158.4, 375.3)	(59.7, 125.3)		(84.2, 161.1)	(54.8, 85.4)	
Stove 2	Kitchen N = 19			Personal N = 18		
	Pre	Post	%Red	Pre	Post	%Red
Geomean	173.4	51.1	70.5	126.3	58.3	53.8
95% CI	(98.7, 304.5)	(27.2, 95.6)		(97.1, 164.3)	(42.2, 80.6)	
BC µg/m ³						
Stove 1	Kitchen N = 24			Personal N = 27		
	Pre	Post	%Red	Pre	Post	%Red
Geomean	8.2	5.6	31.7	5.4	4.1	25.6
95% CI	(6.2, 10.7)	(3.7, 8.2)		(4.0, 7.5)	(3.1, 5.3)	
Stove 2	Kitchen N = 19			Personal N = 18		
	Pre	Post	%Red	Pre	Post	%Red
Geomean	7.4	4.7	36.3	4.7	3.7	20.8
95% CI	(4.7, 11.9)	(2.9, 7.7)		(3.2, 6.8)	(2.7, 5.0)	

All means are in geometric means. %Red is the percentage of reduction for the pre-intervention to post-intervention using the geometric means. PM_{2.5} data is a subset of what was presented in Fitzgerald et al., 2012 (Fitzgerald et al., 2012). Black carbon (BC) reductions were not as much as particulate matter 2.5µm (PM_{2.5}) reductions in terms of percentage.

Table 4. 2 Santiago de Chuco geometric means of the BC/PM_{2.5} ratios of each stove before and after intervention.

BC/PM _{2.5} Ratio				
Stove 1	Kitchen N = 24		Personal N = 27	
	Pre	Post	Pre	Post
Geomean	3.37%	6.42%	4.68%	5.93%
95% CI	(2.65%, 4.29%)	(5.46%, 7.55%)	(3.79%, 5.77%)	(5.04%, 6.97%)
Std Error	0.41	0.52	0.50	0.48
Stove 2	Kitchen N = 19		Personal N = 18	
	Pre	Post	Pre	Post
Geomean	4.29%	9.27%	3.69%	6.33%
95% CI	(3.49%, 5.28%)	(7.48%, 11.49%)	(2.84%, 4.79%)	(5.28%, 7.58%)
Std Error	0.45	1.00	0.49	0.58

Black carbon to particulate matter 2.5 μ m ratio (BC/PM_{2.5} ratio) increased after intervention stoves were implemented.

Table 4. 3 Santiago de Chuco paired t-test of BC concentrations.

Kitchen				
Stove	N	Mean Reduction BC $\mu\text{g}/\text{m}^3$	P-value	95% CL
1	24	2.0	0.005	(.7, 3.2)
2	19	3.5	0.108	(.1, 6.8)
1 & 2	43	2.6	0.004	(1.1, 4.2)
Personal				
1	27	2.2	0.029	(.9, 3.6)
2	18	1.9	0.304	(-.7, 4.6)
1 & 2	45	2.1	0.024	(.9, 3.4)

Black carbon (BC) concentrations had a significant mean decrease after the intervention for both personal and kitchen samples. BC concentrations did not significantly decrease for Stove 2 on its own.

Table 4. 4 Trujillo samples counts used that had reliable BC and PM_{2.5} data.

Number of observations for BC and PM _{2.5}			
	Kitchen	Personal	Secondary Room
Gas	31	31	27
Combo Gas	23	22	22
Combo No Gas	6	4	5
Kerosene	8	7	8
Wood	14	12	13
Coal	12	12	12

Black carbon (BC) and particulate matter 2.5 μ m (PM_{2.5}) sample counts that were used for BC analysis.

Table 4. 5 Trujillo kitchen BC geometric means.

Stove Type	N	Geometric Mean BC μg/m ³	Standard Error	95% CI for Mean	
Coal	12	4.1	0.75	2.9	5.9
Combo gas	23	2.8	0.36	2.1	3.6
Combo no gas	6	4.1	0.96	2.6	6.6
Gas	31	2.4	0.24	2.0	3.0
Kerosene	8	3.4	0.56	2.4	4.7
Wood	14	8.0	1.32	5.7	11.1

Geometric means, standard error, and 95% confidence interval for black carbon (BC).

Table 4. 6 Trujillo kitchen PM_{2.5} geometric means.

Stove Type	N	Geometric Mean PM _{2.5} µg/m ³	Standard Error	95% CI for Mean	
Coal	12	80.2	17.73	51.7	124.4
Combo gas	23	45.2	7.37	32.7	62.5
Combo no gas	6	64.3	17.37	37.6	109.9
Gas	31	40.5	6.26	29.8	55.0
Kerosene	8	46.3	7.60	33.5	64.2
Wood	14	171.8	35.54	113.9	259.1

All PM_{2.5} analyses for Trujillo in this study is a subset of the data presented by St. Helen et al. in 2015 (Helen et al., 2015). Geometric means, standard error, and 95% confidence interval for particulate matter 2.5µm (PM_{2.5}).

Table 4. 7 Trujillo kitchen BC/PM_{2.5} ratio geometric means.

Stove Type	N	Geometric Mean BC/PM _{2.5} Ratio	Standard Error	95% CI for Mean	
Coal	12	5.1	0.69	3.9	6.7
Combo gas	23	6.1	0.65	5.0	7.6
Combo no gas	6	6.4	1.21	4.4	9.3
Gas	31	6.0	1.01	4.3	8.4
Kerosene	8	7.3	0.72	6.0	8.8
Wood	14	4.6	0.54	3.7	5.8

Geometric means, standard error, and 95% confidence interval for black carbon to particulate matter 2.5 μ m ratio (BC/PM_{2.5} ratio).

Table 4. 8 Trujillo gas, non-gas, and city hall comparisons of BC concentrations and BC/PM_{2.5} ratio.

BC $\mu\text{g}/\text{m}^3$			
	Non-gas	Gas	City Hall
Geomean	4.0	2.4	1.9
95% CI	(3.4, 4.8)	(2.0, 3.0)	(1.8, 2.1)
Std Error	0.37	0.24	0.07

BC/PM _{2.5} Ratio			
	Non-gas	Gas	City Hall
Geomean	5.71%	6.00%	7.63%
95% CI	(5.1%, 6.4%)	(4.3%, 8.4%)	(7.0%, 8.3%)
Std Error	0.35	1.0	0.31

Black carbon (BC) to particulate matter 2.5 μm ratio (BC/PM_{2.5} ratio) for non-gas, gas, and city hall samples.

Gas, N = 31; Non-gas, N = 63; and City Hall, N = 84.

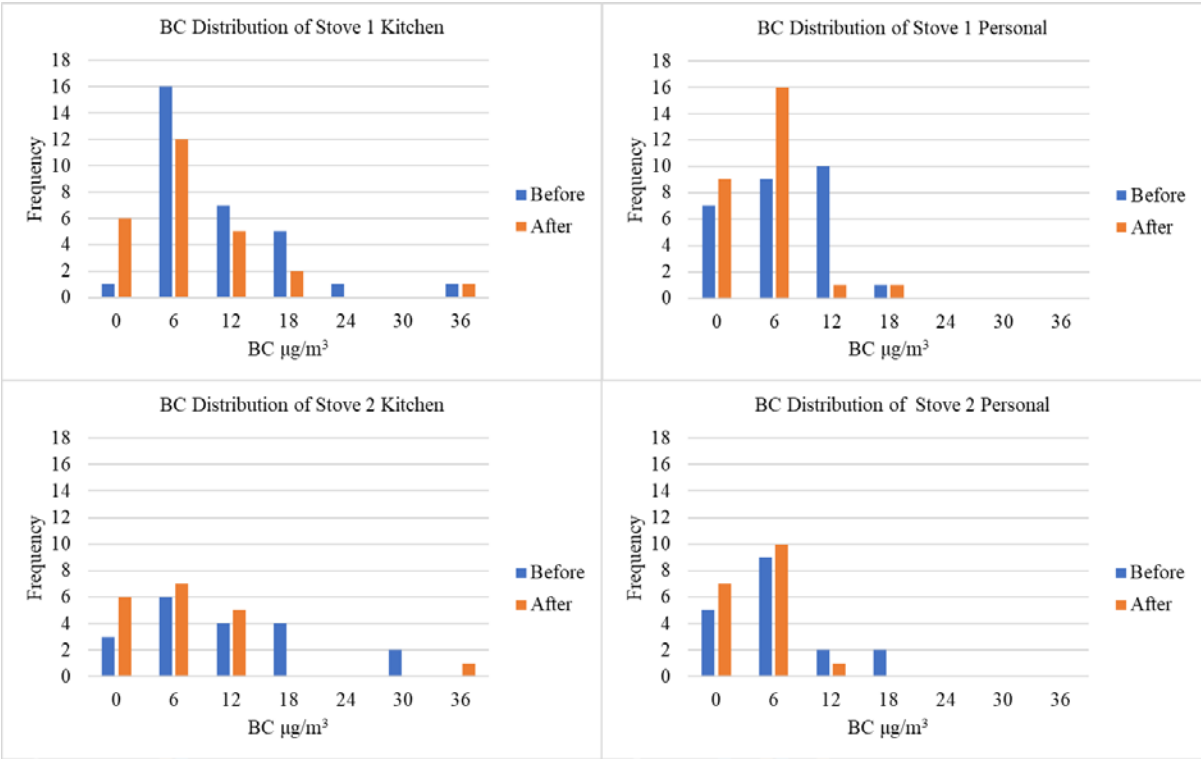


Figure 4. 1 Santiago de Chuco distribution of the concentration of BC. Black carbon (BC) concentrations were right skewed for both traditional and improved cookstoves for Santiago de Chuco.

