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In Field Measurements of Solid Fuel Cookstove Emissions

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In Field Measurements of Solid Fuel Cookstove Emissions

DISSERTATION

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for the degree of

DOCTOR OF PHILOSOPHY

in Mechanical and Aerospace Engineering

by

Jin Dang

Dissertation Committee:
Professor Derek Dunn-Rankin, Chair
Professor Donald Dabdub
Professor Rufus D. Edwards

2016

DEDICATION

To my parents...

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Personal exposure to indoor air pollution from solid-fuel cook-stoves Advances in Aerosol Dosimetry Research	**Oct. 2014**
In-field measurement of combustion emissions from solid fuel cook stoves The 11th International Conference on Carbonaceous Particles in the Atmosphere	**Aug. 2015**
Solid fuel cook stove emissions: effect of intermittent use The Western States Section of the Combustion Institute Fall Meeting	**Oct. 2015**

ABSTRACT OF THE DISSERTATION

In Field Measurements of Solid Fuel Cookstove Emissions

By

Jin Dang

Doctor of Philosophy in Mechanical and Aerospace Engineering

University of California, Irvine, 2016

Professor Derek Dunn-Rankin, Chair

Solid fuel cookstoves have been used as primary energy sources for residential cooking and heating activities for ages, and the practice continues heavily, especially in developing countries. It has been estimated that domestic combustion of solid fuels (wood, animal dung, coal etc.) makes considerable contribution to global greenhouse gas (GHG) and aerosol emissions, degradation in local air quality, and deleterious effects on resident's health. Emissions from in situ solid fuel burning cookstoves have not been well characterized, and the majority of the data collected from simulated tests in laboratories do not reflect stove performance in actual use. This study characterized the in-field emissions of $PM_{2.5}$, carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4), and total non-methane hydrocarbons (TNMHC) from residential cooking events with various fuel and stove types from field sites in the Himalaya area, which includes Nepal, India, Tibet, and Yunnan province, China. Gravimetric filter and gas chromatography analysis were utilized, respectively, to measure $PM_{2.5}$ and gas-phase pollutant concentrations from direct cookstoves emission and indoor microenvironments. Real-time monitoring of $PM_{2.5}$, CO_2, and CO concentration was conducted simultaneously. The corresponding emission factors were calculated based on the field data using the carbon balance approach. The data set provides a unique resource for assessing the relationship between laboratory and in-use cookstove behavior. Detailed statistical analysis of the measurements confirmed the major factors responsible for emission variance among and between cookstoves. These factors include fuel type and cookstove type. A further analysis revealed that cookstove use dynamics (i.e., continuous use versus intermittent use) plays an important role in cookstove emission.

Chapter 1

Introduction

1.1 Emission from Solid fuel Cookstoves

Solid-fuel cookstoves are used all over the world. These cookstoves generally burn biomass or coal as their primary fuel. Biomass has been used directly as a fuel since the harnessing of fire by humans [1] and coal has been used since the second and third century of the Common Era [2]. Biomass fuels fall at the low end of the energy ladder, and consequently require large volumes and mass relative to the energy delivered, and they often produce high levels of combustion emissions. Coal has higher energy density but also contains substantial levels of dangerous compounds, including sulfur and heavy metals. For household energy sources, the energy density ladder can be expressed as: Dung < Crop Residues < Wood < Kerosene < Gas < Electricity [3]. The wide use of solid fuel due to human activity results in significant emission contribution to the atmosphere and indoor air quality. Although switching to a higher energy ladder fuel or adopting new technology like gasification with co-generation provides a cleaner way to acquire energy [4], there are still large populations that use biomass and coal directly as fuel for cooking and heating. It is reported that there are more than two billion people use direct burning of solid-fuel as their primary energy source [5, 6], especially in developing countries. Furthermore, it has been estimated that worldwide domestic combustion of solid fuels from residential use and small scale industry contribute approximately 34% of total black carbon (BC) emissions [7].

Unlike other well studied categories of combustion emission sources such as diesel engines [8, 9, 10], the emission inventory for the residential and small scale industry sector is under-investigated. In particular, depending on the type of fuel, emissions from solid-fuel cookstoves have a complicated make-up which includes Well-mixed Greenhouse Gases (WMGHG) like carbon dioxide and methane, pollutants such as carbon monoxide, sulfur dioxide (mostly when coal is used as the fuel source), hydrocarbons, and particulate matter (PM), as well as small concentrations of volatile organic compounds [6]. The potential radiative forcing from these complex emissions is still unclear, especially for particulate matter [11]. This dissertation study aims to measure cookstove emissions while they are in use to permit more accurate characterization of the potential local and global climate impact from domestic solid fuel combustion.

1.2 The Impact on Climate Change

Radiative Forcing (RF), which is defined as the net change in the energy balance of the Earth system due to some imposed perturbation, is frequently used to describe how various drivers contribute to climate change [12]. According to the Intergovernmental Panel on Climate Change's (IPCC) Fifth Assessments Report (AR5), the total anthropogenic Effective Radiative Forcing (ERF) over the industrial era is 2.3 (1.1 to 3.3) Wm^{-2} and has increased more rapidly since 1970 than during prior decades. The total anthropogenic RF estimate for 2011 according to IPCC AR5 is 43% higher than that reported in AR4 in 2007 [13].

1.2.1 Well Mixed GreenHouse Gas

Within all of the RF contributors, WMGHG made the largest contribution, and emission of carbon dioxide and methane are the most important. The tropospheric mixing ratio of carbon dioxide has increased from 278 (176-280) ppm in 1750 [14] to 390.5 (390.3-390.7) ppm in 2011 [15]. Methane's surface mixing ratio has increased dramatically since pre-industrial eras, from 722 ± 25 ppb in 1750 [16, 17] to 1803 ± 2 ppb in 2011 [12]. This increase is mainly due to the changes in anthropogenic-related CH_4 emissions [18, 19].

1.2.2 Carbonaceous Aerosols

Unlike the clear correlation between RF and each gas species, the effects from particulate matter are more complicated. The effect on climate from PM depends on several factors, including: PM concentration, size distribution, and chemical composition [20]. The PM in the atmosphere affects climate change in many ways. First, depending on the PM optical properties, PM scatter and absorb solar radiation which brings positive or negative RF. Second, aerosols in the atmosphere behave like cloud condensation nuclei and therefore affect local cloud formation. Third, particulates change the intensity and distribution of solar radiation that reaches earth surface. This change in solar influx impacts vegetation and its interaction with the carbon cycle thereby affecting the climate indirectly [21, 22].

The sources of particulate matter are also highly variable. There are natural PM sources such as soil dust, sea salt, biogenic aerosols, and volcanoes, and also anthropogenic PM which includes industrial dust and carbonaceous aerosols (organic and black carbon) [23]. One major source of the carbonaceous aerosols, which is the one of primary concern in this study, is the incomplete products of combustion. Organic Carbon (OC), also known as Organic Matter (OM), and Black Carbon (BC), also known as Elemental Carbon (EC) have different chemical composition which changes the overall refractive index and thus affects how particles interact with solar radiation, particularly as regards how much light is scattered (negative RF) and absorbed (positive RF).

The organic carbon in the atmosphere is a result of both direct emission (primary OC) and secondary organic carbon (SOAs), which is a product from the oxidation of hydrocarbons in the atmosphere [12]. Direct OC emission mostly comes from incomplete combustion while SOAs are formed from the chemical reactions of non-methane hydrocarbons (and their products) with hydroxyl radical (OH), ozone (O_3), nitrate (NO_3), or via photolysis [24]. The scientific understanding of SOAs formation is still limited due to the complexity of the process [25], but significant progress has been made and current urban air quality modeling efforts include some SOA reactions [26]. OC modify aerosols' optical properties by changing the spectral dependence of light absorption which changes its RF [27]. The global mean RF estimation for primary OC is about -0.09 (-0.16 to -0.03) Wm^{-2} and is -0.03 (-0.27 to +0.20) Wm^{-2} for SOAs [12]. As shown in Figure 1.1, though the estimates are highly uncertain, from

1850 to 2000, the emission of OC increased approximately 100% with most of the contribution coming from the burning of biofuel [7].

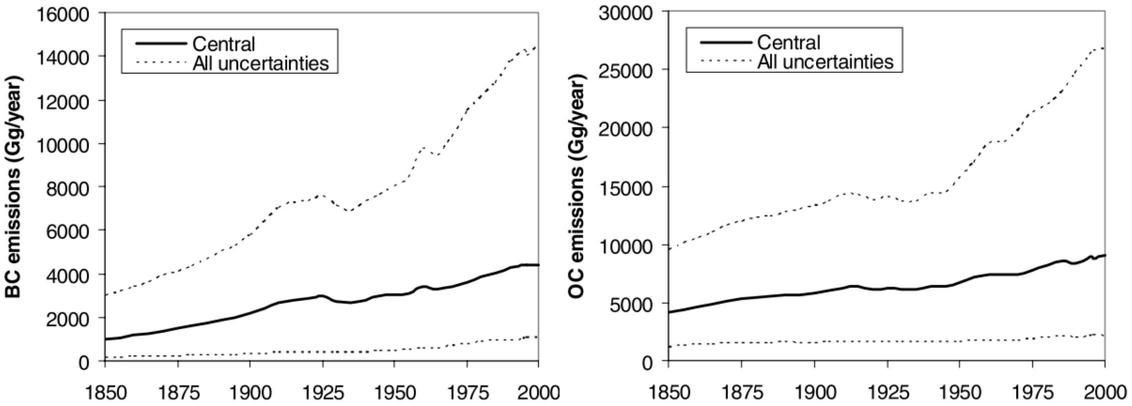


Figure 1.1: Emission of (left) black carbon and (right) organic carbon from 1850–2000 [7]

The primary source of black carbon is the emission from various combustion processes, such as power plants and diesel engines. Depending on the region, the major sources for black carbon emission varies. Globally, the largest source comes from open burning of forest and savannas. Residential solid fuels (coal and biomass) contribute 60 to 80% in Asia and Africa. In Europe and America, diesel engines are the key BC emission source as these engines contribute about 70% [11].

Black carbon is the major component of soot [28], a product from compression ignition engines. The formation mechanism of black carbon from combustion processes is still not completely determined. Generally it is believed the formation of soot strongly relates to carbon/oxygen ratio and Acetylene plays a critical role in the soot formation process [29, 30]. There is an argument regarding effects from charged particles and ions [31, 32], and the link between free radical and soot formation is brought up by

Bittner and Howard [33]. Nevertheless, the Hydrogen-Abstraction–Carbon Addition (HACA) mechanism, as sketched in Figure 1.2, pioneered by Frenklach and coworkers [34, 35, 36], is the most popular model regarding soot formation currently [37].

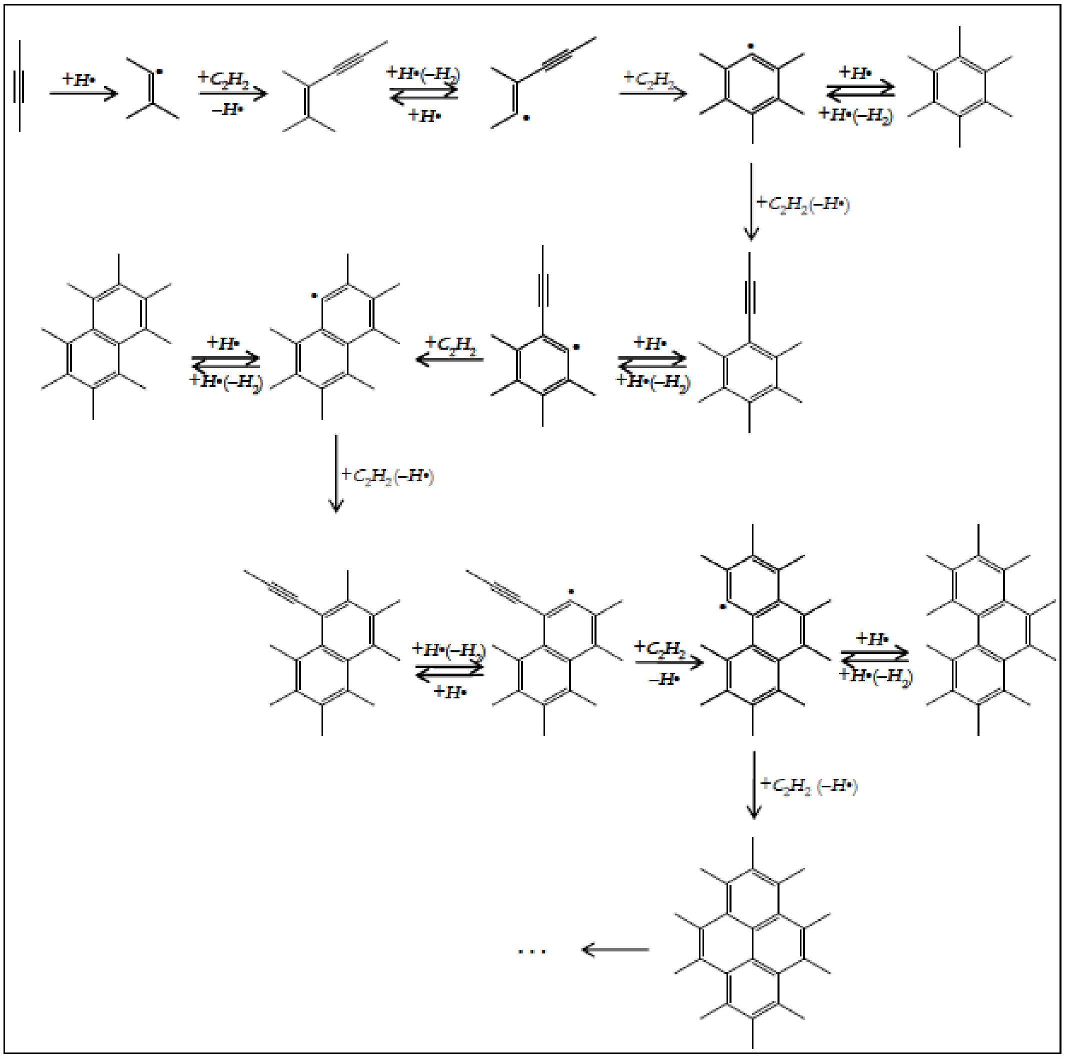


Figure 1.2: The HACA mechanism of aromatics formation and growth [35]

From the perspective of influence to RF, compared with OC, one major difference in optical properties of black carbon is that BC strongly absorbs visible light. IPCC 2011 estimated the RF at +0.20 (+0.05 to +0.35) Wm^{-2} and at 2014, the estimate increased to +0.40 (+0.05 to +0.80) Wm^{-2} [38]. Historically, the emission of BC in 2000 is more than 4 times that in 1850 [7]. On the other hand, the black carbon in snow or ice decreases the surface albedo significantly and therefore leads to a positive RF (though the decrease in albedo is accompanied by increased absorption into snow and ice which increases the potential melting in polar regions). In IPCC 2007, the estimate of this complex contribution is given as $[0.1 \pm 0.1]$ Wm^{-2} with a low level of scientific understanding. In all cases, the high uncertainty associated with aerosol estimates, as seen in Figure 1.3, indicates that it is necessary to have more detailed data of anthropogenic aerosol emission.

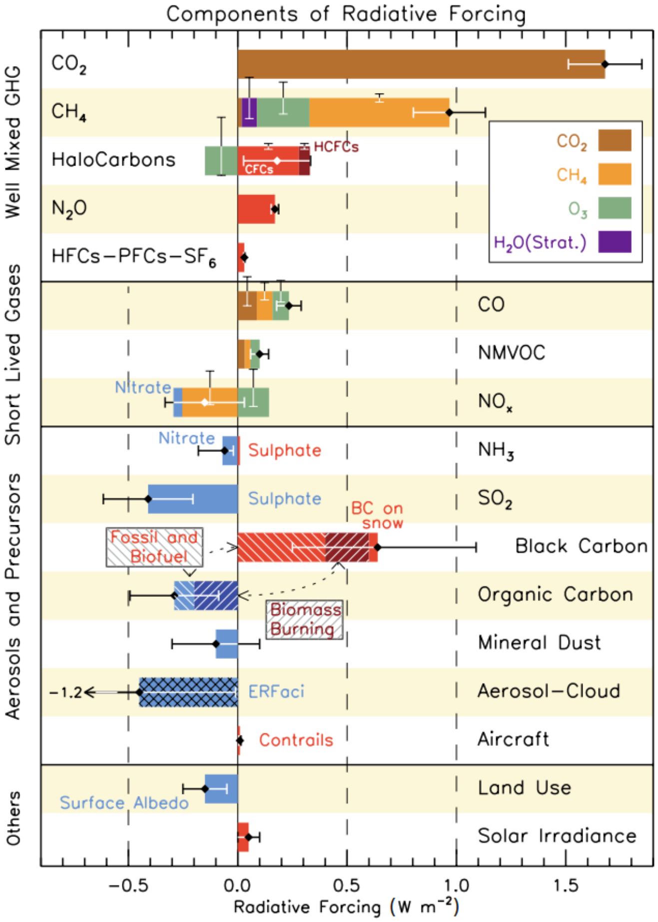


Figure 1.3: Radiative forcing of climate between 1980 and 2011 from AR5 report [12]

1.3 Indoor Air Quality and Resident Health

Air quality and human health are strongly linked. The famous 1952 London smog, which caused more than 4000 deaths [39] (later study indicates more than 12000 additional deaths [40]), is an extreme example. The health related compounds emitted from solid fuel cookstoves include: carbon monoxide (CO), sulfur dioxide (SO_2, coal burning stove), PM and some hydrocarbon components. Household use of solid fuels has led to well-documented high exposures to unhealthy indoor air pollution, particularly for women [41] and children [42]. Significant long-term exposure in environments containing the products of incomplete combustion and particulates found in solid-fuel smoke can cause chronic respiratory illnesses and other adverse health effects. According to World Health Organizations (WHO) estimates, there are approximately 1.6 million premature deaths caused by exposure to solid fuel smoke products each year [43]. A recent study conducted in Yunnan province of China indicates strong correlation between residential coal use and lung cancer occurrence [44, 45].

1.3.1 Gas Phase Pollutants

Carbon monoxide is the most common hazard gas from incomplete combustion. It can be found in the smoke/exhaust produced by all types of fires. The precise and complete mechanisms of carbon monoxide's toxicity is still under investigation [46]. Some known mechanisms include carbon monoxide's binding with hemoglobin, myoglobin and mitochondrial cytochrome oxidase, which results in restriction in oxygen supply [47, 48]. The colorless, tasteless, odorless, and nonirritating nature of carbon monoxide makes it impossible to detect by the exposed human [49]. Among the about

6000 fire related deaths in United States each year, more than half are suspected to have been caused by carbon monoxide poisoning [50]. EPA's eight-hour average permissible exposure limit (PEL) for carbon monoxide is 50 ppm while CDC suggests to reduce it to 35 ppm [51]

Volcanoes are the major natural source of sulfur dioxide. Of more concern is the anthropogenic emission of sulfur dioxide, which is in the products from combustion of sulfur-containing fossil fuels (like coal) [52]. As a major pollutant, sulfur dioxide is a hazard to both the ambient environment and living being's health [53]. Oxidation of sulfur dioxide, which produces sulfur trioxide and sulfuric acid eventually, is the primary path to the formation of acid rain [54]. As regards human health, inhaling sulfur dioxide causes reduction of lung function. The severity varies with individuals [55, 56] and simultaneous exposure to ultra-fine particles enhances the effect [57].

1.3.2 Particulate Matter

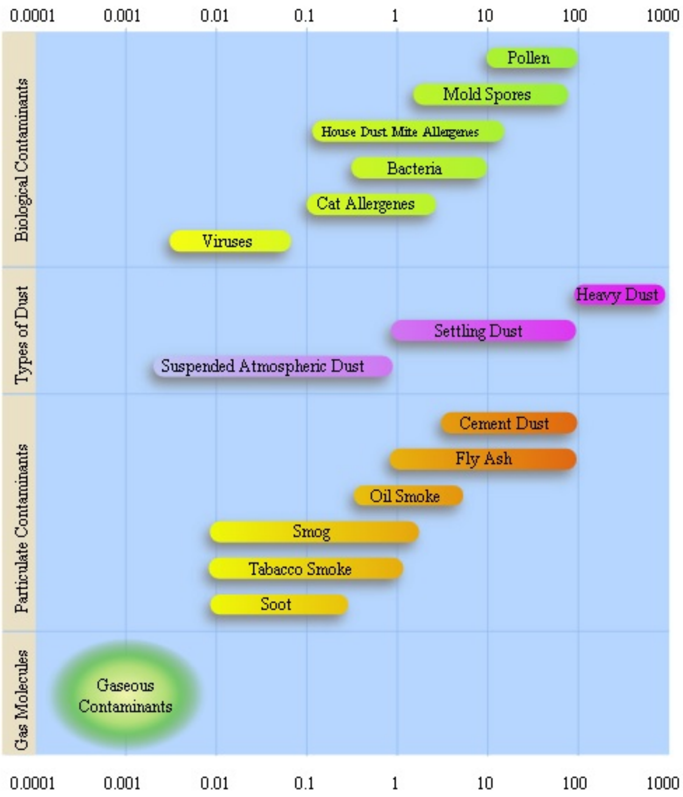


Figure 1.4: Particulate matter size chart [58]

The potential for causing health issues from particulates is strongly related to particle size, which determines how far the particles can penetrate in the respiratory tract, and how efficiently they deposit there. The US EPA particulate matter standard groups particulates into: *inhalable coarse* particles as those larger than 2.5 micrometers, but less than 10 micrometers, and *fine* particles as those less than 2.5 micrometers [59]. Note that the “size” of a particle is a subtle concept unless the particles are perfect spheres, which is often not the case. Hence, the particle size is often reflective of the measurement methods always considering some general connection to an equivalent sphere of standard density. Since inhalability is the concern, it is often aerodynamic equivalent size that is considered, while light scattering measurement methods reflect more an optical equivalent size. Despite this potential shape complexity, most practical particles behave sufficiently closely to spheres to be broadly classified in the $PM_{2.5}$ and PM_{10} domains. $PM_{2.5}$, with smaller size compared with PM_{10}, can reach the gas exchange region inside lung while PM_{10} is mostly filtered out by cilia [60], and thus $PM_{2.5}$ is presumed to have the more direct negative effect on human health. The latest studies suggest $PM_{2.5}$ as a generally better predictor of health effects than PM_{10} [61, 52]. The known health effects from PM include, but not limited to: premature death in people with heart or lung disease, nonfatal heart attacks, irregular heartbeat, aggravated asthma, decreased lung function and other increased respiratory symptoms (irritation of the airways, coughing or difficulty breathing) [62].

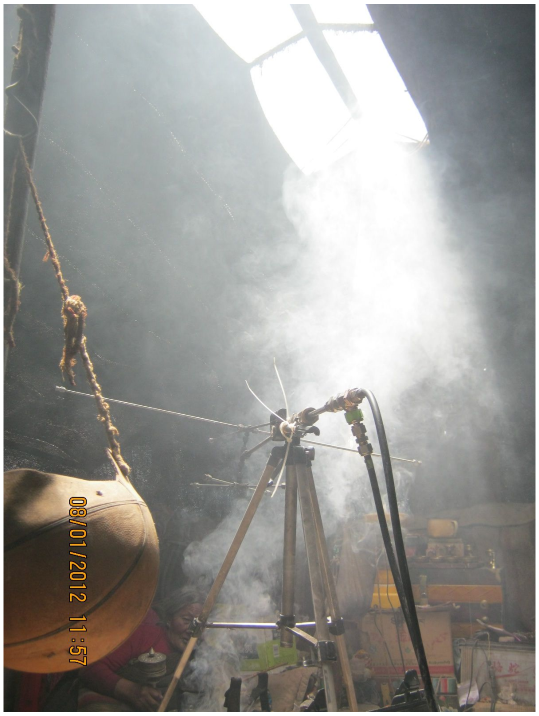


Figure 1.5: The smoke inside a Tibetan tent

Prior studies have addressed these ongoing global climate and public health issues, but there remains large gaps in knowledge regarding the climate and air quality implications of emissions from resident households using solid fuel cookstoves as a primary source of cooking and heating. An example image from such a household is shown in Figure 1.5. Without accurate information from field measurements, the potential contribution to overall emission is likely inaccurately estimated since there is enormous variability among the large populations in the developing countries using cookstoves with solid fuels. A major objective of this dissertation research, therefore, is to use in-field measurements to improve substantially the estimated emission from solid fuel cookstoves.

Chapter 2

Background

2.1 Role of Field Studies

2.1.1 Limitations of Models and Laboratory Tests

Studies of domestic solid fuel combustion emission have been underway for many years, but due to the limitation of technology deployment, the experimental study of biomass combustion emissions started only in the late 20th century [3, 63, 64, 65]. With help from statistical models, an emissions data set covering the historical period of 1850 - 2000 is available for major species which includes: methane, carbon monoxide, nitrogen oxides, total and specialized non-methane volatile organic compounds (NMVOCs), ammonia, organic carbon, black carbon and sulfur dioxide [13]. Unfortunately, the complexity and dispersivity of the emission sources means that the model study does not provide estimates with high accuracy and precision. In particular, several studies indicate that models consistently underestimate the carbon monoxide [66, 67, 68, 69, 70] and black carbon contributions resulting from biomass cookstoves use [71].

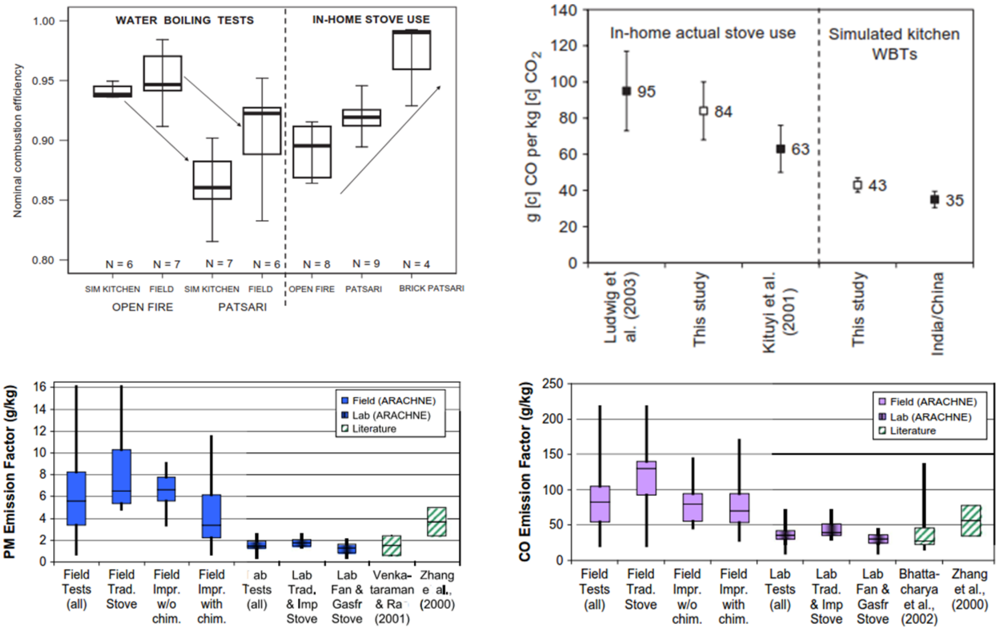


Figure 2.1: Comparison of lab and field measurement from previous studies [72, 73]

Controlled laboratory measurements of solid fuel cookstoves have been made by many groups [73, 74, 75, 76]. The widely used testing protocol includes the Water Boiling Test (WBT) and Kitchen Performance Tests (KPT). However, it is not well-demonstrated that current testing protocols represent the actual everyday cooking and heating activities in homes, and there is still lacking a confirmed explanation regarding the difference between laboratory and in-field measurements [77]. Bailis, for example, reported that laboratory measurements do not agree with in-field KPT [78], with laboratory results generally underestimating in-field outcomes; Roden suggested that traditional stoves produce more particles than expected from previous laboratory studies [79, 80]. As the actual emissions from household cookstoves depend on several variables including: stove type, fuel type, food type, and the behavior of the cooks cooking the food, laboratory experiments with uniformity and repeatability are not similar to everyday cooking and heating activities and therefore may not reflect the in-home conditions, nor the unavoidable variation of resident stove activities. This situation leads to highly uncertain in-field data [81]. Nevertheless, it is important to determine suitable laboratory test configurations that can help evaluate stove performance both for more accurate global estimates of emissions and as a test protocol for the designers of improved solid-fuel stoves. Thus, in order to have a better understanding of household solid-fuel cookstove emissions, in-field study is important and valuable.

2.1.2 Challenge and Significance of In-Field Measurements

The inherent challenges of in-field measurement result in a very limited database available for emissions from residential cookstove activities. Compared with laboratory experiment studies, in-field measurements have significant challenges to acquire high quality data. For example, because most of the residents who use solid-fuel cookstoves as their primary energy source live in rural areas, it is often difficult to access these in-field sites. Also, rural areas that rely on solid-fuel have limited, or even no electrical power supply, which greatly restricts measurement capabilities [79]. Moreover, taking measurements in homes is not as straightforward as doing so in a laboratory since the in-field environment is generally in an active family location. Local coordination plays a critically important role in this process, and it is for this reason that experienced field measurement research teams are invaluable.

Previous studies report that residential cookstoves emissions are highly region dependent [82]. Some of the reasons attributed are the great variety of lifestyle and types of food in different regions. One simple example is that people in many parts of Asia cook smokier food, which leads to higher organic matter emission. This diversity calls for a broader and more complete set of in-field emission data in order to help evaluate the variability accurately. Using the field data from a single site as simple reference from a regional study and applying the information to global models will introduce significant accuracy issues [79].

Figure 2.2: A field view in Nam Co, Tibet, China

Data of this current field study (an example site is shown in Figure 2.2) is mostly collected from hard-to-access areas around the Himalaya region. The Nepal and Tibet, China measurements fill in a major gap in the cookstoves related emission data inventory in these regions. Even more, the sampling campaign in Nam Co of Tibet, China, reached the highest altitude (4730m, approximately 15500 ft) for residential cookstoves emission data so far obtained.

2.2 Measurement Techniques

The complex make-up of exhaust from solid fuel combustion requires various measurement methods. Time-integrated measurement generally can be conducted by collecting samples from the field and then later analyzing them in the laboratory. This approach permits gas samples with gas chromatography analysis [83] and filter samples with gravimetric (particulate matter) [84] or thermal optical analysis (elemental carbon) [85]. Real-time monitoring, depends on the species to be measured, and relies on additional instrumentation. Because the in-house environment is dynamic, the real-time data is necessarily more variable than long-duration integrated measurements. It is also valuable, however, since it shows specific cooking and heating events that are relevant to the accurate interpretation of emissions.

