Supplemental Material

This Supplemental Material document contains additional information on the instrumentation deployed during the measurement of emissions from the selected brick kilns as well as additional figures and tables that are discussed in the manuscript.

1. Fuel types and chemical composition

Table SM1 describes the types and amount (kg) of fuels used for the production of bricks in the three kilns sampled. The majority of the fuel used in the three kilns consisted in diverse types of wood. Diesel is used in the Traditional-fixed kiln only at the beginning of the burning stage to initiate the combustion.

Table SM2 shows the results of the chemical composition analyses of the fuels used during the burning stages of the brick production process for the MK2 and the traditional-campaign kilns in El Refugio, Guanajuato. The table also shows the heat of combustion of fuels and materials used during the production of bricks. Both of these two kilns are located in the same brick production area and use the same pitch for obtaining the clay for the bricks and use similar types of woods for fuels.

Table SM3 shows the results of the chemical composition analyses of the fuels and heat of combustion of materials used during the production of bricks for the traditional-fixed kiln in Abasolo, Guanajuato. The values from these analyses are used in the calculation of fuel, energy and brick-based emission factors following the methods described in the manuscript.

Table SM1. Mass [kg] of fuels used during the firing stage of the brick production.

Fuels	MK2 kiln	Traditional-campaign kiln	Traditional-fixed kiln
Pine	294.4	-	-
Indian laurel	15.5	-	-
Poplar	83.1	165.2	-
Eucalyptus	259.3	107.3	-
Pirul	350.3	1481.7	-
Ficus	171.7	22.5	-
Ash tree	293.1	284.9	-
Mesquite	230.6	741.9	-
Manure[a]	734.4	1568.3	-
Avocado wood	-	-	1784.5
Diesel	-	-	8.3
Sawdust	-	-	5930.7

Table SM2. Chemical composition of fuels and heat of combustion of materials used during the brick production for the MK2 kiln and the traditional-campaign kiln.

Sample	%C	%H	%N	Mass (mg)[a]	H (MJ/kg)[b]
Ash tree	50.68	6.44	0.41	2.5	20.0
Poplar	50.06	6.43	0.67	2.2	18.4
Pirul	46.22	5.99	0.28	2.5	19.3
Pine	48.74	5.35	0.66	2.2	18.9
Indian laurel	48.69	5.75	0.43	2.5	8.1
Ficus	49.62	6.25	0.73	2.4	19.0
Mesquite	48.81	6.19	0.39	2.5	19.5
Eucalyptus	52.93	6.73	0.46	2.4	17.7
Manure	35.49	4.09	2.65	2.3	13.6
Raw brick	1.28	0.64	0.19	1.9	-
Cooked brick	0.11	0.01	0.09	2.3	-
Yellow clay	0.27	0.37	0.1	2.5	-
Black clay	0.86	0.58	0.14	2.1	-
Ashes[c]	7.44	0.05	0.11	2.4	-

[a] Mass used for determining the elemental composition.
[b] H: heat of combustion.
[c] Ashes debris sampled after the burning.

Table SM3. Chemical composition of fuels and materials used during the brick production at Abasolo, Guanajuato, for the traditional-fixed kiln.

Sample	%C	%H	%N	Mass (mg)[a]	H (MJ/kg)[b]
Avocado	50.62	6.79	0.24	2.6	19.9
Sawdust	49.86	5.25	0.41	2.4	18.6
Diesel	84.60	9.70	1.0	-	42.9
Raw brick	0.86	0.4	0.13	2.2	-
Cooked brick	0.13	0.18	0.08	2.4	-
Yellow clay	0.24	0.33	0.13	2.2	-
Black clay	0.81	0.42	0.14	2.5	-
Ashes[c]	2.75	0.06	0.09	2.3	-

[a] Mass used for determining the elemental composition.
[b] H: heat of combustion.
[c] Ashes debris sampled after the burning.