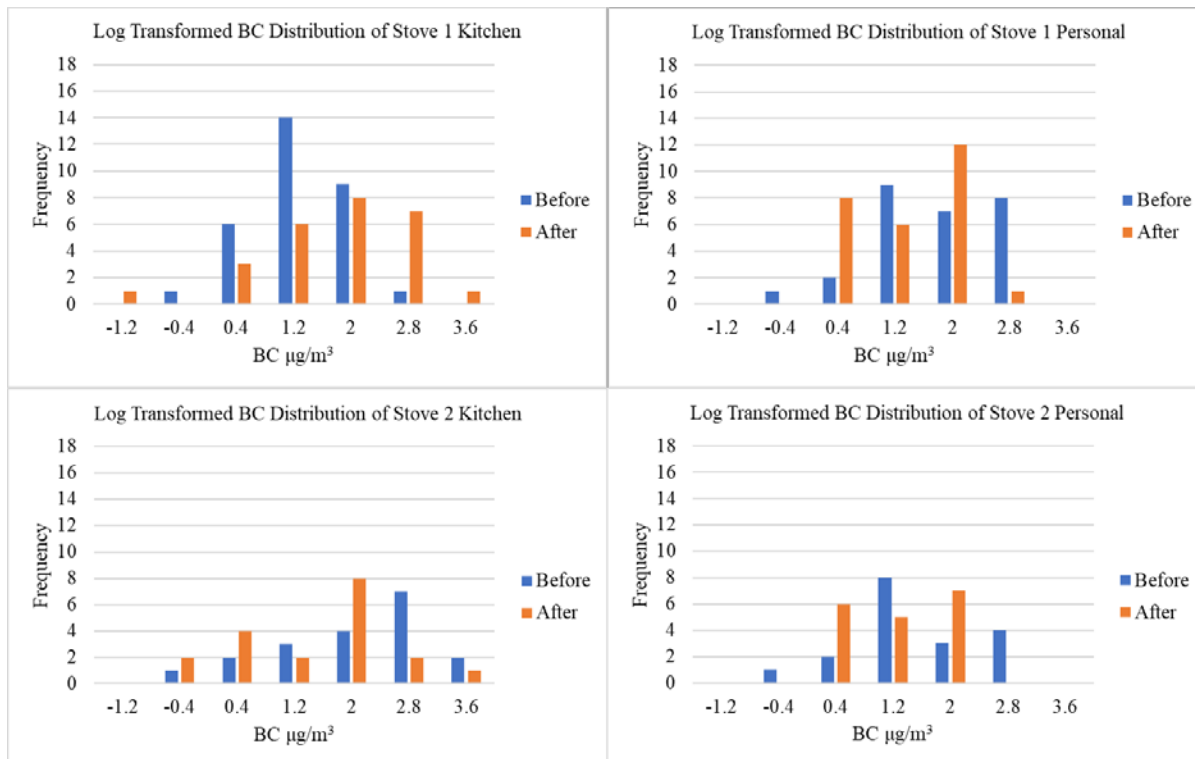


Figure 4. 2 Santiago de Chuco distribution of the log transformed concentration of BC. The natural log of black carbon (BC) concentrations were normally distributed for both traditional and improved cookstoves for Santiago de Chuco.

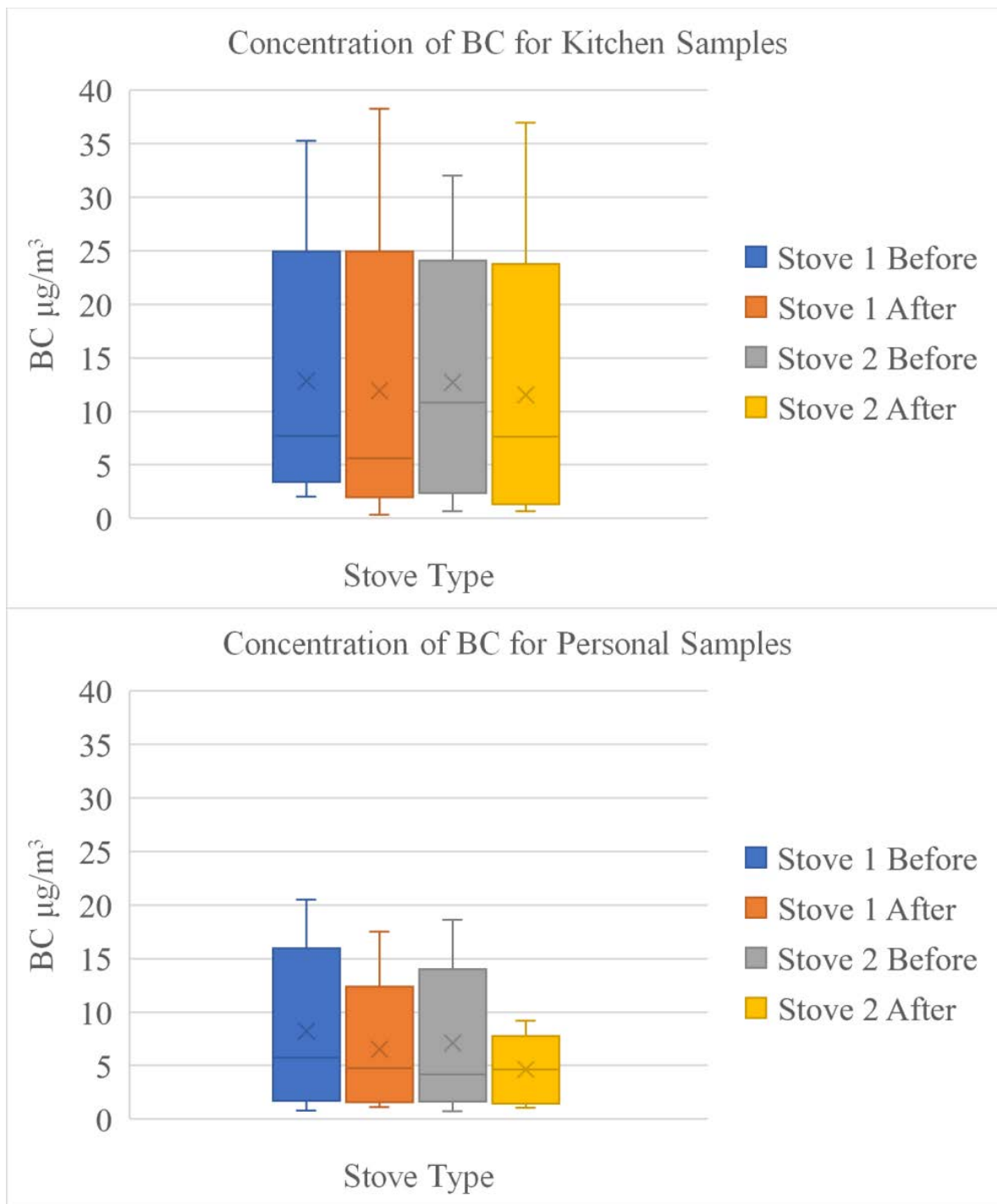


Figure 4. 3 Santiago de Chuco comparison of the concentration of BC in $\mu\text{g}/\text{m}^3$. Black carbon (BC) concentrations decrease after improved stoves were installed. The box is the upper and lower quartiles, the horizontal line is the median, the “X” is the mean, and the whiskers are the minimum and maximum values. Stove 1: Kitchen, N = 24; Personal, N = 27; Stove 2: Kitchen, N = 19, Personal N, = 18.