2.2.1 Gas Analysis Methods

2.2.1.1 Gas Chromotography

Chromatography is a very popular analytical chemistry technique widely used for separating and analyzing compounds. Depending on the state of the so-called mobile phase in the system, there are Gas Chromatography (GC) and Liquid Chromatography (LC). The chromatography phenomenon was first discovered by Russian-Italian botanist Mikhail Tswett in the beginning of the 20th century during his study into separating pigments in green leaves [86, 87, 88]. American petroleum chemist David Talbot was using chromatography in his work of separating hydrocarbon from petroleum at the same time [89, 90]. The invention of GC is generally credited to A.T. James and A.J.P. Martin's paper: *Gas-liquid partition chromatography: the separation and micro-estimation of volatile fatty acids from formic acid to dodecanoic acid* in 1952 [91]. Although theoretically LC can analyze more substances than can GC, the advantages of high resolution, shorter analysis time and lower cost make GC (only for compounds that can be vaporized without decomposition) extremely popular in analytical chemistry.

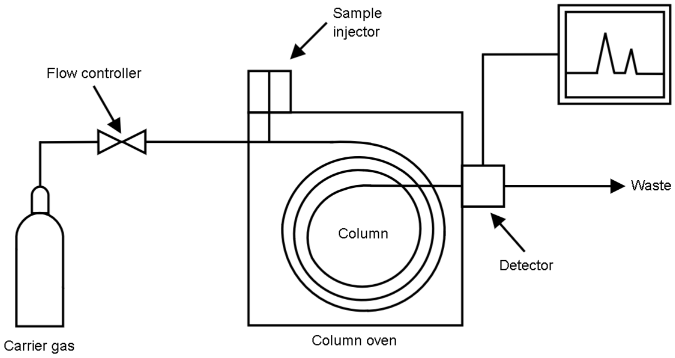


Figure 2.3: GC diagram [92]

As shown in figure 2.3, a typical GC system comprises: a sample injector, carrier gas (mobile phase), column, oven, and detector. The analyte is injected into the column via a sample injector. Carrier gas carries the sample flow through the column. The separation process is completed within the column, which is essentially tubing with a stationary phase coated on the inner surface. The separation is based on the nature of molecular interactions between analyte and stationary phase. For non-polar compounds, the separation is mostly based on volatility. Separation of polar compounds also involves dipole-dipole interactions [93]. Different compounds reach the detector after different retention time, which generates signals as separated peaks on the chromatograph.

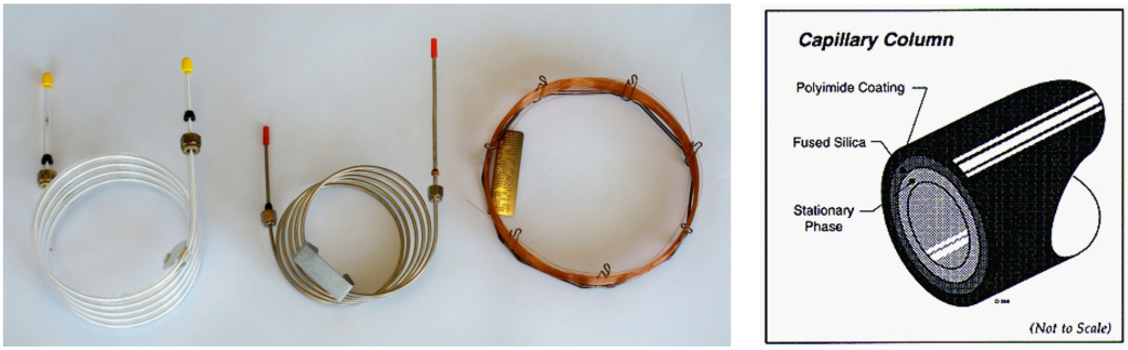
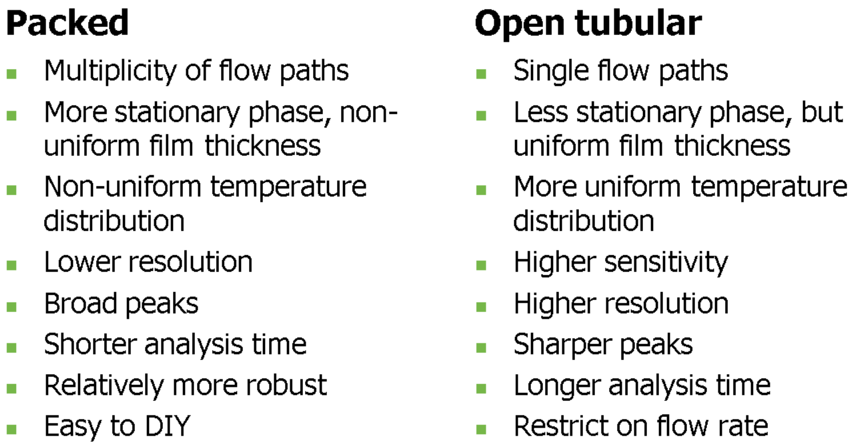


Figure 2.4: Packed and capillary GC Columns [94]

As discussed above, the column is the key to the separation performance of GC. There are two types of column in general: packed and open tubular (also called capillary). Packed columns have existed since the GC was invented, and its characteristic of affordable, robust, and shorter analysis time make it still widely used in tasks that do not require very high resolution [95]. As shown in the Figure 2.4 diagram, a packed column is essentially metal (copper in most cases) tubing packed with a stationary phase. The resolution of a packed column is limited by its length, non-uniform flow/temperature condition, and the resistance to gas flow. Suggested by Martin in 1956 [96], the capillary column, was invented by Golay in 1957 [97] and became popular quickly [98]. Early capillary columns are made from glass which has the disadvantage of fragility [99]. These issues were solved by the invention of fused-silica columns in 1979 [100]. The chromatogram below, Figure 2.1, shows a comparison between packed and capillary columns for a sample of calmus oil. Capillary columns bring significantly higher resolution and sharper peaks.



Packed	**Open tubular**
Multiplicity of flow paths	Single flow paths
More stationary phase, non-uniform film thickness	Less stationary phase, but uniform film thickness
Non-uniform temperature distribution	More uniform temperature distribution
Lower resolution	Higher sensitivity
Broad peaks	Higher resolution
Shorter analysis time	Sharper peaks
Relatively more robust	Longer analysis time
Easy to DIY	Restrict on flow rate

Table 2.1: Comparison between packed and open tubular column

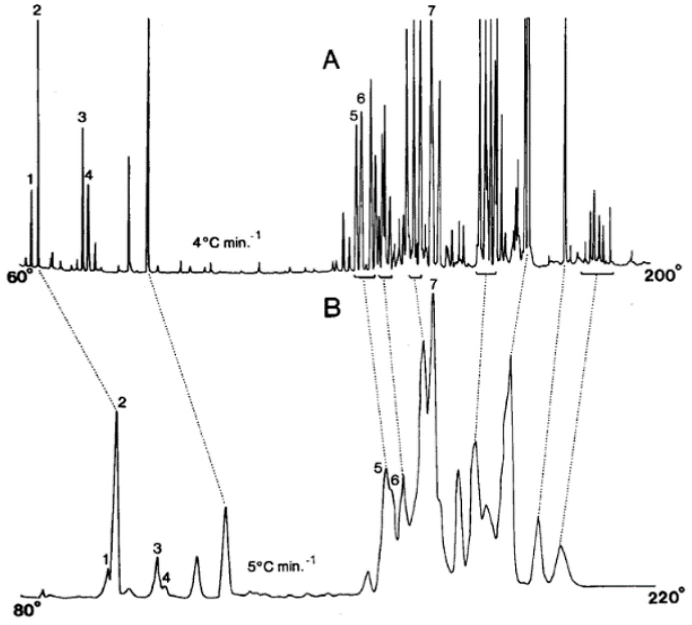


Figure 2.5: Capillary column verses packed column [93]

The mobile phase's function is to blow (or carry) analyte through the column. Hence, one critical requirement is that the carrier gas must not react with the analyte. Thus, most carrier gas selections are in the inert gas group, with hydrogen, helium and nitrogen (Figure 2.6) the most popular three [95]. Another criteria is the diffusivity of carrier gas, which directly affects the interaction with the stationary phase and thus determines the efficiency of column separation [101]. For example, in order to acquire the same level of separation efficiency, with higher diffusivity, a higher gas velocity in the column can used, which will significantly reduce analysis time. Depending on the detector type and individual analysis requirements, other limitations may apply. For example, a helium ionization detector (HID) requires helium as carrier gas to work properly [102].

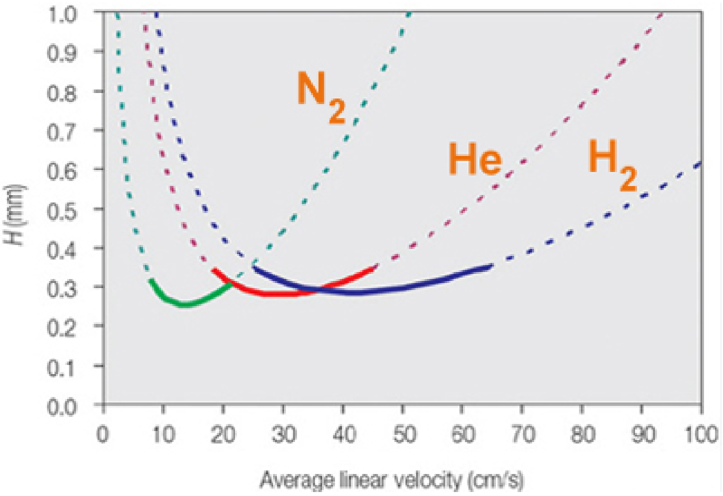


Figure 2.6: Comparison of separation efficiency between carrier gases [95]

Among the various GC detectors, thermal conductivity detectors (TCD) and flame ionization detectors are the most popular. TCD relies on different thermal conductivity from different compounds. Thus, it can respond to almost all types of analytes. But the sensitivity is limited. FID, on the other hand, measures the ion current from organic molecules in a hydrogen flame. With its very high sensitivity, great linearity across wide range and low cost, FID has become the most popular detector for organic carbon. One limitation for FID is that it cannot respond to inorganic substances by itself. In some systems, a methanizer (Figure 2.7) is used to give FID CO and CO_2 detectivity. With a nickel catalyst and an additional hydrogen supply flow, methanizers convert CO and CO_2 to methane before they reach the FID. Sulfur containing gases and unsaturated hydrocarbons (eg, C_2H_4) have a poisoning effect on nickel catalysts, and so the methanizer is not recommended when these compounds exist [103]. Unlike TCD, FID destroys the sample being tested; thus it should be used in the last stage of analysis.

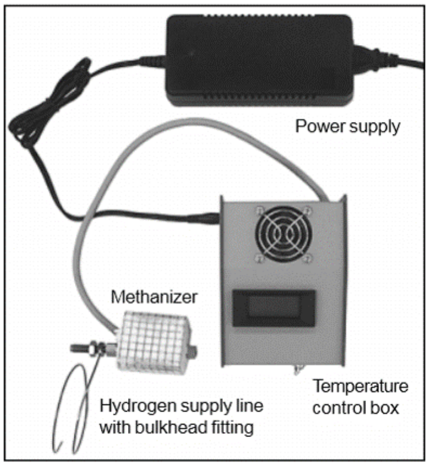


Figure 2.7: Methanizer

There are two calibration methods for chromatography analysis: internal standardization and external standardization [95]. Internal standardization adds a known amount of standard (different with the targeting species) into the sample as a reference. The standard and sample are injected into the GC together. By comparing the detector's responses to the analyte and the reference standard, the concentration of the species in the sample is acquired. Internal standardization generally has higher accuracy, as it eliminates the error between every injection [104]. However, this method requires special processing on the sample (adding standard) which is not always feasible. External standardization injects the standard and sample separately. By injecting a known concentration standard (same with targeting species) at different volume, a calibration curve is obtained. With the response to the analyte and the calibration curve, the analyte concentration can be calculated. External standardization is more convenient to use in many cases. Ensuring exactly the same condition for the injection of standard and sample are critical to acquire accurate result [104, 105, 106].

2.2.1.2 Isopropanol Absorption and Controlled Condensation

The current study does not include detailed measurements of sulfur compounds, but such compounds are known to be significant in solid fuel cookstove emissions and so for completeness the analytical chemistry methods available for such emissions are described herein. Isopropanol absorption and controlled condensation are two standard methods for analyzing sulfur dioxide and sulfur trioxide from stationary sources. EPA method 8 [107] and 8A [108] provide the methods description in details with method 8 emphasizing sulfur dioxide and 8A for sulfur trioxide. The major challenge for these methods is how to sample sulfur dioxide and sulfur trioxide separately.

The idea of isopropanol absorption is based on the recognition that sulfur dioxide and sulfur trioxide have very different solubility in isopropanol: sulfur trioxide dissolves easily in isopropanol while sulfur dioxide does not. As the sampling train schematic (Figure 2.8) shows, the sampled gas mixture passes through four water/ice bath cooled impingers. The first impinger is filled with 80% isopropanol to absorb sulfur trioxide without absorbing sulfur dioxide. The second and third impingers are filled with 3% hydrogen peroxide to absorb and react with sulfur dioxide ($SO_2 + H_2O_2 \rightarrow H_2SO_4$). The fourth impinger is for drying purposes. The main limitation for isopropanol absorption is the relatively high measurement uncertainty in humid or high SO_2 concentration environments. At typical flue gas temperature, some SO_2 will oxidize with the excess oxygen in the flue gas and then react with water (sulfate acid as product), which results in an over estimating SO_3 concentration [109].

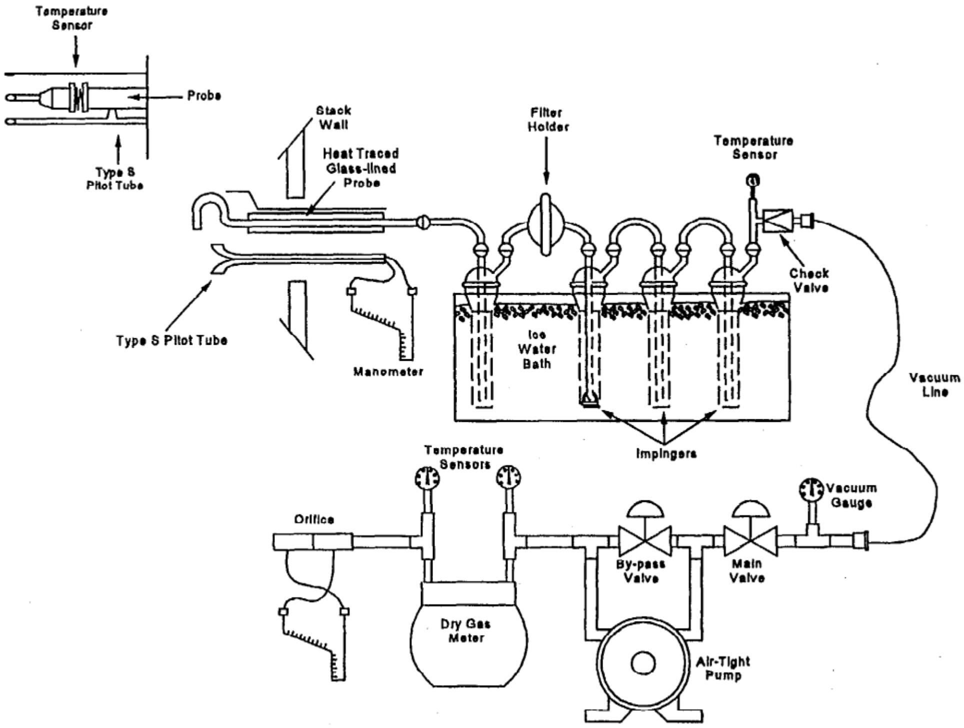


Figure 2.8: The EPA Method 8 SO_x sampling train [107]

The sampling train for controlled condensation in Method 8A is shown in Figure 2.9. The difference between this method and isopropanol absorption is that instead of using isopropanol to absorb sulfur trioxide, controlled condensation utilizes a modified Graham condenser with water cooling at 85 to 95°C. This temperature is higher than the dew point of water, which prevents water vapor from condensing. SO_2 does not react with water/vapor at this temperature also, which prevents this potential interference [110]. When the gas flows through the condenser, with the water cooling, SO_3 gas and sulfate acid vapor instantly condense to droplets. With the help of the centrifugal force created by the spiral flow path, these droplets will attach on to the spiral tubing wall [109]. The glass frit at the end of the condenser collects the relatively large sulfate acid droplets which may not stick on the condenser film at high flow rate. Although controlled condensation is capable of measuring SO_2 and SO_3 simultaneously, reports from studies recommend not to do so as the high flow rate sampling required by controlled condensation does not permit sufficient residence time for the SO_2 absorption, leading to an underestimation of SO_2 [109].

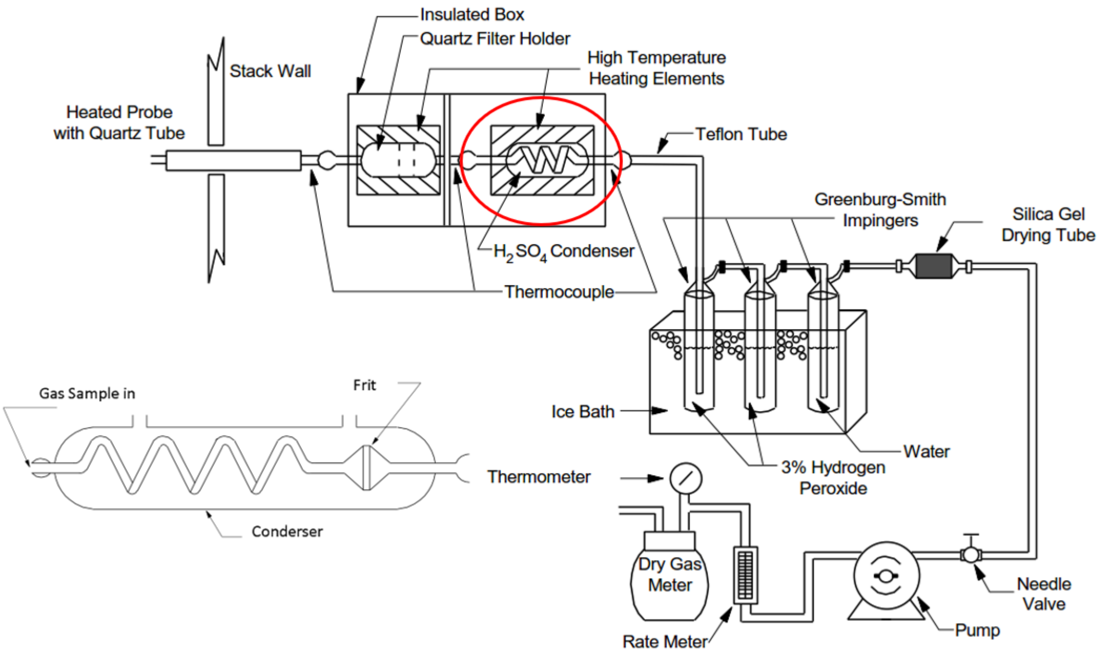


Figure 2.9: The EPA method 8A SO_x sampling train with customized Graham condenser [108]

The SO_4^{2-} content in the collected sample is determined by barium perchlorate titration with a color indicator such as Thorin, Beryllon II, etac. [111, 112]). In the SO_4^{2-} environment, Ba^{2+} will immediately react with SO_4^{2-} forming the precipitate product $BaSO_4$ ($SO_4^{2-} + Ba^{2+} \rightarrow BaSO_4 \downarrow$). After all the SO_4^{2-} has reacted, the extra Ba^{2+} titrated into the solution reacts with indicator and triggers the color change which indicates the end of titration [113]. With total gas volume recorded, SO_x concentration is obtainable. One major challenge of this titration analysis is to determine the end of titration from a subtle color change. The traditional indicator Thorin does not give a sharp enough color change (Figure 2.10). Beryllon II is reported to have better effect [114, 111, 115] but it is still challenging for visual identification. Thus, it is recommended to use an optical spectrometer to assist in the identification of the end of titration. There are also commercial auto-titrators available, with a Spectrasense optrode to sense the color change.

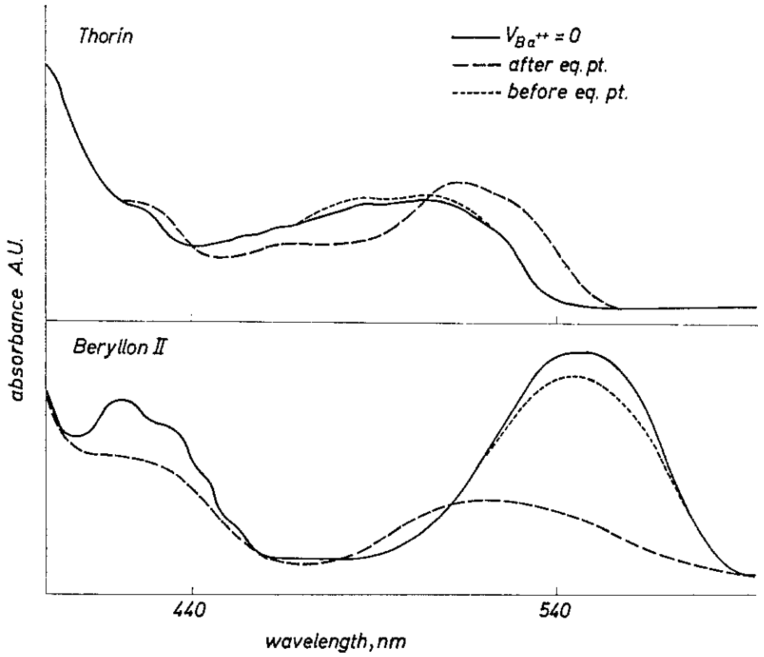


Figure 2.10: Spectra of Thorin and Beryllon II at various stages of titration [114]

The titration condition is also critical to this analysis. The major factors includes pH and isopropanol fraction in the solution. Common indicators (e.g., Thorin, Beryllon II) function within a large pH range. For instance, Thorin is reported to have a functional pH range of 3–10 while Beryllon II is 3–11 (Figure 2.11). Despite the wide range of operation, practical experience suggests that there exists an optimal indicator condition that increases accuracy. According to J. C. Haartz's study, a pH of 3.5 approximately combined with 85% isopropanol in the solution gives the best result, and is considered optimal [116].

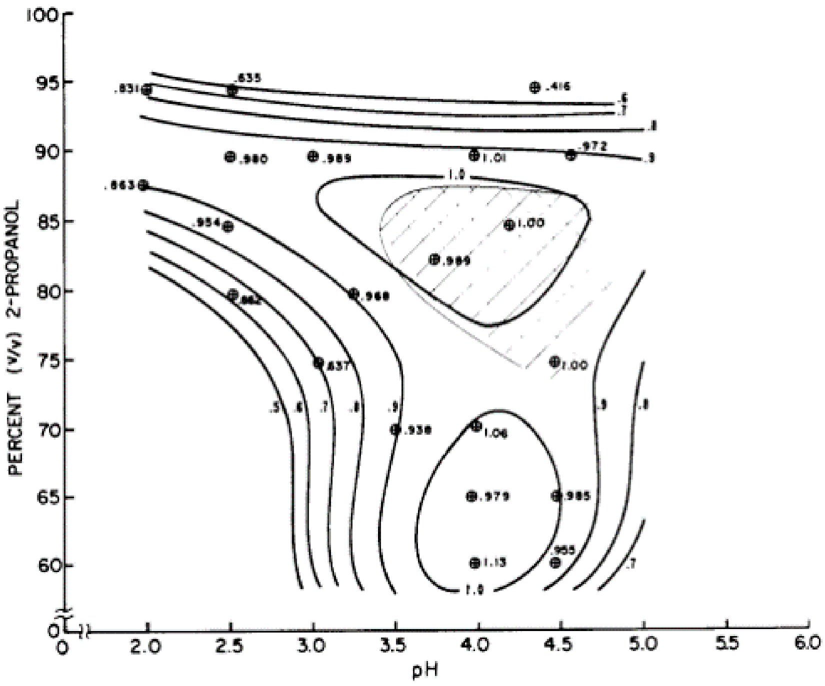


Figure 2.11: Fraction of sulfate recovered as a funtion of pH and % of isopropanol [116]

2.2.2 Particulate Matter Measurements

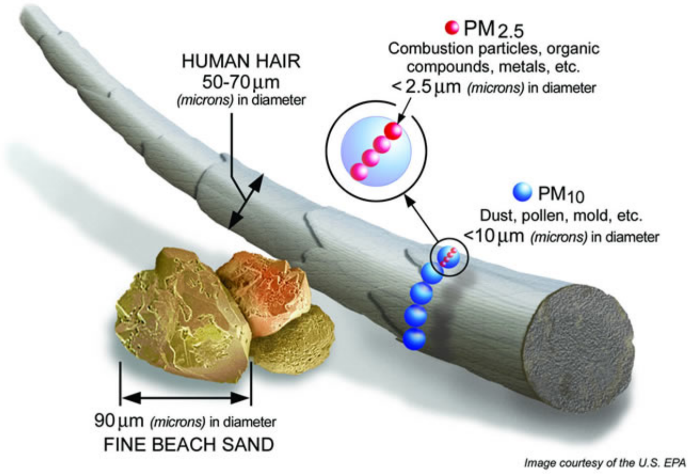


Figure 2.12: Particulate matter: various sizes

The measurements of particulate matter suitable for implementation in the field generally includes two stages: size selection and concentration detection. Size selection of PM is usually realized with impactors, cyclones, and other inertial or gravitational collectors. Concentration measurement techniques generally include three groups of methods: gravimetric, optical and microbalance.

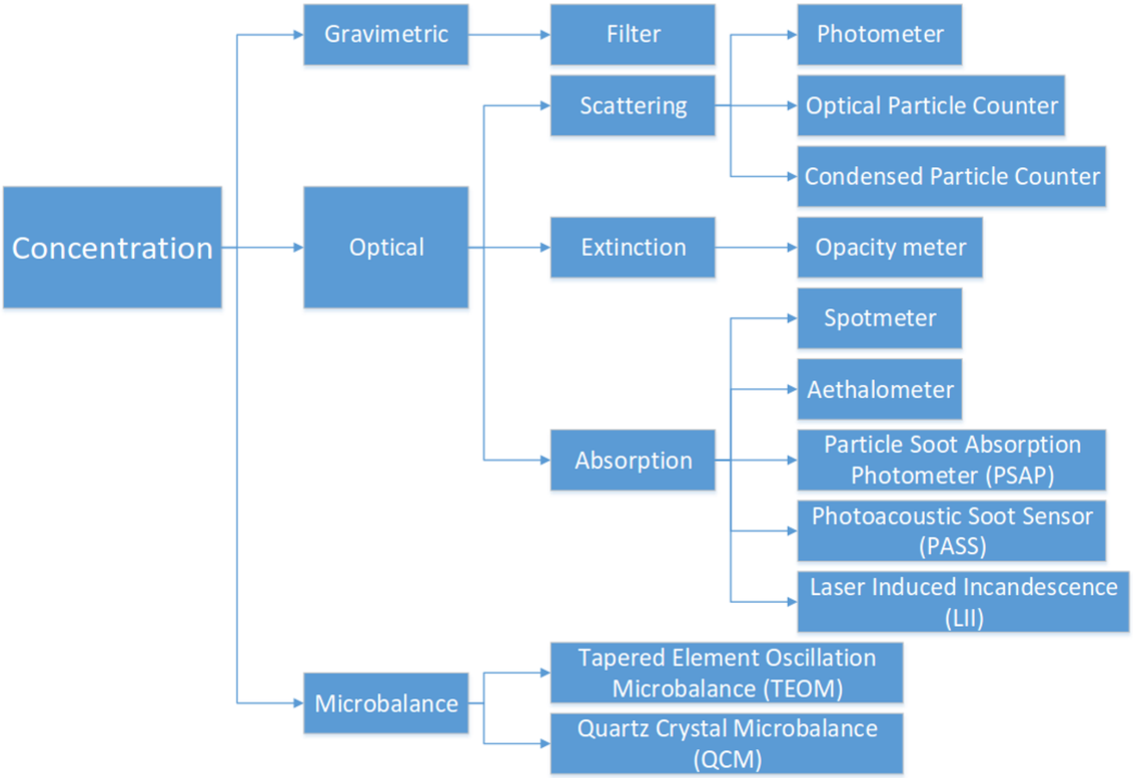


Figure 2.13: PM concentration measurement techniques

2.2.2.1 Particle Size Selection

Cascade impactors and cyclone separators are the most common PM size selection equipment [117]. Both of them are inertial collectors. The figure below describes how a single or multi stage conventional cascade impactor works. Flow containing various sizes of PM travels through the flow path in a impactor. The larger size PM, with higher inertia, will be stopped by the impact plate while smaller size PM with better flow tracking capability will be able to flow through the cascade. To prevent the particle from bouncing on the impactor surface, a small amount of oil is usually applied. With the same principle applies to multiple stage impactors, the particle size distribution can be acquired. There is another type of impactor called a virtual impactor. In contrast with the conventional impactor, a virtual impactor does not have an impact plate. Instead, it utilizes a stagnation, or slow moving air flow [118, 119]. Impactors are usually very compact and work with portable particle instruments.

