Letter to the Editor:

Dear Editor,

We would like to thank the two reviewers for their careful reading and constructive comments.

We are attaching our final response to the reviewers' comments and the revised manuscript, which incorporates the comments and changes suggested by the reviewers.

Thank you in advance for your consideration.

Best regards,

Luisa Molina

Responses to Reviewer 1

Worldwide communications/publications on the environmental properties of brick kiln burns are progressively more detailed (in the sense of number of environmental pollutants measured) and analytic, this paper follows this pattern. Nevertheless, the authors mention a problem of which this reviewer is quite aware and which represents the primary weak point of this paper: variability between burns for a number of reasons, mentioned too briefly in this paper. This variability has been noted in other papers of the author's recent reviews, in kiln research from South Africa and Vietnam, for example. For this paper the problem is more severe than for the others since only one burn for each of several variations of kilns was performed. Either the procedures / materials / specific construction must be specified or. . .a number of complete burns must be monitored to be definitive about various features and quantities. . .anything less is not definitive of the characteristics. What can be done? The authors can make the point more clearly that this represents a sampling and is not a definitive comparative description: to compare, fuel/stacking/similar clays/ brick additives/feeding procedures or knowledge of aging of the kilns (# of previous burns in the same kiln) were not standardized nor described. Complete burns

Response

We thank the reviewer, Dr. Charles Bruce, for his constructive comments on this paper.

The main concern expressed by the reviewer is the inherently large variability of the brick production process. As the reviewer pointed out, a small sampling size is a common issue in the scarcely available literature on brick kilns emissions characterizations worldwide. This is perhaps in part due to the considerable logistical complexity of real world measurements for these sources, but also to the large combination of materials, fuels, kiln types, and operational practices that brick producers use. This further highlights the strong need to increase the number of databases on locally-measured emission characteristics of brick kilns.

As the reviewer pointed out, this issue can be addressed in two ways: either by describing the particular parameters (materials, fuels, operational practices) of the brick production process for each kiln sampled, or by attempting to standardize the processes for the purpose of measurements. However, artisanal production of bricks is by definition not standardized as it depends on the variations of kiln types and burning practices that are generationally learned by producers, and adjusted by clay type and fuel availability. Therefore, we believe it is better to describe in more detail the conditions of the brick-making processes during samplings, as these represent artisanal combustion processes. This will also facilitate future comparisons with other results.

As suggested, we have now included more detailed descriptions of the clay, fuels, and additives used as well as fuel feeding practices during the sampling of the brick kilns. The descriptions have been added in section 6 of the Supplement Material document to keep the readability in the main manuscript. We have also expanded the discussions on the reasons for the variability between burns and further

clarified that the results are not intended to be definitive generalizations of the brick making process but to help in the understanding of the effects of different kiln designs and fuels on gaseous and particulate phase emissions from brick kilns.

As an additional note, although due to the nature of the brick-making process it is not possible to standardize the burning practices for sampling purposes, it is certainly possible to standardize the sampling techniques and analysis protocols used. We recommend this practice in our study by using the methodology recently proposed by the Climate and Clean Air Coalition Brick Production Initiative. This will allow further reducing the uncertainty during the comparison of our results with future studies.

On other issues: 1. Sampling downstream: many papers have made attempts to quantify dispersion in two dimensions. I have to think that they do not understand dispersion theory, another very poorly defined result. Could have been done much better. Next time profile the downwind cross section using instrumented drones or other methods to be more definitive. Just not worthwhile as performed here.

Response

The reviewer's comment suggests that some clarification may be needed in the Methods section. In this paper we have not attempted to quantify the dispersion of air pollutants or obtain the cross section or any sort of spatial representation of the brick kilns emission plumes. We have further clarified this by explicitly stating in the methods section that the well-established plume tracer ratio technique is not meant to address the aforementioned issues but to quantify the emission rates of co-emitted pollutants from a single source. Although the technique has been successfully applied multiple times to other sources (e.g., wastewater treatment plants, industrial stacks, etc.), to our knowledge this technique had never been applied for measuring emissions from brick production and therefore it is worthwhile to compare it with the more traditional filter-based technique.

2. What supplemental documents? This article should stand on its own or on previous publications.

Response

We believe the additional materials provided in the supplement material document will be valuable to the readers. The supplemental material document includes: 1) descriptions of the fuel types and analysis of chemical compositions of fuels and materials used for each kiln; 2) technical characteristics of instrumentation used; 3) additional results on the mechanical resistance analysis of the bricks and emission factors obtained. We have further added a detailed description of the artisanal brick-making process for each kiln. We believe this additional information will allow the reader to more completely understand the context of the samplings.

3. Data on the MK2 will depend on development in three defined intervals; pre-switch, transition to coupled kilns and final the coupled burn. . .all very distinct and not even discussed. Frequency of sampling? Quality of temporal integration?

Response

As described above, detailed information on the artisanal brick-making procedures for the sampled kilns, including the MK2 kiln, has now been added in the Supplemental Material document. The sampling frequency and temporal integration of the samplings are already described in the Methods section.

4. Chemistry: nicely done and informative. . . Just with the previous concerns for representation.

Response

We appreciate the comment from the reviewer. As stated above and in the manuscript, the results of this study should not be considered as generalizations of brick production practices due to the various combination of materials, fuels, kiln types, and operational practices that brick producers use. However, we believe that the results contribute to the understanding of the chemical characterization of emissions from brick kilns and represent valuable additions to the currently scarce literature.

5. Temperature profiles were puzzling, too sparse to analyze.

Response

As mentioned in the manuscript, temperature profiles were obtained at the lower, middle, and upper levels of each kiln using thermocouples and the average results are presented in Figure 3. We have now further clarified in the methods and results sections that the temperature measurements were obtained using four thermocouples at each of the three levels. In other words, we obtained three cross-sections (each at a different level) using 12 temperature measurements for each kiln. The analyses and discussions on the average temperature profiles that we present in the manuscript are directed towards: 1) defining the stages of the brick production process for our chemical analysis purposes, 2) understanding the relations between vertical changes in heating rates inside the kiln and the mechanical resistance of the produced bricks.

As a corollary, our results indicate that the spatial distribution of the internal temperature in the kiln is closely related to quality of the products. Thus we suggest that improving the structural design and thermal energy transfer of brick kilns could be an alternative way of increasing the efficiency of brick kiln production.

6. Spatial representation of the outflow requires time to average in each location. Uncertain how well performed. Like many points is undefined. In summary, should be presented as a first try at comparison but not as definitive.

Response

Our study is not directed towards obtaining the spatial representation of the brick kiln emissions outflow and this has now been clarified in the methods section.

“The second technique used to sample the kilns was based on the tracer ratio method in which the emission rate of the targeted source is obtained by simultaneously measuring in real-time the above-background concentrations of the species of interest and of a selected gas tracer with a known release rate that is co-located at the emission source (Lamb et al., 1995). This method is based on the fundamental assumption that a relatively unreactive mixture of gases emitted from a common location experiences a quasi-perfect co-dispersion and equivalent dilution through the atmosphere. The tracer ratio method does not quantify the dispersion of air pollutants or the spatial representation of the brick kilns emission plumes, but is used to quantify the emission rates of co-emitted pollutants from a single source.”

Responses to Reviewer 2

It is an interesting and well prepared field monitoring work for obtaining the emission factors of various pollutants and PM associated chemical components from brick kilns. It is very helpful for the emission inventory updating and related human health risk assessment research. Also considering the difficulty and the complexity of this type of motoring works, I highly recommend the publication of this manuscript after the following questions are answered and corresponding revisions are done.

Response

We thank the reviewer for the thoughtful comments on the paper.

(1) Please give a sampling frame figure, after Figure 1, to clear show the size of the brick kilns, the relative location of the sampling probe, the relative location of the AML. It is very important for the comparison of the emission factors as the location reflects the dilution extent of the flumes, considering quantitative dilution effect could not be obtained in this study.

Response

We have included in the Supplemental Material document additional figures showing the locations of the samplings and the spatial location of the AML with respect to the kilns. These figures were included in the Supplemental Material document to keep the readability in the manuscript. We have also included additional information on the artisanal brick making procedures for each sampled kiln.

(2) The range of 20-100 m is huge enough for the chemical evolution and variation of flumes. How the authors consider its impact on the emission factors? In Table 1, the OC emission factors are quite different for the two methods. The authors should give clear suggestions that when establishing the emission inventory, which emission factors should be selected.

Response

The typical distances of the AML to the kilns ranged from about 20-100 m, depending on the feasibility to “find” the plume. As stated in the manuscript, the calculation of the emission factors using the tracer sampling technique does not requires the estimation of the dilution of the plumes because the analysis is based on the ratios of the targeted species and the tracer. This is possible due to the very low detection and high precision limits of the instruments on-board the AML. However, as pointed out by the reviewer it is possible that some condensation of SVOCs occurs as the plume cools, thereby increasing the OC content into the particle phase. One possibility to quantify this effect for a future experiment would be through mass balance while measuring individual VOCs both directly at the emission point and downwind together with OC, but this is beyond the scope of our paper. We have now included a paragraph acknowledging this effect and a note in the results tables (Tables 2 and 3). The following paragraph has been added for clarification:

"In this study, condensation of emitted semi-volatile VOCs between the top of the kiln and the sampling location of the mobile laboratory downwind the plume is possible due to the strong temperature gradient, adding organic content to the measured OC. However, quantification of this effect is beyond the scope of this study."

"Results for OC and VOCs obtained with the tracer ratio method include the effects of possible condensation of organics into the particle phase."

(3) I am not clear about how the author obtain the release flow rate of tracers. By AML, you can just obtain the emission concentrations, but not the flow rate information.

Response

We thank the reviewer for pointing out the need to clarify the measurement of the release flow of the tracers. The following paragraph has been added in the manuscript:

"The tracer gas was released from a compressed gas cylinder of pure N_2O located in a separate vehicle. The flow rate was controlled with an MKS mass flow controller (MFC), which was calibrated against a traceable Drycal mass flowmeter several times over the course of the measurement campaign. A 3/8" polyethylene tube extended from the mass flow controller to the desired location, allowing the cylinder and MFC to be located in a close but safe distance from the kiln. Mass flow rates were digitally recorded, and manually logged."