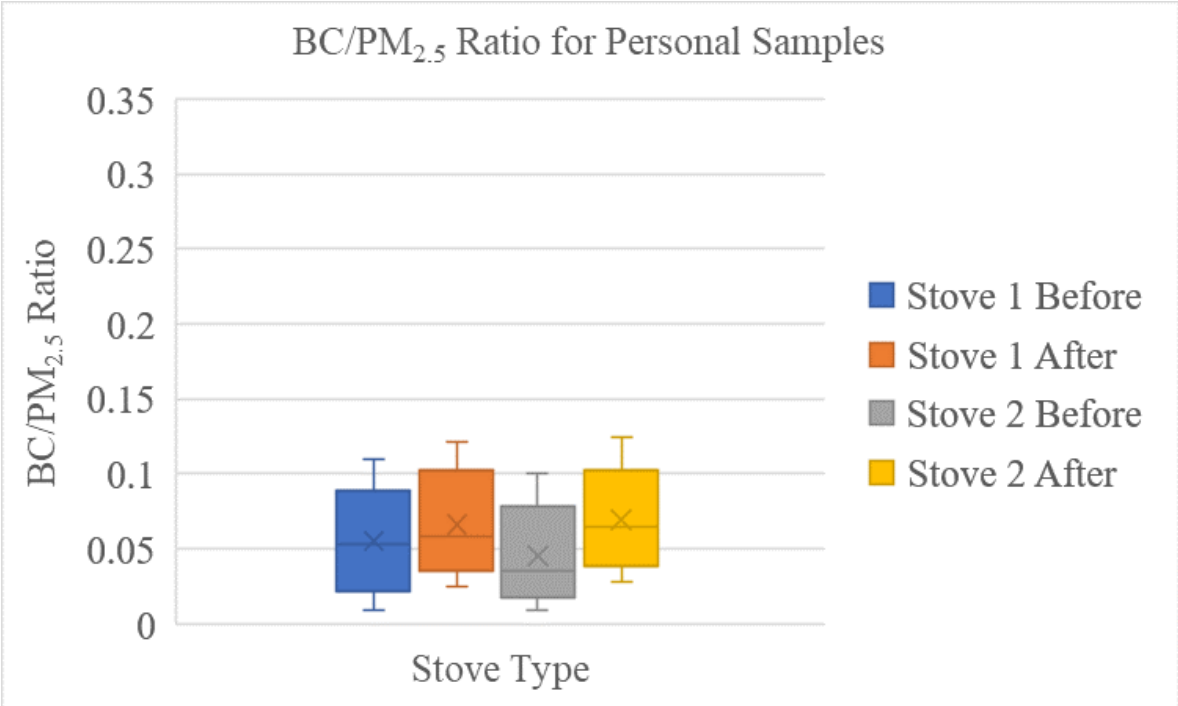
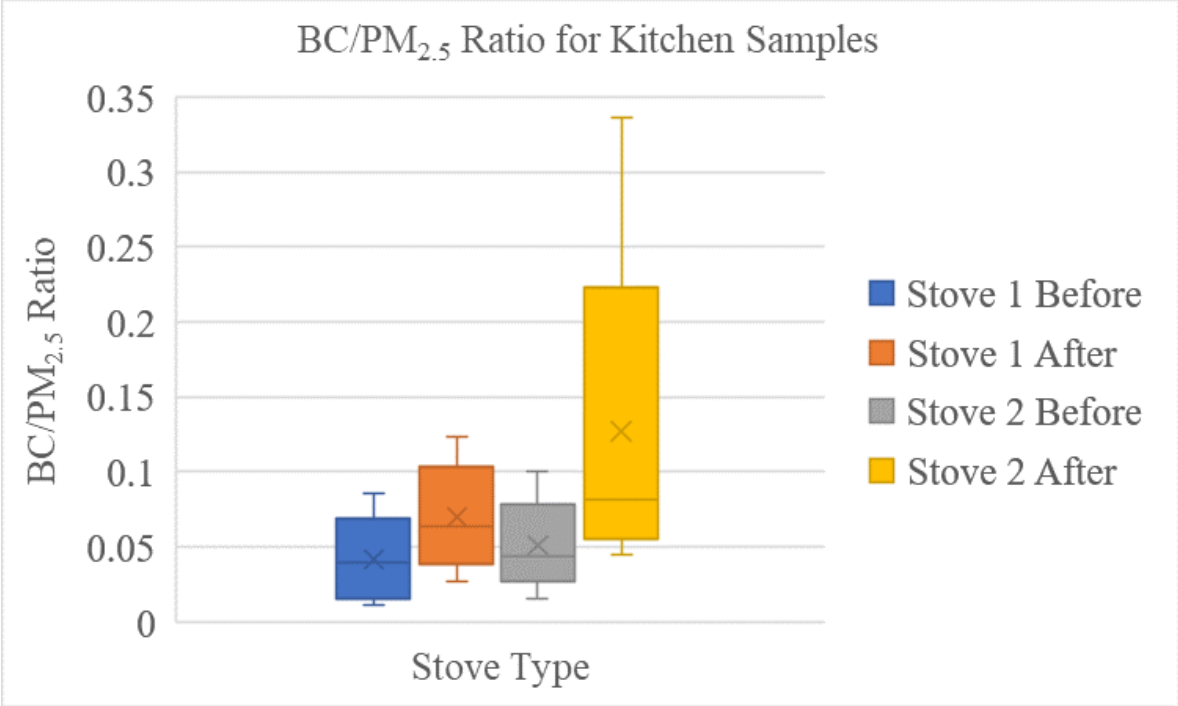


Figure 4. 4 Santiago de Chuco comparison of the BC/PM_{2.5} ratios. Black carbon (BC) to particulate matter 2.5µm ratio (BC/PM_{2.5}) increased after the intervention. The box is the upper and lower quartiles, the horizontal line is the median, the “X” is the mean, and the whiskers are the minimum and maximum values. Stove 1: Kitchen, N = 24; Personal, N = 27; Stove 2: Kitchen, N = 19, Personal, N = 18.