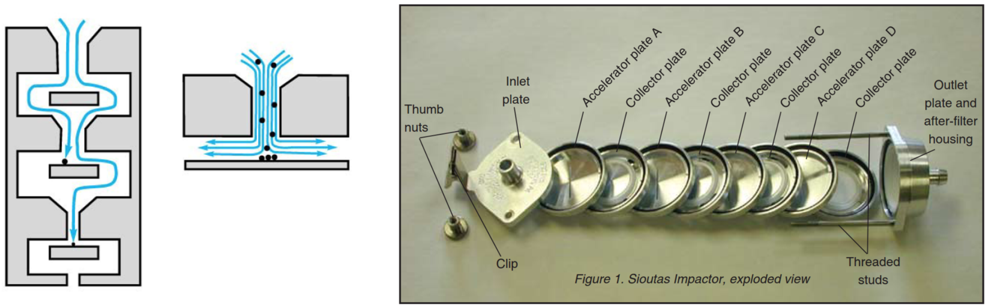


Figure 2.14: Flow inside a cascade impactor and a multiple stage cascade impactor [120]

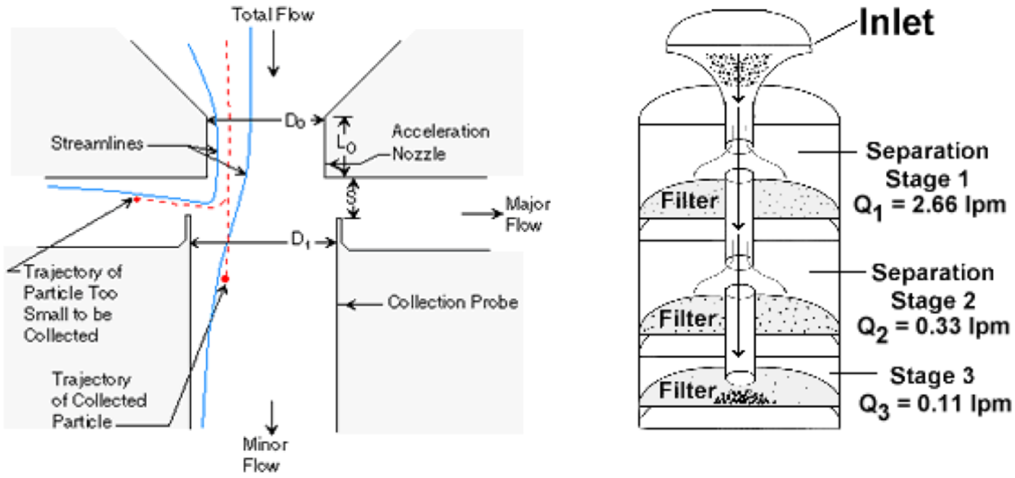


Figure 2.15: Single and multiple stages virtual impactor

Cyclone separators, similar with cascade impactors, are also inertial collectors. However, unlike the cascade impactor which is mostly compact, cyclone separator size varies substantially depending on the usage. There are portable cyclones designed for personal sampling as well as large scale cyclones used for dust filtration in industry.

The main structure of a cyclone separator is a chamber with cylindrical body and a conical section. As the aerosol mixture enters the chamber tangentially, the mixture flows in a helical pattern until it reaches the convergent conical section. Pressure increase from the convergent flow path pushes the flow, together with small particles, up so that they exit from the top of chamber while large/heavy particles get trapped in the catch bin below the lower chamber exit.

Field measurements have additional requirements for instruments, which include, but are not limited to: lightweight, robustness, reliability, durability, and energy efficiency. Both impactors and cyclones work well in field measurements in most cases. For impactors, part of the performance relies on the applied oil film, which gets contaminated as the sampling continues. In this study, due to the requirement of long time (10+ hours) continuous sampling, cyclone separation is used to select particle size.

Figure 2.16: Various cyclone separator and its flow path

2.2.2.2 Gravimetric

Excellent reliability and accuracy brings the gravimetric method the title of ‘gold standard’ for particulate measurement. Gravimetric sampling measurements are a significant component of this disseration’s field measurement data. EPA method 201A provides a detailed methodology about using gravimetric analysis to measure PM_{10} and $PM_{2.5}$ [121]. In order to measure particulate within a specified size range, the gravimetric method is usually combined with particle size selection equipment. A simple gravimetric set up for measuring $PM_{2.5}$ includes: particle size selection equipment (usually impactor or cyclone), sampling pump to providing consistent flow rate, polytetrafluoroethylene (PTFE) membrane filter, and micro balance. The PTFE filter is pre-weighed before the sampling and post-weighed after the measurement. By acquiring the difference between the pre- and post- weight, combining with the volume of total sampled air, the concentration of target PM can be obtained [122].

Figure 2.17: PTFE filter, sampling pump, and micro balance

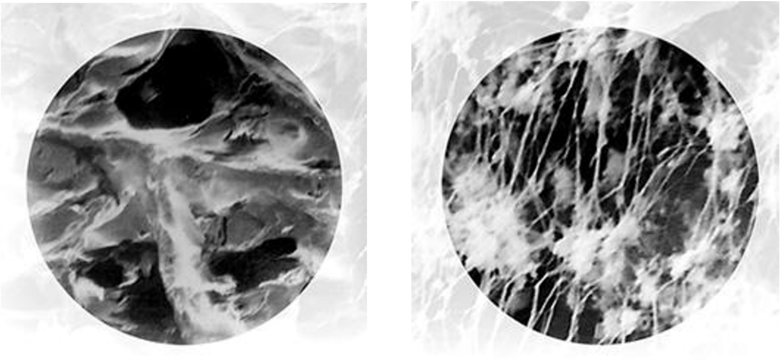


Figure 2.18: PTFE filter under microscope [123]

The air filter itself is a physically simple device, yet the mechanism behind the air filtration process is not. Depending on the particle size range, the responsible filtration mechanisms vary. The major air filtration mechanisms include:

- Impaction: Also named inertia. Large particles with higher mass and inertia tend to travel in a straight line even though the air stream within the air filter is turning to pass the fiber. The impaction mechanism occurs as these large particles hit and stick on the filter fibers.
- Interception: Similar with impaction, but works on smaller particles that do not have enough inertia to hold a straight line trajectory. When the air stream turn to pass through fibers, these particles do not track the air stream perfectly and are intercepted by the fiber.
- Diffusion: For very small particles, the diffusion effect becomes significant and Brownian motion is involved. In this case, particles do not follow the air stream precisely, instead, they move irregularly. This irregular movement increases the probability of particles touching a filter fiber and being trapped.
- Straining: The straining mechanism is relatively straight-forward. When the

particle is larger in most dimensions compared with the distance between fibers, the particle will not be able to pass through and will be stopped by the filter.

- Electrostatic Attraction: Usually used to enhance the capability of capturing fine particles for coarse filters. The downside of electrostatic attraction is that filter will lose electrostatic charge over time as particles captured on the surface neutralize their electrostatic charge, which results in degrading filtration efficiency [124].

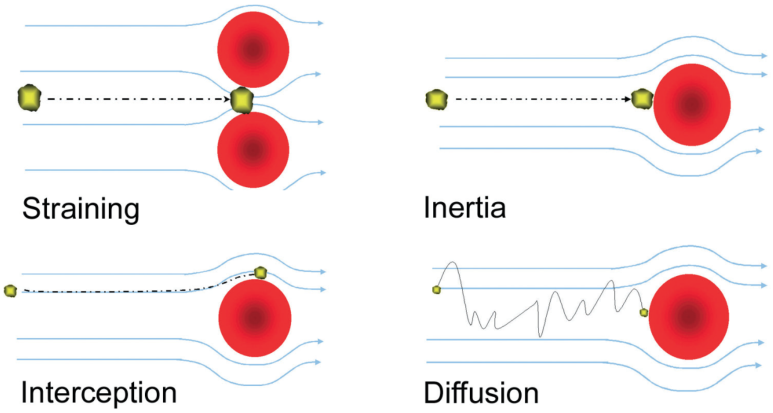


Figure 2.19: Schematic of major filtration mechanism [124]

2.2.2.3 Optical

Optical methods are widely adopted for particulate measurements. Based on their principle, these methods can be subgrouped into scattering methods, extinction methods and absorption methods.

2.2.2.3.1 Scattering

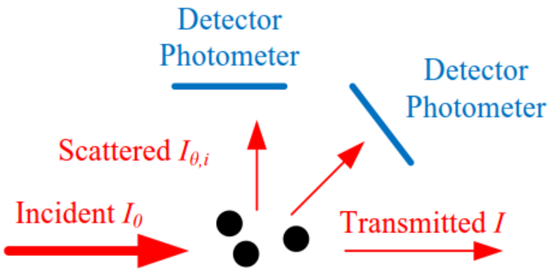


Figure 2.20: Schematic of light scattering on particles [125]

Instruments using a scattering method include photometers, optical particle counters and condensed particle counters. The light scattering pattern and intensity are function of particle size factor, which is defined as the ratio between particle size and the wavelength of the light source. Note again that size here is not a precise measure since the particle might have irregular shape. Rather size refers to an optically scattering equivalent size. As the wavelength of the light source (laser in most cases) is known, by acquiring the scattering light information from one or more angles, the particle size and concentration is obtainable. The typical angles of choice include 90°, 45°, or less than 30° [126, 127]. The whole scattering particle measurement system can be as simple as a light source plus detector and a data acquisition system. Therefore, it is possible to have very compact designs for the PM instrument based on the scattering method. This advantage makes scattering methods very popular in portable PM monitoring equipment. The scattering based instruments used in this study include TSI DustTrak Aerosol Monitor (8520 and 8530 model) and UCB Particle Monitor. The choice is made mainly on availability as these monitors are usually costly. The UCB Particle Monitor is basically a data logger integrated with smoke detector and it does not provide particle size selection capability. The TSI DustTrak Aerosol Monitor provides good real time information for background level

PM concentration. For direct cookstoves emission monitoring, dilution is required to prevent over range saturation issues.

$$Particle\ Size\ Factor: \quad \alpha = \pi\frac{d}{\lambda} \tag{2.1}$$

The downside for scattering methods is mainly limited accuracy. As the optical property of the particle itself (composition, shape, etc.) greatly affects the scattering pattern, additional calibration/correction is always required when measuring PM from different sources [128, 129]. By 2015, there is only one scattering based PM monitor (GRIMM EDM 180 Dust Monitor) approved by the EPA as an EPA Federal Reference and Equivalent Methods (FRM and FEM) [130].

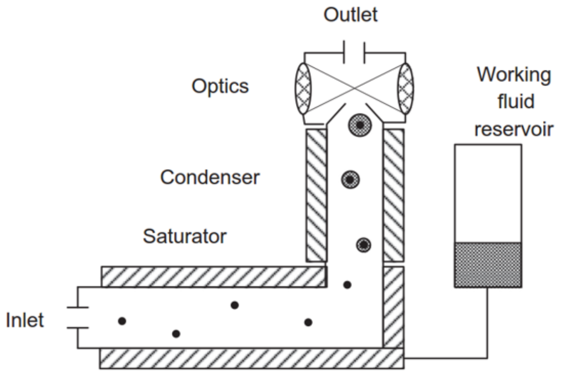


Figure 2.21: Continuous flow condensation particle counter [125]

In comparison with light scattering methods for particle sizing, an optical particle counter instead has a measurement volume, which is formed by the intersection of focused beam, that is small enough to ensure that only one particle is illuminated at each time. In this way, optical particle counters give the count of particles instead of concentration. Condensation particle counters let the particle grow to micron size before taking the measurement. Common methods used to achieve ‘particle growth’ include: adiabatic expansion of the aerosol-vapor mixture, conductive cooling, or mixing of cool and warm saturated air [131, 132].

Figure 2.22: Examples of scattering based instruments: A UCB Particle Monitor [133]; B Shinyei PPD42NS dust sensor; C DustTrak II Aerosol Monitor; D SidePak Personal Aerosol Monitor; E Dylos Particle Counter

2.2.2.3.2 Extinction

The extinction method, as the name indicates, measures the extinction of light from particles. As $extinction = scattering + absorption$ [134], extinction methods actually measure the ‘opacity’ of the particles. And the equipment based on extinction are also named opacity meters. As shown in Figure 2.23, the detector is placed behind the particles being measured. The incident light gets scattered and absorbed by the particles, and the rest is collected by the detector. Similar with scattering methods, extinction methods also strongly depend on light wavelength, particle shape and composition. Correction factors are usually required for particles from different sources.

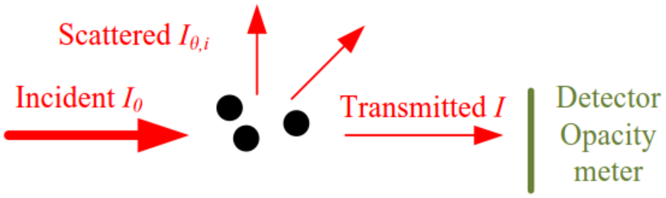


Figure 2.23: Schematic of extinction methods [125]

2.2.2.3.3 Absorption

As black carbon has a strong absorption of light, absorption methods are very popular in black carbon detection, especially in automobile exhaust (high black carbon fraction in the PM emission) analysis. Its popularity brings more variation compared with scattering and extinction methods. Instruments such as Spotmeter, Aethalometer, Particle Soot Absorption Photometer (PSAP), Photoacoustic Soot Sensor (PASS), and Laser Induced Incandescence (LII) are all based on the light absorption effect of particles, but with different approaches. Spotmeter, Aethalometer and PSAP use the filter based absorption method while PASS and LII rely on the heating effect from particles' absorption of light.

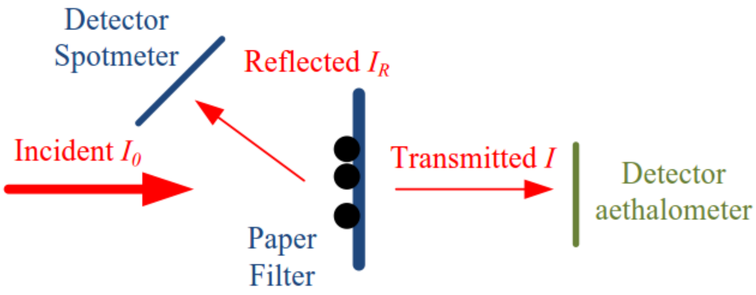


Figure 2.24: Schematic of absorption methods [125]

The spotmeter, also called a reflectometer or smoke meter, records the ratio of light reflected by two paper filters: the first one is exposed to particles and the second one is blank which acts as reference. PSAP and Aethalometer work in a similar way [135]. But unlike the Spotmeter which measures reflection, PSAP and Aethalometer measure the change of light transmission at multiple wavelengths from two quartz filter [136, 137, 138].

Figure 2.25: Aethalometer and PSAP

PASS and LII do not need filters, as these methods rely on the heating effect when particles absorb light. PASS is based on the photoacoustic principle: absorption of modulated light heats up the particles and the conduction of this heat to the surroundings generates pressure waves [139]. PASS uses a microphone as the detector and captures the pressure waves. In LII, a short laser pulse is shot into a particle [140, 141] or an ensemble of particles [142] to heat up the particles to just below the carbon sublimation temperature. By measuring the subsequent incandescence decay with a photomultiplier, and creating a reference with a radiation model and soot optical properties [143], the concentration of particles is determined.

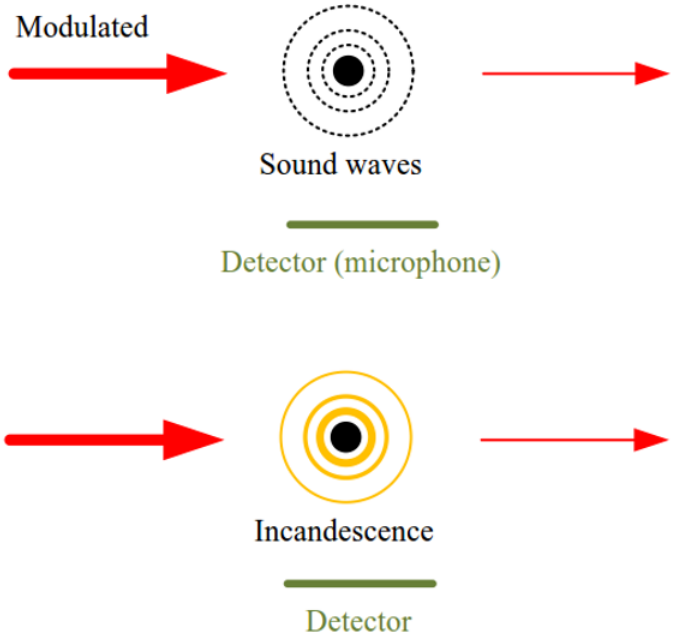


Figure 2.26: Principle of PASS and LII [125]

Due to instrumental limitations, the black carbon monitoring in this study is using the filter method with thermal optical analysis. The collaborating sampling team from the University of Illinois Urbana-Champaign (UIUC) carried out a few real time black carbon measurements with PSAP and Aethalometer. For the in-field cookstoves measurement, PSAP from Radiance Research is a well tested instrument which provides good measuring range though it requires frequent filter change. But its size and weight greatly limits its mobility. Furthermore, the high energy consumption makes it hard to deploy in rural settings. In contrast, the Aethalometer is more portable and energy efficient, but with limited upper detection limit.

2.2.2.4 Microbalance

Microbalance methods are based on the change of resonance frequency of an oscillating element when its mass changes; for instance, when particulate is collected on this oscillating element [144, 145]. Microbalance methods have excellent resolution but are very sensitive to environment conditions such as humidity and pressure, which limits their use in combustion exhaust measurements. Common microbalance methods include Tapered Element Oscillation Microbalance (TEOM) and Quartz Crystal Microbalance (QCM).

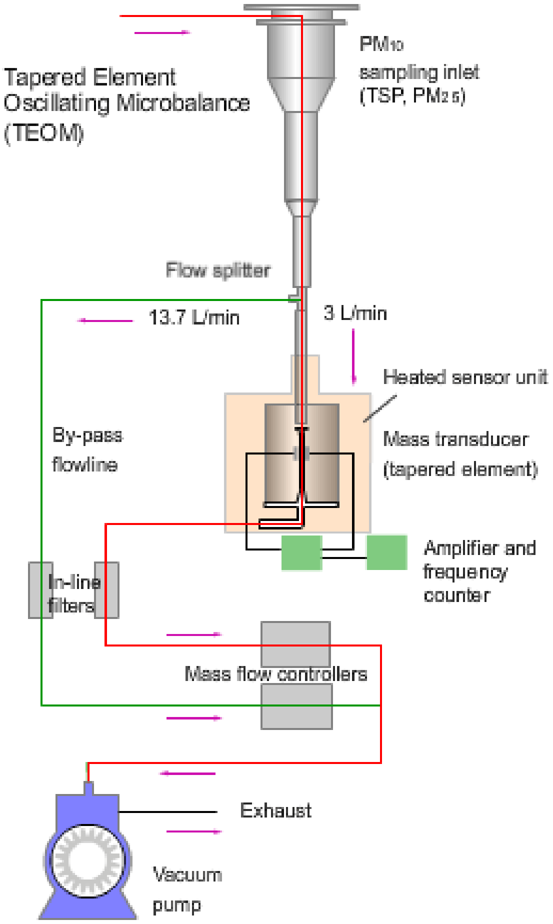
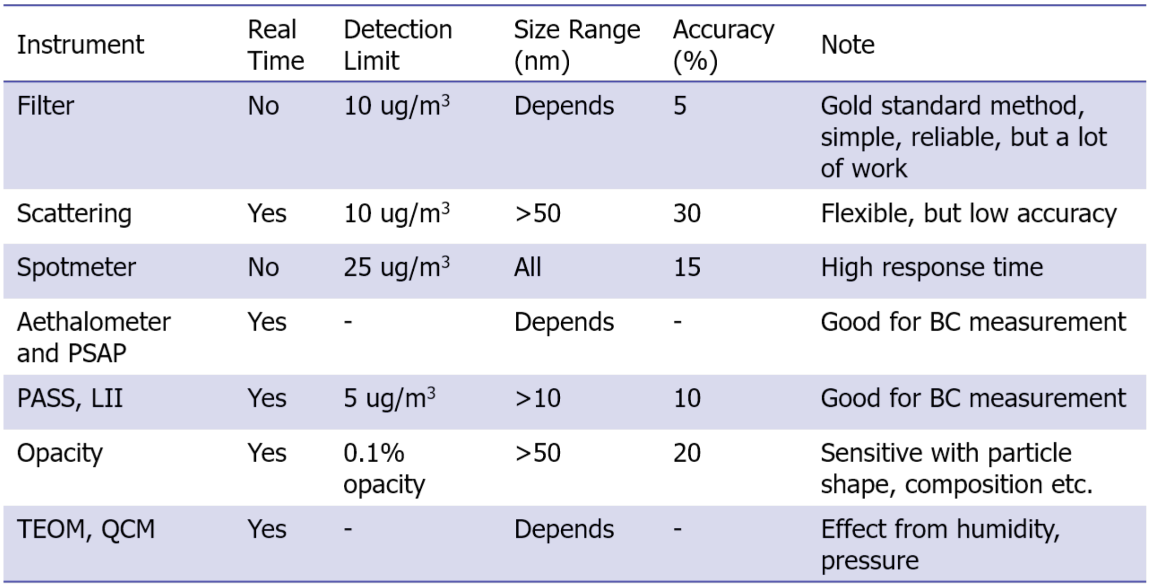


Figure 2.27: How the TEOM instrument operates [146]

Figure 2.27 shows how the TEOM instrument operates. The flow splitter works as a particle size cutter which only allows PM within a certain size range to enter the microbalance. The oscillating element in the TEOM is a tapered quartz wand with a filter attached at its tip. As particles accumulate onto this filter, the frequency of the tapered quartz wand's oscillation changes. By measuring this frequency, the mass concentration of PM is obtained [147, 148, 149, 150, 151]. TEOM requires a high level of mechanical and thermal decoupling from its environment and water (vapor) or volatile material may lead to inaccurate results [152]. QCM works in a similar way, but the oscillating element is a thin quartz crystal resonator. Its resonance frequency changes as particles deposit on it by electrostatic precipitation [153].

Figure 2.28: TEOM Particulate Mass Monitor (Series 1400)

The microbalance method can be consider as a ‘real time gravimetric analysis’. Other than optical methods which are sensitive to particle optical properties, microbalance instruments measure the PM mass directly. However, the oscillation mechanism inside make these instruments very sensitive to vibration, and require a steady set up when it is running. Additionally, its environment sensitive characteristics also prevent its usage in the field. As shown in Figure 2.28, microbalance instruments are mostly used in stationary measurement.



Instrument	Real Time	Detection Limit	Size Range (nm)	Accuracy (%)	Note
Filter	No	10 ug/m^3	Depends	5	Gold standard method, simple, reliable, but a lot of work
Scattering	Yes	10 ug/m^3	>50	30	Flexible, but low accuracy
Spotmeter	No	25 ug/m^3	All	15	High response time
Aethalometer and PSAP	Yes	-	Depends	-	Good for BC measurement
PASS, LII	Yes	5 ug/m^3	>10	10	Good for BC measurement
Opacity	Yes	0.1% opacity	>50	20	Sensitive with particle shape, composition etc.
TEOM, QCM	Yes	-	Depends	-	Effect from humidity, pressure

Table 2.2: A comparison of various PM concentration measurement techniques

2.3 Field Instrument for Cookstoves

Instrumentation is major challenge in solid fuel cookstoves in-field emission measurement. As described in section 2.2, in-field measurements require instruments to be: lightweight, robust, reliable, durable, energy efficient, and affordable (if possible). Due to the small market, there are few off-the-shelf instruments designed for in-field cookstoves emission test. Automobile exhaust analysis instruments are partially capable of analyzing cookstove emissions as there similar components from cookstoves and internal combustion engines emissions. But the concentrations are far different in cookstoves with much higher dynamic range in most cases.

2.3.1 Comparison: Cookstoves vs Internal Combustion Engines

Automobile internal combustion engines' (ICE) design are usually aiming at a certain type of fuel, or fuels with similar properties (e.g. gasoline and E85). The fuel properties determine the appropriate thermodynamics cycle that the engine design is based on: the Otto cycle for spark ignition engine (Atkinson cycle is essentially a modified Otto cycle with different expansion and compression ratio [154]) and Diesel cycle for compression ignition engine [155]. Thus, engines have relatively low tolerance for fuel variability and, by design with the corresponding fuel, they work in close-to-optimal conditions. Furthermore, to ensure fuel purity, on an automobile ICE, before the fuel enters the combustion chamber through fuel injector, it has been refined and purified in an oil plant, filtered at the gas station and filtered again by the automobile fuel filter.

Figure 2.29: Gasoline spray from a fuel injector

Solid fuel cookstoves are another story. According to the field experience from this study, no matter what kind of fuel a stove is designed to burn with, the user of the stove will use anything flammable with the stove. As fuel type is one of the most critical factors that affects combustion emission [3], this introduces additional complexity in the solid fuel cookstoves emission characterization. Due to these complexities, there are also few numerical simulation studies available for solid fuel cookstoves combustions.

Compared with automobile ICE, the combustion process of solid fuel cookstoves is imprecise and inhomogeneous. In an automobile ICE, before the fuel reacts with air, the electronic control unit (ECU) calculates the amount of fuel needed based on the air flow rate, and adjusts the fuel injectors' duty cycle to inject the required amount of fuel into the intake manifold (port injection) or cylinder (direct injection). The fuel injectors atomize the fuel into very fine aerosols (Figure 2.29), which greatly increases the reaction surface area. Solid fuel cookstoves behave more random in their working condition. The air fuel ratio is adjusted by operators feeding fuel or blowing air. As the fuel itself does not have a consistent make up, it is impossible to realize complete combustion precisely. The incomplete combustion products and unburned fuels then exhaust as part of the emissions. Another issue with solid fuel cookstoves is the 'cleanliness' of the burner. The ash and char from burning may contribute to part of the emission as the flow is created by the combustion process. A study of stoves in India and China indicates that whether cookstoves are cleaned or not significantly affects their emissions [74]. Although the dust is mostly large particles and usually has short resident time in the atmosphere, they form a very harsh environment for sampling instruments.

Finally, there is no available test protocol for solid fuel cookstoves that can well represent its actual usage. The most well known testing protocol for cookstoves is the water boiling test (WBT) [156]. The idea is basically testing the stove performance via boiling a certain amount of water and calculating the efficiency with fuel information recorded. The general testing procedure is shown in Figure 2.30. The test includes a cold start, a hot start and a 45 minutes simmer phase. One argument for WBT is that there are very limited simulations on cooking activities other than boiling water [72, 73]. Other testing protocols, such as the Kitchen Performance Test (KPT) [157] and Controlled Cooking Test (CCT) [158], do record a real cooking process and the associated information such as food type and amount, but they do not provide a standardized testing procedure.

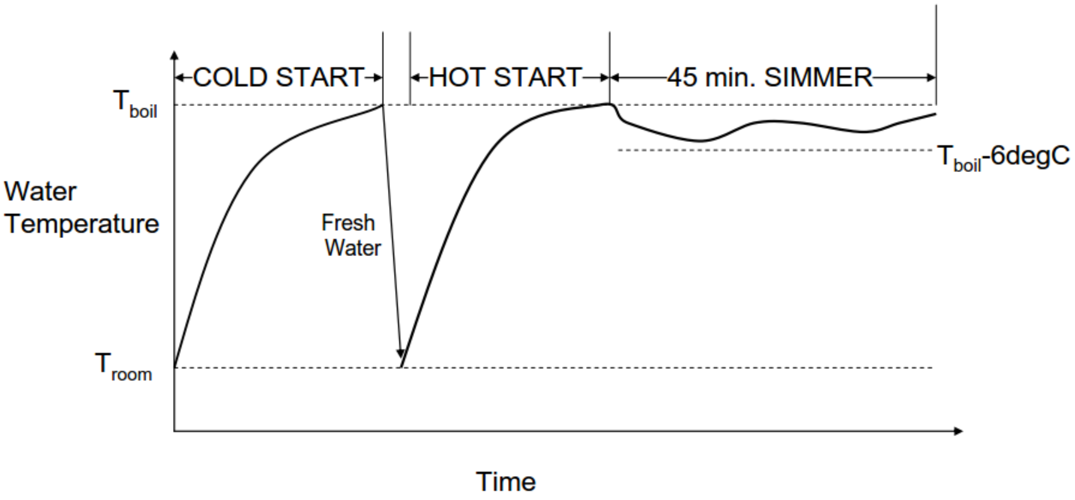


Figure 2.30: Water boiling test [159]

Although it is not perfect, standardized automobile emission tests are much more well-studied. Both the New European Driving Cycle [160] Figure 2.31 and the Federal Testing Procedure (Figure 2.32, common known as FTP-75) [161] include various phases like cruise, cold and hot start. Within each phase, there are small cycles of acceleration and deceleration that represent different working conditions in actual use. To achieve more representative measurements in the lab, more comprehensive lab testing protocols are needed. Establishing a comprehensive testing protocol requires a large amount of data from actual use, which is what is lacking for solid fuel cookstoves.