(4) I wonder whether the emission concentration is too high for the detection of SP-AMS. Please give detailed operating procedures for the switch of BC and other components monitoring by SP-AMS during the whole sampling period.

Response

The SP-AMS is able to handle high concentrations of particulate matter routinely. It is frequently used in source studies where organics and black carbon may be higher than 100 $\mu g/m^3$ (Massoli et al., 2012; Zavala et al., 2017). The SP-AMS does use the same laser as an SP2 system but it uses the laser for a different purpose. In the case of the SP-AMS it is simply using the laser to heat the particle beam creating gas phase molecules which are then ionized by reaction with electrons being emitted by a tungsten filament. This measurement technique is really not negatively impacted as concentrations increase.

Regarding switching related to BC there is no switch between measurement modes. The following paragraph has been added in the Methods section:
"The SP-AMS acquires data in 1 second mode during which it obtains an average mass spectrum sampling from 12-1000 m/z. The mass spectrum is then processed and high resolution fits are applied to

peaks (e.g., C_3 at m/z 36 or C_3H_7 at m/z 43) to distinguish between BC and organics. All fit peaks are summed, counted as a particular species and then that species is quantified for each second. There are 2 vaporizers simultaneously heating particles so that gas phase molecules are then available to ionize by reaction with electrons. The laser vaporizer heated particles with a 1064-nm laser while the conventional AMS vaporizer was also present and after passing through the laser vaporizer the particle beam impacted the conventional vaporizer which was heated to 600 ˚C. Inorganic species such as sulfate and nitrate are not vaporized by the 1064-nm laser but were vaporized by a conventional heater."

References:

Massoli, E. C. Fortner, M. R. Canagaratna, L. R. Williams, Q. Zhang, Y. Sun, J. J. Schwab, A. Trimborn, T. B. Onasch, K. L. Demerjian, C. E. Kolb, D. R. Worsnop, J. T. Jayne.: Pollution gradients and chemical characterization of particulate matter from vehicular traffic near major roadways: Results from the 2009 queens college air quality study in NYC, P., Aerosol Science and Technology, 46, 1201-1218, 2012.

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(5) Whether the MCE is of significant differences between the MK2 and Traditional kilns. The one cycle test in this study may be limited. The authors should better describe this.

Response

We have expanded our discussion on the differences between measured modified combustion efficiency (MCE):

"The MK2 and the traditional-campaign kilns presented similar average MCE2 values (0.94 - 0.96) that were higher than for the traditional-fixed kiln (0.91 – 0.92). This is reflected in the much higher CO emission factors for the traditional-fixed kiln in comparison with the other two kilns, indicating overall smaller combustion efficiency. In our study the BC/OC ratios were 5.2, 0.9, and 3.8 for the MK2, traditional-campaign, and traditional-fixed kilns, respectively; whereas the corresponding BC/OC ratios in Christian et al. (2010) ranged from 5.29 to 8.15. Methane, methanol, and acetic acid fuel-based emission factors for the traditional-fixed kiln are 3-5, 2-8, and 5 times higher, respectively, than those reported by Christian et al. (2010). These higher emission factors are consistent with the lower average MCE of 0.910 obtained in this study compared to the average MCE of 0.968 for the traditional-fixed kiln sampled reported by Christian et al. (2010). As a comparison, Stockwell et al. (2016) reported a much higher average MCE value of 0.994 for the zig-zag coal-fueled brick kiln sampled."

References:

Christian, T. J., Yokelson, R. J., Cárdenas, B., Molina, L. T., Engling, G., and Hsu, S.-C.: Trace gas and particle emissions from domestic and industrial biofuel use and garbage burning in central Mexico, Atmos. Chem. Phys., 10, 565–584, doi: 10.5194/acp-10-565-2010, 2010.

Stockwell, C. E., Christian, T. J., Goetz, J. D., Jayarathne, T., Bhave, P. V., Praveen, P. S., Adhikari, S., Maharjan, R., DeCarlo, P. F., Stone, E. A., Saikawa, E., Blake, D. R., Simpson, I. J., Yokelson, R. J., and Panday, A. K.: Nepal Ambient Monitoring and Source Testing Experiment (NAMaSTE): emissions of trace gases and light-absorbing carbon from wood and dung cooking fires, garbage and crop residue burning, brick kilns, and other sources, Atmos. Chem. Phys., 16, 11043-11081, https://doi.org/10.5194/acp-16-11043-2016, 2016.

Black Carbon, Organic Carbon, and Co-pollutants Emissions and Energy Efficiency from Artisanal Brick Production in Mexico

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Abstract. In many parts of the developing world and economies in transition, small-scale traditional brick kilns are a notorious source of urban air pollution. Many are both energy inefficient and burn highly polluting fuels that emit significant levels of black carbon (BC), organic carbon (OC) and other atmospheric pollutants into local communities, resulting in severe health and environmental impacts. However, only a very limited number of studies are available on the emission characteristics of brick kilns; thus there is a need to characterize their gaseous and particulate matter (PM) emission factors to better assess their overall contribution to emissions inventories and to quantify their ecological, human health, and climate impacts. In this study, the fuel-, energy-, and brick-based emissions factors and time-based emission ratios of BC, OC, inorganic PM components, CO, SO_2, CH_4, NO_x, and selected volatile organic compounds (VOCs) from three artisanal brick kilns with different designs in Mexico were quantified using the tracer ratio sampling technique. Simultaneous measurements of PM components, CO and CO_2 were also obtained using a sampling probe technique. Additional measurements included the internal temperature of the brick kilns, mechanical resistance of bricks produced, and characteristics of fuels employed. Average fuel-based BC emission factors ranged from 0.15 – 0.58 g/kg-fuel whereas BC/OC mass ratios ranged from 0.9 - 5.2, depending on the kiln type. The results show that both techniques capture similar temporal profiles of the brick kiln emissions and produce comparable emission factors. A more integrated inter-comparison of the brick kilns' performances was obtained by simultaneously assessing emissions factors, energy efficiency, fuel consumption, and the quality of the bricks produced.

1 Introduction

Artisanal clay brick production using small-scale traditional kilns is a highly polluting activity occurring in developing countries and economies in transition to manufacture building materials. Moreover, traditional brick production is a serious local health hazard to the residents of the poor neighborhoods that typically host brickyards, as well as to brick makers

themselves. Impacts of toxic emissions on brick producers' respiratory health and the environment have been documented in a number of studies (e.g., Zuskin et al., 1998; Co et al., 2009; Martínez-Salinas et al., 2010; Kaushik et al., 2012). Although production zones are clustered at the periphery of -or even within- urban areas, laborers and their families often lack access to adequate public services including clean water, basic sanitation facilities, health services, transport, and education infrastructure. Brick producers often sell the bricks to intermediaries and the economic revenue for producers can be marginal. These conditions contribute to the perpetuation of severe environmental and social injustice problems.

The most current estimates suggest that about 1.5 trillion clay bricks are produced annually, with 90% of the global production generated by Asian countries, and with only a small fraction (less than 10%) of global brick production using modern mechanized technology (CIATEC, 2015). However, being predominantly an informal industrial sector, there are substantial uncertainties in the number, types, fuels, and characteristics of kilns used for this activity. The lack of reliable activity data and emission factors makes it difficult to quantify the overall contribution of brick production to local and regional emissions inventories and to assess the ecological, human health and climate impacts.

Efforts in Mexico to reduce the impacts of bricks production include the promotion of technologically improved kilns and survey-based field studies to improve the activity data for this sector (Cardenas et al., 2012). The few data available indicate that fuels and the characteristics of raw materials vary based on their cost and availability. The estimated number of brick kilns in Mexico is about 17,000, of which 75% are "traditional-fixed" type with permanent walls that delimit the space of accommodation of the bricks to be cooked; 22% are "traditional-campaign" kilns in which the raw bricks give shape to the kiln, and only < 3% are mechanically industrialized or of new design (CIATEC, 2015). One of the new designs is a double dome version of the original Marquez Kiln (MK) developed by R. O. Marquez (2002) called MK2 which involves covering the kiln with a dome and channeling the output flow through a second loaded kiln for its additional filtration of the effluents (Bruce et al., 2007). However, there is a need for an integrated assessment of the emissions and energy performance of traditional and new kiln designs as well as the identification of the economic, social and technical barriers to adopt new technologies by brick producers (Schmidt, 2013).

The general steps of brick production include clay preparation, molding, drying, and firing. The firing process itself is divided into burning, smoldering, and cooling stages. Nevertheless, the whole process is artisanal rather than standardized, learned by experience, and locally adjusted depending on the soil characteristics, kiln design, and available fuels. In Mexico, biomass is the predominant fuel used in the production of bricks, although it is often combined with other hazardous and highly polluting materials including waste oils, textiles, tires and plastics (CIATEC, 2015). This results in low efficiency combustion and high levels of gaseous and particulate matter (PM) pollutants that are difficult to quantify in an emissions inventory.

Brick kiln emissions are suspected to be a major source of black carbon (BC) and other PM components at the local scale in developing countries. However, there are no reliable estimates of global emissions from brick kilns. Based on a very limited number of measurements and expert judgment, Bond et al. (2013) estimated that industrial coal combustion provided about 9% of global BC emissions in 2000, although that figure includes brick production as well as small boilers, process heating for lime kilns, and coke production for the steel industry. In Mexico, the 2008 National Emissions Inventory (2008-MNEI) suggests emissions of 2.9, 0.5, and 19.7 Gg of $PM_{2.5}$, NO_x, and volatile organic compounds (VOCs), respectively, from brick kilns (SEMARNAT, 2012). Nevertheless, these estimates were obtained using emission factors from the AP-42 US-EPA database that may not apply to kiln technologies and operating conditions in Mexico. There is a need to reduce the uncertainties associated with the estimation of emissions from brick production.