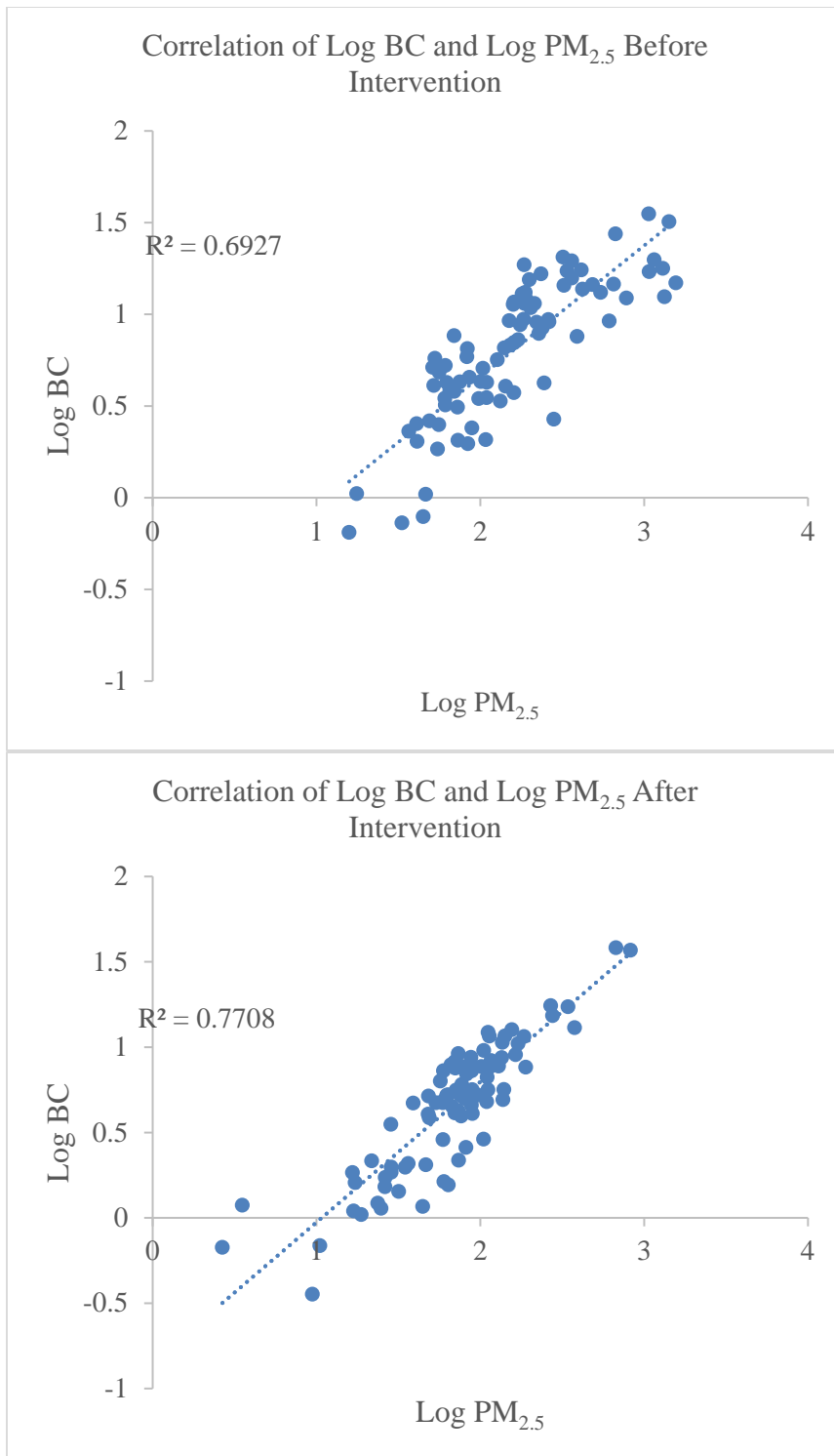


Figure 4. 5 Santiago de Chuco correlations of the log transformed PM_{2.5} and BC. Strong correlations were seen for both the traditional and improved stove between particulate matter 2.5 μ m (PM_{2.5}) and black carbon (BC). Personal and kitchen samples were combined for this analysis, N = 87.

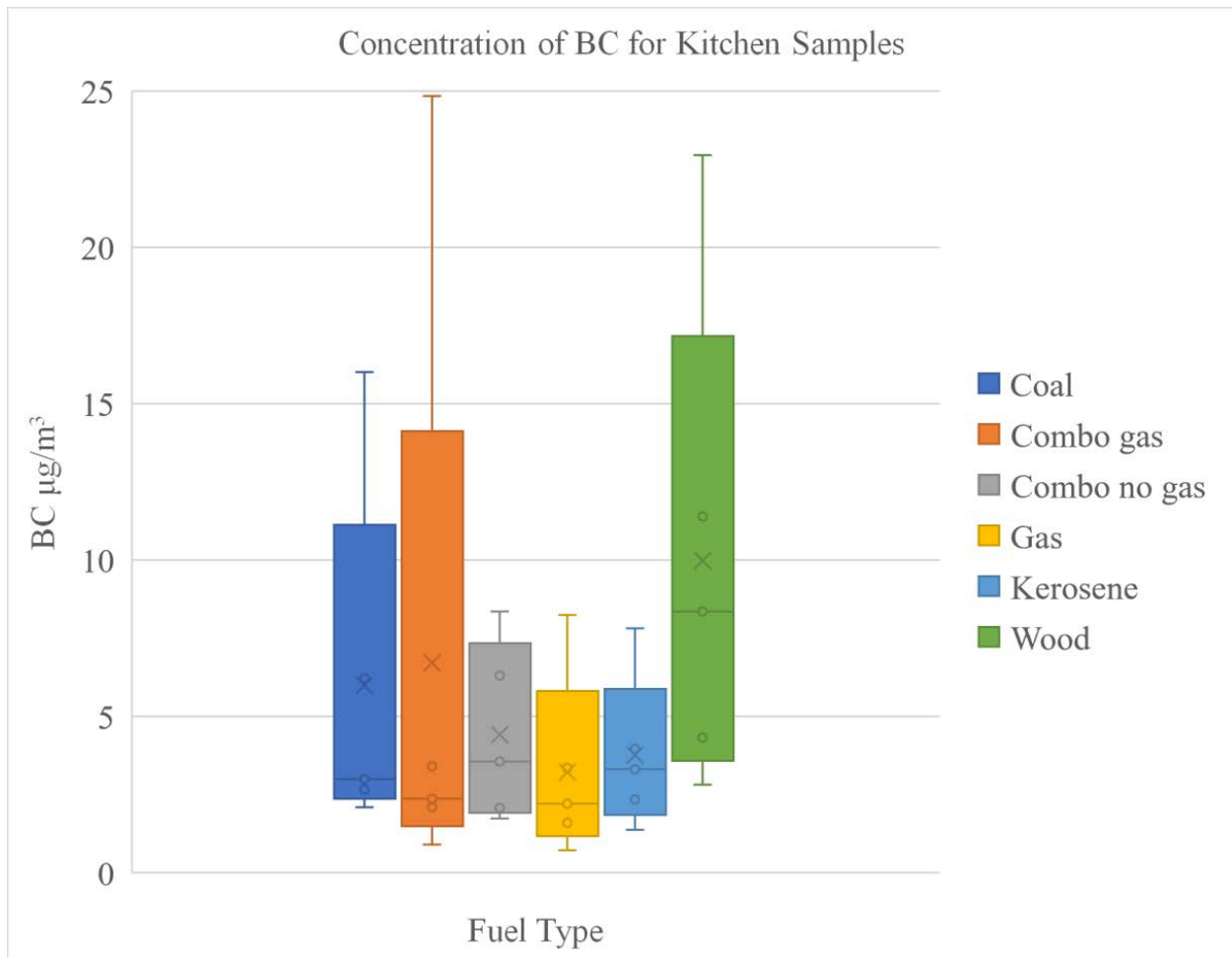


Figure 4. 6 Trujillo kitchen BC concentrations.

Black carbon (BC) concentrations for the six fuel types in Trujillo.

The box is the upper and lower quartiles, the horizontal line is the median, the “X” is the mean, and the whiskers are the minimum and maximum values.

Coal, N = 12; Combo gas, N = 23; Combo no gas, N = 6; Gas, N = 31; Kerosene, N = 8; Wood, N = 14.

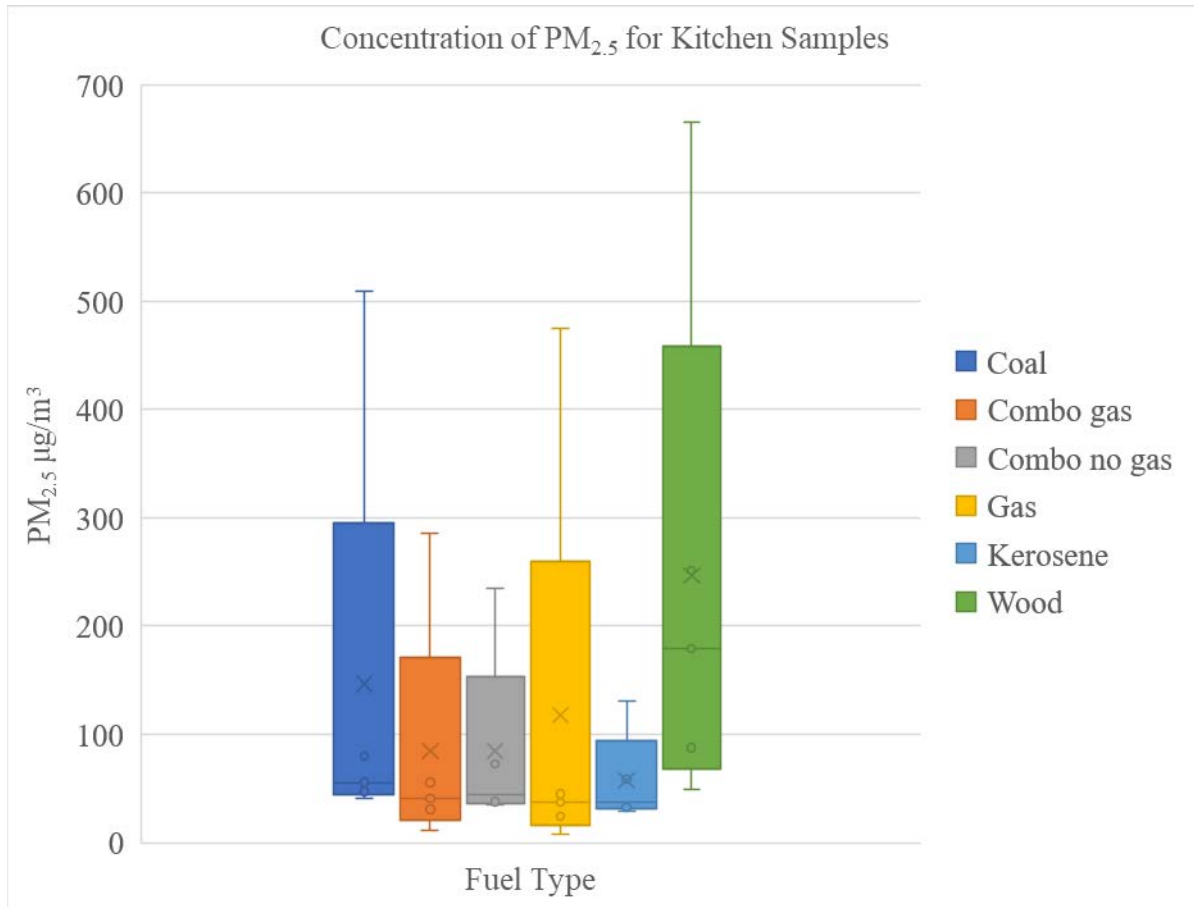


Figure 4. 7 Trujillo kitchen $PM_{2.5}$ concentrations.