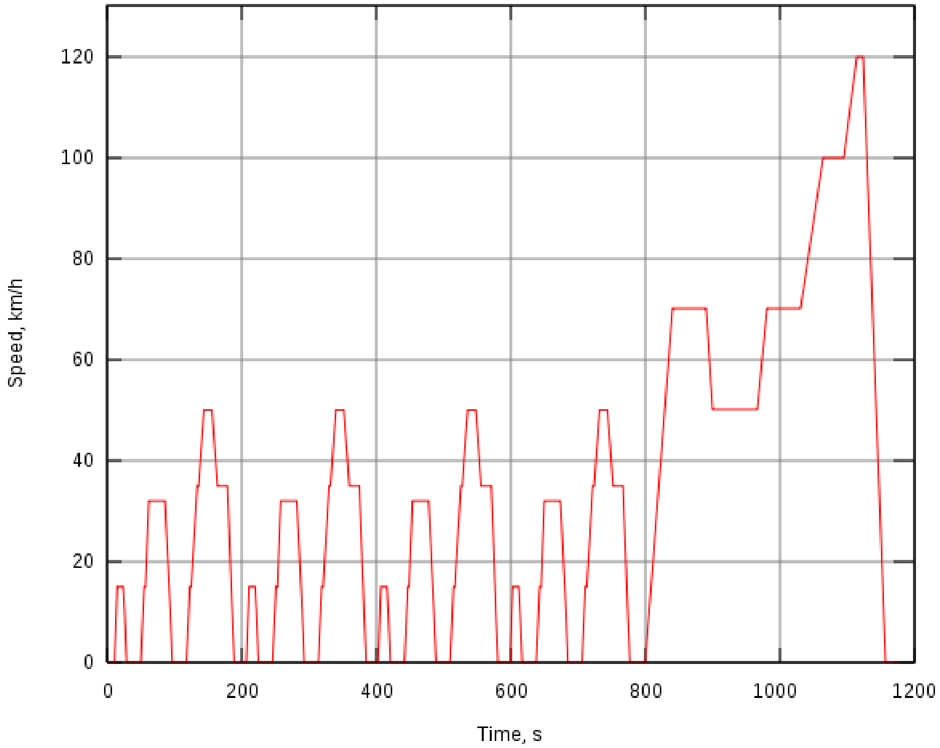


Figure 2.31: New European Driving Cycle [160]

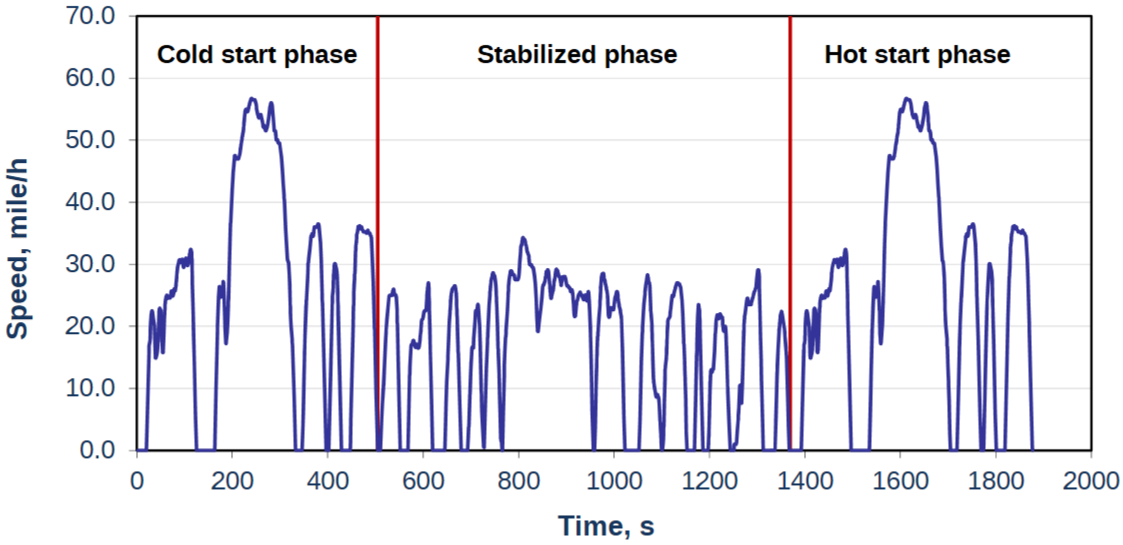


Figure 2.32: US EPA Urban Dynamometer Driving Schedule (FTP-75) [161]

2.3.2 State of the Art in Field Measurements of Cookstoves

A significant challenge for in-field solid fuel cookstoves emission monitoring is the instrumentation, especially for stoves with chimneys. The dynamic range of emission is so wide that it is very hard to keep instruments working at their designed or optimized condition. This issue becomes most challenging when dealing with PM measurements [162]. In the open-fire cases (an open fire is the simplest variety of solid fuel cook stove), as the smoke plume is naturally diluted by the background ambient air, the concentration of gas phases is automatically reduced to a working range acceptable for gas analyzers. As discussed in section 2.2, the in-field real time monitoring of PM generally relies on optical methods (absorption and scattering), and the contamination effects from the PM greatly limits the range and durability of optical instruments. Filter based absorption instruments, for example, the Particle Soot Absorption Photometer (PSAP) from Radiance Research, is capable of measuring reasonably high PM concentration but it requires the operator to change the filter frequently to keep the instrument from overloading. Field experience indicates that the frequency of filter changes for the PSAP can be as short as a few seconds per filter while the cookstove is in use. Such frequent filter changes would mean an intrusive measurement that could itself disrupt the realism of the cookstoves use [163]. The size and weight of the PSAP also limits its use in the field. Scattering based instruments such as the DustTrak from TSI is delicate for portability and the 250 mg/m^3 range is far away from enough for the solid-fuel cookstoves emission measurement task. The measurements with chimney stoves presents even more severe situations, as there are extremely high concentrations inside the chimney.

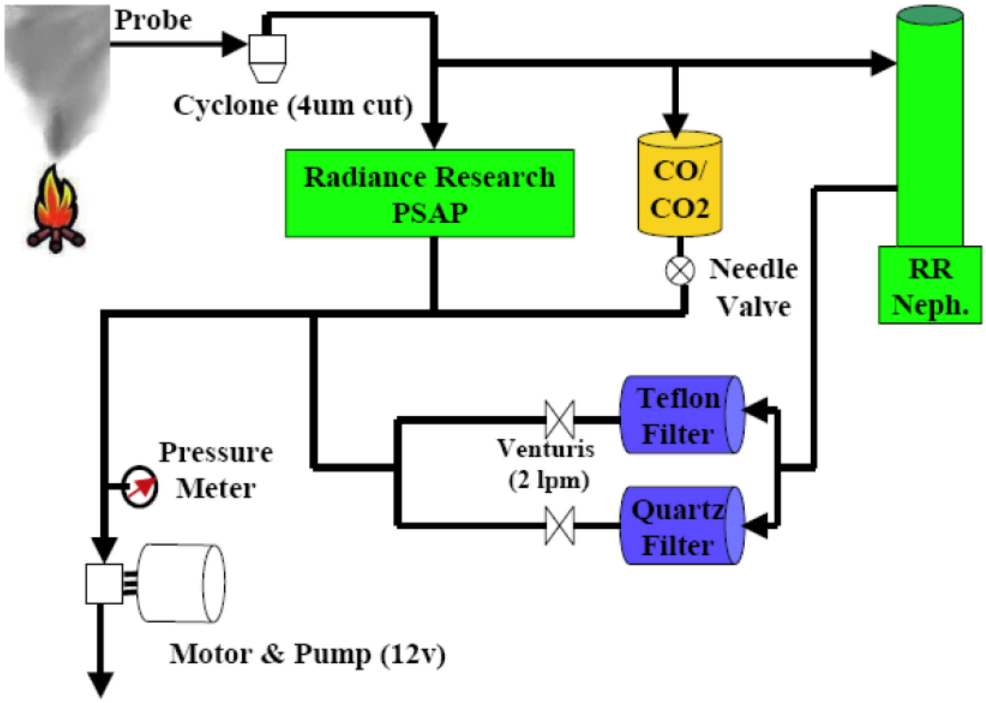


Figure 2.33: The ARACHNE system from University of Illinois Urbana Champaign (UIUC) [79]

In order to measure a full range of solid fuel cookstoves emissions, a comprehensive measurement system is required. The ambulatory real-time analyzer for climate and health-related noxious emissions (ARACHNE) system developed by Dr Tami C. Bond from UIUC is a typical system designed for solid fuel cookstoves measurements [79, 164]. This system measures real-time absorption and scattering by particles, carbon monoxide, and carbon dioxide concentrations. It also includes a gravimetric set up to collect filters for PM and EC/OC analysis. As shown in Figure 2.33, a cyclone is used to select the size range and a PSAP measures real-time particle absorption and Nephelometer for scattering. The Teflon filter is used to collect PM samples while quartz filters are used for EC/OC samples. In the original design, the whole system is powered by an automobile 12V battery with power inverter and is capable of approximately two hours continuous measurement.

Figure 2.34: The original ARACHNE system in the field [79]

The ARACHNE system is used by the collaborator in this study and joint measurements were made in Nepal, Tibet and Yunnan in China. This system provides comprehensive emission measurement capability with decent measurement range. But it still has difficulty with capturing the peak PM concentration when measuring stoves with chimneys. The ARACHNE system has been revised several times. The original design [79] did not provide much mobility (Figure 2.34) which limited its deployment in the field. The version used in the Nepal measurement has significant improvements in mobility (Figure 2.35 left), but still requires additional labor for transportation. The PSAP and automobile battery are the major mobility limiter. In the Yunnan, China campaign, the ARACHNE system used a TSI Aethalometer instead of the heavy PSAP and used a compact Li-on battery rather than the automobile battery (Figure 2.35 right). These modifications greatly increased its portability with the exchange of a lower real time black carbon measuring range and shorter time of endurance. The measurement system used in the current study is modified from ARACHNE based on the availability of real time instruments. Details of the experiment set up are explained in the methodology chapter.

Figure 2.35: The revisions of ARACHNE system from UIUC

Another comprehensive system emission measurement system was developed by Desert Research Institute (DRI) [165]. This system was designed for general stationary and mobile sources and its outstanding dilution control brings very high upper detection limits for real-time PM. This is a sophisticated system (Figure 2.36) which measures a full range of compounds includes real-time monitoring of: aromatics, CO, CO_2, NO, NO_2, SO_2, O_2, PM size distribution and concentration, and also integrated sample collection of: specific VOCs, NH_3, SO_2 and H_2S gases, as well as elemental carbon, organic carbon, and specific organic compounds [166, 167]. However, due to its complexity, it requires extensive installation time and brings extraordinary challenge in transportation. This space consumptive set up also interferes with household cooking activity, which make it more suitable for long term stationary measurement rather than field deployment.

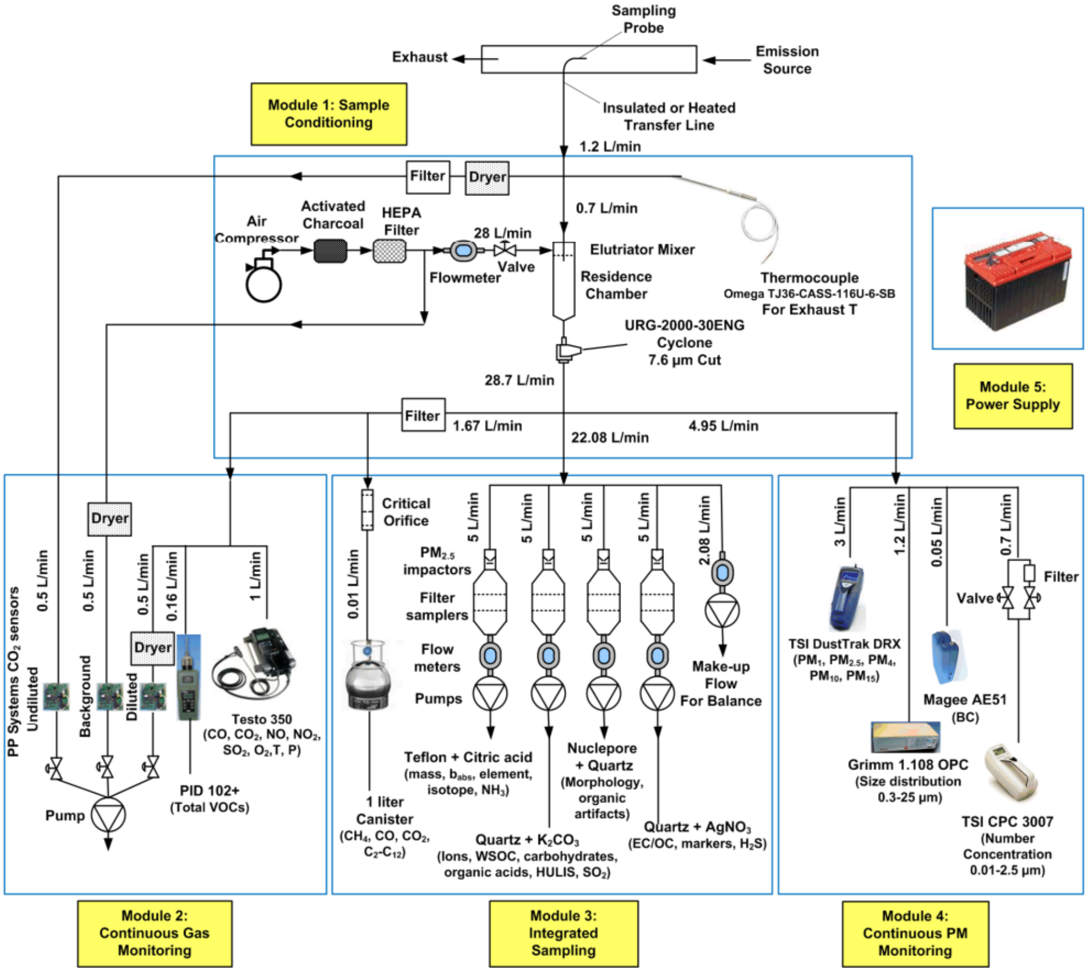


Figure 2.36: Multipollutant dilution sampling and measurement system from [165]

After evaluating the measurement methods available, and considering the challenges of in field use, the current field study, based on the measurement objective and instrument availability, uses a GC to analyze the collected samples for integrated measurement. The real time carbon dioxide and carbon monoxide are monitored by a TSI Q-Trak 7575 CO/CO_2 monitor. A Drager PAC 7000 monitor with SO_2 sensor are used to acquire real-time SO. Integrated $PM_{2.5}$ sample is collected with PTFE filter and analyzed with gravimetric method. A TSI DustTrak Aerosol Monitor is adopted to monitor Real-time $PM_{2.5}$ concentration. Dilution is applied to prevent the high concentration flue gas saturate real time instruments. The detailed set up is explained in the methodology chapter.

Chapter 3

Methodology

The entire study includes in-field measurements, sample analysis and field measurement system improvement. The objective species in this study include: carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4), non-methane total hydrocarbon (NMTHC), sulfur dioxide (SO_2) and fine particles ($PM_{2.5}$). Real-time continuous monitoring of carbon dioxide, carbon monoxide, sulfur dioxide and $PM_{2.5}$ was conducted in the field. $PM_{2.5}$ and gas samples were collected in the field and brought back after each field study. Gravimetric filter and gas chromatography analysis were utilized to measure $PM_{2.5}$ concentration and levels of gas-phase pollutants through post measurement analysis. The field measurement system set up was continuously modified during measurement campaigns to improve accuracy and reliability, and to satisfy the specifics of each field configuration (i.e., stove and fuel type, and the surrounding environmental conditions). A detailed description of the approach is discussed below.

3.1 In Field Sampling

Globally, the emission to the environment from household cookstoves activity largely depends on the regional population density. Himalaya Mountain, as one of the largest fresh water resources in the world, has a population of more than 2 billion people living on the rivers that originate from this source. It has been reported that the glacier area in the Tibetan Plateau decreased approximately 15% within the past 30 years and the affected population may exceed 2 billion [168]. The high population density in the nearby area leads to significant contribution of emission from domestic residential combustion. Hence, the field sites for this study are selected to be in several different Himalaya region countries which includes: Nepal, India, and the China (Tibet autonomous region and Yunnan province). The local natural and humanistic environmental conditions will be introduced separately.

Field site location	Starting	Ending	Duration	Total sample acquired
Nepal	Nov 2011	Jan 2012	7 weeks	46
Tibet	July 2012	Sept 2012	6 weeks	38
Yunnan	June 2013	Aug 2013	6 weeks	40
Mongolia - Pilot study	Jan 2012	Feb 2012	3 weeks	N/A
Mongolia - Starting	Oct 2012	Nov 2012	3 weeks	218
Mongolia - Ending	Jan 2013	Feb 2013	4 weeks	

Table 3.1: Field campaign schedule

Table 3.1 shows the schedule and length of time for the field works. In general (except

Mongolia), each campaign take around 2 months with about 6 weeks measurement time and 1 or 2 weeks for pre- and post- preparation. The target of approximately 60 households were selected to participate in the emission tests. The UIUC team shares about 1/4 of the total 60 households due to sampling train and schedule availability. The Mongolia measurements are mostly finished by local sampling team. A pilot study was first conducted for verifying feasibility. The second travel is mostly for training purpose with in-field tutorial. The last travel contains some measurements together with local sampling team and the wrap up after the campaign completed. The basis for the selection of households included the ability to measure a variety of region specific primary and secondary stove and fuel types. Depending on the given sites, there were also constraints and considerations taken into account regarding household selection. Based on instrument availability, a sampling train was designed and built to achieve comprehensive in-field measurements. The train includes in-line sampling filters and real time instruments to measure different parameters. One of the important elements of this research is that each field site requires variations driven by the distinctiveness of each location. Hence, a detailed field study protocol will be introduced in a site-by-site manner.

Figure 3.1: The geographical location of our field sites [169]

3.1.1 Nepal

Research conducted in Nepal was a joint cooperation with a University of Illinois, Urbana-Champaign (UIUC) sample team and the locally collaborating Centre for Rural Technology, Nepal (CRT/N), a non-governmental organization focused on the development and promotion of technologies to improve the livelihood of rural people. Household selection was carried out by CRT/N. While the traditional open-fire stove is considered to be the most popular stove in Nepal, the selection of households for emission tests were mainly based on geographical features (i.e. mid-hills area in the mid-northern region; plains in southern of Nepal) and variety of fuel used.

Typically, there are three types of fuel used in Nepal: wood, dung, and agricultural residue (Figure 3.2). The mid-hills area has an abundant source of trees, where wood is mostly used as the primary source of fuel. However, in the plains area, the existence of larger scale agriculture makes animal dung and agricultural residue the primary fuel.

Figure 3.2: Left to right: openfire stove in Nepal; dung used as fuel; Agricultrial residue as fuel; external view of sampling set up

The sampling system for Nepal is the initial design as Nepal is the first campaign site where this study is conducted. The diagram for the sampling train is shown in Figure 3.3. After the probe, the emission sample travels through a length (depends on the stove, typically around 2m) of conductive tubing where it enters the sample train. The particle loss through 3m of this tubing was measured at about 2% by the UIUC sample team [170]. A cyclone cuts off particles larger than 2.5um at a fixed flow rate (1.5 L/min). The first branch of the train collects elemental carbon (EC), organic carbon (OC), and gas samples. The EC/OC sample are collected with a 47 mm quartz filter. The gas sample is collected with a 200L Kynar bag. As the requested sample duration is from the start of breakfast cooking to the end of dinner cooking, which is typically around 13 to 15 hours according to the Nepali habits and customs in village, the flow rate is a major constraint at 200 ml/min with a SKC pocket sampling pump so that it is possible to collect all the gas with the 200L bag. The second branch includes one 37 mm, PTFE filter and one 47 mm quartz filter to collect PM samples and EC/OC in the gas phase. The filtered gas goes through a TSI Q-Trak 7575 CO/CO_2 monitor and Drager PAC 7000 monitor with an SO_2 sensor to acquire real-time CO, CO_2 and SO_2 information. The flow rate for the second branch is initially set at about 800 ml/min. The third branch is for a DustTrak aerosol monitor. Considering that the real time PM monitor is less capable with high concentration, which is more likely to exceed the maximum range, a dilution pump is connected with the DustTrak to provide clean air. The flow rate which the DustTrak draws from the cyclone needs to satisfy the 1.5 L/min requirement of the cyclone. The dilution pump provides compensation flow to match the flow setting on the DustTrak.

The background sample train is relatively simple. As the background concentration of both PM and gas phases is much more stable compared with emissions from cookstoves, we did not carry on real-time monitoring for background. As shown in Figure 3.3, the background train only contains the filter/gas sample collection components with a similar design to that in the emission train.

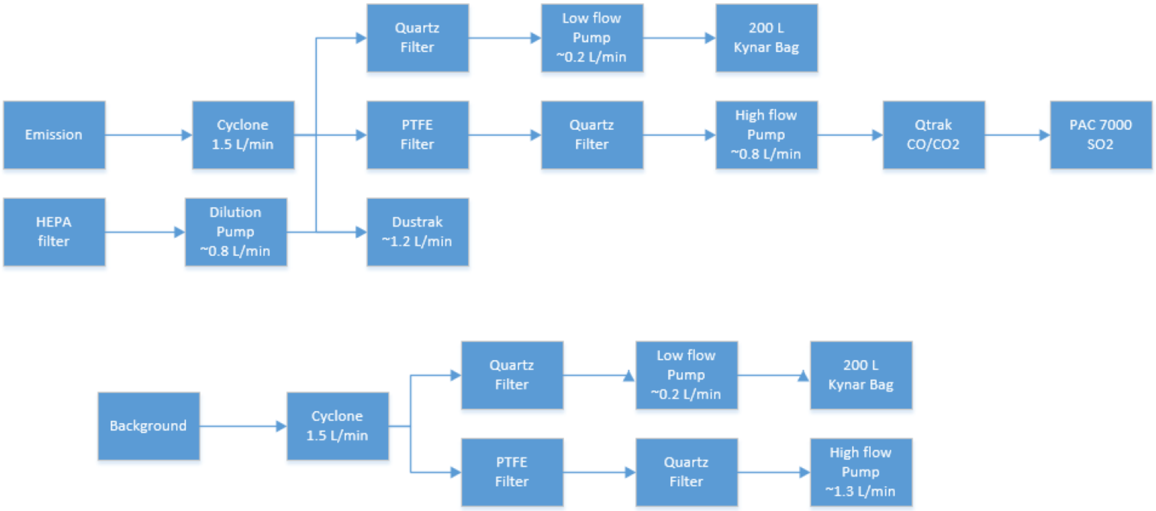


Figure 3.3: Sampling train design for Nepal site measurement

Measurements during the Nepal campaign experienced extended difficulties and challenges. One consistent challenge was the limited power supply. As all of the instruments are battery powered, we did not expect a power supply from the participating household. However, a stable power source at the local lodging place is critical to keep instruments well charged after every days task. Unfortunately, Nepal is a country with country-wide energy shortages. There are always hours of scheduled power outage every day, even in the capital city (the field site where we stayed most of the time has an average power off for about 10 hours per day, at various times). As the instrument batteries get drained day-by-day until they cannot complete a full day measurement, for each week, one day is taken off in order to fully charge all the instruments.

3.1.2 Mongolia

Cookstoves in Mongolia are also being used as heating stoves. The extremely cold weather during winter (-40°C to -30°C) means that the stoves are continuously being used most of the time. Mongolia has an abundance of coal mines, which makes coal the primary fuel for local residents. The excessive amount of exhaust from household coal burning during the heating season leads to heavy polluted air in the surrounding areas. The participating household in Mongolia was selected by our local cooperator according to their previous survey about stove usage. There are several different brands of stoves in Mongolia, but in general, they have similar design and they all have a chimney.

Figure 3.4: The pollution in Ulaanbaatar, Mongolia

As the field measurements in Mongolia were taken in the capital city, Ulaanbaatar, many of the local residents work during the day time and the households might be empty. In order to catch the period when the stove is used, Overnight measurements are conducted in Mongolia. The instruments were set up in the evening of the first day and collected the next morning. As it is not welcome to stay at households late in the evening or visit them in the early morning, the overnight measurement actually extended the duration to approximately 15 hours. Fortunately, the power supply in the household was mostly reliable which greatly helped with the measurement.

Due to the flow issue identified in the Nepal measurements, and to accommodate the chimney stove in Mongolia, the sampling train (Figure 3.5) is modified. The pilot study in Mongolia indicated that PM concentration within the chimney is too high for the real-time PM monitor. To avoid the risk of instrument failure, real-time PM monitoring is not conducted for stove emission this time. To fix the unstable flow issue from Nepal, instead of only diluting the real-time PM monitor, a global dilution pump is utilized. The sample collection (filter and gas bag) configuration is the same as before, except a separate pump is connected with a cyclone to maintain the required 1.5 L/min flow rate. With the help of a TESTO 350 flue gas analyzer, it is possible to acquire real-time CO, CO_2 and NO_2 from the chimney directly. The DustTrak aerosol monitor and the Q-Trak CO/CO_2 monitor are used for background measurements.

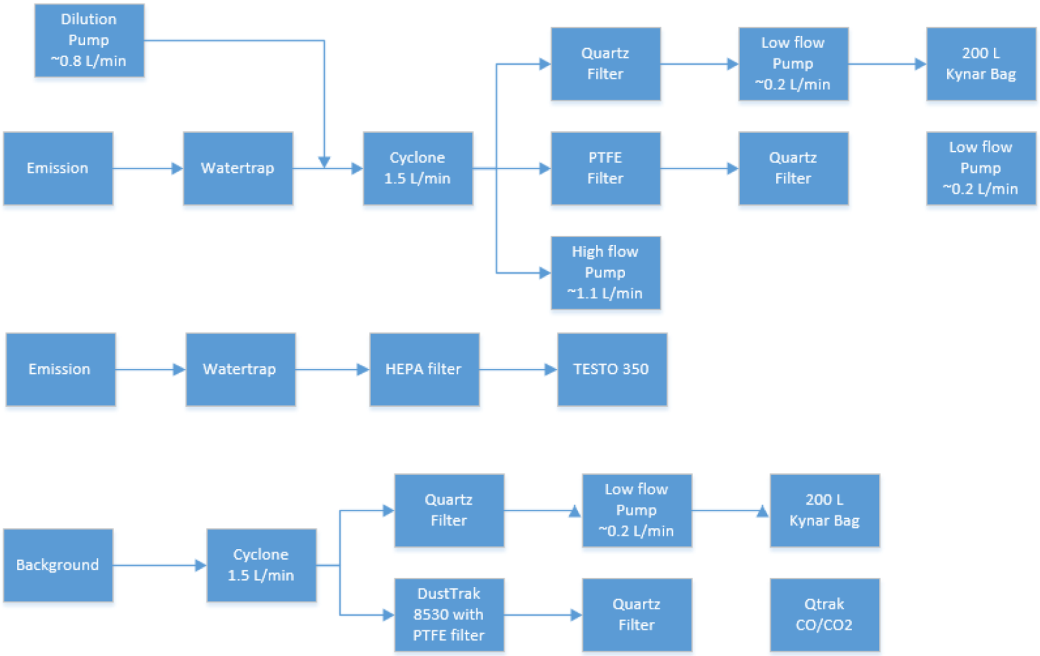


Figure 3.5: Sample train for the Mongolia site measurement

As mentioned before, the outside temperature in Mongolia during the winter season is extremely low, which brought some issues to our measurement and also affected the transportation of the instrument. The initial sample plan was to put metal tubing into the chimney. However, the low temperature outside plus high humidity within the chimney resulted in the instant freezing of water vapor which clogged the tubing. In the end, the sampling is conducted by drilling holes into the indoor section of the chimney and replaced that section after the measurement finished. Also, the Kynar bag used to collect gas samples became brittle at low temperature. Leak checks were conducted every time when the Kynar bag was not well inflated, but the pump was in working condition, after sampling. Once leaks were found, the in-field fix was to tape to seal the leaking area to keep the system working.

3.1.3 China

There are two field campaign conducted in China. The first one is in the Tibet autonomous region and the second in Yunnan province. The extraordinarily harsh working environment in Tibet demonstrated the robustness of the current set up. Thus, the set up is adopted to the Yunnan measurement without any major modification.

3.1.3.1 Tibet Autonomous Region in China

For the research in Tibet, China cooperated through the Institute of Tibetan plateau Research, Chinese Academy of Sciences. Due to the limitation of the local environment, two regions, Nam Co, and Linzhi, are chosen as the sites in which to conduct the in-field measurements.

Nam Co area has an extremely high elevation (approximately 4700 m). As the poor plant and animal sources make most biomass scarce, local residents mostly rely on yak dung as their primary fuel. Most of the local residents lead a traditional nomadic life, with a Tibetan tent as their shelter. The tourist industry being developed in the Nam Co area absorbed some residents to join the tour business. Due to their more settled living style, these people built fixed or semi-fixed households instead of traditional tents. There are two types of stoves being used in the Nam Co area. A traditional open fire stove and an improved chimney stove. The open fire stove is mostly used by nomadic residents, as it has better portability. All the fixed and semi-fixed households are using an improved chimney stove nowadays. There is not much space for household selection. As the population is very sparse in the Nam Co area, we tried our best to take measurements in whatever household we could find.

The high elevation in Tibet not only challenged the experimentalists physical strength but also gave instruments a hard time. The ambient pressure at 4700 m altitude (Nam Co) is measured at approximately 0.55 - 0.6 atm. As sampling pump uses mass flow controllers to maintain and adjust flow rate, at low pressure like 0.55 atm, in order to maintain the same mass flow with sea level conditions, the required volume flow rate is almost doubled. For example, the volume flow rate for the pocket pump at 200 ml/min at sea level produces an actual volume flow rate measured in Nam Co between 100 – 150 ml/min. To achieve 200 ml/min at Nam Co, the pump has to work much harder than it does at sea level. The harder the pump works, the faster the battery drains. Additionally, the high concentration emissions from chimney stoves is always challenging. Catching peak values is very difficult because the dilution flow in our sampling train cannot be set too high since as the dilution flow gets close to the cyclone flow, the emission flow from the probe becomes unstable.

The Linzhi area has much lower elevation (approximately 3300 m) compared with Nam Co. Lower elevation brings richer plant and animal sources. As a result, wood becomes the primary fuel for the Linzhi residents. The well-developed agriculture and tourist industry significantly improved the living condition of local residents. All the residents have well-built houses and well-designed chimney stoves (different from the one in Nam Co). As there is a uniformity of households, stove and fuel type, the selection of participating household in the Linzhi area is mostly based on regional considerations. All the measured households in the Linzhi area are located in the two villages which are close to the Linzhi Research Station, Chinese Academy of Sciences.

Figure 3.6: Up left: traditional Tibetan tent; up right: Linzhi household; bottom left: traditional Tibetan open fire stove; bottom right: Tibetan chimney stove in Nam Co.

3.1.3.2 Yunnan Province in China

The study in Yunnan province is cooperative with the Center for Disease Control and Prevention (CDC) of Qujing City. Yunnan is a rich coal province with good growing weather which brings an abundance of forestry and agricultural resources (elevation approximately 2000 m). As a result, residents in Yunnan province have various fuels to choose from: coal, wood, corn, pine needles, and agriculture residue. However, people mostly use wood, corn, pine needles, or other biomass fuel to start the fire and they then use coal to keep the stove burning. Hence, coal is considered as the primary fuel in Yunnan province. The household selection is mostly based on coal distribution. Qujing CDC has conducted comprehensive investigations on the relationship between coal usage and lung cancer occurrence in the past decades. According to their database about the distribution of various sub-categories of coal (e.g., gas fat, smoky, coking, and smokeless), covering all of the mainstream coal types is the main consideration while selecting participating households.

The stove usage situation in Yunnan province is quite different from the other sites. As Yunnan province is relatively developed compared with Tibet and Nepal, there are well-constructed electricity grids in this area, which provides local residents reliable and affordable power sources. As a result, many residents in the village actually already switched to electric stoves for their primary cooking. Solid fuel stoves are still widely used for heating during the cold weather season, especially for those families with senior people. Our research is conducted during the summer, which brought some difficulties in finding households where solid fuel stoves were still in use. Fortunately, there are enough senior people staying in the village who use solid fuel stoves for heating and cooking even in summer, and also some households use solid fuel stoves to prepare food for animals (electric stoves are not large enough for this task), we managed to find enough participating households.

The solid fuel cook stoves used in Yunnan generally are of three different types: high stove, low stove, and portable stove. The high stove is a chimney stove, which is mainly use for cooking (before the electric stove became popular); the low stove is rarely in use nowadays. It is good for heating the floor and also for making some simple food. The old style low stove does not have a chimney (we did not find any old style low stoves in use during out study). A newer low stove has similar design with the high stove, but it sits lower to ground level. The portable stove is still popular in villages, especially among senior people, as it is good for heating and easy to carry around.