A limited number of studies exist on the emission characteristics of brick kilns. Le and Oanh (2010) measured the emission rates of CO, SO_2 and PM in two kilns in Vietnam. Christian et al. (2010) measured the emission factors of multiple gases and PM composition, including BC and organic carbon (OC), from three traditional brick kilns in Mexico. Maiz et al. (2010) determined emission factors for several types of dioxins, furans and other persistent organic pollutants (POPs) from two types of artisanal brick kilns. Umlauf et al. (2017) determined various POPs in soil, bottom ash and products from brickmaking sites in Kenya, Mexico and South Africa. Fifteen kilns in India and two in Vietnam representing five types of kiln designs were sampled for their CO, CO_2, SO_2, (Rajarathnam et al., 2014) and their $PM_{2.5}$ and elemental carbon (EC) emission factors and optical properties (Weyant et al., 2014). Stockwell et al. (2016) measured a "zig-zag" kiln and a batch-type clamp kiln burning coal as fuel in Nepal to obtain emission factors for a large suite of gases and PM composition. Overall, the results from these studies indicate that emission factors are highly variable and depend on fuel type, feeding patterns, fraction of internal and external fuel, and kiln designs. Despite the widespread use of brick kilns in Latin American countries there have been very limited studies on the emission impacts of kiln designs and fuels employed.

Due to the intensity of the emission fluxes, the high temperatures involved, and the varied geometry of the kilns, there are considerable technical challenges associated with the measurement of emission factors from brick kilns. Recently, based on a review of the available studies, the Climate and Clean Air Coalition (CCAC) Brick Production Initiative has developed guidelines for the measurement of brick kilns emissions and energy performance (Weyant et al., 2016). The guidelines include procedures for the isokinetic probe sampling of effluents in kiln stacks when they are available, and the use of an array probe in the open plume above the kiln to apply the carbon mass balance method (Thomson et al., 2016).

As part of the pilot field measurement campaign to characterize the emissions from key sources of Short-Lived Climate Forcers in Mexico (SLCF-2013 Mexico), we measured the emissions factors for BC, OC, the inorganic PM components, CO, SO_2, NO_x, CH_4, and selected VOCs from a traditional-fixed kiln, a traditional-campaign kiln, and a MK2 kiln in Mexico using a tracer ratio method sampling technique, allowing the examination of the emission plume's evolution as it transits downwind

from the source. The tracer ratio method (Lamb et al., 1995) has been used to measure emissions from other similar types of industrial and area sources. To our knowledge, this technique had never been applied for measuring emissions from brick production. Simultaneous measurements of PM components, CO and CO_2 were obtained using the sampling probe technique, thus allowing a unique comparison between the two different techniques. Additional measurements included the internal brick kilns temperature, energy efficiency, mechanical resistance of bricks produced, and chemical composition of fuels employed. The emissions were measured both during the firing and subsequent smoldering stages, providing insight into the effects of different kiln designs and fuels on gaseous and particulate phase emissions from brick kilns.

2 Methodology

2.1 Brick kilns sampled

Table 1 lists the characteristics of the brick kilns sampled and Fig. 1 shows the kilns. A description of their operation processes as well as the sampling location for each kiln is presented in the Supplemental Material document. The MK2 kiln and the traditional-campaign kiln were measured in El Refugio, a community of brick producers located in the periphery of Leon, Guanajuato. The traditional-fixed kiln was measured in a separate community of brick producers in Abasolo, Guanajuato. Measurements took place during the dry season on March 12-16, 2013. Close collaboration with the local authorities and the brick producers' associations allowed us to establish an agreement that other kilns would not be fired during the measurement period to minimize the influence from nearby sources. The selected kilns were operated by experienced brick producers under real-world operating conditions, with fuels types and practices they commonly use.

A random sample of 60 bricks were identified, measured, and weighed before the firing took place for each kiln. At the end of the firing, these same bricks were again measured, weighed and sent to a laboratory to test their mechanical resistance and water absorption content following the corresponding NMX-CC-404-ONNCCE-2012 Mexican standard (ONNCCE, 2012). Samples of fuels and raw materials were collected before the firing to determine carbon content and heating value of combustion for the fuels. The determination was carried out with an Elemental Analyzer PE-2400 Series1 and a microbalance. An acetanilide standard was used to calibrate the equipment and obtain the sample's carbon content. Heating value of combustion was determined using ASTM standards (ASTM 1995) with a Parr-1108 calorimetric pump operating with excess of oxygen to assure complete combustion of the sample. The results of these analyses are presented in Tables SM1-SM3 in the Supplemental Material document. Four t~~T~~hermocouples were installed at each of the lower, middle, and upper levels ~~of the kiln~~ to obtain three cross sections and to determine the temperature profile~~s~~ inside the kilns during ~~its~~ their operation. These three levels were defined as follow: 0.4 m above the combustion chamber for the lower level, 0.3 m below the last layer of bricks for the upper level, and half the distance between the lower and upper levels for the middle level.

2.2 Sampling techniques

Two sampling techniques were used to obtain the emission factors of pollutants generated from the brick kilns. In the sampling-probe technique, a temporary scaffold was built on the side of the kiln for equipment and technicians, and a probe was installed on top of the kiln and connected to a sensor sampling train containing real-time sensors and filters for PM collection. This sampling technique is possible due to the relatively low velocities of the exhaust so that an isokinetic flow train is not required (Weyant et al., 2016). During the few seconds right after exiting the kiln and before they are well mixed downwind, the emission plumes on top of the kiln can vary substantially in intensity and composition. This implies that the location of the sampling probe on top of the kiln is of key importance to the representativeness of the filter measurement. To account for this effect, the sampling probe was mounted on a rotating crane that was continuously spinning slowly on top of the kiln (see Fig. 1).

An inertial mass separator with a cut-point of 2.5 μm was used to obtain the $PM_{2.5}$ fraction of PM collected on 47-mm diameter quartz filters. The $PM_{2.5}$ filters were replaced approximately once an hour depending on the pressure drop on the sampler. After the samplings, the filters were thermally stabilized and sent to the laboratory for gravimetric and EC and OC composition analysis using thermal/optical transmittance (TOT) and reflectance (TOR) analysis (Chow et al., 2004) using the IMPROVE_A protocol (Chow et al., 2007). Although the EC measured by the thermal/optical methods is not technically considered as BC (Petzold et al., 2013), in this paper we refer to EC by TOR as a surrogate of BC as the light-absorbing carbon in the measured PM. Since the collection filters were heavily loaded and had homogenous deposits, analysis of anions (chlorides, nitrates, sulfates) and cations (ammonium and water- soluble sodium and potassium) analyses by ion chromatography were performed. Laboratory analyses showed that field blank concentrations were low in relation to those in source samples, averaging < 5 % for OC and < 0.1% for BC.

Exhaust flow in the sampling train was measured using a piston flowmeter and directed to a Continuous Emissions Monitoring System (CEMS) with a Fourier-Transform Infrared Spectrometer (FTIR) to measure CO_2 and CO and to a flame ionization detector (FID) analyser to measure total gaseous organic compounds (TOG). Instrument specifications and sampling calibration protocols are described in Tables SM4-SM5 in the Supplemental Material document. The gaseous carbon concentration in standard conditions are used in the carbon mass balance method together with the measured carbon content of the fuels (see Tables SM2-SM3) to obtain fuel-based emission factors (EF_{fuel}, g/kg-fuel) of a pollutant (p) emitted (Thomson et al., 2016) as shown in Eq. (1).

$$EF_{fuel,p} = \frac{[p]}{[CO_2]\frac{M_C}{M_{CO_2}} + [CO]\frac{M_C}{M_{CO}} + [OC] + [BC]} w_c \quad (1)$$

In Eq. (1), w_c (g/kg-fuel) represents the measured effective fuel carbon fraction in dry basis, M_C, M_{CO2} and M_{CO} represent the molecular weight of carbon, CO_2 and CO, respectively. Energy-based emission factors (EF_{energy}, g/MJ) and brick-based emission factors (EF_{brick}, g/kg-brick) are calculated using EF_{fuel}, the measured effective fuel heating value in dry basis (w_f, MJ/kg-fuel), and the specific energy consumption (SEC, MJ/kg-brick), respectively, as shown in Eqs. (2) and (3).

$$EF_{energy,p} = EF_{fuel,p} w_f{}^{-1} \quad (2)$$

$$EF_{brick,p} = EF_{energy,p} SEC \quad (3)$$

In Eq. (3), SEC is calculated by multiplying the fuel mass consumption rate (kg-fuel/day) by w_f and dividing by the brick production rate (kg-bricks/day).

The second technique used to sample the kilns was based on the tracer ratio method in which the emission rate of the targeted source is obtained by simultaneously measuring in real-time the above-background concentrations of the species of interest and of a selected gas tracer with a known release rate that is co-located at the emission source (Lamb et al., 1995). This method is based on the fundamental assumption that a relatively unreactive mixture of gases emitted from a common location experiences a quasi-perfect co-dispersion and equivalent dilution through the atmosphere. The tracer ratio method does not quantify the dispersion of air pollutants or the spatial representation of the brick kilns emission plumes, but is used to quantify the emission rates of co-emitted pollutants from a single source. The source's emission rate (*ER*, l/s, standard conditions) can be estimated using the relationship between above-background concentrations of the species *p* emitted and the tracer C_t multiplied by the known tracer's release flow rate R_t (l/s, standard conditions) as shown in Eq. (4):

$$ER_p = \frac{[p]}{[C_t]} R_t \quad (4)$$

Using the scaffold built for the measurements, the tracer was released at a constant rate close to the top of the kiln so that the kiln's emissions and the released tracer were simultaneously transported downwind and measured by the instruments on-board the Aerodyne Mobile laboratory (AML). For this study nitrous oxide (N_2O) and ethyl acetate ($C_4H_8O_2$) were used as tracers ~~gases~~ for the measurement of the *ER* due to their low atmospheric reactivity and the ability of the AML to measure their concentrations very accurately and with high sensitivity. The tracer gas was released from a compressed gas cylinder of pure N_2O located in a separate vehicle. The flow rate was controlled with an MKS mass flow controller (MFC), which was calibrated against a traceable Drycal mass flowmeter several times over the course of the measurement campaign. A 3/8" polyethylene tube extended from the mass flow controller to the desired location, allowing the cylinder and MFC to be located in a close but safe distance from the kiln. Mass flow rates were digitally recorded, and manually logged. ~~For this study nitrous oxide (N_2O) and ethyl acetate ($C_4H_8O_2$) were used as tracer gases for the measurement of the *ER* due to their low atmospheric~~

~~reactivity and the ability of the AML to measure their concentrations very accurately and with high sensitivity.~~ The $C_4H_8O_2$ emission tracer was generated by bubbling air through a bottle containing the compound. While it was co-located with the known N_2O emission, its direct release rate was uncertain. Thus, only the N_2O tracer was used to quantify brick kiln emission rates. The $C_4H_8O_2$ served as an auxiliary tracer identified when the AML was downwind of plumes from the kiln of interest, rather than from other sources in the area. Furthermore, it independently diagnosed the tracer plume characteristics directly with the instrumentation used to measure VOCs of interests, as described below.