Particulate matter 2.5µm ($PM_{2.5}$) for the six fuel types in Trujillo.

The box is the upper and lower quartiles, the horizontal line is the median, the “X” is the mean, and the whiskers are the minimum and maximum values.

All $PM_{2.5}$ analyses for Trujillo were presented by St. Helen et al. in 2015, and $PM_{2.5}$ used in this study is a subset of that data (Helen et al., 2015).

Coal, N = 12; Combo gas, N = 23; Combo no gas, N = 6; Gas, N = 31; Kerosene, N = 8; Wood, N = 14.

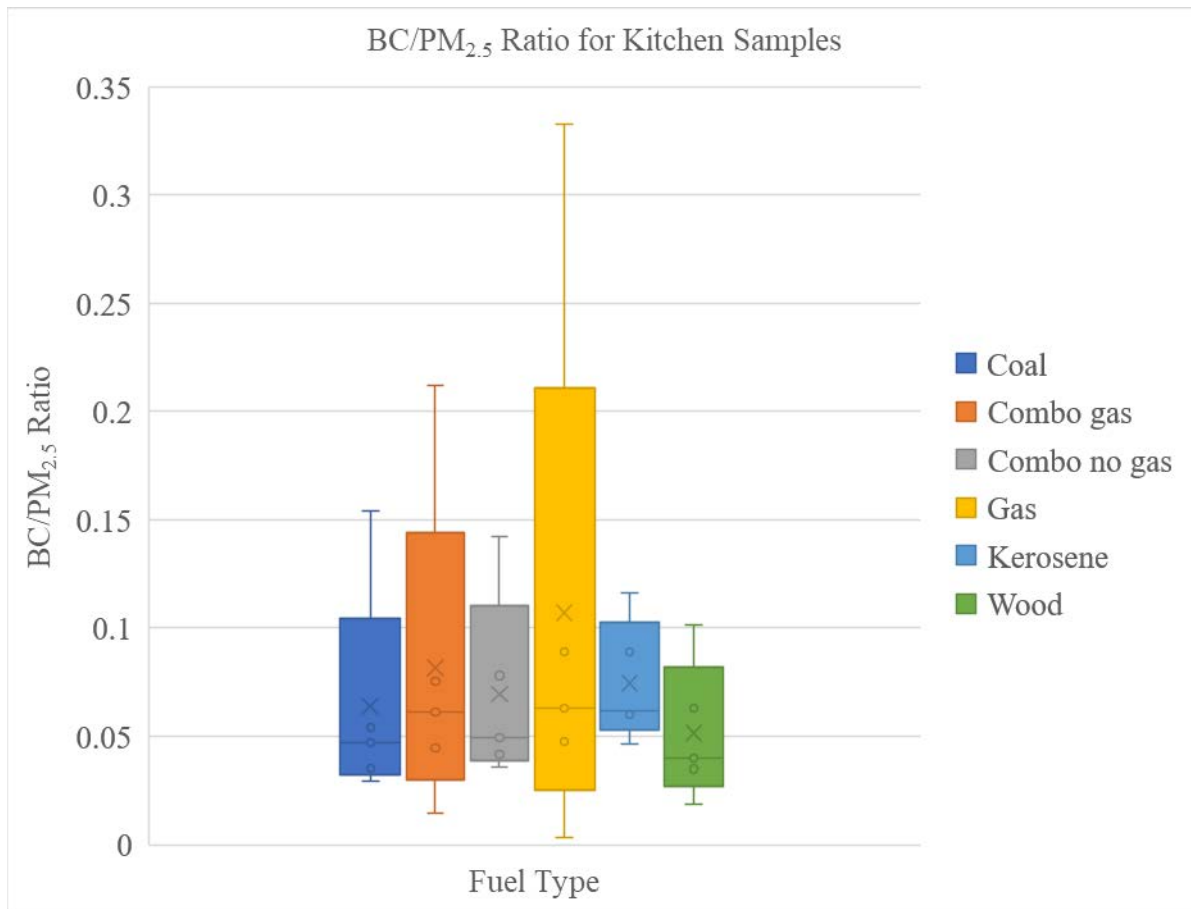


Figure 4. 8 Trujillo kitchen BC/PM_{2.5} ratios.

Black carbon (BC) to particulate matter 2.5µm ratio (BC/PM_{2.5}) for the six fuel types in Trujillo. The box is the upper and lower quartiles, the horizontal line is the median, the “X” is the mean, and the whiskers are the minimum and maximum values.

Coal, N = 12; Combo gas, N = 23; Combo no gas, N = 6; Gas, N = 31; Kerosene, N = 8; Wood, N = 14.

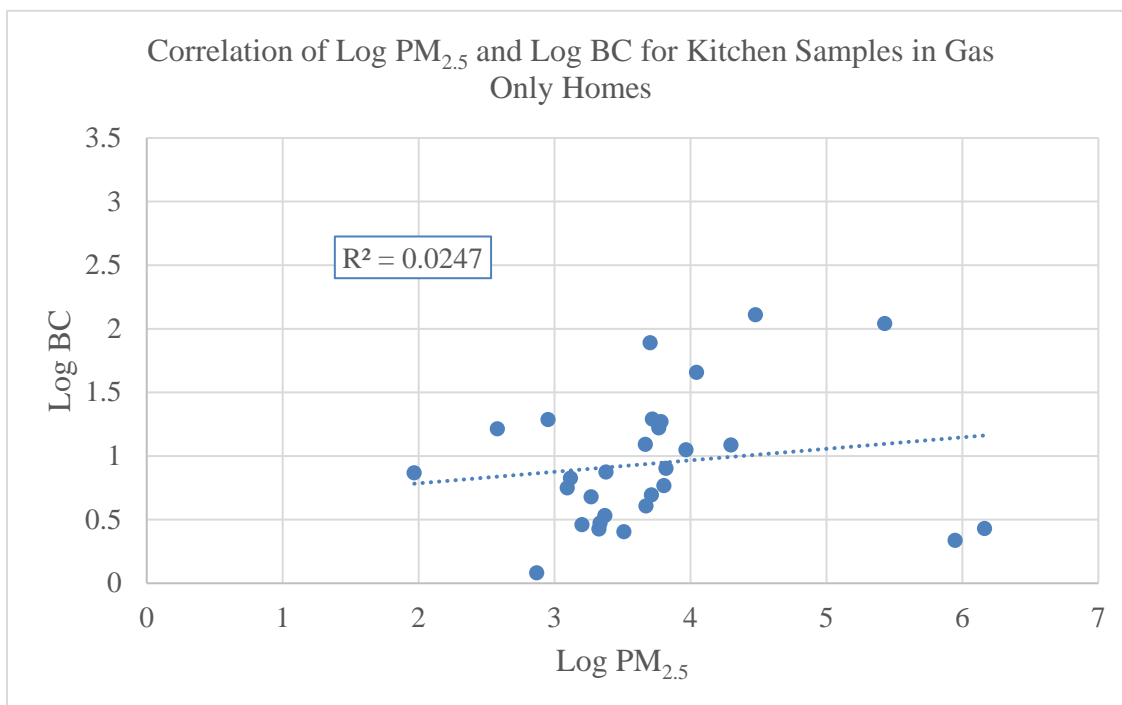
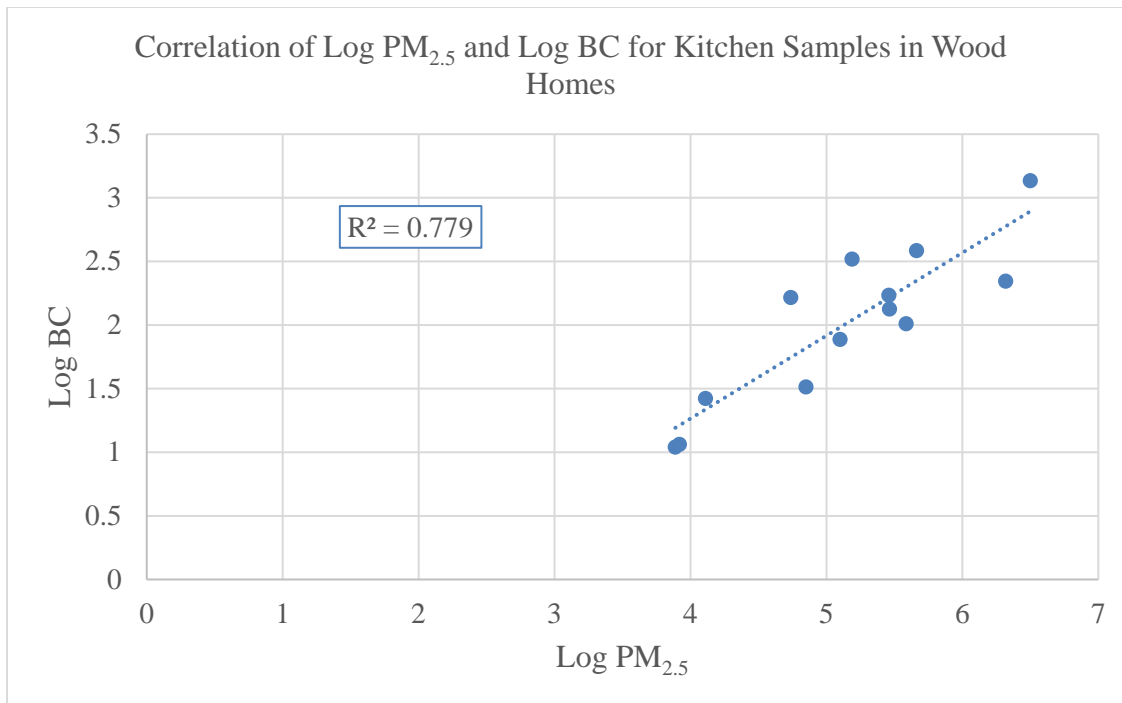