Figure 3.7: Left: high stove; middle: portable stove; right: low stove

The sampling train set up for Tibet and Yunnan are similar. The global dilution design from the Mongolia sampling system is kept and with DustTrak aerosol monitor to make up the cyclone flow. The filter and gas bag sampling part of the train did not change. As the sampling duration in Tibet and Yunnan are much shorter than in Nepal and Mongolia due to transportation restriction, a smaller Kynar bag was used to collect the gas sample.

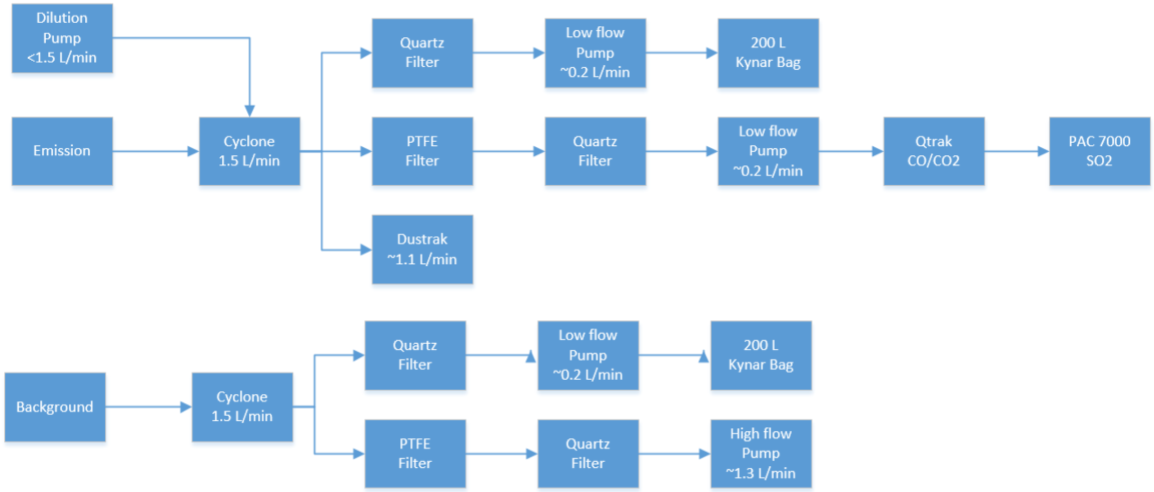


Figure 3.8: Sample train of Tibet and Yunnan measurement

3.2 The Carbon Balance Method

The measurement and analysis rely on the carbon balance method. This method is developed by Crutzen et al. [171] and is commonly used for biomass combustion emission studies [172]. This method calculates the emission factor based on the carbon processed in fuel consumption and the ratio between pollutants in the exhaust gas [79, 6]. A detailed explanation of the carbon balance method is attached in Appendix A. In order to achieve a representative measurement, the sample is taken after the plume gets well-mixed [73]. Prior study indicated that emissions take less than 2.5 seconds to reach phase equilibrium [173]. In our set up for open-fire stoves, the sample probe is located about 1m above the stove, which leaves about 3 to 4 seconds residence time for the plume to stabilize before reaching the probe. For the chimney stove measurements, as the length of the chimney is mostly more than 2m long and the flow inside the chimney is turbulent ($Re > 4000$) [73], we assume the emissions are well-mixed within the chimneys and we collect our sample from the chimney outlet.

3.3 Post Measurement Analysis

The post measurement analysis includes gravimetric analysis for the $PM_{2.5}$ sample (PTFE filter) and gas chromatography analysis for the gas sample. The analysis of the EC/OC (quartz filter analysis) is conducted by our collaborators in the UIUC group.

3.3.1 Gravimetric Analysis

Gravimetric analysis is applied to the PTFE filters collected from field measurements. Before heading to the field, the PTFE filters are weighed and sealed (pre-weights). A post weight is conducted after the measurement in the field with the PM sample collected on the filter. With the recorded flow information and the weight difference between pre and post analysis, the $PM_{2.5}$ emission is calculated. The detailed gravimetric analysis protocol is described in Appendix D.

3.3.2 Gas Chromatography Analysis

Gas chromatography analysis is applied to the collected gas sample to investigate the concentration for interesting gas species, which include carbon dioxide, carbon, monoxide, methane and total hydrocarbon (THC). The detection of carbon dioxide and carbon monoxide are achieved with a flame ionization detector (FID) plus nickel catalyst methanizer (SRI Instruments, USA). The THC analysis is accomplished using a blank column plus FID. This approach takes advantage of the fact that the FID responds only to hydrocarbons [174]. A detailed GC analysis protocol is available in

Appendix E.

In this study, the gas samples obtained from field are stored in metal-coated multilayer Tedlar (MMT) bags and the exact sample volume are unknown and not unified. In this case, adding standards into the sample will require separate calibrations for each individual sample, which is not practical. Thus external standardization is selected to calibrate the GC analysis. Calibration gases with known concentrations of target gas species are used to generate the calibration curve.

Chapter 4

Results and Discussion

The heart of the dissertation is the unique data set accomplished with the multiple remote site field campaign completed. As alluded to in the prior chapters, each measurement exercise faced site-specific challenges which, combined with the natural variation in stove type, fuel, and stove use, produce significant variability in the results. This made the post-measurement processing very important for stable, reproducible, and statistically significant results.

4.1 Data Report

The finalized database includes modified combustion efficiency (MCE) and emission factors for: carbon dioxide, carbon monoxide, methane, non-methane total hydrocarbon, and $PM_{2.5}$ for each sample from the four field sites. The emission factors are calculated with the carbon balance method, which is described in appendix A. Modified combustion efficiency is defined as the ratio between carbon in the form of carbon dioxide to that in the forms of carbon dioxide. MCE is commonly used as an approximation of normalized combustion efficiency. Since most of the carbon emissions are in form of CO_2 and CO, MCE provides a robust approximation to the normalized combustion efficiency (NCE) [72].

$$MCE \equiv \frac{[CO_2]}{[CO_2] + [CO]} \tag{4.1}$$

There are three types of emission measurement for cookstoves:

- Meals test: this type of measurement is conducted during each meal in the same household. Each meal test is considered as one separate sample. This test is focusing on the emission during one cooking event.
- 1-Day test: this type of measurement performs a continuous one day measurement (before breakfast to after dinner) in one household. Each full day measurement is considered as one sample. This test provides a typical full day emission information.
- 3-Day test: reviewer three 1-Day tests in the same household to investigate the variation within same household between different days.

Not all if these three types of measurement are conducted in every field site due to supply allowance and feasibility so the results are introduced in a site-by-site manner. A complete and comprehensive dataset is acquired in this study. This section contains the statistical summaries and the corresponding explanation and discussion.

4.1.1 Nepal

Figure 4.1: The stove and fuels used in Nepal

The measurements results from Nepal contain 81 samples from 45 households and 9 small scale industries. Nine samples are invalid due to instrument failure in the field. The cookstoves being measured in Nepal are uniformly traditional open fire type for all households. Fuel types include wood, animal dung, and agricultural residue. 10 samples are measured in the mid hills region, while the rest are from the plains area. The small scale industries being measured include small food service, candy making, and pottery workshop. Stoves being used in restaurants are very similar to household stoves, except they are a larger size. Candy making and pottery workshops use special stoves (Figure 4.2).

Figure 4.2: Left: candy making, middle: individal pottery workshop, right: outdoor pottery stove

location	Residence type	Stove type	Fuel type	Measurement	# of samples
Mid hills	House	Open fire	Wood	Meals	2
	House	Open fire	Wood	1-Day	2
	House	Open fire	Wood	3-Day	2
Plains	House	Open fire	Wood	Meals	2
	House	Open fire	Wood	1-Day	4
	House	Open fire	Wood	3-Day	6
	House	Open fire	Dung	Meals	5
	House	Open fire	Dung	1-Day	9
	House	Open fire	Dung	3-Day	0
	House	Open fire	Agricultural Residue	Meals	4
	House	Open fire	Agricultural Residue	1-Day	9
	House	Open fire	Agricultural Residue	3-Day	1
Total					46

Table 4.1: Nepal households summary

The regular living style for village residents in Nepal brings clear emission pattern throughout the day. Figure 4.3 shows an example of typical real-time CO_2 concentration, with significant CO_2 concentration peaks appearing at each meal time. The statistical summary for emission factors and MCE are shown in Table 4.2.

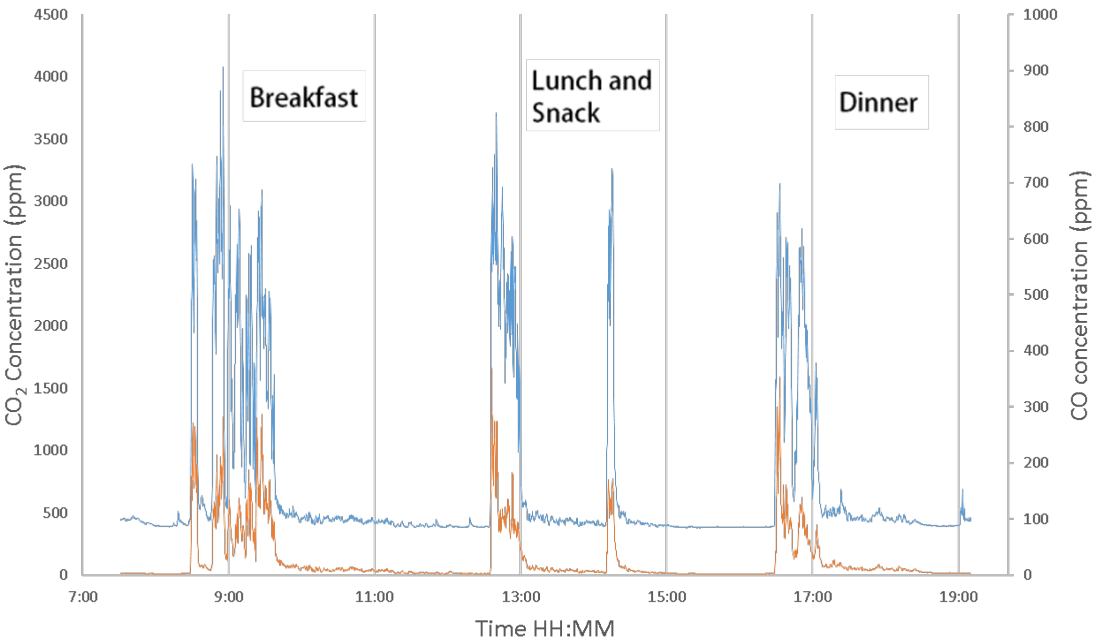


Figure 4.3: Example of typical real-time CO_2 and CO concentration for an open fire stove in Nepal

	Sample amount	MCE	EF CO_2 [g/kg fuel]	EF CO [g/kg fuel]	EF $PM_{2.5}$ [g/kg fuel]	EF CH_4 [g/kg fuel]
Wood stove at mid-hill	8	0.888±0.009	1171.5±22.2	94.4±7.7	2.8±0.7	40.6±4.2
Wood stove at plain	18	0.892±0.003	1175.4±19.2	89.2±1.5	2.9±0.6	30.7±2.8
Dung stove at plain	19	0.874±0.006	1086.3±10.6	99.4±4.8	5.9±0.8	17.4±2.6
Agri Rez at plain	20	0.904±0.002	1134.6±10.9	76.8±2.2	2.3±0.3	11.2±2.8
All wood stove	26	0.891±0.003	1174.2±14.7	90.8±2.5	2.9±0.5	33.7±2.4
All households	65	0.89±0.003	1136.3±8.6	89±2.1	3.6±0.4	22±1.9
Small scale industries	7	0.846±0.018	1091.6±15.4	128.5±20.1	5.3±3.2	24.4±5.1

Table 4.2: Statistical summary for Nepal measurement

4.1.2 Tibet

A summary of Tibet measurement is shown in Table 4.4. Due to households availability and the brutal environment, measurement in Tibet comes with smaller sample amount and lower success rate. 47 samples are collected with 9 of them ending up invalid due to instrument failure, mostly pump issues. As discussed in section 3.1.3.1, in order to achieve the same mass flow rate, the load on pumps are much higher when ambient pressure is low (0.55 – 0.6 atm at approximately 15,000 ft).

location	Residence type	Stove type	Fuel type	Measurement	# of samples
Nam Co	Tent	Open fire	Yak dung	1-Day	4
	Tent	Chimney	Yak dung	1-Day	4
	Prefab house	Chimney	Yak dung	1-Day	12
	Stone house	Chimney	Yak dung	1-Day	6
	SSI	Chimney	Yak dung	1-Day	2
Linzhi	Garret	Chimney	Wood	3-Day	4
	Garret	Chimney	Wood	1-Day	8
Total					38

Figure 4.4: Tibet household summary

The living condition in different regions of Tibet varies, which made the fuel, stove, and household types distribute homogeneously with region. In Nam Co, yak dung is the only fuel. Household types include Tibetan tent, pre-fab house, and stone house. The mainstream stove is the chimney type, except some tents still use the traditional open fire bucket stove. In Linzhi, all the residents live in well constructed garrets, burning wood with chimney stoves. The chimney stoves being used in Linzhi have a very artistic external design, which gives them some visual design function. There were 2 small scale industry measurements conducted in Nam Co. Both were small restaurants with exactly the same type of stoves used in local households.

Figure 4.5: The household, stove, and fuel in Tibet

The sparse population and limited transportation capability restricted the sampling time in each household. Unlike the full day measurements conducted in Nepal which usually lasted more than 12 hours, Tibet testing time was limited to around 6 hours. Figure 4.6 shows an example of real time pollutant concentration in Nam Co and Linzhi. The emission pattern from Tibet does not show the obvious cooking events presented as does the one in Nepal. This difference is attributed to the lifestyle of Tibetan residents. Particularly in Nam Co area, the nomad life does not have a regular daily meal schedule (breakfast, lunch, snack, and dinner) at all. As shown in Figure 4.6, the daytime stove activity in Tibet does not give obvious patterns representing regular cooking events. Also, the cold weather in these high altitude regions encourages local residents to use cookstoves for heating purposes as well. The statistical summary for the Tibet measurements is shown in Table 4.3.

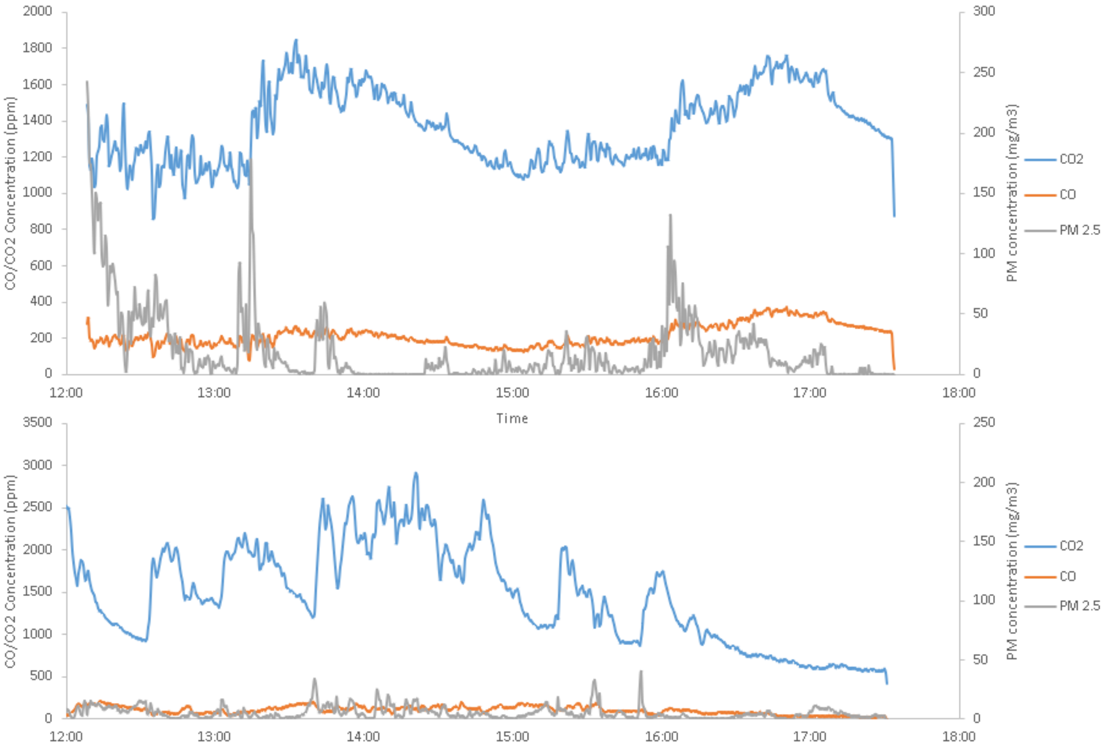


Figure 4.6: Typical real time emission in Tibet, above: Nam Co; below: Linzhi

	Sample amount	MCE	EF CO_2 [g/kg fuel]	EF CO [g/kg fuel]	EF $PM_{2.5}$ [g/kg fuel]	EF CH_4 [g/kg fuel]
Dung, open fire stove in tent	3	0.73±0.075	1298.8±148.3	303.1±80.8	18.5±10.2	32.4±7
Dung, chimney stove in tent	2	0.9±0.071	1590.4±176.3	107.1±76.4	26±26	5.8±1.6
Dung, chimney stove in house	15	0.91±0.018	1632.4±38.1	96±20	14.7±4.1	22±4.6
Wood, chimney stove in house	15	0.84±0.035	1282.9±64.4	150.7±31.5	18.6±3.8	9.8±1.3
All dung	22	0.89±0.021	1579±41.5	127.7±23.2	16.3±3.6	24.1±3.8
All household	35	0.87±0.02	1451.6±44.9	137.8±19.6	17.3±2.7	16.7±2.5
All SSI	2	0.89±0.046	1587.5±97.5	122.6±51.5	16.1±7.7	46.1±5.7
Overall	37	0.87±0.019	1459±42.9	137±18.6	17.2±2.6	18.3±2.6

Table 4.3: Statistical summary for Tibet measurement

4.1.3 Yunnan

Figure 4.7: Left: high stove; middle: portable stove; right: low stove

Table 4.4 shows the summary of the Yunnan measurements. The Yunnan measurement set contains 50 samples from 2 counties with 10 villages. There are 7 invalid samples. The household types in Yunnan are uniform while stove type varies. Although the well-developed electric grid prompts the usage of electric stoves, solid fuel stoves are still widely used, especially during winter and within senior residences. The typical solid fuel stoves being used in Yunnan include:

- High stove (HS): Dominate cookstove type before electric stove became popular. Still widely used for cooking. Especially when preparing large amounts of food.
- Portable stove (PS): Open fire bucket stove, designed to burn beehive coal. Local residents use it for other fuel too. Popular in heating, boiling water, and preparing simple food.
- Low stove (LS): Also called a floor stove. Not very common. Good for heating up the floor.

Coal and various agricultural residue dominate the fuel sources in Yunnan province. On one side, as one of the major coal-rich province in China, coal is easy to find at low cost and therefore becomes the primary fuel for local residents; on the other side, agriculture is well developed as it is supported by the appropriate weather and natural environment. As a result, there are plenty of agricultural residues that could be used as lighters to start the fire, or even use as fuel. Most of the local residents use coal and agricultural residue together. The most common scenario is using agricultural residue (corn cob) to start the fire and using coal to sustain it. After the stove gets stable, agricultural residue can be used to adjust the stove working condition.

location	Residence type	Stove type	Fuel type	Measurement	# of samples
Fuyuan	House	High stove	Coal	1-Day	13
	House	High stove	Coal	3-Day	2
	House	Portable stove	Coal	1-Day	5
	House	Portable stove	Coal	3-Day	1
	House	Low stove	Coal	1-Day	1
Xuanwei	House	High stove	Coal	1-Day	7
	House	High stove	Coal	3-Day	1
	House	Portable stove	Coal	1-Day	8
	House	Portable stove	Coal	3-Day	1
	House	Low stove	Coal	1-Day	1
Total					40

Table 4.4: Yunnan household summary

Real time monitoring is also conducted in Yunnan. Figure 4.8 shows an example of the pollutant concentration through out the day. The two major peak emission event groups indicate the traditional breakfast and lunch event in a Chinese village. The dinner cooking event, which usually happens at 6pm approximately, could not be monitored due to local collaborator's unavailability. The smaller peak at around 3pm is normally caused by water boiling or a snack event. As corn is often used as the stove starter, the moisture content in it generates a large amount of smoke at the starting stage of each cooking event; this process shows a strong $PM_{2.5}$ peak concentration at the beginning of every cooking event, while the concentration of CO and CO_2 does not show the same behavior.

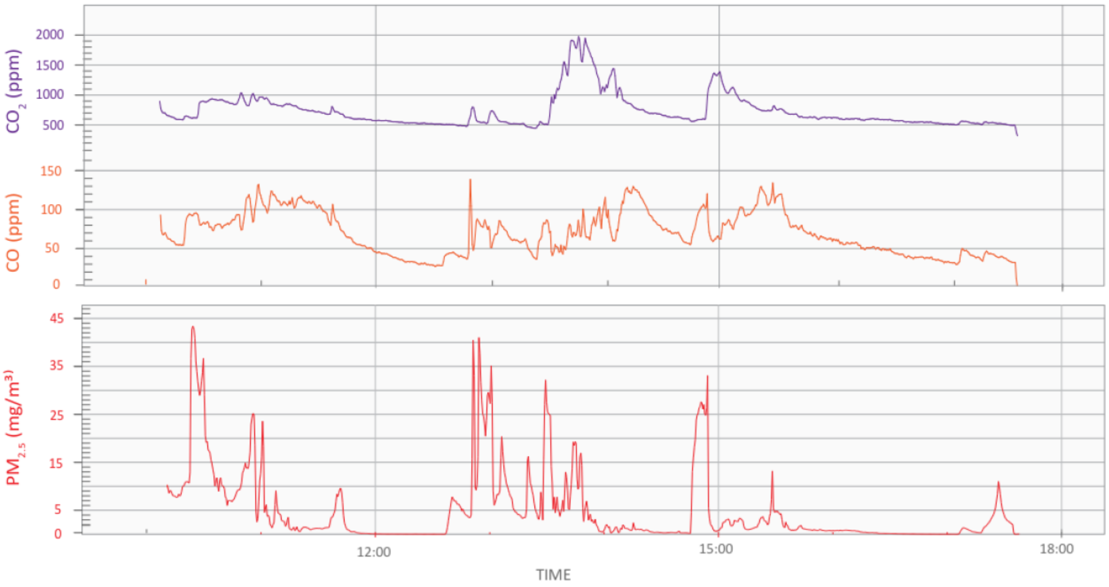


Figure 4.8: Typical real-time emission pattern for CO_2, CO, and $PM_{2.5}$ in Yunnan

Table 4.5 is the summary for the Yunnan dataset. As mentioned in the previous paragraph, the mixed fuel usage is very popular in Yunnan. The native definition of emission factor determined that it is very sensitive to fuel consumption [65]. Thus, it is important to separate the case of using agricultural residue as a lighter only and using coal as the major energy source, and using both agricultural residue and coal as the energy source. Based on observations in the field, the threshold value of $2kg$ agricultural residue consumption is selected as the criteria of whether a household is using agricultural residue as lighter only. In the case of more than $2kg$ of agricultural residue consumed, the emission factors are calculated based on the weight of total fuel (coal plus agricultural residue). In the other case, only coal consumption is considered in the emission factor calculation.

	Sample amount	MCE	EF CO_2 [g/kg fuel]	EF CO [g/kg fuel]	EF $PM_{2.5}$ [g/kg fuel]	EF CH_4 [g/kg fuel]
High stove in Fuyuan	15	0.827±0.027	1528.4±174.5	195±30.7	16.6±3.5	83.6±17.8
Portable stove in Fuyuan	6	0.871±0.031	1973.5±217.4	199.1±60.6	12.1±2.3	106.3±24.3
Low stove in Fuyuan	1	0.852	1379.0	152.8	32.1	89.7
High stove in Xuanwei	9	0.858±0.014	1573.7±251.2	172±35	21.8±8.6	61.6±11.2
Portable stove in Xuanwei	11	0.882±0.007	1457.4±269.8	125.2±25.4	13.3±4.3	88.6±20.9
Low stove in Xuanwei	1	0.897	2437.4	178.3	2.4	54.7
Overall Fuyuan	22	0.84±0.021	1643±137.5	194.2±25.9	16.1±2.6	90.1±13.7
Overall Xuanwei	21	0.872±0.007	1553.9±178.9	147.8±20.2	16.4±4.3	75.4±12.1
Overall high stove	24	0.838±0.018	1545.4±140.8	186.4±22.9	18.5±3.8	75.3±11.9
Overall portable stove	17	0.878±0.011	1639.5±196.1	151.3±27.3	12.9±2.8	94.8±15.7
Overall low stove	2	0.874±0.023	1908.2±529.2	165.6±12.8	17.2±14.9	72.2±17.5
Overall all	43	0.856±0.011	1599.5±111	171.5±16.7	16.2±2.5	82.9±9.1

Table 4.5: Statistical summary for Yunnan measurement

In order to explore the effect from mixing agricultural residue (mostly corn cob) together with coal, the correlation of modified combustion efficiency at different mixing ratio is plotted in Figure 4.9. The mixing ratio here is defined as the fraction of coal consumption (kg) in the total fuel consumption (kg). The reason use MCE as the indicator is that the emission factor is a normalized quantity that is defined as grams of emission compounds per kilogram of fuel consumption. With emission factor being calculated, the fuel type information has been already chosen. If using emission factor for CO_2 or CO, since the emission factor for these carbon compounds largely depends on the carbon fraction in the fuel, the correlation extracted from the emission factor of carbon compounds verses fuel mixing ratio will be aliased by the more significant correlation between emission factor and fuel type (strictly, the carbon fraction in the fuel). While the modified combustion efficiency, which is essentially a comparison of how much carbon is emitted in CO_2 and CO form, does not rely on fuel information. The result in Figure 4.9 shows that MCE distributes evenly through the whole fuel mixing ratio range, which implies the mixing ratio does not have a significant effect on the stove performance.

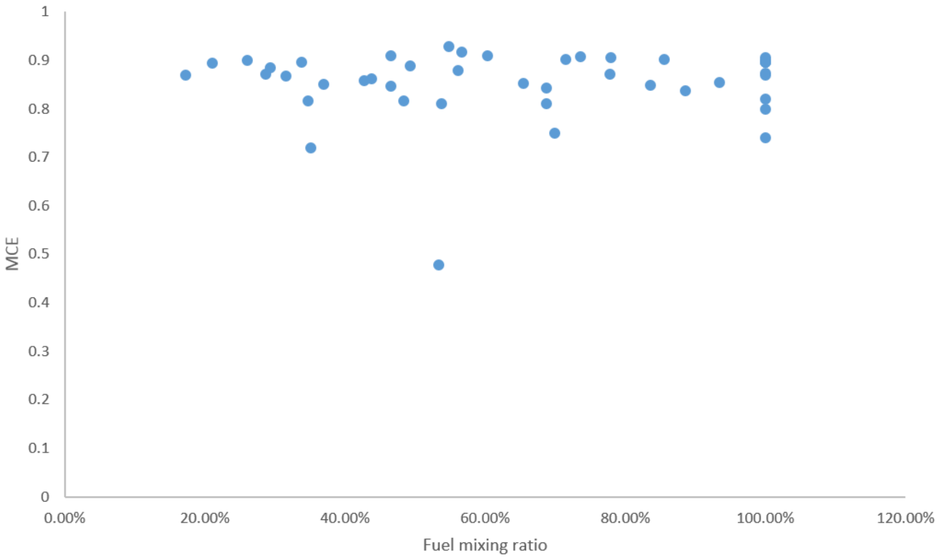


Figure 4.9: MCE at different fuel mixing ratio

4.1.4 Mongolia

The Mongolia measurement is accomplished together with a trained local sampling team. With their help, the Mongolia campaign was able to acquire 157 valid samples from 236 measurements. Unlike other campaigns which are all taken from low population density rural villages. The Mongolia measurements are carried out in the population dense area of the capital city, Ulaanbaatar. Solid fuel stoves are popular in Mongolia as the heating stove due to extremely cold weather during winter (outdoor ambient temperature approximately $-40°C$). The tests are conducted overnight to follow local residents' stove usage schedule (since they are out of the home for work during daytime). Sampling duration is 15 – 16 hours. Table 4.6 gives the summary for the Mongolia measurements.

location	Residence type	Stove type	Fuel type	Measurement	# of samples
Ulaanbaatar	House	Dul	Coal	1-Day	19
	House	Khas	Coal	1-Day	37
	House	Traditional	Coal	1-Day	34
	House	Ulzii	Coal	1-Day	38
	Ger	Dul	Coal	1-Day	23
	Ger	Khas	Coal	1-Day	0
	Ger	Traditional	Coal	1-Day	33
	Ger	Ulzii	Coal	1-Day	34
Total					218

Table 4.6: Mongolia household summary

Figure 4.10: Wood and Coal used in Mongolia

Figure 4.11: Households in Mongolia and the heating wall

Mongolia holds approximately 10% of the known coal reserves in the world [175]. Hence, coal is very affordable and easy to access locally, which makes the fuel usage for the Mongolia measurements very simple. All the samples in this study use coal as primary fuel with wood a sa lighter (Figure 4.10). There is no open fire stove in Ulaanbaatar, as ventilation has a negative effect on keeping rooms warm. The various chimney stoves are all commercial products. In some households, a heating wall is constructed from the stove exhaust to obtain better heating effects (Figure 4.11). A special type of household, a Ger, also called a Yurt, is popular in Mongolia. This round tent-shaped shelter is the traditional residence from the nomad history of Mongolia. It is still widely used, especially among senior people.