The AML incorporates real-time data acquisition and data display capabilities so that *in-situ* decisions by the investigators can be made to move the laboratory in and out of the emission plumes that are identified by tracer detection. This is a key element for the successful application of this technique since the dilution and advection of the kiln emissions are dictated by local meteorological conditions that can vary in short time scales. The mobile laboratory was typically positioned between 20-100 m from the kiln during the tracer ratio measurements. The tracer ratio method allows the unequivocally identification of emission plumes from the targeted kiln at various time periods of its operation process; this in turn allows to further apply the mass carbon method to the identified plumes following Eqs. (1-3) to obtain fuel, energy, and brick-based emission factors that can be compared to those obtained with the filter-based technique.

The instrumentation on-board the AML included a soot particle aerosol mass spectrometer (SP-AMS) developed by Aerodyne Research Inc. (Onasch et al., 2012), which measured BC and OC using laser-induced incandescence of absorbing soot particles to vaporize both the coatings and BC cores of exhaust soot particles within the ionization region of the AMS (Dallman et al., 2014). The SP-AMS also measured other inorganic PM components including nitrates, sulfates, ammonium, and chlorides corresponding to a particle size range of 50 – 600 nm. The SP-AMS is able to handle high concentrations of particulate matter routinely. It is frequently used in source studies where organics and black carbon may be higher than 100 $\mu g/m^3$ (Massoli et al., 2012; Zavala et al., 2017). The SP-AMS acquires data in 1 second mode during which it obtains an average mass spectrum sampling from 12-1000 m/z. The mass spectrum is then processed and high resolution fits are applied to peaks (e.g., C_3 at m/z 36 or C_3H_7 at m/z 43) to distinguish between BC and organics. All fit peaks are summed, counted as a particular species and then that species is quantified for each second. There are 2 vaporizers simultaneously heating particles so that gas phase molecules are then available to ionize by reaction with electrons. The laser vaporizer heated particles with a 1064--nm laser while the conventional AMS vaporizer was also present and after passing through the laser vaporizer the particle beam impacted the conventional vaporizer which was heated to 600 ˚C. Inorganic species such as sulfates and nitrates are not vaporized by the 1064-nm laser but were vaporized by a conventional heater. In this study, we refer to PM emission factors obtained with the AML as the sum of BC, OC and inorganic components simultaneously measured with the SP-AMS.

The AML measured N_2O, CH_4, C_2H_6, SO_2, CO and acetylene (C_2H_2) using Tunable Infrared Laser Differential Absorption Spectrometers (TILDAS); NO/NO_y were measured using a Thermo Electron 42i chemiluminescent detector modified for fast-

response; a LiCor 6262 Non-Dispersive Infrared (NDIR) instrument measured CO_2; and a Proton Transfer Reaction Mass Spectrometry (PTR-MS) using H_3O^+ as the ionization reagent was operated in multiple ion detection mode to measure selected VOCs (Rogers et al., 2006). Species measured with the PTR-MS included methanol, acetonitrile, acetaldehyde, acetone, benzene, toluene, acetic acid, ethyl acetate, C2-benzenes (sum of C_8H_{10} isomers: xylenes, ethylbenzene, and benzaldehyde), and C3-benzenes (sum of C_9H_{12} isomers and C_8H_8O isomers). Calibrations of these instruments were checked using certified gas standards. Other instruments on-board the mobile laboratory included a global positioning system (GPS), a sonic anemometer, and a video camera. Further details on the AML instruments detection limits and sensitivities are presented in Table SM5 of the Supplemental Material document.

3 Results

The average fuel-based emission factors (g/kg-fuel) obtained with both the sampling probe and tracer ratio techniques are shown in Table 2. The table also shows the modified combustion efficiency (MCE) that is obtained as the ratio of CO_2 to (CO_2 + CO) concentrations and thus is a useful indicator of the combustion efficiency. The corresponding brick- and energy-based emission factors for the three kilns are shown in Tables SM6 and SM7, respectively, in the Supplemental Material document. Table 2 also shows the average emission rates (g/min) obtained for the three kilns with the tracer ratio technique.

As shown in Table 2, the relative variability of emission rates is much higher compared to the variability of fuel-based emission factors. Time-based emission rates are highly variable particularly during the burning stage because they strongly depend on the fuel-feeding practices including the amount and type of fuel used, as well as the operator's decision of when to add fuel. The lower variability of the fuel-based emission factors compared to emission rates indicates that the normalization of the emissions of combustion by-products effectively takes into account the variations in the thermal energy employed in the cooking process. In addition, since estimations of integrated emissions burden using emission rates depend on the total brick production time, emission rates are not a good indicator to compare the environmental performance of the kilns. However, emission rates can be useful during the development of emissions inventories as inputs in air quality models to better understand the time-based chemical evolution of the emitted species at local and urban scales.

A comparison of temporal profiles of CO, BC, and OC fuel-based emission factors for the traditional-fixed kiln between the two techniques is shown in Fig. 2. Comparisons of the temporal profiles for all measured pollutants are shown in Fig. SM1, SM2 and SM3 for the MK2, traditional-campaign, and traditional-fixed kilns, respectively, in the Supplemental Material document. The results show that in general both techniques capture comparable temporal profiles of the kiln emissions while the magnitudes of the emission factors are remarkably similar. As the fuels used in the three kilns were mostly wood, the resulting identities of VOCs emitted are similar to those from biomass burning. Furthermore, the temporal profiles shown in Figs. SM1-SM3 indicate that high levels of VOCs can be emitted not only during the burning stage of the brick cooking process

but also during the smoldering and cooling stages. Measurements in this pilot study focused primarily on the burning stages and only included partial periods of the smoldering and cooling stages. Therefore, a complete characterization of VOC emissions for brick kilns would require the measurement of the full brick-cooking period.

The data from the tracer ratio technique show that there is large short-term variability of the emission factors for both gaseous and particulate pollutants during the burning stage of the cooking process; this variability is only partially captured by the filter-based sampling probe technique. On the other hand, whereas the sampling probe technique continuously measures the kiln's emissions in ~1-hour intervals, the tracer technique strongly depends on the capability to position the mobile laboratory downwind at a distance ranging from approximately 20-100 m from the kiln, depending on wind speed, and is not feasible during stagnant wind conditions. Thus, with the tracer ratio technique there may be unavoidable gaps in the data needed to fully characterize the kiln's emissions for the entire process. As shown in Fig. SM1, the MK2 kiln presented the largest data gaps with the tracer ratio technique and thus, the obtained emission factors in Table 2 may not represent the complete brick production process with this technique. Therefore, in our subsequent discussions and for the comparison of particulate emission factors we have used the results obtained with the sampling probe technique because all the available comparable studies with PM data used filter-based measurements. This includes emission factors for $PM_{2.5}$, BC, OC, and all the inorganic and ionic PM components. However, in this study all sampled VOCs, SO_2, NO_x, and CH_4 were obtained using only the tracer ratio technique and thus these results are used in the comparisons.

Major components of $PM_{2.5}$ for the MK2 and the traditional-campaign kilns are distinctively different than for the traditional-fixed kiln. As described, the two former kilns belong to a different brick production community (El Refugio) and used similar mix of fuels and batches of clay, whereas the traditional-fixed kiln used mostly avocado wood and a different batch of clay as it is located in a different community (Abasolo). Total carbon corresponded to 9.3, 12.5, 51.1 % in mass of $PM_{2.5}$ for the MK2, the traditional-campaign, and the traditional-fixed kilns, respectively. Correspondingly, BC accounted for 7.8, 6.0, and 40.5 % of PM2.5 for the three brick kilns. Chloride (31.9 %, 42.4%), ammonium (12.7 %, 20.4%), potassium (9.8 %, 2.5%), and sulfate (7.0 %, 2.0%) were the predominant mass components in $PM_{2.5}$ for the MK2 and the traditional-campaign kilns, respectively, whereas the sum of these four components amounted to only 8.9% in mass of $PM_{2.5}$ for the traditional-fixed kiln.

The measured ionic contents are quite high for the MK2 and the traditional-campaign kilns, the sum is greater than the BC + OC content. This indicates that either the ash content of the fuels is quite high or that these non-combustible inorganics are abundant in the brick material. The chloride content is especially elevated, which is often seen when trash containing plastics are burned. In our measurements we controlled the fuels types feed to the kilns and no chlorinated materials were used. Since the clay used for these two kilns was obtained locally in the same brick production community, it is possible that it may be already contaminated with PM deposition resulted from continued trash-burning practices during brick production over the

years. This suggests that environmental and health impacts of brick production can be further persistent even after the banning of trash burning practices.