Figure 4. 9 Trujillo wood and gas BC and PM_{2.5} correlations. (Top) Wood, N = 13 stove correlation of the log transformed particulate matter 2.5 μ m (PM_{2.5}) and black carbon (BC) kitchen concentrations. (Bottom) Gas, N = 29 stove correlation of the log transformed PM_{2.5} and BC kitchen concentrations. All PM_{2.5} analyses for Trujillo is a subset of the presented data by St. Helen et al. in 2015 (Helen et al., 2015).

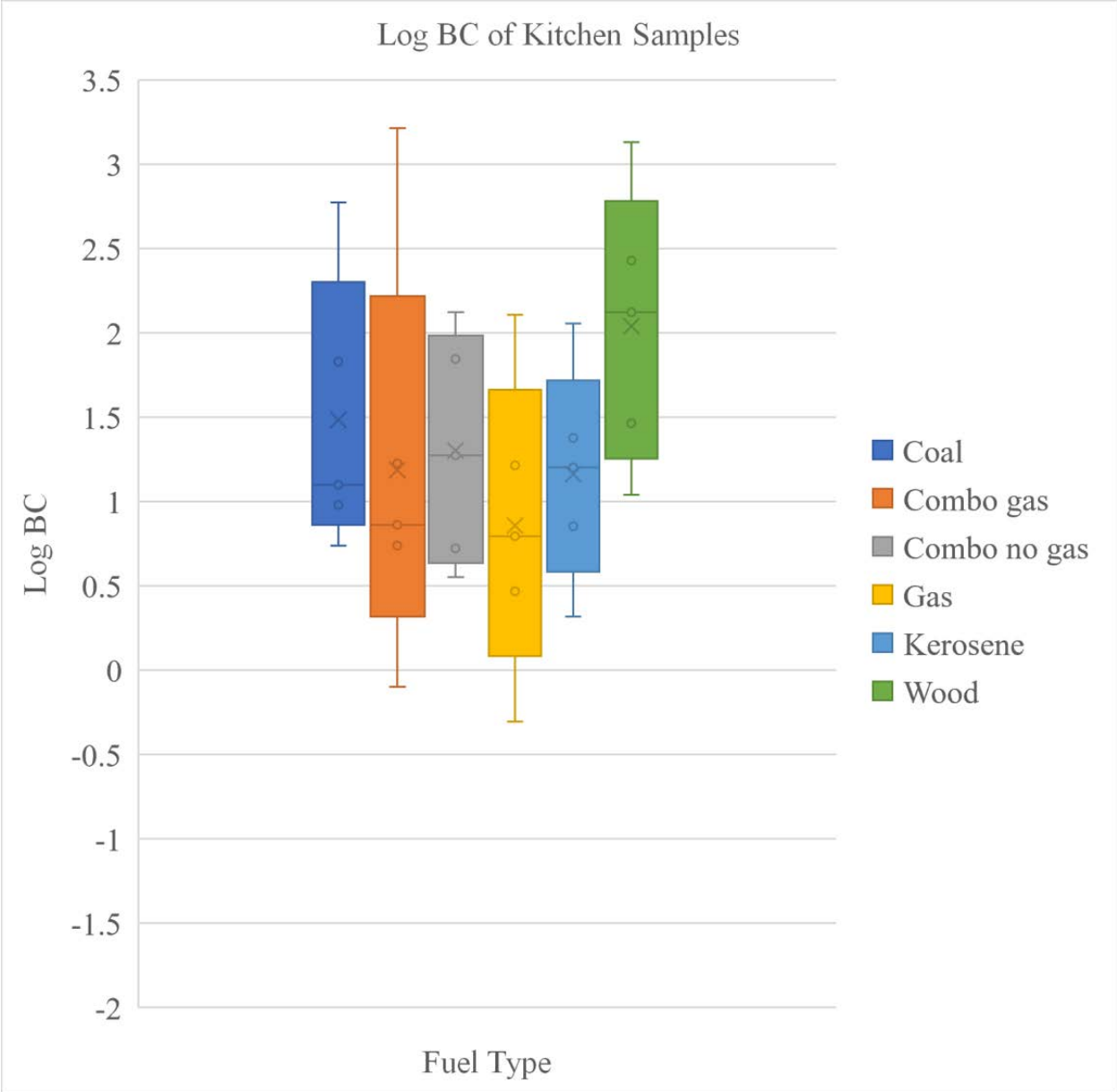


Figure 4. 10 Trujillo log BC ANOVA results for fuel types from the kitchen sample. Natural log transformed black carbon (BC) concentrations for Trujillo kitchen samples were significantly different among the fuel types ($P < .0001$). The box is the upper and lower quartiles, the horizontal line is the median, the “X” is the mean, and the whiskers are the minimum and maximum values. Coal, N = 12; Combo gas, N = 23; Combo no gas, N = 6; Gas, N = 31; Kerosene, N = 8; Wood, N = 14.