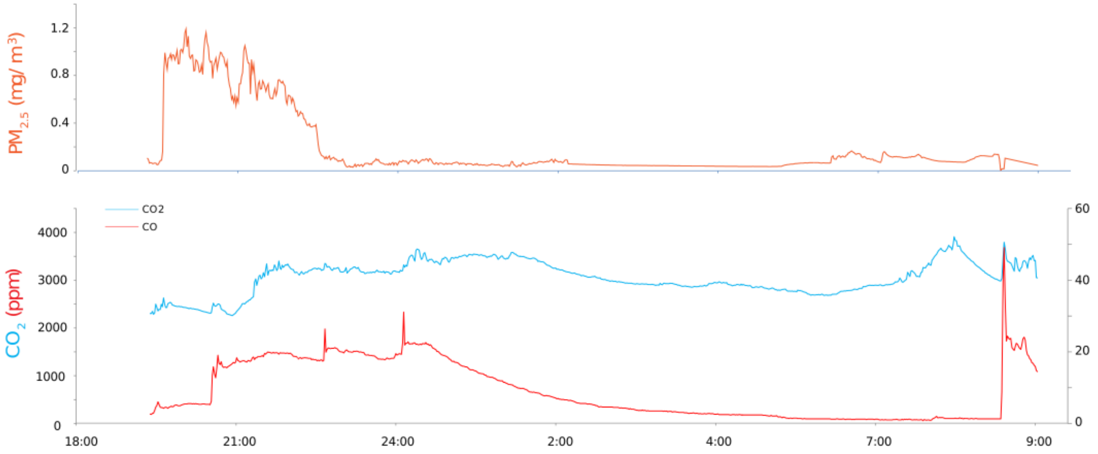
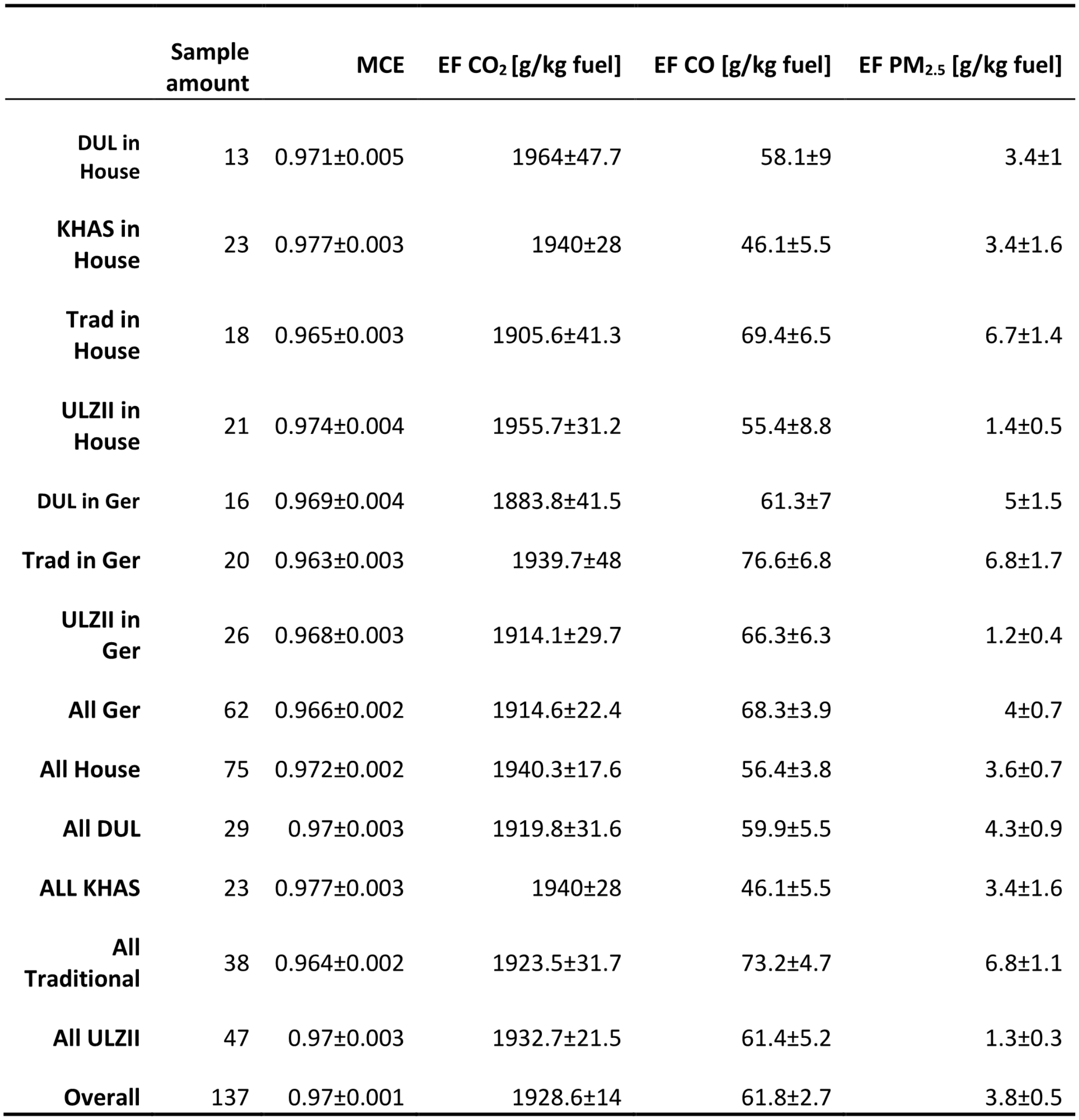


Figure 4.12: Typical real-time indoor air pattern for CO_2, CO, and $PM_{2.5}$ in Mongolia

Figure 4.12 shows typical real time indoor air concentration of CO_2, CO, and $PM_{2.5}$ in Mongolian households. As the measurements are conducted overnight, it shows a very different pattern compared with other sites. The test usually starts at dinner time when the stove is in an active status, producing peak concentration for all major emission compounds. At around mid-night, the residents go to sleep, and the stove activity declines until the next morning when residents wake up and refuel the stove.

The $PM_{2.5}$ concentration shows quicker response to residents' indoor activity, while it take few hours for CO_2 and CO to drop to the low point after people go to sleep.



	Sample amount	**MCE**	**EF CO_2 [g/kg fuel]**	**EF CO [g/kg fuel]**	**EF $PM_{2.5}$ [g/kg fuel]**
DUL in House	13	0.971±0.005	1964±47.7	58.1±9	3.4±1
KHAS in House	23	0.977±0.003	1940±28	46.1±5.5	3.4±1.6
Trad in House	18	0.965±0.003	1905.6±41.3	69.4±6.5	6.7±1.4
ULZII in House	21	0.974±0.004	1955.7±31.2	55.4±8.8	1.4±0.5
DUL in Ger	16	0.969±0.004	1883.8±41.5	61.3±7	5±1.5
Trad in Ger	20	0.963±0.003	1939.7±48	76.6±6.8	6.8±1.7
ULZII in Ger	26	0.968±0.003	1914.1±29.7	66.3±6.3	1.2±0.4
All Ger	62	0.966±0.002	1914.6±22.4	68.3±3.9	4±0.7
All House	75	0.972±0.002	1940.3±17.6	56.4±3.8	3.6±0.7
All DUL	29	0.97±0.003	1919.8±31.6	59.9±5.5	4.3±0.9
ALL KHAS	23	0.977±0.003	1940±28	46.1±5.5	3.4±1.6
All Traditional	38	0.964±0.002	1923.5±31.7	73.2±4.7	6.8±1.1
All ULZII	47	0.97±0.003	1932.7±21.5	61.4±5.2	1.3±0.3
Overall	137	0.97±0.001	1928.6±14	61.8±2.7	3.8±0.5

Table 4.7: Statistical summary for Mongolia measurement

4.2 Discussion and Comparison of Results

4.2.1 Efficiency and Emissions

Figure 4.13 compares the modified combustion efficiency for wood burning cookstoves between this study (with uncertainties) and several previous works, including both the water boiling test and the measurement of actual stove usage. The MCE measured from actual stove use in the field is consistently lower compare with those measured from standard water boiling tests. A comparison for CO emission factor (Figure 4.14) gives similar results. The measurements on actual stove use in homes gives significantly higher CO emission, and larger uncertainty, than the WBTs. The Nepal results from Weyant et al. are collected together with this study by the UIUC sampling team [163], with a similar mean value but much larger uncertainty, which is likely due to the smaller sample number collected by the UIUC team.

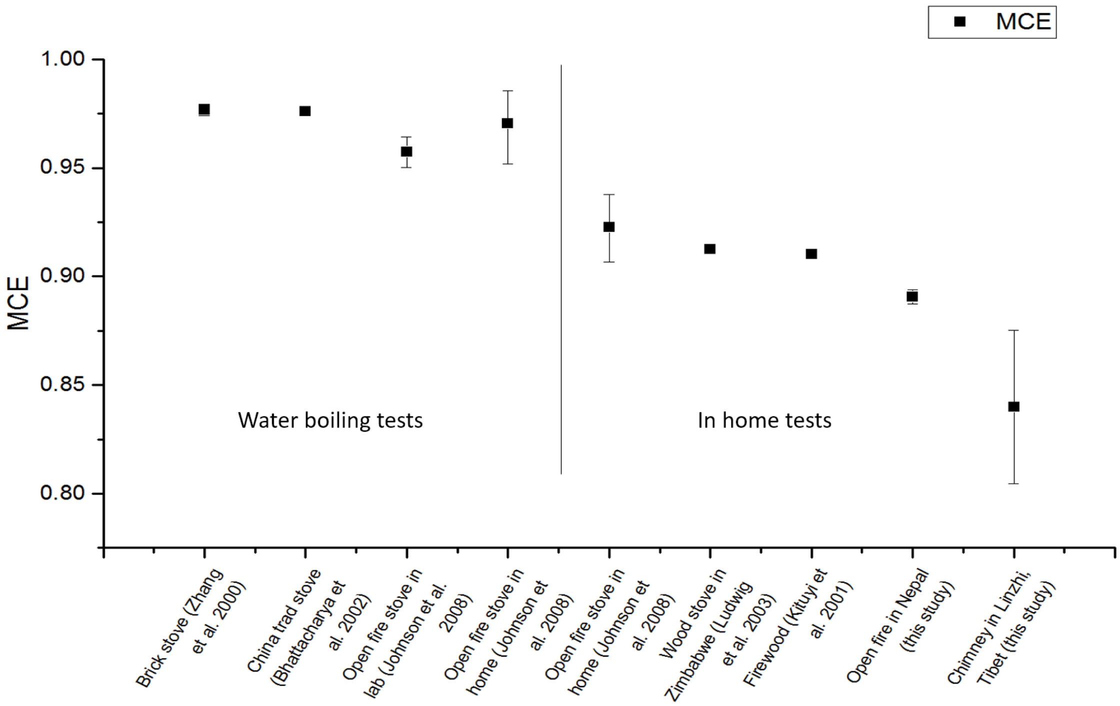


Figure 4.13: The MCE comparison

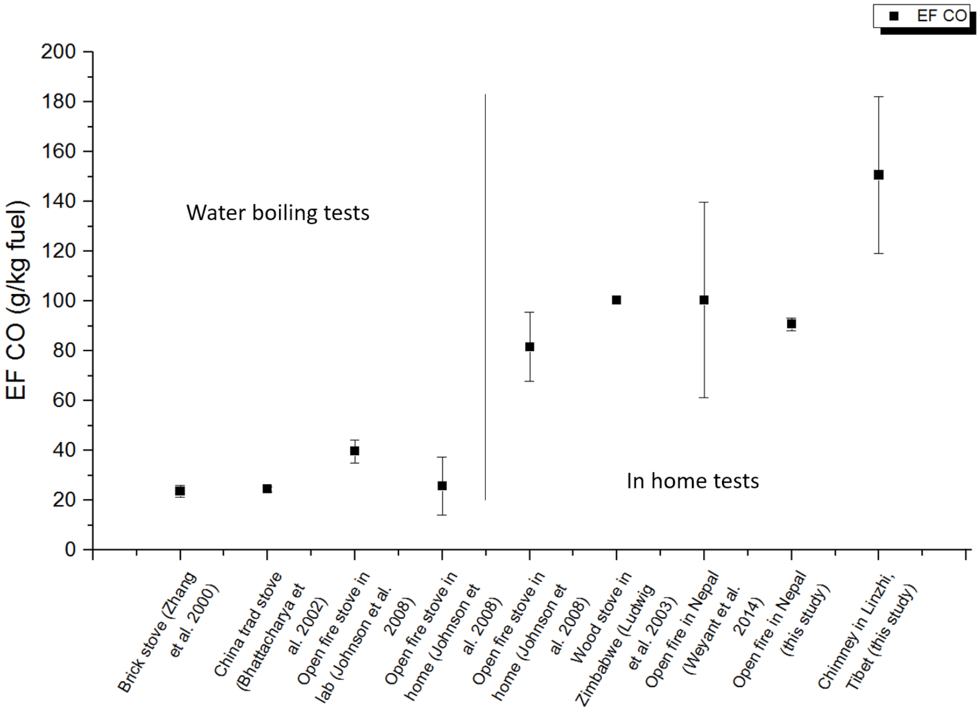


Figure 4.14: The CO emission factor comparison

Figure 4.15 compares the MCE from different regions with different fuels in this study. The MCE results from all regions with all different fuels are similar, with the Mongolia site an exception, it being significantly higher than all other sites. Coal stoves in Mongolia are primarily used for heating. Unlike the cookstoves in other sites, which are only lit during cooking events, the heating stoves in Mongolia are kept on all the time. This more constant working condition is the potential reason for their high overall MCE.

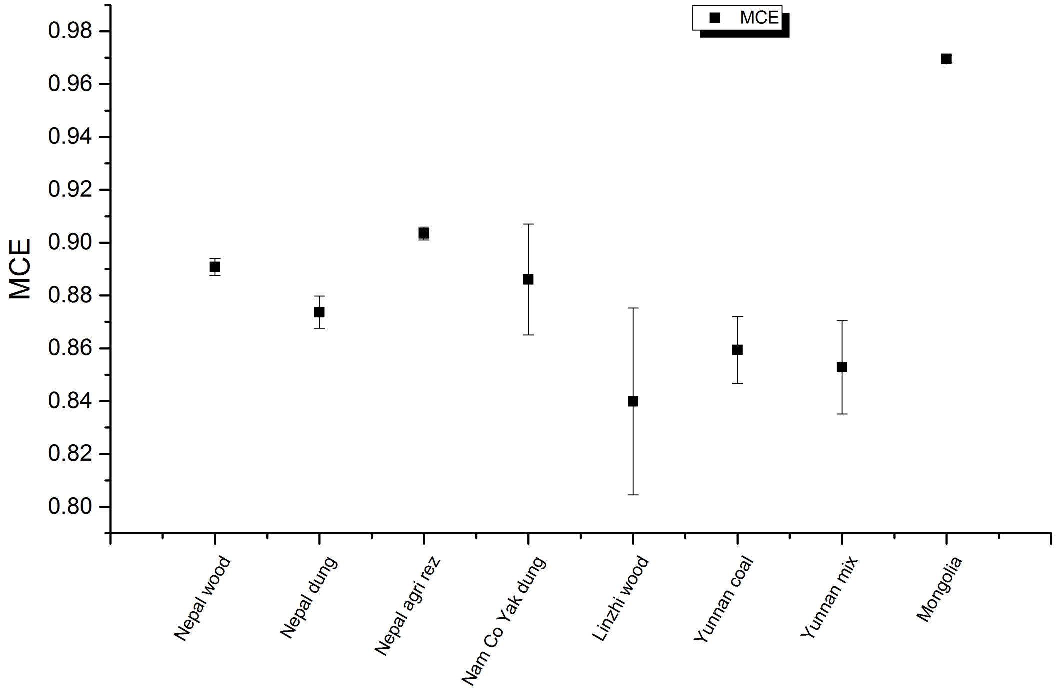


Figure 4.15: Comparison of MCE between sites and fuels

The CO_2 emission factor is a good reference for carbon emission as most of the emission comes out in form of CO_2. As has been well-addressed, fuel makes a big difference in the carbon emission. One major reason for this is the carbon content in fuel, which directly affects the emission factor of carbon compounds. For example, woods and agricultural residues normally have the carbon content at about 50%.

The carbon content for coal can be over 90 % [184]. Comparing the CO_2 emission factor for the wood and agricultural stoves (Nepal, Tibet) and coal stoves (Yunnan, Mongolia), the carbon emission from coal stoves are significantly higher (Figure 4.17).

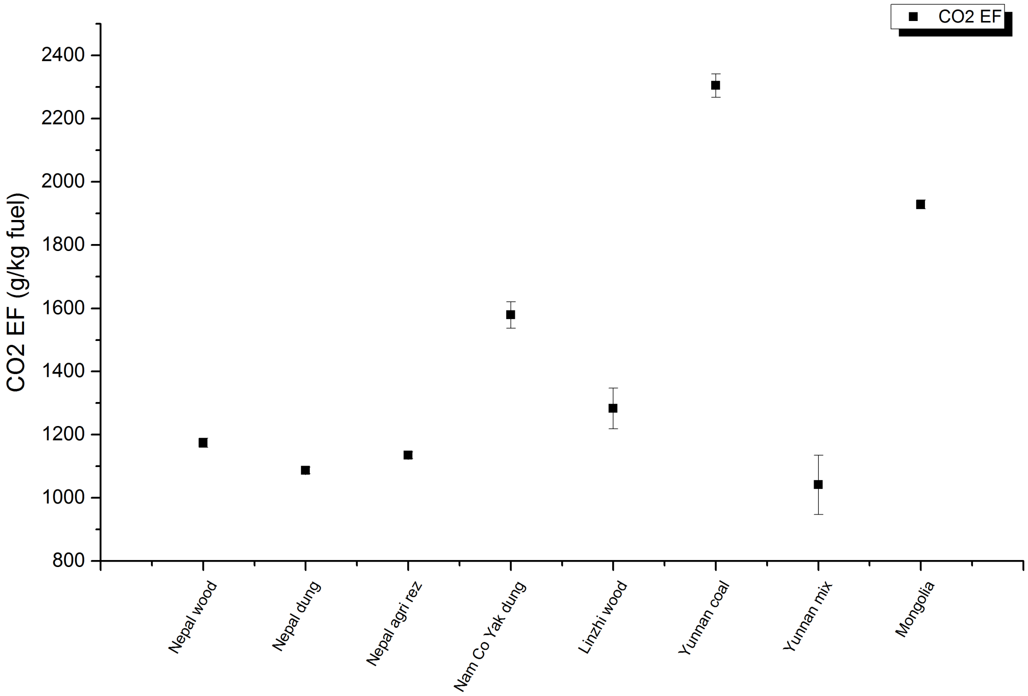


Figure 4.16: Comparison of CO_2 between sites and fuels

CO and $PM_{2.5}$ are the major products of incomplete combustion, and they are closely related to indoor air quality and resident health. One challenge for CO and $PM_{2.5}$ measurements are the associated uncertainties, especially for $PM_{2.5}$. In Nepal, dung stoves show higher CO and $PM_{2.5}$ emission than wood and agricultural residue stoves, which matches with the general opinion of dung as a more ‘dirty’ fuel. But the yak dung stove in Nam Co, Tibet gives lower CO and $PM_{2.5}$ than wood stoves in Linzhi, Tibet. As discussed in the methodology chapter, the stoves in Nam Co, Tibet, due to the harsh environment (high altitude, cold), are partially used as heating stoves. This difference on ‘how the stove is used’ may explain this unusual behavior. Among all the field sites in this study, Yunnan coal stoves have the highest CO and $PM_{2.5}$ emission factor. According to the local CDC, the field sites in Yunnan province, Fuyuan and Xuanwei county, all have high occurrence of lung cancer.

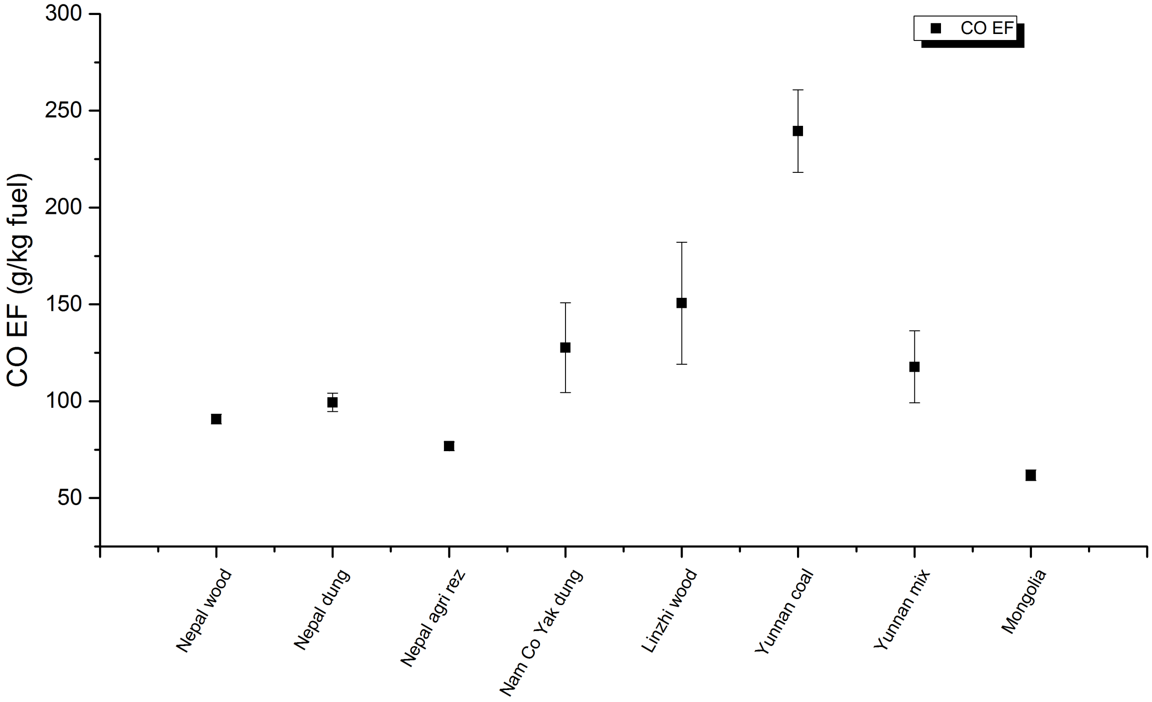


Figure 4.17: Comparison of CO between sites and fuels

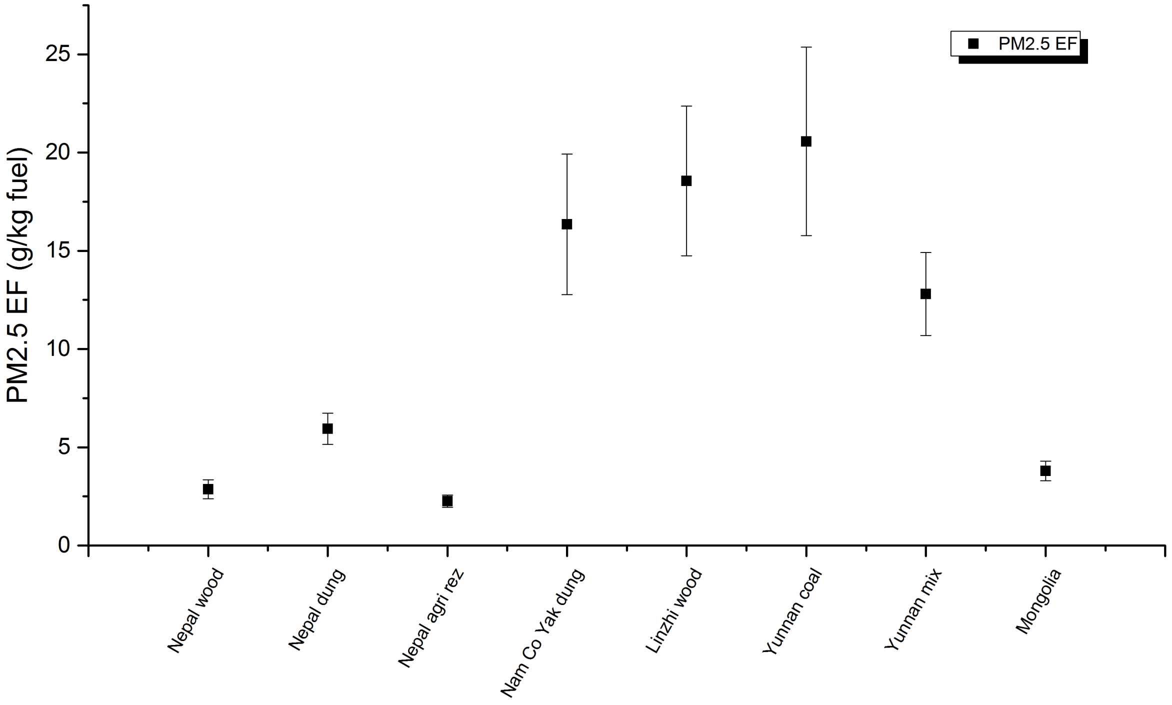


Figure 4.18: Comparison of $PM_{2.5}$ between sites and fuels

It is interesting to note Nepal's low uncertainty compared with other sites. Comparing with the emission from cookstove combustion, the background value (ambient) is relatively consistent. The stoves in Nepal are all open fire design, which will involve natural dilution by ambient air. This process will lower the signal to noise ratio. However, in this case, the signal itself varies, but the noise level is more stable. Thus the result is less variation between each sample, and this leads to a lower uncertainty.

4.2.2 Carbon Particulate Emission

The study of elemental carbon and organic carbon is a separate section of this dissertation because it has distinctively different character than the other measurements. For example, the EC/OC work involved a strong collaborative component from the

UIUC team, where they were responsible for the core values of these measurements. This meant that the creative resolution of the typical issues faced during in-field measurements (as described earlier) were handled by others, and the documentation of such subtle activities is often less complete than when measurement campaigns are carried out by a single entity. In addition, the EC/OC particulate measurements are inherently noisier than gas measurements and total particulate measurements because they are often less uniformly mixed at the sampling zone (the complete mixing into the atmosphere occurs over longer time). Hence, the clearly valid sample number of EC and OC is much smaller than for the other species discussed in previous paragraphs. Nevertheless, the EC/OC data is a critical component of the uncertainty in climate forcing so it is important to include even the limited validated data obtained. Figure 4.19 shows a summary of the EC and OC measurement.

Location	Fuel	Sample amount	EF EC [g/kg fuel]	EF OC [g/kg fuel]
Nepal	Wood	28	0.53±0.18	1.68±0.35
Nepal	Dung	18	0.43±0.14	1.97±0.32
Nepal	Agricultural Residue	16	0.59±0.10	0.88±0.14
Tibet, China	Yak Dung	10	0.25±0.05	15.41±2.54
Tibet, China	Wood	2	0.11±0.05	16.03±14.48
Yunnan, China	Coal	16	1.46±0.47	10.09±2.71
Yunnan, China	Mix	18	0.51±0.17	7.02±1.26

Figure 4.19: Summary of elemental carbon and organic carbon result

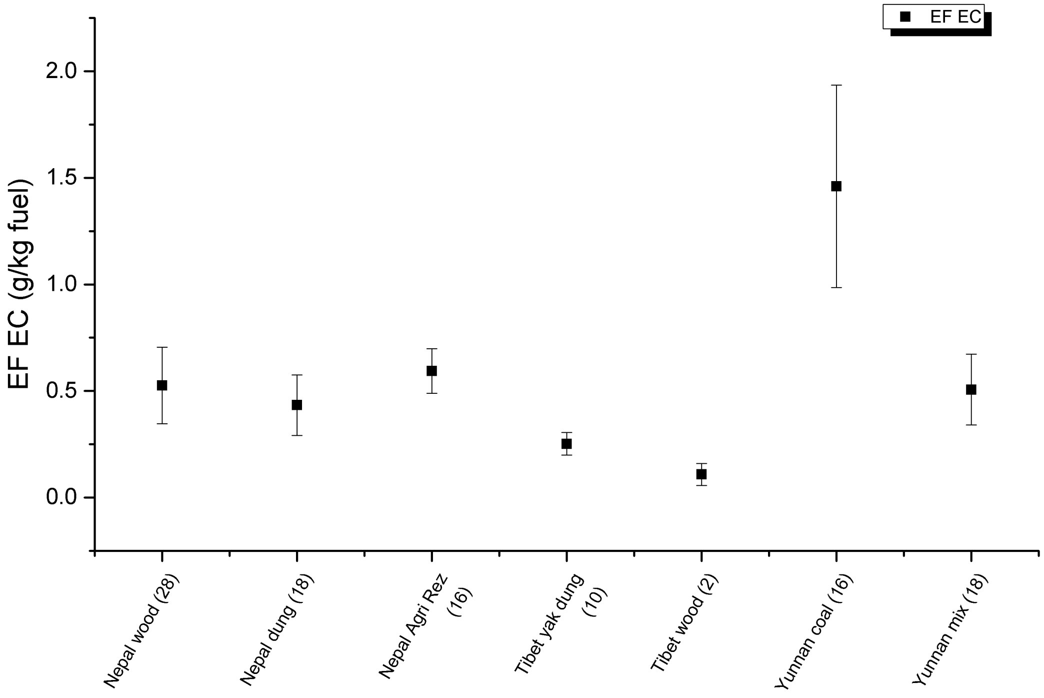


Figure 4.20: Comparison of elemental carbon between sites and fuels

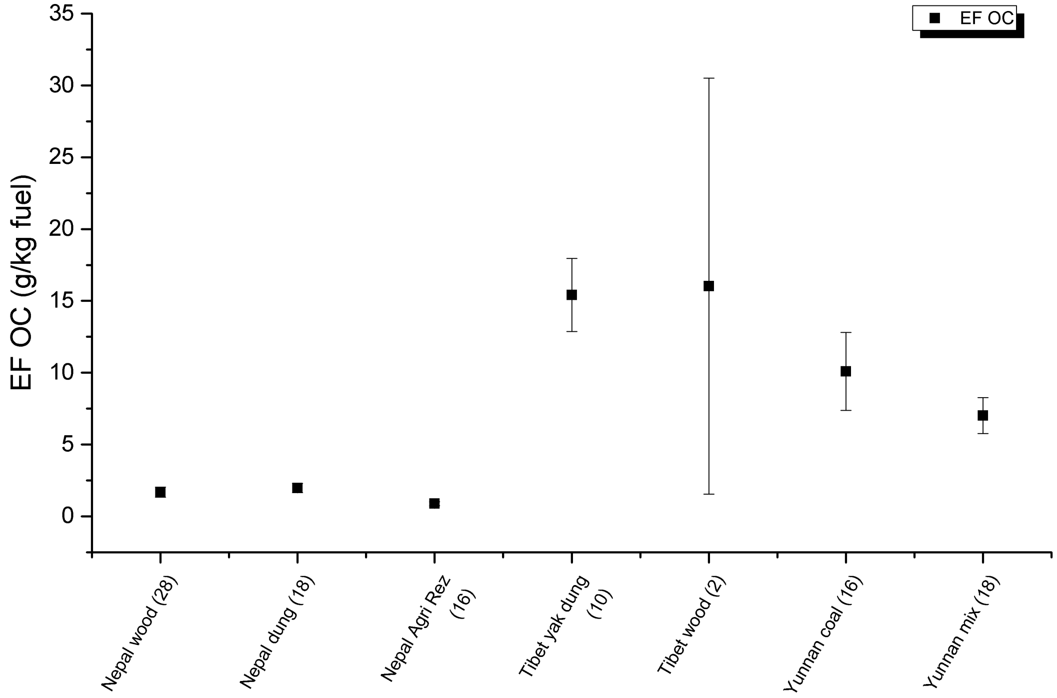


Figure 4.21: Comparison of organic carbon between sites and fuels

Figure 4.20 and 4.21 show a comparison of EC and OC emission factors through all field sites and fuels. The coal stoves in Yunnan, China produces the highest elemental carbon emissions, even considering its high uncertainty, while other stoves burning agricultural-based fuel have a similar result. Figure 4.21 shows that the stoves in Nepal, whatever fuel is using, emit less OC across all the field sites. Figure 4.22 is a plot of EC and OC ratio for the different regions and fuel combinations, as the EC to OC ratio is usually of more interest.