Fluorides, bromides and other halogens are not typically high in ambient filter-based PM samples but they may be present in trace amounts in clay. Previous work has shown that fluorides from brick kilns can have adverse effects on vegetation and crops (Ahmand et al., 2012). Emission factors of particulate fluorides in this study were small (1.1-2.2 x 10^{-3} g/kg-fuel), suggesting that it was not present in large amounts in the raw brick materials. None of the wood used during the burning stage had paint or solvents on it, thus ruling out possible contributions of halogens or metals from wood fuels. Nevertheless, it has been reported that these materials can be used as part of wood waste products utilized as fuels by brick producers in Mexico (CIATEC, 2015).

It should be noted that during these measurements both methane and ethane emissions were quantified aboard the AML. The ethane measurement is an important complement to methane because it is a marker for non-biogenic methane emissions. Interestingly, the mass ratio of ethane to methane was consistently 0.06-0.075 between the three brick kiln types despite the substantial variation of the CH_4 emission ratio. This indicates that the ethane production is strongly linked to the methane production, and the ratio is not strongly dependent on the brick kiln operation.

4 Discussions

4.1 Brick cooking process

The physical and chemical changes occurring in the bricks during the cooking process are associated with the burning, smoldering and cooling stages, which are in turn determined by changes in thermal energy transfer rates within the kiln, and are closely related to the final quality of the cooked bricks. In describing the brick cooking process, we define the burning stage as the time passed since the firing starts until the feeding of fuel is stopped, the smoldering stage as the time when the maximum temperature at the top of the kiln is reached minus the burning time, and the cooling stage as the time when the temperature at the bottom of the kiln reaches a stable minimum minus smoldering time. The temporal profiles of temperature at the lower, middle, and upper levels of the kilns and the brick cooking stages are shown in Fig. 3. The corresponding rates of heating and cooling are obtained as the time derivatives of the temperature profiles.

The data show that the cooking of bricks results from vertical transfer of thermal energy inside the kiln starting from the beginning of the burning stage when temperatures at the bottom layers rise quickly with very high heating rates. In general, higher temperatures are reached inside the traditional-fixed kiln, followed by the traditional-campaign and the MK2 kilns. The bricks located in the middle and upper layers of the kiln start their cooking process only after sufficient thermal energy is transferred from the bottom layer. Interestingly, in the case of the MK2 and the traditional-campaign kilns this can occur during

the burning stage, but for the traditional-fixed kiln the cooking of bricks at the middle and upper layers occur only during the smoldering and cooling stages.

During the burning stage at the bottom of the kiln, the heating rate is much higher and smoother in the case of the traditional-fixed kiln compared to the traditional-campaign kiln, whereas the MK2 kiln shows highly variable but overall decreasing heating rates. This critical difference in the heating process at the burning stage is likely due to the physical arrangement of bricks and the design of the kiln. The traditional-fixed kiln seems to be particularly efficient in its vertical thermal energy transfer inside the kiln as temperatures in the middle and upper levels reach similarly high values (and at comparable heating rates) as those at the bottom even after the burning stage has finished.

The primary effect of the initial period of the burning stage is to remove all the remaining moisture from the bricks. At the beginning of the process this is done only at the bottom layers as temperatures do not reach high values in the middle and upper layers until much later. Once the moisture is removed and the temperatures continue rising, the carbonaceous organic material contained in the clay is removed by combustion. The raw materials for the three kilns are comparable in mass and type of clay used, but the traditional-campaign and the MK2 kilns use about 3.5 wt.% of manure whereas the traditional-fixed kiln use 8 wt.% of sawdust (see Table 1). These materials are additives that the brick producers use during the clay preparation process, mixing them with water and crushing them until the mixture is ready for molding. These organic additives effectively act as internal fuel during the brick cooking process and affect the quality and mechanical condition of the bricks (Martínez and Jiménez, 2014).

As temperatures continue to rise, the hydroxyl groups that are combined with the chemical compounds forming the clay begin the process of dehydroxylation, which effectively releases water and other volatile compounds at about 450 ºC (Osornio-Rubio et al., 2016). Figure 3 shows that the traditional-fixed kiln reaches dehydroxylation much faster than the MK2 and traditional-campaign kilns. At about 573 ºC (T_v in Fig. 3) the silica contained in the clay changes its α–quartz structure to a β-quartz structure, effectively expanding the volume of the clay (Heaney and Veblen, 1991). If the temperatures throughout the brick are not homogenous around T_v, cracks in the brick can form due to the mechanical stress of different volume expansion (Wayant et al., 2016).

Above Tv the clay begins the actual vitrification process in which clay particles melt to form a glassy bond, ultimately giving strength to the brick during the cooling stage. Brick producers have learned by experience the importance of not extending the vitrification process more than what is needed as overheating may distort the shapes of the bricks. Similarly, if the vitrification is not achieved homogenously within the brick, the mechanical resistance and thus the quality of the final product will be smaller. The time that the bricks are exposed to temperatures above T_v is 1.9 and 1.2 times larger for the traditional-campaign kiln compared to the traditional-fixed and MK2 kilns, respectively. Therefore, of the three kilns the traditional-fixed kiln

exposes the bricks to temperatures above T_v for much shorter periods of time. In addition, the time-integrals of the temperature profiles above T_v of the traditional-fixed kiln are at least half the magnitude of the corresponding time-integrals for the traditional-campaign and MK2 kilns, indicating that much less thermal energy is transferred inside the traditional-fixed kiln for vitrification.

4.2 Comparison among sampled kilns

The environmental performance of the brick kilns can be assessed in terms of the relative magnitude of the emission factors during the brick production process. The use of fuel-based emission factors to compare brick kilns performance is adequate when similar fuels are used among different kilns and when bricks have similar physical characteristics. In contrast, energy-based emission factors are adequate comparison indicators when fuels types are substantially different because they take directly into account the effective heating value of the fuels employed. Brick-based emission factors are adequate comparison indicators between kilns when the mass and size of the bricks produced are substantially different. Nevertheless, regardless of the type of emission factor used, an integrated assessment of the brick kilns performance should also incorporate other parameters, such as energy efficiency, fuel consumption, combustion efficiency, production time, and the quality of bricks produced, among others.

Figure 4 shows an inter-comparison of the relative performance of the three sampled kilns along with the specific energy consumption, fuel consumption, modified combustion efficiency, and measured brick's mechanical resistance as a surrogate for bricks' quality. In order to compare the relative environmental performance of the three kilns, we have normalized the fuel-based emission factors with the corresponding average of the three kilns for each pollutant in Fig. 4. Regardless of the base (fuel mass, brick mass, or energy) employed, the normalization effectively allows the simultaneous comparison of emissions factors for multiple pollutants that differ by orders of magnitude while providing information on their relative magnitudes.

The results show that the traditional-fixed kiln had lower modified combustion efficiency, lower fuel (wood) consumption, and slightly higher specific energy consumption compared to the other two kilns. The results of the measured mechanical resistance of the bricks produced are shown in Table SM8 of the Supplemental Material document. The traditional-fixed kiln also produced bricks with an average mechanical resistance almost half of that compared to the traditional-campaign kiln, in agreement with the much higher time-integral of the temperature profile above T_v for the traditional-campaign kiln and suggesting a more efficient vitrification process. Thus, although bricks from the traditional-fixed and MK2 kilns complied with the Mexican standard, the much higher mechanical resistance in the traditional-campaign kiln indicates that its bricks were produced with higher quality.

Low combustion efficiency is related to higher pollutant emissions produced during incomplete combustion. The traditional-fixed kiln had the highest emissions factors for CO, BC, as well as CH_4, C_2H_6, CH_3OH, C_2H_3N, and C_2H_4O but emitted

substantially smaller inorganic PM components. Conversely, CO, BC and OC emission factors were much smaller for the MK2 kiln compared to the traditional-campaign and traditional-fixed kilns, but had the highest inorganic PM components. Although the latter minimally contribute in mass to the overall emissions, ionic species may be important contributors to chemical processes in the atmosphere involving wet deposition. The measured SEC values were similar for the three kilns, with 10% variation among them, because the fuels used had similar heating values. In addition, since the combustion efficiency for the MK2 and the traditional-campaign kilns are somewhat similar in magnitude, the results indicate that the traditional-campaign kiln produced bricks of much higher quality while performing more efficiently in energy consumption and combustion efficiency than the other kilns.

4.3 Comparison with other studies

Very few studies are available on the chemical characteristics of emission factors for brick kilns. Previous work by Christian et al. (2010) includes measurements of multiple gases and PM composition for three traditional-fixed kilns in Mexico that used wood waste products as fuel. Of the five types of kiln designs measured by Rajarathnam et al. (2014) and Weyant et al. (2014) in India and Vietnam, only the down-draft kiln type used wood as fuel while the rest used mostly coal. Both the "zig-zag" and clamp kilns measured by Stockwell et al. (2016) in Nepal also used coal as fuel. Jayarathne et al. (2017) recently reported the particle-phase results of the same kilns measured by Stockwell et al. (2016). Of these studies, Stockwell et al. (2016) and Christian et al. (2010) report fuel-based energy factors whereas Rajarathnam et al. (2014) and Weyant et al. (2014) report energy-based emission factors, allowing a proper inter-comparison with our results. Tables 3 and 4 show a comparison of the energy-based and fuel-based emission factors, respectively, with those obtained in other studies.

Table 3 shows that the specific energy consumption for brick kilns using coal as fuel in the studies of Rajarathnam et al., (2014) and Weyant et al., (2014) are much smaller than for those measured in this study, due to the much higher energy density content of coal versus wood. SO_2 emission factors for coal-firing kilns are higher than those of wood-firing kilns; coal having larger sulfur content than wood. Nevertheless, the major difference between emissions factors among the kilns seems to be caused by the kiln design. The improved designs for the zig-zag and vertical shaft kilns are related to substantially smaller emission factors than the other kilns, indicating large environmental benefits by the use of more efficient brick kiln technologies. Thus, addressing the complex economic, social, and technical barriers surrounding the adoption of more efficient technologies can produce substantial environmental and health benefits.