2. Instruments

Table SM4 shows the characteristics of the instruments deployed for the sampling of brick kilns using the sampling-probe described in the manuscript. Additional peripheral equipment used included filter, probe, hot pump, gas conditioner, distribution lines, gas diluter, temperature controller, flow calibration standards, and autonomous data acquisition system, among others.

Table SM4. Characteristics of the instruments deployed for the measurement of emission factors of the kilns using the sampling-probe technique.

Instrument	Pollutants measured	Specifications
Fourier-Transfer Infrared Spectrometer (FTIR)	CO_2, CO	Gasmet Technologies Oy, model DX 4000 Path length: 5 m Linearity error: < 2%
Flame Ionization Detector Analyzer (FIDA)	Total organic compounds	California Analytical Instruments, model 300 HFID Range: 0 – 300 µmol/mol as CH_4 Linearity error: < 1%
$PM_{2.5}$ Ambient Air Sampler	$PM_{2.5}$	BGI Incorporated, model: PQ 200 air sampler with very sharp cyclone. Quartz filters were thermally stabilized and sent to the laboratory for gravimetric and PM composition analysis using thermal/optical analysis.

Quality control procedures during the sampling-probe technique included:

- Interference Testing Analyzers, prior to first sampling;
- Calibration error test at the beginning of each sampling day of each analyte, in zero, low, middle, and high range concentration levels;
- Bias test for each analyte at the beginning and at the end of each sampling day, using Zero and High-Range calibration gases;
- Drift Test on each analyte at the end of each sampling day, using Zero and High-Range calibration gases;
- Sample interference was maintained at 50ºC to prevent condensation of water and/or hydrocarbons, as well as to prevent reactions between compounds;
- Sample cell on the FTIR analyzer was heated to 50ºC;
- Use of certified calibration gases with 2% uncertainty;
- A traceable calibrated gas dilution system (fixed point) was used to deliver different levels of concentration and evaluate the linearity of the analyzer;

Table SM5 shows the instruments deployed by the Aerodyne mobile laboratory (AML), the corresponding pollutants measured, and their associated detection limits for the measurement of emission factors for the three sampled kilns using the tracer ratio technique as described in the manuscript.

Table SM5. Characteristics of instruments deployed by the AML.

Instrument	Pollutants measured	Detection limit by pollutant
Tunable Infrared Laser Differential Absorption Spectrometers (TILDAS)	Carbon monoxide (CO) and nitrous oxide (N_2O); ethane (C_2H_6); methane isotopes ($^{13}CH_4$ and $^{12}CH_4$), sulfur dioxide (SO_2), and acetylene (C_2H_2).	Typical detection limits are 0.1 ppbv in 1-s, each of the pollutants quantified in this work is detected in plume encounters well above the detection limit.
Proton Transfer Reaction Mass Spectrometer (PTRMS)	Oxygenates, aromatics.	Typical detection limits are 0.3 – 0.8 ppbv depending on compound in 1-s of integration time.
Soot Particle Aerosol Mass Spectrometer (SP-AMS)	70 nm – 600 nm aerodynamic diameter aerosol, composition resolved into black carbon; sulfate; nitrate; ammonium; chloride and organic PM.	300 ng/m^3 in 1-s integration time.
Thermo Electron 42i chemiluminescent detector	NO, NO_y	0.4 ppbv in 1-s integration time for each species.
LiCor 6262 Non-Dispersive Infrared (NDIR)	CO_2	300 ppb in 1-s integration time. Plume enhancements in excess 5 ppm were quantified.

3. <u>Brick-based and energy-based emission factors</u>

Tables SM6 and SM7 show the average brick-based emission factors EF (g/kg fuel) and energy-based emission factors (g/MJ), respectively, obtained with the sampling probe (SP) and tracer ratio (AML) techniques for the sampled three kilns. The calculations were obtained following the procedures described in the manuscript.

Table S6. Average brick-based emission factors EF [g/kg-brick] obtained with the sampling probe (SP) and tracer ratio (AML) techniques for the three sampled kilns[1].