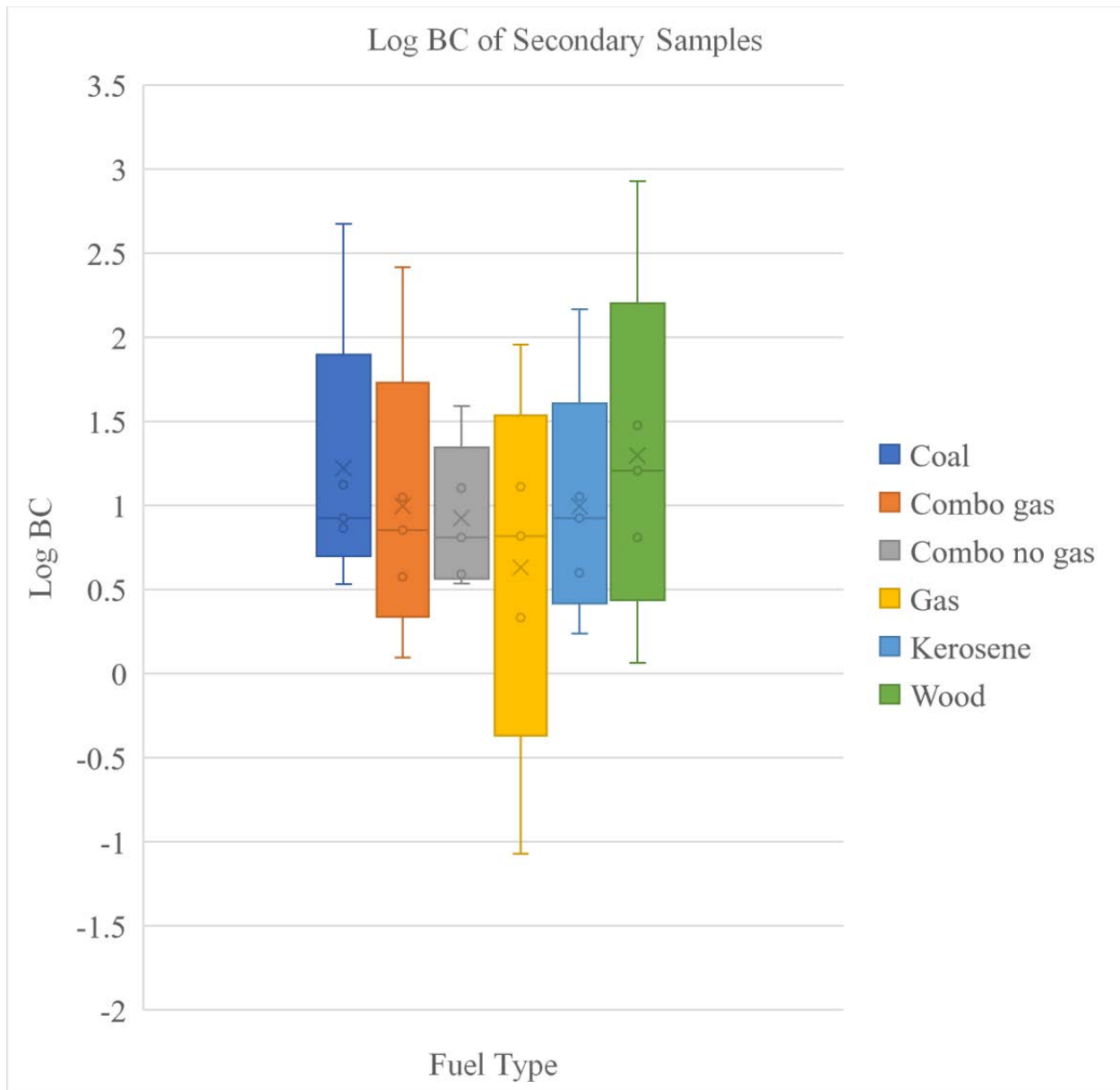


Figure 4. 11 Trujillo log BC ANOVA results for fuel types from the secondary room sample. Natural log transformed black carbon (BC) concentrations for Trujillo secondary room samples were significantly different among the fuel types ($P = 0.0485$).

The box is the upper and lower quartiles, the horizontal line is the median, the “X” is the mean, and the whiskers are the minimum and maximum values.

Coal, N = 12; Combo gas, N = 22; Combo no gas, N = 5; Gas, N = 27; Kerosene, N = 8; Wood, N = 13.

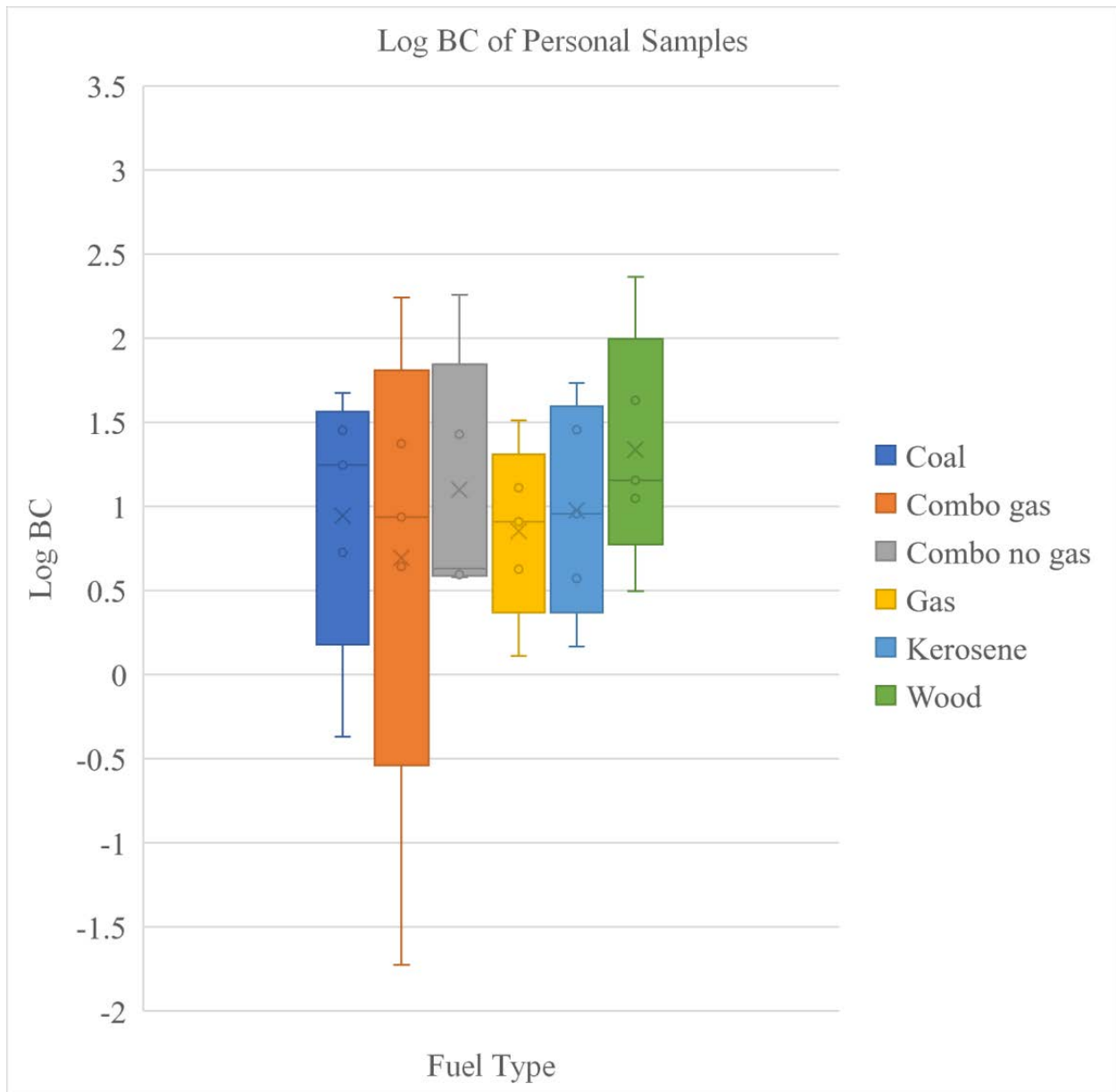


Figure 4. 12 Trujillo log BC ANOVA results for fuel types from the personal sample. Natural log transformed black carbon (BC) concentrations for Trujillo personal samples were not significantly different among the fuel types ($P = 0.2834$). The box is the upper and lower quartiles, the horizontal line is the median, the "X" is the mean, and the whiskers are the minimum and maximum values. Coal, $N = 12$; Combo gas, $N = 22$; Combo no gas, $N = 4$; Gas, $N = 31$; Kerosene, $N = 7$; Wood, $N = 12$.

CHAPTER 5

DISCUSSION AND CONCLUSION

Santiago de Chuco and Trujillo Study Conclusions

A goal of providing cleaner stoves is to lower the concentration of PM_{2.5} exposure to provide better health outcomes. The components of PM_{2.5} have different toxicities, with BC being a major component of interest for health. Although the total concentrations of BC decreased, the ratio of BC to PM_{2.5} increased after the intervention stove was installed. The kitchen ratios of BC/PM_{2.5} averaged 4.1% for the traditional stove, and 8.5% for the intervention stove. This increased ratio brings up the concern that intervention stoves may not provide as much of a health benefit as expected, but the overall decrease of BC concentration would still provide a substantial benefit.

Understanding the similarities and differences of other cookstove studies is important in order to provide a comprehensive knowledge of interventions. Downward's study in the Yunan province in China had personal BC concentrations of 18 µg/m³ for wood, 14 µg/m³ for smoky coal, and 6.2 µg/m³ for smokeless coal (Downward et al., 2016). Curto's study in rural Mozambique had personal BC concentrations of 18.6 µg/m³ for kerosene users and 9.9 µg/m³ for electricity users (Curto et al., 2019). In Santiago de Chuco, the traditional stove average was 7.9 µg/m³ and the intervention average was 5.1 µg/m³. Trujillo non-gas stoves had an average of 4.0 µg/m³, and gas had an average of 2.4 µg/m³. The average BC concentrations from Santiago de Chuco and Trujillo were lower than in the above studies, except for the smokeless coal stoves from Yunan.