The emission factors in this study are closer to the values reported for the down-draft kiln by Rajarathnam et al. (2014) and Weyant et al. (2014) and to the results by Christian et al. (2010) due to similarities in kiln designs and fuels (wood) employed. However, there are differences in the emission factors that suggest substantial inter-variability of emissions even when fuels and kilns designs are similar. The average BC and OC emission factors obtained in this study for the traditional-fixed kiln of 0.54 and 0.14 g/kg-fuel, respectively, are within the lower range of the values reported by Christian et al. (2010), whereas the

corresponding BC and OC energy-based emission factors are 2-12 times lower than those reported by Weyant et al. (2014) for the down-draft wood-fueled kiln. In the study of Weyant et al. (2014), the sample streams were diluted and cooled before measuring whereas our filter-based measurements were not diluted. Similarly, in the study of Stockwell et al., (2016) the emissions were sampled downwind of the stack after natural dilution and cooling. As gas-to-particle mass transfer processes are likely to occur under strong temperature gradients, different sampling techniques can further contribute to observed differences. In this study, condensation of emitted semi-volatile VOCs between the top of the kiln and the sampling location of the mobile laboratory downwind the plume is possible due to the strong temperature gradient, potentially adding organic content to the measured OC. However, quantification of this effect is beyond the scope of this study.

The MK2 and the traditional-campaign kilns presented similar average MCE values (0.94 - 0.96) that were higher than for the traditional-fixed kiln (0.91 – 0.92). This is reflected in the much higher CO emission factors for the traditional-fixed kiln in comparison with the other two kilns, indicating overall smaller combustion efficiency. In our study the BC/OC ratios were 5.2, 0.9, and 3.8 for the MK2, traditional-campaign, and traditional-fixed kilns, respectively; whereas the corresponding BC/OC ratios in Christian et al. (2010) ranged from 5.29 to 8.15. Methane, methanol, and acetic acid fuel-based emission factors for the traditional-fixed kiln are 3-5, 2-8, and 5 times higher, respectively, than those reported by Christian et al. (2010). These higher emission factors are consistent with the lower average MCE of 0.910 obtained in this study compared to the average MCE of 0.968 for the traditional-fixed kiln ~~sampled~~ reported by Christian et al. (2010). As a comparison, Stockwell et al. (2016) reports a much higher average MCE value of 0.994 for the zig-zag coal-fueled brick kiln sampled.

Overall, the comparison of the results in this study with the available literature reports indicate that there is substantial variability among brick kiln designs and fuel types. The observed variability is also the result of the combination of materials, fuels, kiln types, and operational practices that brick producers use. However, d~~D~~ue to the small sampling size, it is not possible to ~~distinguish~~ infer from the data the contribution of fuel types and kiln design to the overall variability of emissions during brick production. Therefore, although both the traditional-campaign and traditional-fixed kilns are widely used in Mexico, caution should be taken ~~into~~ in generalizing the results to other brick production regions with different fuels and operation practices. The results from this study are not intended to provide definitive generalizations of the brick making process, but to help in understanding the effects of different kiln designs and fuels on gaseous and particulate phase emissions from brick kilns. Nevertheless, since the number of studies with chemical composition of brick kiln emissions is so small, the results of this study represent valuable additions to the current literature.

5 Conclusions

Despite the widespread use of brick kilns in Mexico and other Latin American countries, there have been very few studies on their emission characteristics. An important part of the brick production in Mexico is still done by using traditional brick kilns

that are operated with artisanal methods and thus the individual kiln's performance depends on the producer's operation skills, kiln design, and available materials and fuels. This diversity in operating conditions can result in large intra-variability on the pollutant emissions characteristics from brick kilns even when using similar designs and fuels. Therefore, there is a need for additional emissions measurements from brick production to better constrain the uncertainties of emissions estimates and mitigate their environmental and human health impacts. Since the tracer ratio method is not limited by mass saturation constrains, the results from this pilot project suggest that the tracer technique can be an alternative option to the filter-based sampling probe technique in understanding the temporal profile of the chemical composition of brick kilns emissions.

The results of this study showed that a well-designed and operated MK2 kiln produced lower $PM_{2.5}$, BC, CO, and OC emission factors, the traditional-campaign kiln overall had the lowest sampled VOCs emission factors, whereas the traditional-fixed kiln had the lowest inorganic PM component emission factors. However, we have shown that non-environmental parameters can be used to quantitatively evaluate the performance of brick kilns. The traditional-campaign kiln had good energy efficiency performance and produced bricks with the highest quality, likely due to a better vitrification process. The MK2 kiln had a short cooking time and similar energy consumption to the traditional fixed and campaign kilns. Despite its higher internal temperatures, smaller fuel consumption, and shorter burning time, the traditional-fixed kiln produced lower quality bricks and with overall high emissions of combustion products. As both energy-efficient and low-emissions brick kilns are needed to mitigate the impacts from these sources, further studies should address the benefits of potential upgrades in the mechanical design of kilns to further improve their fuel consumption and energy efficiency.

Disclaimers:

The authors declare that they have no conflict of interest.

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Table 1. Summary of the characteristics of kilns sampled.

Parameter	Traditional-fixed kiln	Traditional-campaign kiln	MK2 kiln
Burning time[a] [hr]	3.8	20.5	17.6
Soaking time[b] [hr]	17.1	14.4	19.2
Cooling time[c] [hr]	10.2	23.1	12.5
Total raw bricks [pc]	21780	9898	5135
Bricks rejected [%][d]	0.20	1.8	2.8
Mass of raw brick [kg]	3.59 ± 0.05	4.44 ± 0.16	4.55 ± 0.16
Mass of cooked brick [kg]	3.03 ± 0.04	3.95 ± 0.25	4.11 ± 0.16
Moisture content in raw bricks [wt.%]	15.6	11.2	9.6
Carbon content in raw brick [wt.%]	0.86	1.28	1.28
Carbon content in cooked brick [wt.%]	0.13	0.11	0.11
Raw materials [wt.%]	clay (92), sawdust (8)	clay (96.4), manure (3.6)	clay (96.6), manure (3.4)
Fuels[e]	wood, diesel, sawdust	wood, manure	wood, manure

[a] Time passed since the firing starts until the fuel feeding is stopped.

[b] Time when the maximum temperature at the top of the kiln is reached minus burning time.

[c] Time when the temperature at the bottom of the kiln reaches a stable minimum minus smoldering time. It takes about 48 hours for a kiln to homogenously cool off back to ambient temperature.

[d] Percentage of bricks either broken or fractured after burning, thus rejected for sale.

[e] See Supplemental Material document for specific types, quantities, and chemical composition of fuels.

Table 2. Average modified combustion efficiency (MCE), fuel-based emission factors EF [g/kg fuel], and emission rates ER [g/min] obtained with the sampling probe (SP) and tracer ratio (AML) techniques.[1]

	MK2			Traditional-campaign			Traditional-fixed		
	SP	AML		SP	AML		SP	AML	
	EF-fuel	EF-fuel	ER	EF-fuel	EF-fuel	ER	EF-fuel	EF-fuel	ER
MCE	0.96	0.94		0.95	0.94		0.91	0.92	
	(0.02)	(0.04)		(0.02)	(0.03)		(0.02)	(0.02)	
CO_2	1583	1595		1527	1597		1668	1658	
	(28)	(58)		(28)	(54)		(40)	(43)	
CO	44.4	65.4	270.7	50.5	65.3	553.7	105.2	105.3	8500.2
	(18)	(526)	(902)	(17)	(43)	(1040)	(24)	(36)	(9588)
TOC[2]	2.0			5.0			14.6		
	(2)			(4)			(2)		
CH_4		2.39	11.90		3.34	28.0		5.92	551
		(2.6)	(28)		(2.9)	(53)		(2.2)	(699)
NO		1.02	4.3		1.05	13.8		0.76	43.4
		(0.9)	(8)		(2.1)	(71)		(0.3)	(31)
NO_2		1.7	7.4		0.93	7.8		1.01	53.8
		(1.8)	(18)		(1.4)	(27)		(0.6)	(36)
SO_2		1.0	3.6		0.27	1.1		0.13	8.7
		(1.4)	(8)		(0.3)	(2)		(0.1)	(9)
$PM_{2.5}$[3]	1.94	1.66	3.9	4.62	2.28	17.5	1.32	1.26	171.9
	(0.6)	(0.8)	(2)	(4.3)	(1.8)	(15)	(1.3)	(2.2)	(152)
BC	0.15	0.67	1.6	0.28	0.73	3.4	0.54	1.03	149.4
	(0.1)	(0.5)	(3)	(0.2)	(0.6)	(5)	(0.8)	(2.2)	(377)
OC[4]	0.03	0.52	1.5	0.3	1.18	12.6	0.14	0.18	19.5
	(0.03)	(0.6)	(5)	(0.7)	(1.7)	(38)	(0.1)	(0.2)	(31)
Fullerene ($x10^{-3}$)		31.0	84.5		26.8	150.1		8.1	912.4
		(39)	(183)		(30)	(252)		(12)	(1820)
Ammonium ($x10^{-3}$)	246.3	96.8	155.2	942.2	66.7	240.6	2.9	6.6	312.5
	(105)	(64)	(225)	(1068)	(69)	(442)	(2)	(5)	(349)
Nitrate ($x10^{-3}$)	1.4	23.4	68.4	10.7	12.3	69.7	3.4	4.8	393.6
	(1)	(33)	(173)	(17)	(20)	(197)	(2)	(6)	(691)
Sulfate ($x10^{-3}$)	135.5	121.3	315.1	91.9	68.8	302.1	48.8	21.6	1721.7
	(96)	(203)	(678)	(36)	(104)	(620)	(59)	(19)	(2240)
Chloride ($x10^{-3}$)	617.2	234.1	305.2	1956.3	226.8	936.8	21.7	10.5	649.7
	(200)	(153)	(397)	(2095)	(227)	(1766)	(14)	(4)	(624)
Sodium ($x10^{-3}$)	27.2			21.9			15.3		
	(15)			(9)			(12)		
Magnesium ($x10^{-3}$)	0.67			1.34			1.11		
	(0.4)			(0.8)			(0.8)		
Potassium ($x10^{-3}$)	189.3			114.7			44.0		
	(146)			(74)			(65)		
Calcium ($x10^{-3}$)	5.5			7.9			5.3		