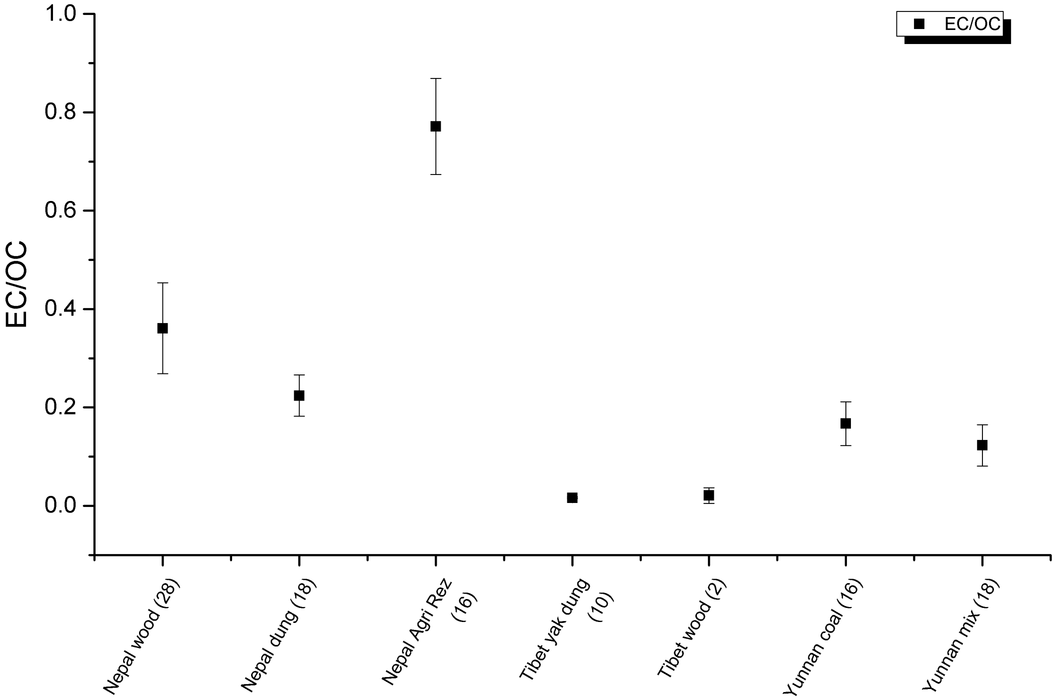


Figure 4.22: Comparison of EC/OC ratio between sites and fuels

As in the discussion above, the elemental carbon emission relates closely to the carbon content in the fuel: higher carbon fuel such as coal produces more EC during the combustion process. Organic carbon seems more affected by the stove type. The distinctly different behavior of the Nepal stoves appear to result from the open fire design, where all the other sites have stoves with chimneys. From the perspective of combustion chemistry, as discussed in section 1.2.2, the formation of soot, which is mostly elemental carbon, is largely related to the production of acetylene (C_2H_2). The agricultural-based fuels (wood, dung, agricultural residue, etc.) are essentially a mixture of hydrocarbons. In the combustion process, before soot (EC) is produced, the long hydrocarbons (larger C number) break up into shorter hydrocarbons (smaller C number) until acetylene. For a stove that does not burn fuel completely (which is common for cookstoves), the decomposition reactions for some molecules can stop before reaching the acetylene stage. In this case, organic carbon is emitted. Elemental carbon, on the other hand, that reactions reach the key soot precursor acetylene, which represents more complete combustion as compared to high OC emission combustion. Looking back at the modified combustion efficiency (Figure 4.15), the open fire stoves in Nepal have overall higher MCE among all other field sites (exclude the pure heating stove in Mongolia). This suggests that the ratio of EC & OC emission from cookstoves may logically correlate with the combustion efficiency of the stove: that is, higher EC at higher efficiency and more OC at lower efficiency.

4.3 Combustion Intermittency

As has been well documented, the primary effect on solid fuel cookstoves' performance and emission is fuel type [3]. Fuel variability alone, however, is not sufficient to explain all of the observed measurement variation, and it is likely, therefore, that there are secondary factors impacting significantly stove emission performance. These secondary factors are difficult to mimic in a laboratory measurement. For example, stove activities in households can be affected by a series of variables which may include family size, food type, chef's skill level and so on. Some of these variables can be very hard to introduce into controlled laboratory experiments. A comprehensive statistical analysis of our large in-field data set [176] showed, as others have found, that fuel type is a primary factor in emissions. In addition, however, there appeared to be a consistent trend where emissions were higher (when normalized to fuel consumption) when the stove was used more infrequently. This behavior is reminiscent of the emission challenges from internal combustion engines during the initial startup when the system is cold. Previous study has acquired the information between fraction of carbon emission and modified combustion efficiency for three types of stove in Mexico [177]. In this study, in order to quantitatively evaluate the effect from stove usage, we propose a parameter 'continuity factor', which provides combined information comprising the fraction of time the stove is being used, the number of event cycles during the sampling time span, and the fluctuation of combustion in the stove while it is being used.

The intermittency analysis is based on the data set obtained from a series of field measurement campaigns that include not only those already described but others from around the world. The field sites include: Nepal, Mongolia, India, Mexico and the Tibet area of China. We analyze the real time information of carbon dioxide (CO_2), carbon monoxide (CO) and $PM_{2.5}$ emission during stove working hours to explore the intermittency and its effect on the modified combustion efficiency (MCE) and emission factors (EF).

As with many other combustion systems, it is likely that most of the incomplete combustion products are generated during the starting and ending stages. The stove works best in continuous burning conditions. The results suggest that a larger fraction of total cookstove operating time spent under continuous burning (lower portion for the starting and ending stages), the higher the overall efficiency and the lower incomplete combustion emissions should be (after considering fuel type variability). In the case of residential use cookstoves, the number of events (meals) is directly related to the number of starting and ending processes. With the assumption that for each event, the starting and ending process takes approximately the same amount of time, more events will lead to a higher fraction of starting and ending, lowering the overall efficiency and raising the emissions. Thus, in this preliminary study, the continuity factor is: within total sampling time, the fraction of time (over total sampling time) when the stove is actually being used, weighted by the inverse of stove event (cooking event) number. The cooking events are identified based on the real time CO_2 concentration measured (figure 2). Samples with higher continuity factor to have higher MCE and lower incomplete combustion products (CO and $PM_{2.5}$).

$$Continuity\ Factor \equiv \frac{stove\ working\ time}{total\ sampling\ time} \times \frac{1}{number\ of\ events}$$

The first hint of the effect from combustion intermittency comes from the comparison of data from different sites. Figure 3 shows the overall MCE from Tibet of China, India, Mexico, and Mongolia, separated by regions. Despite all other factors like fuel type and stove type, it is obvious that the MCE in Mongolia is significantly higher than at other sites. According to the background study and observation, one special thing in Mongolia is that these stoves are primarily used for heating instead of cooking. Which means unlike those cooking stoves which will be turned off after the cooking event ends, the heating stove stays on all the time. To further explore the effect from combustion intermittency, a quantitative intermittency analysis is applied to the data set from Nepal.

VARIABLE	FUEL	N	MEAN	STD.DEV	UNCERTAINTY	RELATIVE UNCERTAINTY
MCE	WOOD	20	0.88	0.02	0.01	0.99%
	DUNG	14	0.88	0.03	0.01	1.54%
	AGRICULTURAL RESIDUE	14	0.90	0.01	0.01	0.64%
CO EF	WOOD	20	95.39	16.81	7.52	7.88%
[g/kg fuel]	DUNG	14	99.05	19.83	10.60	10.70%
	AGRICULTURAL RESIDUE	14	79.92	9.88	5.28	6.61%
PM EF	WOOD	20	4.23	5.33	2.38	56.29%
[g/kg fuel]	DUNG	14	7.00	3.38	1.80	25.78%
	AGRICULTURAL RESIDUE	14	2.23	1.35	0.72	32.26%

Table 4.8: Nepal measurement summary for MCE CO and $PM_{2.5}$

The main reason for choosing the Nepal dataset is the same household type and stove type through all the samples, which minimizes the confounding effects from these factors. Typically, there are three types of fuel used in Nepal: wood, dung, and agricultural residue (Figure 3.2). Table 4.8 gives the summary of MCE, emission factor of CO and $PM_{2.5}$, categorized by fuel type and with statistical uncertainty calculated. Comparing the MCE and CO emission factors by fuels, stoves with dung have the lowest efficiency and highest CO emission, which matches with previous studies [79, 3, 178]. The $PM_{2.5}$ emission factors for dung stoves are about six times higher than stoves with wood and agricultural residues as fuel. However, the high uncertainty level indicates there are considerable other factors involved as well [7].

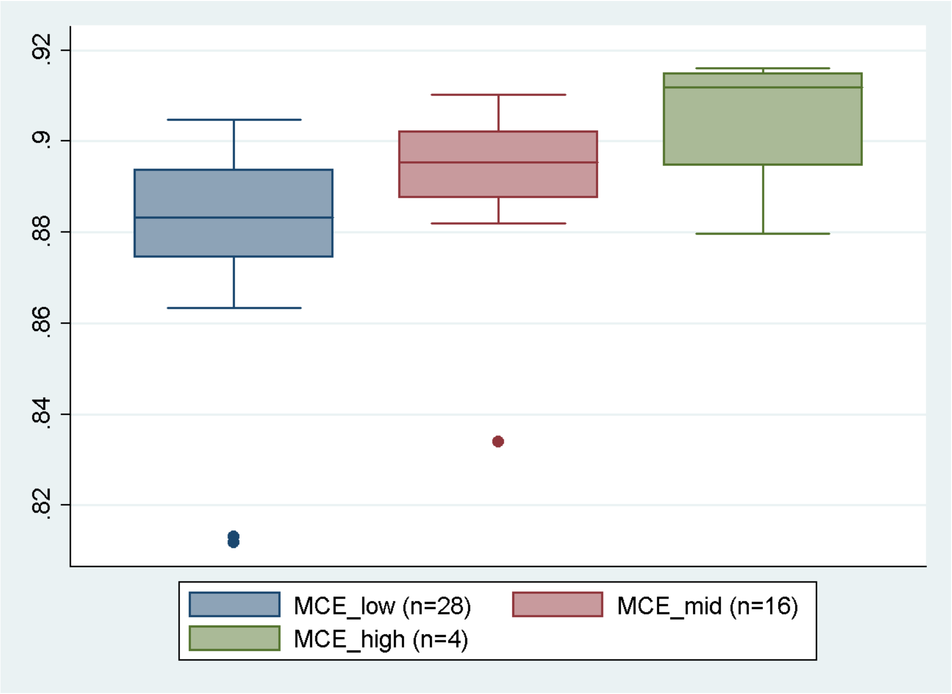


Figure 4.23: MCE comparison for various continuity factor

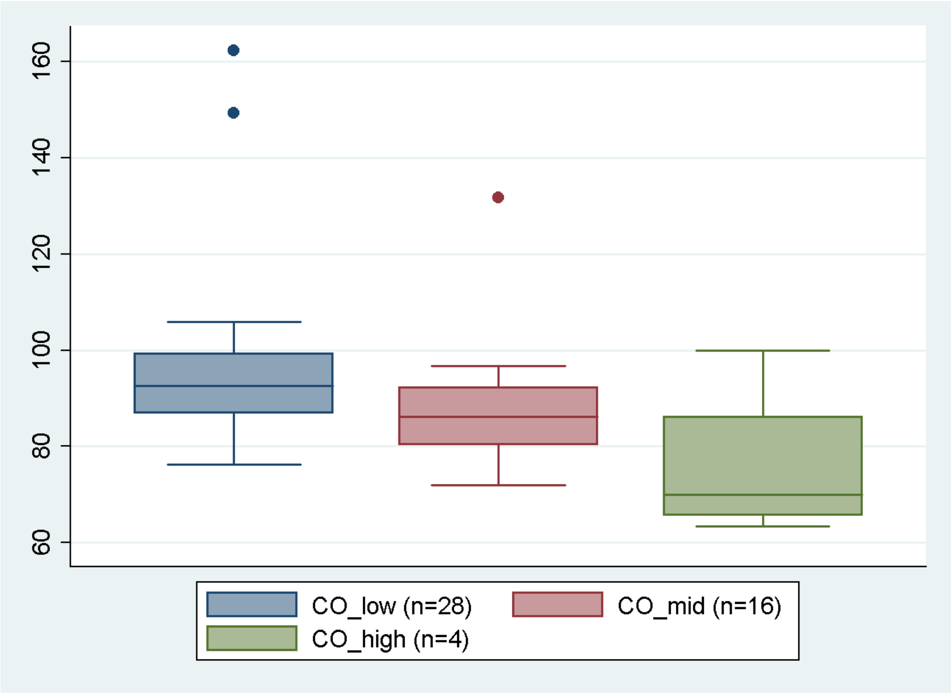


Figure 4.24: CO emission factor comparison for various continuity factor

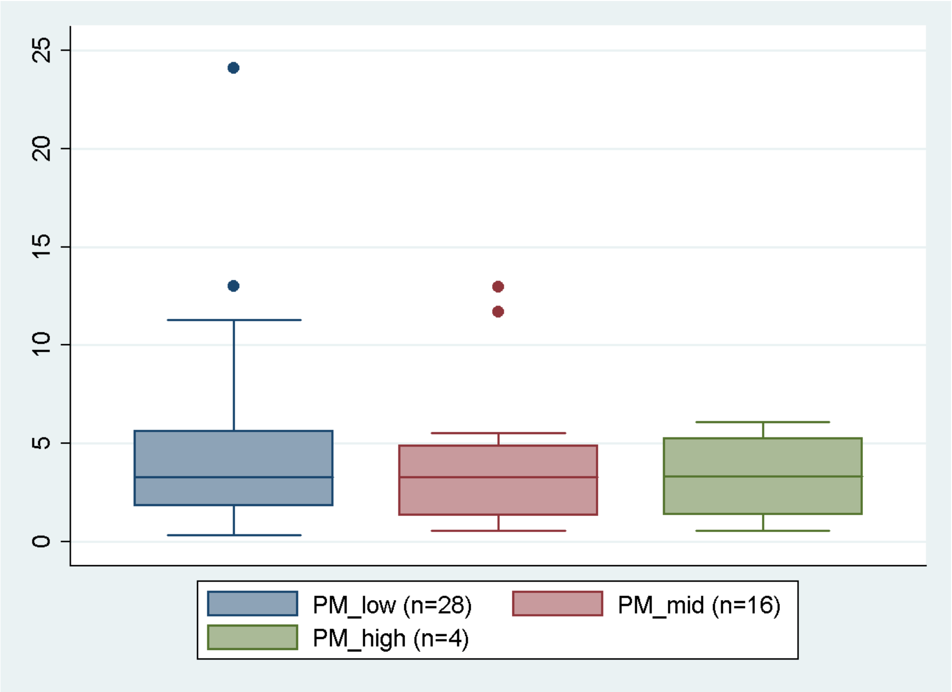


Figure 4.25: $PM_{2.5}$ emission factor comparison for various continuity factor

Figures 4.23, 4.24, and 4.25 show the comparison between different levels of continuity factor. The range of continuity factor for this data set is from 0.2 to 0.8. Considering the sample size within each subgroup, the low continuity group contains samples with continuity factor smaller than 0.1 with a mean value around 0.07; The mid level group ranges from 0.1 to 0.3 (mean value: 0.17) while the high level group is beyond 0.3 (mean value: 0.53). The results of MCE and CO emission factor are promising. As expected, continuity factor increases, which indicates the portion of starting and ending are less, lead to a higher combustion efficiency and lower major incomplete combustion product emissions. As for the result of $PM_{2.5}$, there is no obvious pattern, but the uncertainty and variability are very high which obscures moderate effects.

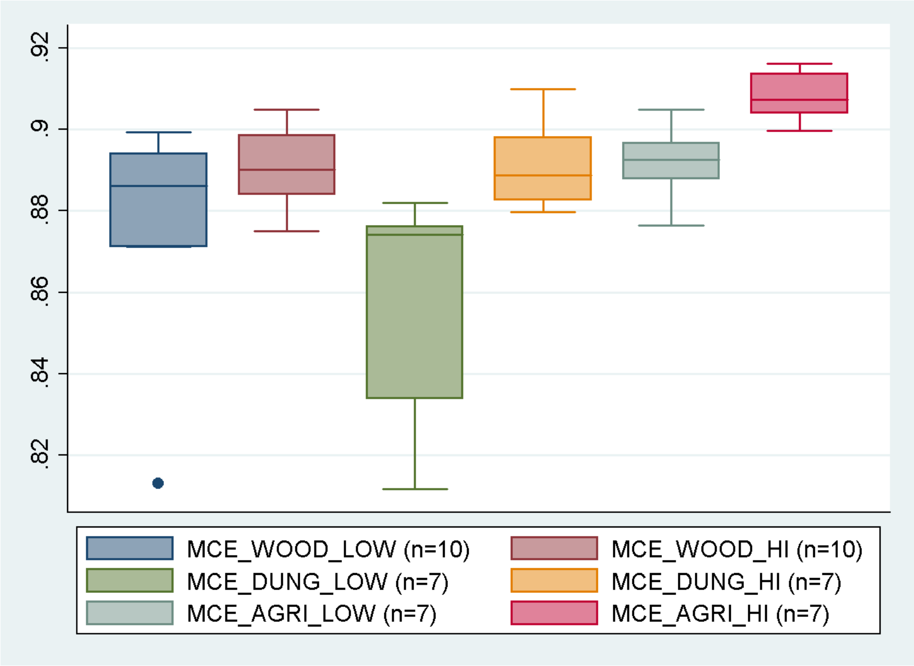


Figure 4.26: MCE comparison for various continuity factor within each fuel category

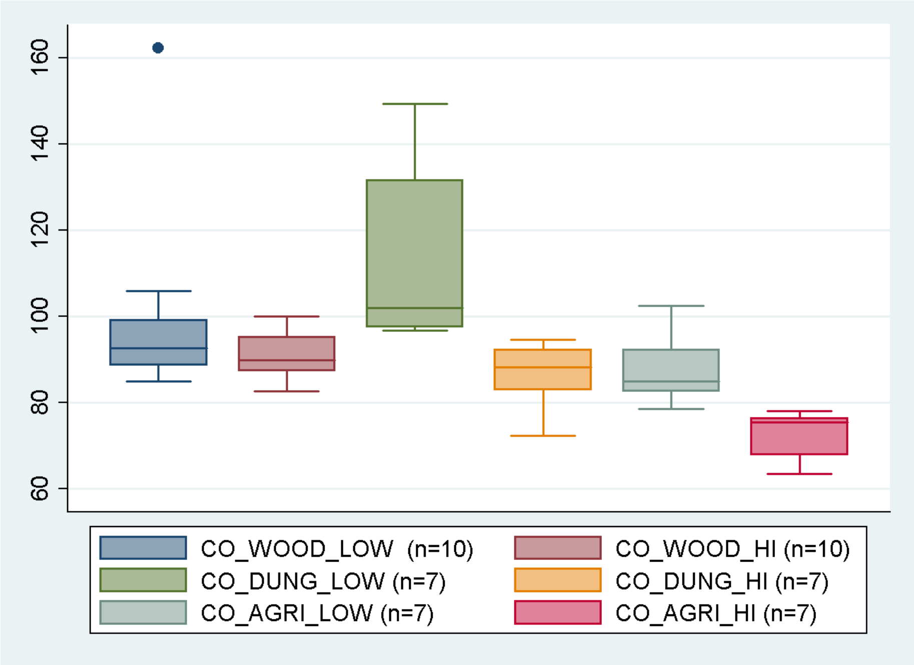


Figure 4.27: CO emission factor comparison for various continuity factor within each fuel category

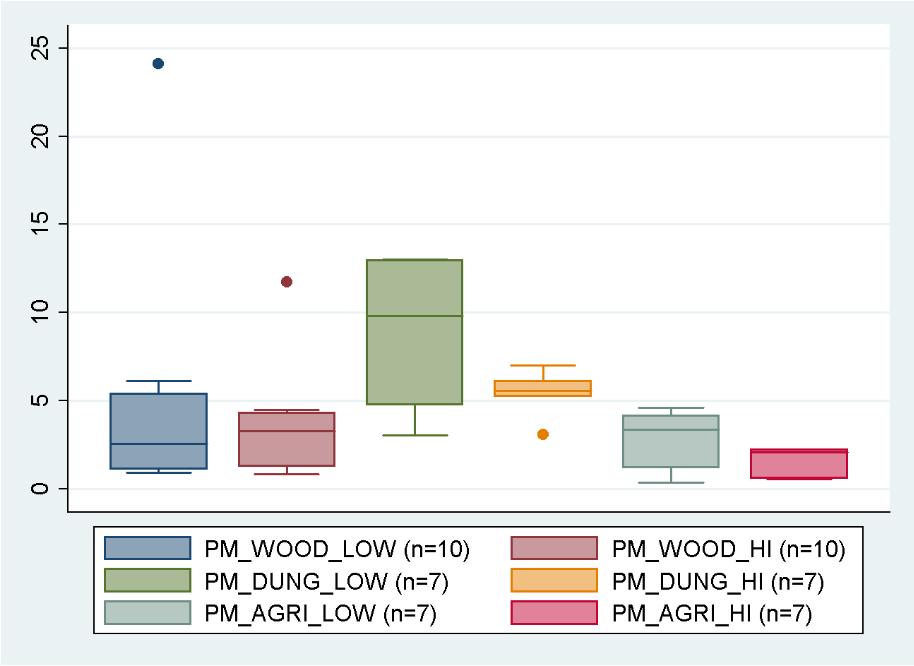


Figure 4.28: $PM_{2.5}$ emission factor comparison for various continuity factor within each fuel category

As mentioned before, one primary effect on solid fuel cookstoves combustion is the fuel type. In order to exclude this interference, the intermittency analysis is applied within each fuel category. One challenge associated with this approach is: since the total pool size is divided by three (roughly), the decreased sample amount within each subgroup will introduce more uncertainty. To alleviate this negative effect with limited samples, the samples within each fuel category are grouped into two intermittency levels. The comparison of MCE, CO and $PM_{2.5}$ emission factor with different intermittency level in each fuel group is shown in Figure 4.26, 4.27, and 4.28. With the effect from fuel type isolated, the MCE and CO result gives similar but clearer correlation with the overall comparison above, in agreement with the hypothesis of stove activity as a secondary effect. Dung and agricultural residue stove $PM_{2.5}$ emission seems to have the same pattern. however, the disagreement from wood and agricultural residue stoves, plus the high uncertainty of $PM_{2.5}$ data requires further study.

Chapter 5

Conclusion

A series of in-field emission measurements for solid fuel cookstoves have been conducted. Emission factor for major compounds (CO_2, CO, $PM_{2.5}$, and CH_4) with their statistical uncertainties are calculated with the carbon balance method. The acquired emission database fills the blank of the inventory for the household cookstoves emission in the corresponding regions. The challenge of field measurement limits its deployment and the study about resident emission mostly relies on modeling and lab tests. However, these field data provide important information for both model tuning and exploring more representative lab test protocols.

A non-dimensional parameter 'continuity factor' is established to describe residential stove activity quantitatively. The correlations between continuity factor and MCE as well as CO emission factor are demonstrated by the analysis on the data set from Nepal sites. The result from both overall analysis and the analysis within each fuel category agrees with an hypothesis that for residential stove usage, higher continuity factor indicates higher overall combustion efficiency and lower major incomplete combustion emissions. There is no obvious link between continuity factor and $PM_{2.5}$ emission factor, but uncertainty is a major issue for $PM_{2.5}$ measurements which makes the analysis very challenging. In order to verify the effect on $PM_{2.5}$ emissions, a larger sample size is required. This current study suggests that some recognition of intermittent stove use should be part of such a protocol.

There is no strong link being found between household cookstove emission and outdoor ambient air quality from this study. Most of the field sites (Nepal, Tibet and Yunnan in China) have very clean outdoor air but high cookstove emissions and very smoky indoor air. The reasons include short resident time of most cookstove PM and in natural villages, the population is still sparse compare with big cities. Ulaanbaatar in Mongolia does have serious air pollution issues, but these are more likely attributed to the capital city's high population density and the existence of other heavy industries, such as mining, which is very popular in Mongolia.

The impact on indoor air quality from residential cookstoves emission is substantial. Even with chimney stoves, the indoor emission concentrations are significantly higher than those in the ambient when the stove is running. In Mongolia, the background CO_2 concentration reaches 3000 ppm, which is almost 10 times that in ambient atmosphere. CO, which is a toxic gas species, also has above 100 ppm background level in some households. For those residents using agricultural residue as fuel or lighter, the enormous smoke generated from the beginning stage of fire is sometimes oppressive with penetrating odor. In the Yunnan province of China, especially Xuanwei county, which is one of the field sites in this study, the lung cancer occurrence ranked in the top 3 in the whole China, and studies relating coal use and lung cancer occurrence has been underway for decades [45].

The method of controlling emissions that is being deployed in large scale industry, such as carbon capture, does not fit the resident emission case well. For distributed emission sources like in villages, a carbon capture facility is not cost effective, which gives low energy efficiency ratio [179]. Prompting better stoves to the rural villages is a useful approach in easing the health threats from solid fuel cookstoves emissions. Some examples include biogas stoves which use biogas (CH_4 is the major compounds) generated from agricultural residue and electric stoves. Besides the cost aspect, one widely existing challenge in these improved stove promotion activities is the inertia of using the existing stove. that is, residents tend to keep their traditional way of cooking unless there is an obvious, severe, and well-demonstrated con. One example is the lung cancer occurrence in Yunnan villages, and the correlated popularity of electrical stoves locally.

A major contribution of this work is the unique information from in field measurements. These measurements show the real variability of cookstove use and caution against simple methods to incorporate cookstove emissions in global climate models. The results show clearly that in the mean, real life cookstove use emits more than occurs under laboratory and controlled conditions. Nevertheless, the measurements continue to show that fuel type is a critical variable in cookstove performance. However, the effect from stove activity, such as the fluctuation during combustion process and the start and stop stages, should be considered in modeling and designing controlled laboratory experiment. This field dataset provides a good reference for the potential future research that includes but not limit to regional modeling, laboratory testing protocol design, and so on.

Appendices

A Carbon Balance Method

The carbon balance method is developed by Crutzen et al. [171] and has been widely employed in biomass combustion emission studies [74, 76, 79, 180, 181, 182, 183]. The method is based on the mass balance of carbon in the combustion process. As shown in equation A.1, C_f is the carbon mass in fuel, C_a is the unburned carbon remaining in ash and char, and C_T is total carbon mass in the emissions. C_T includes the carbon mass in each species. In this study, the considered species includes carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4), total non-methane hydrocarbon ($TNMHC$), and total suspended particles (TSP).

$$C_f - C_a = C_T \tag{A.1}$$

where

$$C_T = C_{CO_2} + C_{CO} + C_{CH_4} + C_{TNMHC} + C_{TSP} \tag{A.2}$$

Combine and rearrange the two equations:

$$\frac{C_f - C_a}{C_{CO_2}} = 1 + \frac{C_{CO}}{C_{CO_2}} + \frac{C_{CH_4}}{C_{CO_2}} + \frac{C_{TNMHC}}{C_{CO_2}} + \frac{C_{TSP}}{C_{CO_2}} \tag{A.3}$$

$$= 1 + K \tag{A.4}$$

and

$$K = \frac{C_{CO}}{C_{CO_2}} + \frac{C_{CH_4}}{C_{CO_2}} + \frac{C_{TNMHC}}{C_{CO_2}} + \frac{C_{TSP}}{C_{CO_2}} \tag{A.5}$$

Thus,

$$C_{CO_2} = \frac{C_f - C_a}{1 + K} \tag{A.6}$$

The emission factor E_m for a pollutant is defined as the mass of the pollutant emitted per mass of fuel consumed (M) [74]. The emission factor for carbon in CO_2 can be calculated with the equation:

$$E_{m.C_{CO_2}} = \frac{C_f - C_a}{(1 + K)M} \tag{A.7}$$

and the emission factor for CO_2 is:

$$E_{m.CO_2} = \frac{C_f - C_a}{(1 + K)M} \cdot f_{CO_2} \tag{A.8}$$

where f_{CO_2} is a factor for converting carbon mass to the compound mass, which can be calculated with the molecular mass of the corresponding compound.

$$f_x = \frac{(MW)_x}{(MW)_C} \tag{A.9}$$

In the case of CO_2, as the molecular weight of CO_2 is 44 and that for carbon in CO_2 is 12, $f_{CO_2} = 3.67$. For other compounds in the emissions.

$$E_{m.X} = E_{m.C_X} \cdot \frac{(MW)_X}{12} \tag{A.10}$$

and

$$\begin{aligned} E_{m.C_X} &= \frac{C_X}{C_{CO_2}} \cdot E_{m.C_{CO_2}} && \text{(A.11)} \\ &= \frac{C_X}{C_{CO_2}} \cdot E_{m.CO_2} \cdot \frac{12}{(MW)_{CO_2}} && \text{(A.12)} \end{aligned}$$

Substitute equation A.12 into equation A.10:

$$\begin{aligned} E_{m.X} &= \frac{C_X}{C_{CO_2}} \cdot E_{m.CO_2} \cdot \frac{12}{(MW)_{CO_2}} \cdot \frac{(MW)_X}{12} && \text{(A.13)} \\ &= \frac{C_X}{C_{CO_2}} \cdot E_{m.CO_2} \cdot \frac{(MW)_X}{(MW)_{CO_2}} && \text{(A.14)} \end{aligned}$$

Equation A.14 gives the emission factor for compounds X. In actual usage, as the mass ratio of compounds $\frac{X}{CO_2}$ is easier to obtain than the mass ratio of carbon $\frac{C_X}{C_{CO_2}}$, the calculation can be further simplified:

$$\begin{aligned} \frac{C_X}{C_{CO_2}} &= \frac{X \cdot \frac{12}{(MW)_X}}{CO_2 \cdot \frac{12}{(MW)_{CO_2}}} && \text{(A.15)} \\ &= \frac{X}{CO_2} \frac{(MW)_{CO_2}}{(MW)_X} && \text{(A.16)} \end{aligned}$$

Substitute equation A.16 into equation A.14.

$$\begin{aligned} E_{m.X} &= \frac{X}{CO_2} \frac{(MW)_{CO_2}}{(MW)_X} \cdot E_{m.CO_2} \cdot \frac{(MW)_X}{(MW)_{CO_2}} && \text{(A.17)} \\ &= \frac{X}{CO_2} \cdot E_{m.CO_2} && \text{(A.18)} \end{aligned}$$

The major advantage of using the carbon balance method to calculate the emission factor is that this approach requires the measurement of emission ratios (to carbon dioxide) rather than absolute mass for each compound. With the assumption of the flue gas stream being well mixed, this method provides great flexibility for probe position and also excludes the interference of natural dilution from surrounding air [74, 73].