Decrease of BC Exposure and Health Impacts

Janssen estimated that a decrease of $0.55 \mu\text{g}/\text{m}^3$ of elemental carbon would lead to an increased life expectancy of 3.6 months. Although elemental carbon and black carbon are not always at a 1:1 ratio, they have very high correlations (Janssen Nicole et al., 2011). The decrease of BC by $2.63 \mu\text{g}/\text{m}^3$ for the improved stove in Santiago de Chuco and $1.41 \mu\text{g}/\text{m}^3$ decrease of BC comparing gas to all other stoves in Trujillo would more than meet what is needed to increase life expectancy. However, the increase in life expectancy is based on decreased exposure to traffic emissions. The lack of research into the health impact of BC exposure due to cookstoves was noted by Downward and colleagues. Most of the studies focused on BC from traffic and not cookstoves (Downward et al., 2016), mainly due to the focus on developed nations and urban settings.

Cookstove Impacts on Sigma and the Loading Effect

Changes in the sigma come from a variety of factors such as the density, size, shape, and aggregation of black carbon particles (Bond et al., 2013). One of the main causes of the change to sigma is due to “coating” of material that is not black carbon, such as organic mass, minerals, and nitrates (Drinovec et al., 2017; Lioussse, Cachier, & Jennings, 1993). Some of these same materials may be found inside of the black carbon cores as well. The deposits can occur at the creation of the BC particle or due to atmospheric aging. These outer layers impact the optical properties of BC by either directing light towards the core, or by diverting light away. Typically, when other components form a shell around BC, light is directed towards the light-absorbing portion of the particle.

One of the properties of pollutant collection on filters is that the pollutant will begin to fill up the matrixes of the filter. This overall would not have much impact on gravimetric data.

As the matrixes of the filter fill up, some of the additional pollutants would be masked from transmission of light. This masking is the loading effect, and it leads to an underestimation of the pollutant, and is the case for BC. The fresh collection of BC from cookstoves is expected to have a reduced amount of coating, which would lead to a higher loading effect. BC collected after atmospheric exposure and aging would have an increased amount of coating, which would lead to a smaller loading effect (Drinovec et al., 2017). BC particles from diesel emissions are smaller in size compared to wood stoves. This smaller size of BC particle leads to a smaller loading effect (Drinovec et al., 2017).

Black carbon emissions gathered within close proximity to cookstoves would be expected to have different properties than atmospheric black carbon. BC goes through an aging process in the atmosphere. BC gathered at the source would not have the same aging impacts if they are properly stored and away from UV exposure (Bond et al., 2013). The kitchen BC from Santiago de Chuco and Trujillo would not have had time to mix with other components in the atmosphere, so this needs to be considered when evaluating sigma values. BC from ambient sources have more time in the atmosphere before they are collected by samplers. This would also mean that the central site data for Trujillo may need its own sigma if the BC from the central site would have more BC that has aged in the atmosphere. Black carbon that has aged typically has a higher sigma value, which would lead to a lower calculated BC concentration (Bond et al., 2013).

Limitations

The main limitation of the scope of this research is the lack of scans with the SootScan on the filters before exposure. This scan would have provided a baseline IR transmission for each filter and could be used as a blank value in the ATN calculation. This correction would work on an individual sample basis and could lead to a decrease or increase in BC concentration. An

additional change that was not done was using a filter loading correction. This would have the biggest impact on filters that have an ATN above 125. Magee Scientific has provided information on the use of the SootScan, neutral density filters, and comparison to elemental carbon. Some of the results from this analysis can be seen in Figure 5. 1. Santiago de Chuco had 22 filters and Trujillo had 12 filters that had attenuations above 125. This may have led to an underestimation of BC, as the correction factor accounts for overloading of filters. The correction was not done due to the current uncertainty of the value of the correction factor for BC originating from cookstoves. A counter to the underestimation is that using optical methods of measuring equivalent BC often is biased towards over estimating BC (Bond et al., 2013).

BC concentrations were only measured with a 48-hour time integrated sample, which provides a basis for daily and long-term exposure. However, peak concentrations during stove use can reach into the hundreds of $\mu\text{g}/\text{m}^3$, such as in a study by Kar and colleagues which had a mean of $335 \mu\text{g}/\text{m}^3$ for the traditional stove, $224 \mu\text{g}/\text{m}^3$ for a natural draft stove, and $78 \mu\text{g}/\text{m}^3$ for a forced draft stove (Kar et al., 2012). Santiago de Chuco had real time $\text{PM}_{2.5}$ measurements for some of the homes, so an extrapolation of BC concentration could be made. The challenge to this extrapolation is that the BC content changes throughout the burning of biomass, as the temperature and flow of air changes while burning. Not all improved stoves will decrease BC concentrations, such as with a natural draft stove design in India, where a traditional mud stove and natural draft stove had no significant difference in BC concentration during cooking time (Kar et al., 2012).

Summary

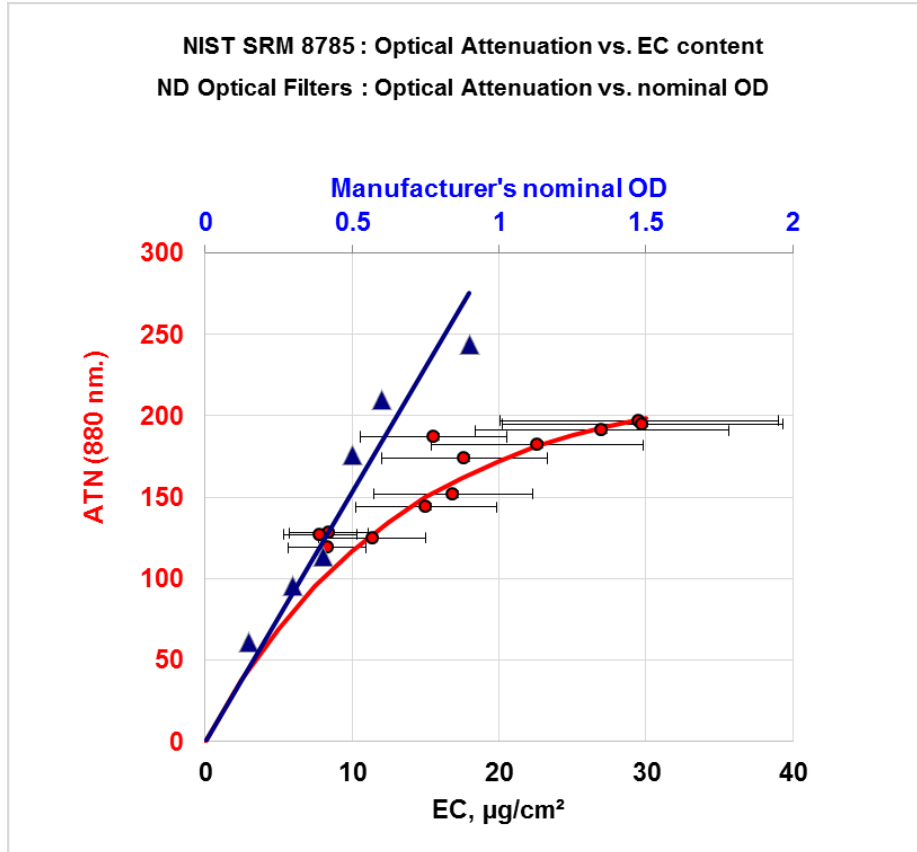
Use of the SootScan can provide an efficient method of gathering black carbon data from archived filters. Although a lack of data from unexposed filters will lead to less accurate data, a representative blank filter is still able to be used to provide insights into black carbon concentrations for archived filters. As more data sets become available and further analysis on black carbon concentrations from cookstoves are completed, improved sigma values and correction factors can be used.

The comparison of the stoves of Santiago de Chuco and Trujillo show that significant decreases of black carbon concentrations are obtainable for cookstoves in both rural and urban environments. Switching fuels to LPG appears to be the most effective for lowering BC exposure, but substantial benefits can still be obtained with an intervention stove that still uses wood. New designs of intervention stoves should still be considered that decrease both the concentration of black carbon and the BC/PM_{2.5} ratio. The decrease of BC exposure that was measured from the studies in Santiago de Chuco and Trujillo are potentially enough to provide health benefits to the affected individuals.

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Y-axis: Optical Attenuation measured at 880 nm using the Model OT21 Optical Transmissometer;

Upper X-axis: Nominal optical density (at 550 nm) of glass elements;

Lower X-axis: Elemental Carbon content of SRM 8785 filters, reported by NIST using the 'IMPROVE' thermal-optical analysis protocol.

Figure 5. 1 Magee Scientific results from neutral density filters, ATN, and elemental carbon measurements. (Magee Scientific, 2014).

The linearity of optical attenuation (ATN) to elemental carbon (EC) decreases as the ATN goes past 125. Figure 5. 1 is used courtesy of Magee Scientific.