	(4)				(4)				(3)			
Fluoride ($x10^{-3}$)	1.1				2.2				1.2			
	(1)				(2)				(1)			
Chloride ($x10^{-3}$)	617.2				1956.3				21.7			
	(200)				(2095)				(14)			
Bromide ($x10^{-3}$)	5.0				23.6				1.0			
	(2)				(38)				(1)			
Ethane		0.15	0.6			0.21	1.1			0.44	30.0	
		(0.2)	(1)			(0.2)	(3)			(0.1)	(29)	
Methanol		1.99	18.7			1.19	5.1			3.25	185.3	
		(2)	(119)			(2.3)	(18)			(1.2)	(151)	
Acetonitrile		0.24	1.1			0.15	0.7			0.46	30.7	
		(0.2)	(2)			(0.1)	(1)			(0.2)	(34)	
Acetaldehyde		1.13	5.8			0.54	2.2			2.18	146.9	
		(1.2)	(12)			(0.4)	(3)			(0.5)	(129)	
Acetone		1.28	6.3			0.61	2.6			0.91	70.2	
		(1.5)	(12)			(1.9)	(14)			(0.3)	(79)	
Acetic acid		2.64	11.6			0.89	2.0			1.04	38.2	
		(3.1)	(22)			(2.6)	(4)			(0.8)	(20)	
Benzene		0.84	3.8			0.66	3.4			0.5	58.3	
		(0.9)	(7)			(0.7)	(6)			(0.3)	(83)	
Toluene		0.93	5.3			0.42	1.9			0.28	20.0	
		(0.8)	(11)			(0.9)	(7)			(0.2)	(20)	
C2Benzenes		1.01	5.6			0.54	2.1			0.19	11.5	
		(1.1)	(11)			(1.5)	(10)			(0.1)	(11)	
C3Benzenes		0.86	4.7			0.45	1.7			0.13	7.4	
		(1.)	(10)			(1.2)	(10)			(0.1)	(7)	

[1] Emission factors obtained with the filter technique represent 1-hr continuous measurements of the brick production process, whereas those obtained with the tracer technique represent sporadic sampling times of a few tens to hundreds of seconds. See text and supplemental material for sampling details. Values in parenthesis are 1 standard deviation. See the Supplemental Material document for the corresponding energy and kg-brick based emission factors.

[2] Total organic carbon measured as methane equivalent.

[3] PM mass and its components from the AML results represent PM in the range 50-600 nm.

[4] Results for OC and VOCs obtained with the tracer ratio method include the effects of possible condensation of organics into the particle phase.

Table 3. Comparison of energy-based emission factors (g/MJ) measured in this study with other studies.

kiln type	This study			Rajarathnam et al., (2014) and Weyant et al., (2014)[a]						
	MK2	Traditional campaign	Traditional fixed	Fixed chimney Bull's trench	Natural draft zig-zag	Forced draft zig Zag	Vertical shaft	Down-Draft	Vertical shaft[b]	Tunnel[b]
Fuels	Wood	Wood	Wood, diesel, sawdust	Coal, wood, others	Coal, wood, others	Coal	Coal	Wood	Coal	Coal
SEC[c]	2.07	2.16	2.22	1.1 - 1.46	1.02 - 1.21	0.95 - 1.11	0.95	2.91	0.54	1.47
$PM_{2.5}$	0.11 (0.04)	0.27 (0.2)	0.07 (0.1)	0.07-0.23	0.03-0.19	0.03-0.05	0.053	0.17	0.16	0.163
BC	0.01 (0.01)	0.02 (0.01)	0.03 (0.04)	0.08-0.18	0.008-0.029	0.004-0.019	0.002	0.06	0.002	0.001
OC[d]	0.002 (0.002)	0.018 (0.04)	0.007 (0.006)	0.004-0.008	0.00-0.012	0.00-0.012	0.030	0.024	0.00	0.00
SO_2	0.058 (0.08)	0.016 (0.02)	0.007 (0.003)	0.39 (0.92)	0.06 (1.52)	0.23 (1.00)	0.11 (0.19)	<0.1 (0.04)	1.78 (0.01)	0.49 (0.03)
CO	2.57 (1)	2.94 (1)	5.56 (1.3)	2.96 (0.91)	0.32 (0.97)	1.96 (0.76)	4.39 (0.39)	5.17 (0.04)	2.93 (0.12)	1.56 (0.26)
CO_2	91.4 (2)	88.9 (2)	88.1 (2)	86.8-108.2	96.0-102.7	88.1-99.6	83	93.3	110.4	111.2

[a] Emission factors for CO_2, OC, BC (obtained as EC), and $PM_{2.5}$ are reported by Weyant et al., (2014); CO and SO_2 are reported by Rajarathnam et al., (2014). Numbers in parenthesis for Rajarathnam et al., (2014) and represent the ratio of standard deviation to the mean whereas in this study the values in parenthesis represent the 1 standard variation.

[b] These two kilns were measured in Vietnam, whereas the rest of kilns in Rajarathnam et al., (2014) and Weyant et al., (2014) were sampled in India.

[c] SEC indicates Specific Energy Consumption in MJ/kg-brick.

[d] Results for OC obtained with the tracer ratio method include the effects of possible condensation of organics into the particle phase.

Table 4. Comparison of fuel-based emission factors (g/kg-fuel) measured in this study with other studies.

	This study[a]			Stockwell et al., (2016), Jayarathne et al., (2017), Nepal		Christian et al., (2010), Mexico
kiln type	MK2	Traditional-campaign	Traditional-fixed	Clamp	Forced draft zig Zag	Traditional-fixed
Fuels	Wood	Wood	Wood, sawdust	Coal, hardwood	Coal, bagasse	Sawdust, wood waste
$PM_{2.5}$	1.94 (0.6)	4.62 (4.3)	1.32 (1.3)	10.7 (1.6)	15.1 (3.7)	1.2 – 2.0[b]
BC	0.15 (0.1)	0.28 (0.2)	0.54 (0.8)	0.0172	0.112	0.596-1.5
OC	0.03 (0.03)	0.3 (0.7)	0.14 (0.1)	6.74	1.05	0.073-0.283
SO_2	1. (1.4)	0.27 (0.3)	0.13 (0.1)	13	12.7	
CO	44.4 (17.7)	50.5 (16.7)	105.2 (24.3)	70.9	10.1	25.7-55.7
CO_2	1582 (28)	1526 (28)	1668 (40)	2102	2620	1736-1787
NO	1.02 (0.9)	1.05 (2.1)	0.76 (0.3)	bdl	1.28	
NO_2	1.7 (1.8)	0.93 (1.4)	1.01 (0.6)	0.297	0.0821	
CH_4	2.39 (2.6)	3.34 (2.9)	5.92 (2.2)	19.5	0.0873	1.13-2.16
C_2H_6	0.15 (0.2)	0.21 (0.2)	0.44 (0.1)	5.37	0.00206	
CH_3OH	1.99 (2.)	1.19 (2.3)	3.25 (1.2)	1.77	0.112	0.39-1.42
CH_3COOH	2.64 (3.1)	0.89 (2.6)	1.04 (0.8)	0.43	0.471	0.21
C_6H_6	0.84 (0.9)	0.66 (0.7)	0.5 (0.3)	1.68	0.00825	
$C_6H_5CH_3$	0.93 (0.8)	0.42 (0.9)	0.28 (0.2)	1.05	0.0028	
C_3H_6O	1.28 (1.5)	0.61 (1.9)	0.91 (0.3)	-	0.146	
C_2H_4O	1.13 (1.2)	0.54 (0.4)	2.18 (0.5)	0.0413	0.0694	

[a] Numbers in parenthesis represent 1 standard variation. Values in Crhistian et al, (2010) represent range of averages. "bdl" indicates below detection limit; "-" indicates concentrations were not greater than background.

[b] Estimated from measurements of OC, EC, metals, and ions (but not sulfate).

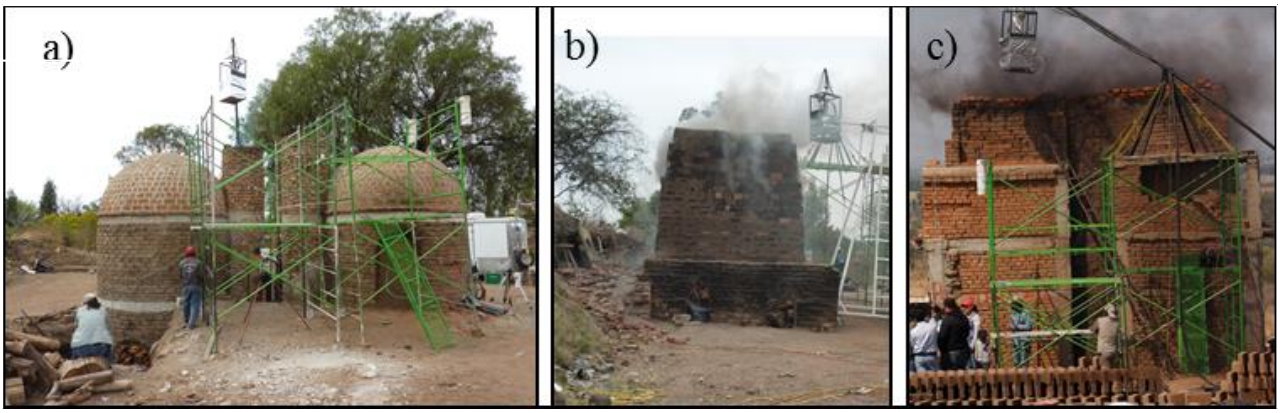

Figure 1. Brick kilns sampled: a) MK2 kiln in El Refugio, Guanajuato, b) Traditional-campaign kiln in El Refugio, Guanajuato, c) Traditional-fixed kiln in Abasolo, Guanajuato.