The emission factor calculation with the carbon balance method is based on the carbon content in the consumed fuel. Thus, the fuel consumption information and carbon fraction in the fuel are critical. In this study, for agriculture based fuel, such as wood and agricultural residue, the carbon content is assumed to be 50%. According to the study conducted by Gaur and Reed [184], this approximation is fairly uniform among pine and oak. Figure A.1 provides the fuel reference information used in this study.

	NCV (MJ/kg)	% Carbon	Char NCV	Char % Carbon	Fraction of fuel carbon assumed to remain as char
Wood	19.0	50%	29.5	95%	0.01
Charcoal	28.2	95%	28.2	95%	0.005
Paper/cardboard	19.0	50%	29.5	95%	0.01
LPG	44.7	82%	-		0
Kerosene	39.7	85%	-		0
Rice husks	-		-		0.01
Corn Cobs	-		-		0.01
Crop residues (general)	13.4	50%	29.5	95%	0.01
Dung	12.3	50%	29.5	95%	0.01
Biogas	-		-		0
Plastic	-		-		0
Ethanol	26.7	52%	-		0
Methanol	21.1	38%	-		0
Coal	23.5	75%	29.5	95%	0.005
palm/dung	13.38	50%	29.5	95%	0.01

Figure A.1: The fuel reference table [184]

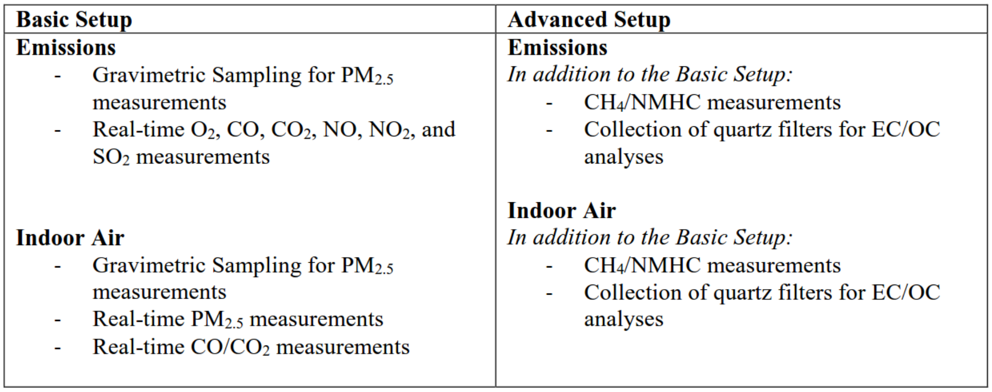
B Standard Operating Procedure for Emissions & Indoor Air Sampling

1. Statement of Purpose

   This protocol describes the instrumentation and general procedures used for stove emissions measurement conducted in Ulaanbaatar, Mongolia.

2. Equipment requirement

   Two types of setup were used in the measurement of emissions.



Basic Setup	**Advanced Setup**
Emissions - Gravimetric Sampling for $PM_{2.5}$ measurements - Real-time O_2, CO, CO_2, NO, NO_2, and SO_2 measurements	**Emissions** *In addition to the Basic Setup:* - CH_4/NMHC measurements - Collection of quartz filters for EC/OC analyses
Indoor Air - Gravimetric Sampling for $PM_{2.5}$ measurements - Real-time $PM_{2.5}$ measurements - Real-time CO/CO_2 measurements	**Indoor Air** *In addition to the Basic Setup:* - CH_4/NMHC measurements - Collection of quartz filters for EC/OC analyses

Qty. Basic	Qty Adv.	Abbreviation	Description
1	1	TESTO	Testo 350 M/XL or 350 Flue Gas Analyzer
1	1	DT	TSI DustTrak II Aerosol Monitor
1	1	QT	TSI Q-Trak 7565/7575 CO & CO2 Monitor
1	1	CYCLONE	BGI Triplex Cyclone
2	2	AC PUMP	SKC PCXR8 or XR5000 Universal Pump
1	2	LP	SKC Pocket Pump
2	2	TF	37mm PTFE (Teflon) 2.0um Pore Size Filters (loaded into cassettes)
-	4	QZ	47mm Quartz Filters
1	2	0.5L BAG	0.5L FlexFoil Gas Sampling Bag
1	2	200L BAG	200L Tedlar/Kynar Gas Sampling Bag
1	1	HEPA	HEPA Filter Capsule
2	2	WATERTRAP	Water Trap

2.1. Basic setup

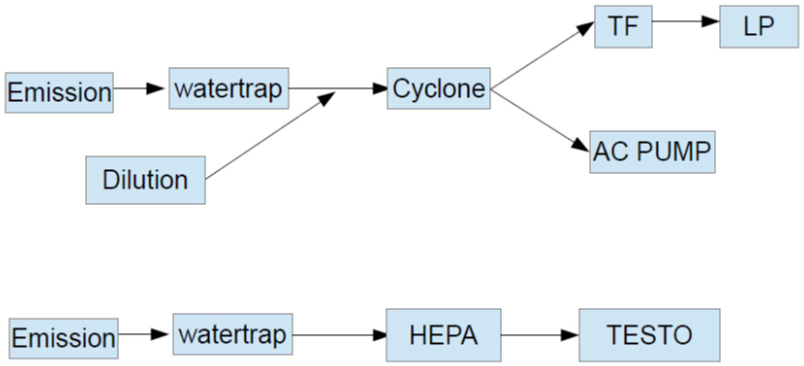


Figure B.2: Basic Emission Sampling Train

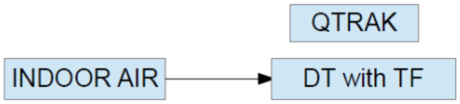


Figure B.3: Basic Indoor Air/Background Sampling Train

2.2. Advanced setup

3. Preparation of instruments prior to transport to sampling site

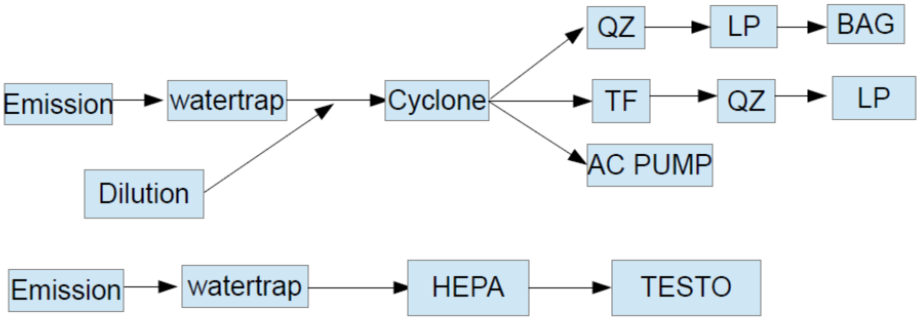


Figure B.4: Advanced Emission Sampling Train

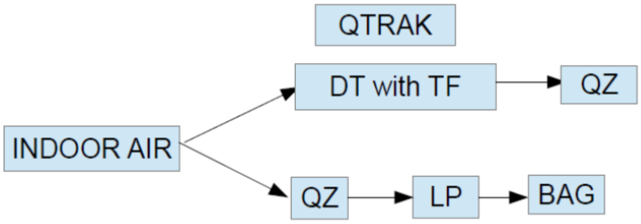


Figure B.5: Advanced Indoor Air/Background Sampling Train

3.1. A unique sample identification number should be assigned to each household, based on a household survey, which will have emission and indoor air tested. All instrument IDs and pump IDs are to be recorded by each sampling team.

3.2. Filter preparation

  3.2.1. Quartz filters should be loaded properly in the conductive filter cassette before transporting to field locations.

  3.2.2. All PTFE filters are preloaded into the filter cassettes and are kept sealed before each measurement. Filter IDs are to be recorded.

3.3. All instruments and pumps should be fully charged before each sampling period.

4. Installation of instruments at sampling site

4.1. Household information needs to be recorded (household ID, stove type, resident type, etc.)

- 4.2. Record the fuel type and perform an initial fuel weighing as specified on the *Sampling Train Datasheet*
- 4.3. Find a location to set up the sampling equipment (upon approval of household owner) and perform the setup.
  - 4.3.1. Placement and installation of emissions sampling train-setup
    - 4.3.1.1. Emissions train should be placed near the stove without causing any potential interference with household members.
    - 4.3.1.2. Assess the stove to determine how the probe should be installed.
      - 4.3.1.2.1. A 1/4″ drilled hole may be required for insertion of probe into the flue and repaired/restored following sampling measurements.
      - 4.3.1.2.2. Make sure that the tubing of the probe is clear of debris. Unclog and clean, if necessary.
    - 4.3.1.3. Placement and installation of indoor air sampling train setup
      - 4.3.1.3.1. The indoor air train should be placed away from the stoves, doors, and windows.
      - 4.3.1.3.2. The sampling probe is installed within the breathing zone (approx. 1.2m)
  - 4.3.2. Measure and record the required initial (pre-measurement) flow rates.
  - 4.3.3. Make certain the all real-time instruments are working properly and record the start time.
  - 4.3.4. Take a photo of the household and sampling train setup for the record.

5. Retrieval of instruments at sampling site.

- 5.1. Record stop time

- 5.2. Check all instruments for normal functionality. Record any issues on the *Sampling Train Datasheet*.
- 5.3. Remove PTFE filters from pump and/or instrument and cap both ends of the filter cassette. Remove quartz filters from the black conductive cassettes and package them into the filter petrislides, seal with Teflon tape.
- 5.4. Record final (post-measurement) flow rate and pump sampling duration (time elapsed).
- 5.5. Stop all the real time instrument and pump.
- 5.6. Perform a final fuel weighing.
- 5.7. Transfer the collected gas sample from 200L gas sampling bag into 0.25L MMT gas sampling bag.
  - 5.7.1. 0.25L MMT bag needs to be "washed" with sample gas three times before the transfer.
  - 5.7.2. Deflate the 200L gas sampling bag, once finished.

6. Quality Assurance/Quality Check (QA/QC)
   - 6.1. Field blanks are conducted for both quartz and PTFE filters.
   - 6.2. Calibration gas bags are shipped to the field and returned to location of gas analysis for QC checks.

7. Post-measurement data uploading and instrument maintenance/cleaning
   - 7.1. Charge all batteries and instruments
   - 7.2. Upload data from all real-time instruments to field laptop and backup data.
   - 7.3. Transcribe written field data from *Sampling Train Datasheet* to PDF version of the datasheet.

- 7.3.1. Synchronization of datasheet and all field data (i.e. DustTrak, Q-Trak data files, etc.) to online cloud storage for backup and accessibility.
- 7.3.2. Take a photo of the original datasheet as backup.

7.4. Post-sampling filter and gas bag handling

- 7.4.1. Quartz filter requires cold storage
- 7.4.2. PTFE filter needs to be sealed
- 7.4.3. Gas sampling bags should be kept away from sharp items to prevent puncture of bags.

7.5. The DustTrak II $PM_{2.5}$ impactor requires cleaning after each measurement.

- 7.5.1. Consult user manual for step-by-step instructions.

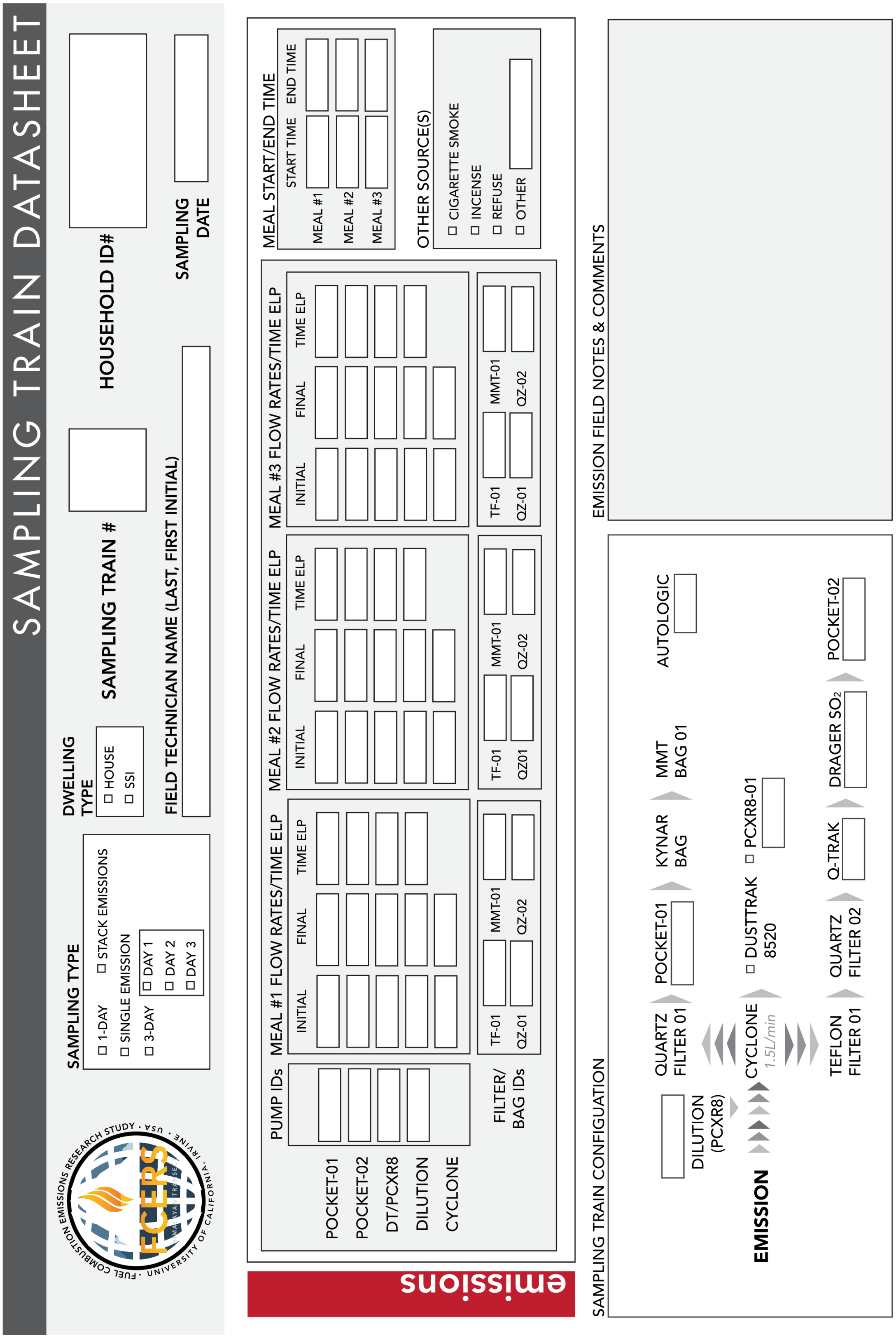
7.6. Check the internal filters for DustTrak II, Testo Gas Analyzer, and pumps.

- 7.6.1. Replace filter, if necessary.

7.7. For gas bag measurements, if the 200L gas sampling bag was not well inflated from the last measurement, perform a leak check in the lab.

- 7.7.1. Re-seal the bag if there are any leaks.

C Field Sampling Datasheet



SAMPLING TRAIN DATASHEET

FUEL COMBUSTION EMISSIONS RESEARCH STUDY · USA · UNIVERSITY OF CALIFORNIA, IRVINE · FCERS

SAMPLING TYPE
☐ 1-DAY ☐ STACK EMISSIONS
☐ SINGLE EMISSION
☐ 3-DAY ☐ DAY 1 ☐ DAY 2 ☐ DAY 3

DWELLING TYPE
☐ HOUSE
☐ SSI

SAMPLING TRAIN #

HOUSEHOLD ID#

FIELD TECHNICIAN NAME (LAST, FIRST INITIAL)

SAMPLING DATE

emissions

	PUMP IDs
POCKET-01	
POCKET-02	
DT/PCXR8	
DILUTION	
CYCLONE	

MEAL #1 FLOW RATES/TIME ELP

INITIAL	FINAL	TIME ELP

MEAL #2 FLOW RATES/TIME ELP

INITIAL	FINAL	TIME ELP

MEAL #3 FLOW RATES/TIME ELP

INITIAL	FINAL	TIME ELP

FILTER/ BAG IDs

Meal #1		Meal #2		Meal #3	
TF-01		TF-01		TF-01	
MMT-01		MMT-01		MMT-01	
QZ-01		QZ01		QZ-01	
QZ-02		QZ-02		QZ-02	

MEAL START/END TIME

	START TIME	END TIME
MEAL #1		
MEAL #2		
MEAL #3		

OTHER SOURCE(S)
☐ CIGARETTE SMOKE
☐ INCENSE
☐ REFUSE
☐ OTHER

SAMPLING TRAIN CONFIGUATION

EMISSION

DILUTION (PCXR8)

CYCLONE 1.5L/min

QUARTZ FILTER 01

POCKET-01

KYNAR BAG

MMT BAG 01

AUTOLOGIC

☐ DUSTTRAK 8520 ☐ PCXR8-01

TEFLON FILTER 01

QUARTZ FILTER 02

Q-TRAK

DRAGER SO_2

POCKET-02

EMISSION FIELD NOTES & COMMENTS

SAMPLING TRAIN DATASHEET

SAMPLING TYPE

☐ 1-DAY ☐ STACK EMISSIONS
☐ SINGLE EMISSION
☐ 3-DAY ☐ DAY 1
☐ DAY 2
☐ DAY 3

DWELLING TYPE

☐ HOUSE
☐ SSI

SAMPLING TRAIN #

HOUSEHOLD ID#

FIELD TECHNICIAN NAME (LAST, FIRST INITIAL)

SAMPLING DATE

background

	PUMP IDs	MEAL #1 FLOW RATES/TIME ELP			MEAL #2 FLOW RATES/TIME ELP			MEAL #3 FLOW RATES/TIME ELP		
		INITIAL	FINAL	TIME ELP	INITIAL	FINAL	TIME ELP	INITIAL	FINAL	TIME ELP
POCKET-03										
PCXR8-02										
DILUTION										
CYCLONE										

FILTER/ BAG IDs	MEAL #1				MEAL #2				MEAL #3			
	TF-02		MMT-02		TF-02		MMT-02		TF-02		MMT-02	
	QZ-03		QZ-04		QZ-03		QZ-04		QZ-03		QZ-04	

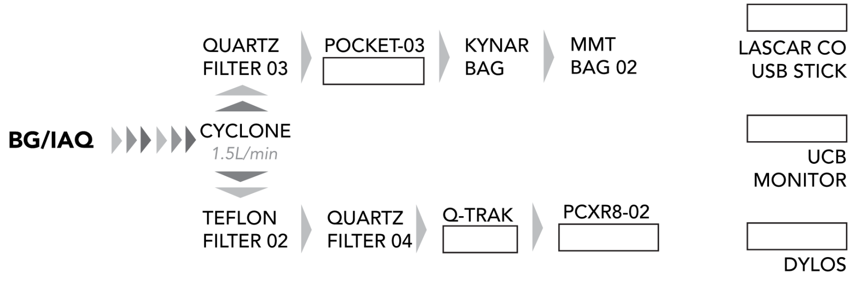
MEAL START/END TIME

	START TIME	END TIME
MEAL #1		
MEAL #2		
MEAL #3		

OTHER SOURCE(S)

☐ CIGARETTE SMOKE
☐ INCENSE
☐ REFUSE
☐ OTHER

SAMPLING TRAIN CONFIGUATION



BG FIELD NOTES & COMMENTS

SAMPLING QUESTIONNAIRE

SAMPLING DATE

SAMPLING TYPE
☐ 1-DAY ☐ SINGLE EMISSION
☐ 3-DAY ☐ STACK EMISSIONS

DWELLING TYPE
☐ HOUSE
☐ SSI

SAMPLING TRAIN #

HOUSEHOLD ID#

MEAL/ACTIVITY

DESCRIPTION OF ACTIVITY

CURRENT HH
ADULTS
CHILDREN

DURATION
ESTIMATED
ACTUAL

FUEL TYPE(S)
☐ WOOD
MOISTURE READINGS
1 2 3
STARTING WT
ENDING WT
TYPE

☐ COAL
STARTING WT
ENDING WT
☐ GAS FAT
☐ 1/3 COKING
☐ SMOKELESS
☐ SMOKY
☐ OTHER

☐ OTHER
STARTING WT
ENDING WT

STOVE TYPE
☐ CHIMNEY
☐ HIGH STOVE (HS)
☐ LOW STOVE (LS)
☐ PORTABLE STOVE (PS)
☐ OTHER

STOVE USE/ACTIVITY

MEAL/ACTIVITY

DESCRIPTION OF ACTIVITY

CURRENT HH
ADULTS
CHILDREN

DURATION
ESTIMATED
ACTUAL

FUEL TYPE(S)
☐ WOOD
MOISTURE READINGS
1 2 3
STARTING WT
ENDING WT
TYPE

☐ COAL
STARTING WT
ENDING WT
☐ GAS FAT
☐ 1/3 COKING
☐ SMOKELESS
☐ SMOKY
☐ OTHER

☐ OTHER
STARTING WT
ENDING WT

STOVE TYPE
☐ CHIMNEY
☐ HIGH STOVE (HS)
☐ LOW STOVE (LS)
☐ PORTABLE STOVE (PS)
☐ OTHER

STOVE USE/ACTIVITY

MEAL/ACTIVITY

DESCRIPTION OF ACTIVITY

CURRENT HH
ADULTS
CHILDREN

DURATION
ESTIMATED
ACTUAL

FUEL TYPE(S)
☐ WOOD
MOISTURE READINGS
1 2 3
STARTING WT
ENDING WT
TYPE

☐ COAL
STARTING WT
ENDING WT
☐ GAS FAT
☐ 1/3 COKING
☐ SMOKELESS
☐ SMOKY
☐ OTHER

☐ OTHER
STARTING WT
ENDING WT

STOVE TYPE
☐ CHIMNEY
☐ HIGH STOVE (HS)
☐ LOW STOVE (LS)
☐ PORTABLE STOVE (PS)
☐ OTHER

STOVE USE/ACTIVITY

D SOP for Gravimetric Filter Sampling

1. Statement of Purpose
    1.1. Overview of filter handing, preparation, sampling, and analysis for gravimetric measurements.
2. Standard equipment & supplies
    2.1. 37mm SKC PTFE Filter with a 2.0 m pore size (SKC Inc., cat. 225-1709)
    2.2. 37mm SKC 2-Piece Clear Styrene Cassette (SKC Inc., cat. 225-2050LF)
    2.3. BIOS 510M Defender Primary Standard Flow Calibrator, 50 to 5000 ml/min
    2.4. BGI Triplex Cyclone (SCC 1.062) - $PM_{1.0}$, $PM_{2.5}$ & Respirable
    2.5. SKC PCXR8 AirChek Universal Air Sampling Pump (SKC Inc., cat. 224-PCXR8)
    2.6. SKC PocketPump Twin-Port Air Sampling Pump (SKC Inc., cat. 210-1002A)
    2.7. CAHN Model 29 Electrobalance (repeatability of 1.0g)
3. Balance room location characteristics
    3.1. Environmentally-controlled laboratory room
    3.2. Balance stationed on vibration-free table
    3.3. Mean temperature: $20 - 30 \pm 2°\text{C}$ over 24 hours
    3.4. Mean humidity: $30 - 40\%$ RH $\pm 5\%$ over 24 hours
4. Gravimetric analysis
    4.1. Filters are equilibrated before weighing as specified in section 5.1.

    - 4.2. Filter is passed between two polonium ionizing strip (StaticMaster Ionizing Unit, Model No. 2U500) for removal of electrostatic charges.
    - 4.3. Each PTFE filter is weighed three times, and repeated if not within ±3.0g
    - 4.4. Values are recorded in milligrams to 3 decimal places.
    - 4.5. Collected field data (i.e. sampling duration, difference in pre- and post-weight, etc.) is analyzed and $PM_{2.5}$ concentrations are calculated in milligrams per cubic meter (mg/m^3).

5. Filter conditioning and Quality Check (QC)
    - 5.1. For pre- and post-sampling weighing, filters are conditioned/equilibrated in the controlled environment for a minimum of 24 hours.
    - 5.2. Both pre- and post-sample weighing is carried out on the same balance.
    - 5.3. Balance room laboratory filter blanks and 100mg standard weight are utilized as QC checks.
    - 5.4. Field blanks are collected for QC checks.
        - 5.4.1. Cassette-loaded PTFE filters are transported to the field office, and are then uncapped and recapped during calibration and setup of pumps before being taken out into the field.

6. Pre-sampling filter preparations
    - 6.1. PTFE filters are inspected, equilibrated, pre-weighed, and loaded into 37mm 2-piece clear styrene cassettes (SKC Inc., cat. 225-2050LF). Filter weighing procedures specified in section 4.1-4.4.
    - 6.2. Filter identification
        - 6.2.1. All cassette-loaded PTFE filters are tagged with a unique identification barcode. LOCATION_TF000 (i.e. MNG_TF042)

7. Field measurements
    7.1. BGI Triplex Cyclone was used in conjunction with programmable sampling pumps set at specified flow rates for a combined flow rate of 1.5L/min.
    7.2. Pump flow rates are measured with a BIOS 510M Defender Primary Standard Flow Calibrator to verify accuracy before and after sampling.
        7.2.1. Flow rates are recorded before and after each sampling period.
        7.2.2. Time elapsed (sampling duration) of each pump are recorded.
8. Filter transport & storage
    8.1. Exposed PTFE filters/cassettes are capped and refrigerated at 4°C, until post-weighed.
9. Post-sampling preparations
    9.1. Post-sampling exposed filters are removed from cassettes and transferred to petrislides prior to post-weighing.
    9.2. Exposed filters are equilibrated, inspected, and post-weighed. Filter weighing procedures specified in section 4.1-4.4.
10. Reference
    10.1. Environmental Protection Agency (EPA). (1998). Quality Assurance Guidance Document, Method Compendium: $PM_{2.5}$ Mass Weighing Laboratory Standard Operating Procedures for the Performance Evaluation Program.

E SOP for Gas Sampling Methodology

1. Statement of Purpose
    1.1. Overview of gas sampling bag handing, preparation, and gas chromatography analysis.
2. Standard equipment & supplies
    2.1. 0.5L FlexFoil Gas Sampling Bag (Calibrated Instruments Inc., USA)
    2.2. 200L Kynar Gas Sampling Bag (Analytical Specialties, Inc., USA)
    2.3. SKC PCXR8 AirChek Universal Air Sampling Pump (SKC Inc., cat. 224-PCXR8)
    2.4. SKC PocketPump Twin-Port Air Sampling Pump (SKC Inc., cat. 210-1002A)
    2.5. BIOS 510M Defender Primary Standard Flow Calibrator, 50 to 5000 ml/min
    2.6. Agilent 6890N Gas Chromatograph with FID
3. Gas bag identification
    3.1. All 0.5L gas sampling bags are tagged with a unique identification barcode. LOCATION_MMT000 (i.e. MNG_MMT042)
4. Standard calibration gas
    4.1. Standard predetermined concentrations (ppm) of specific gases (CO, CO2, and CH4)
        4.1.1. Carbon Monoxide (1,000ppm) in Nitrogen balance (Air Liquide America Specialty Gases LLC, USA)

        - 4.1.2. Carbon Dioxide (1,600ppm) in Nitrogen balance (Air Liquide America Specialty Gases LLC, USA)
        - 4.1.3. Methane (100ppm) in Nitrogen balance (Air Liquide America Specialty Gases LLC, USA)
        - 4.1.4. Carbon Dioxide (3% Vol.), Carbon Monoxide (2,500ppm), and Methane (400ppm) in Helium balance (Air Liquide America Specialty Gases LLC, USA)

5. Field measurements
    - 5.1. Pump flow rates are measured with a BIOS 510M Defender Primary Standard Flow Calibrator to verify accuracy before and after sampling.
        - 5.1.1. Flow rates are recorded before and after each sampling period.
        - 5.1.2. Time elapsed (sampling duration) of each pump are recorded.

6. Quality Assurance (QA) and Quality Check (QC)
    - 6.1. Calibration gases are loaded into 0.5L FlexFoil gas sampling bags and are brought into the field and remains with other field gas samples until the end of the sampling period
        - 6.1.1. The standard gas concentrations will be analyzed to determine any potential contamination or interference during transport of the gas samples.

7. Gas chromatography analysis
    - 7.1. CO2, CO, and CH4 were analyzed using a Agilent 6890N gas chromatograph with a flame ionization detector (FID) equipped with a nickel (Ni) catalyst methanizer (SRI Instruments, USA), with the following columns used: Molecular Sieve 5A Porous Layer Open Tubular Capillary Column

(Restek, cat no. 19720) and Agilent J&W Scientific GS-CarbonPLOT column (Agilent, cat no. 113-3133).

7.2. A 100L gastight Hamilton syringe (Hamilton, USA) was used to inject 100L from the 0.5L FlexFoil gas sampling bags.

7.3. Seven-point calibration curves were made for the quantification of gaseous species using dilutions of NIST traceable gas standard mixture and individual gas standards.

7.4. Samples were randomly selected for duplicate analysis.

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