5

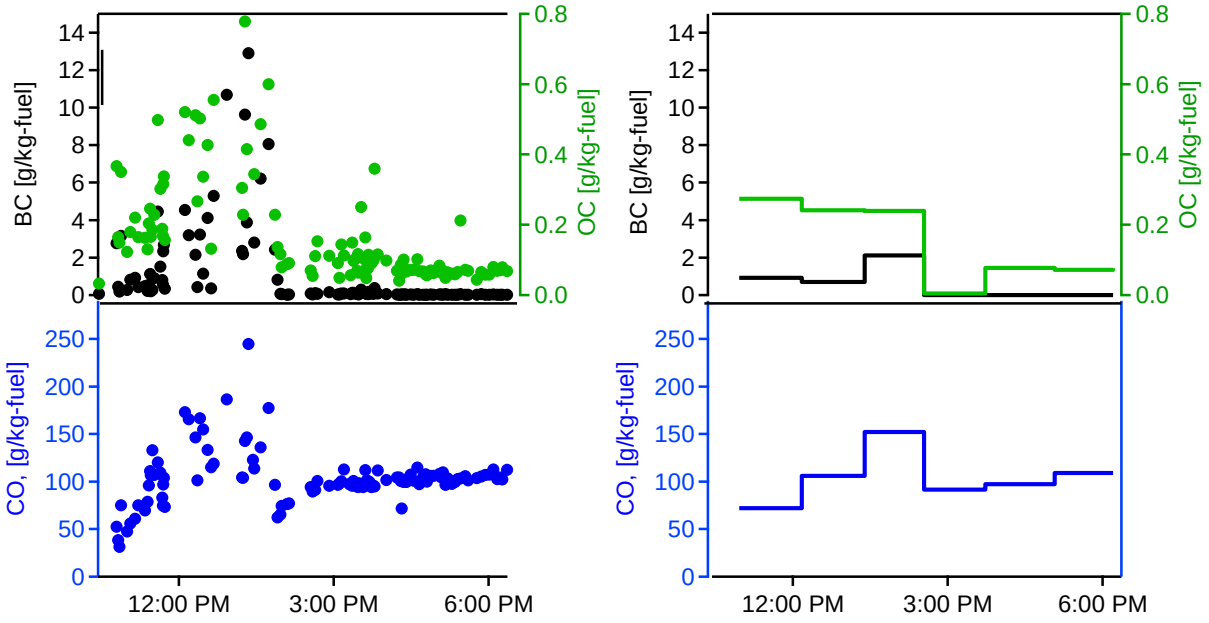

Figure 2. Temporal profiles of fuel-based CO, BC, and OC emission factors (g/kg-fuel) for the traditional-fixed kiln obtained with the AML and the tracer ratio technique (left panels) and with the sampling probe technique (right panels).

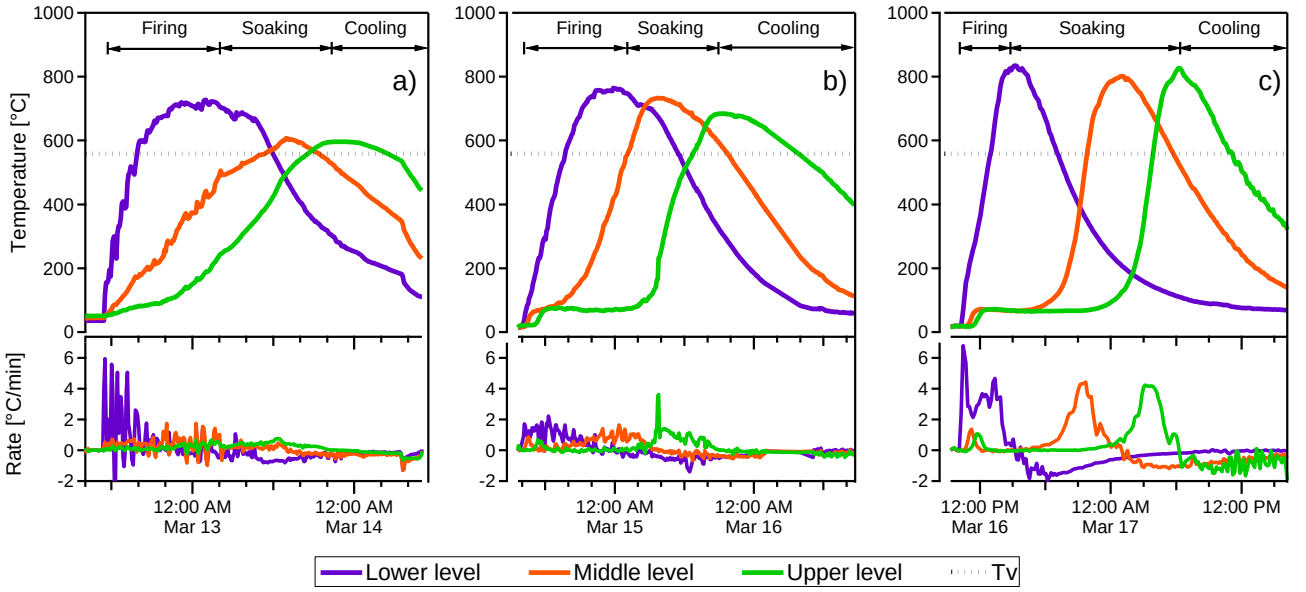

Figure 3: Temperature profiles (top panels) and temperature change rates (bottom panels) for: a) MK2, b) Traditional-campaign, and c) Traditional-fixed brick kilns for the lower, middle, and upper levels of the kilns. Horizontal dotted line represents T_v, the temperature for the quartz inversion process (573 °C). The figures also indicate the stages of burning, smoldering, and cooling for each kiln, as defined in the text.

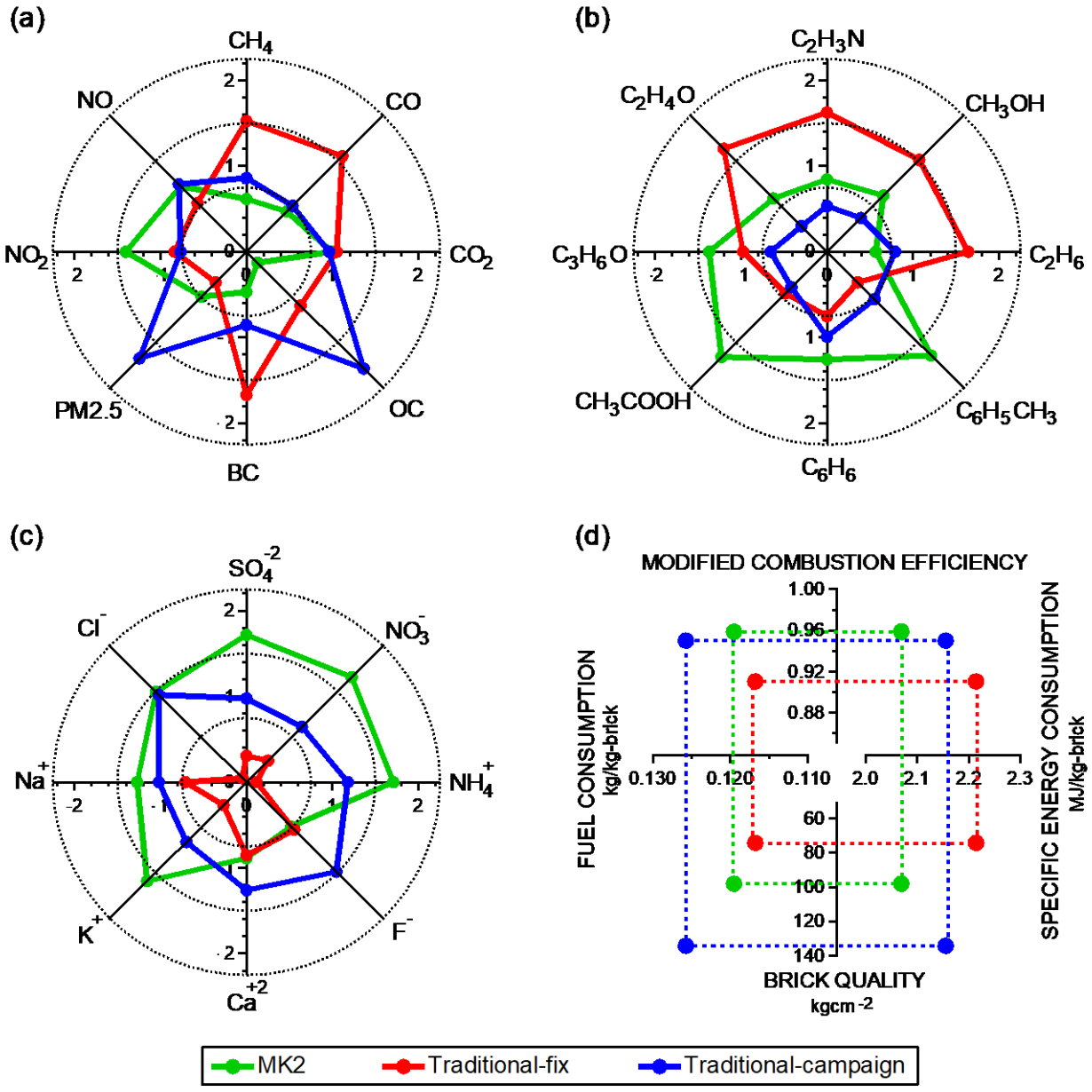

Figure 4: Inter-comparison of emission factors normalized to the average of the three kilns by pollutant for a) CO, CO_2, NO, NO_2, OC, BC, $PM_{2.5}$, CH_4; b) sampled VOC species; and c) inorganic components. Panel d) compares the modified combustion efficiency, specific energy consumption, fuel consumption and brick quality for the three sampled kilns.