	MK2		Traditional-campaign		Traditional-fixed	
	SP	AML	SP	AML	SP	AML
CO_2	189.4 (3)		192.1 (3)		195.4 (5)	
CO	5.32 (2.1)	7.83 (6.2)	6.36 (2.1)	8.21 (5.4)	12.33 (2.8)	12.34 (4.2)
TOC[2]	0.24 (0.3)		0.63 (0.6)		1.71 (0.2)	
CH_4		0.29 (0.3)		0.42 (0.4)		0.69 (0.3)
NO		0.12 (0.1)		0.13 (0.3)		0.09 (0.)
NO_2		0.2 (0.2)		0.12 (0.2)		0.12 (0.1)
SO_2		0.12 (0.2)		0.03 (0.04)		0.02 (0.01)
$PM_{2.5}$[3]	0.23 (0.1)	0.2 (0.1)	0.58 (0.5)	0.29 (0.2)	0.16 (0.2)	0.15 (0.3)
BC	0.02 (0.02)	0.08 (0.1)	0.03 (0.03)	0.09 (0.1)	0.06 (0.09)	0.12 (0.3)
OC	0.003 (0.004)	0.062 (0.071)	0.038 (0.092)	0.148 (0.216)	0.016 (0.013)	0.021 (0.02)
Fullerene ($x10^{-3}$)		3.7 (5)		3.4 (4)		0.9 (1)
Ammonium ($x10^{-3}$)	29.5 (13)	11.6 (8)	118.5 (134)	8.4 (9)	0.3 (0.3)	0.8 (1)
Nitrate ($x10^{-3}$)	0.2 (0.1)	2.8 (4)	1.3 (2)	1.6 (3)	0.4 (0.2)	0.6 (1)
Sulfate ($x10^{-3}$)	16.2 (12)	14.5 (24)	11.6 (5)	8.7 (13)	5.7 (7)	2.5 (2)
Chloride ($x10^{-3}$)	73.9 (24)	28. (18)	246.1 (264)	28.5 (29)	2.5 (2)	1.2 (1)
Sodium ($x10^{-3}$)	3.3 (2)		2.8 (1)		1.8 (1)	
Magnesium ($x10^{-3}$)	0.08 (0.04)		0.17 (0.1)		0.13 (0.1)	
Potassium ($x10^{-3}$)	22.7 (17)		14.4 (9)		5.2 (8)	
Calcium ($x10^{-3}$)	0.7 (0.5)		1. (1)		0.6 (0.4)	
Fluoride ($x10^{-3}$)	0.1 (0.1)		0.3 (0.3)		0.1 (0.1)	
Chloride ($x10^{-3}$)	73.9 (24)		246.1 (264)		2.5 (2)	
Bromide ($x10^{-3}$)	0.6 (0.3)		3.0 (5)		0.1 (0.1)	
Ethane		0.018 (0.02)		0.027 (0.02)		0.052 (0.01)
Methanol		0.238 (0.24)		0.15 (0.29)		0.381 (0.14)
Acetonitrile		0.028 (0.03)		0.019 (0.01)		0.054 (0.02)
Acetaldehyde		0.135 (0.15)		0.068 (0.05)		0.255 (0.06)
Acetone		0.153 (0.18)		0.077 (0.24)		0.106 (0.04)
Acetic acid		0.316 (0.37)		0.112 (0.32)		0.122 (0.09)
Benzene		0.1 (0.11)		0.083 (0.08)		0.059 (0.04)
Toluene		0.111 (0.09)		0.053 (0.11)		0.032 (0.02)
C2Benzenes		0.121 (0.14)		0.068 (0.19)		0.022 (0.02)
C3Benzenes		0.103 (0.12)		0.056 (0.16)		0.015 (0.01)

[1] Values in parenthesis are 1 standard deviation.
[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.

Table S7. Average energy-based emission factors EF [g/MJ] obtained with the sampling probe (SP) and tracer (AML) techniques for the three sampled kilns[1].

	MK2		Traditional-campaign		Traditional-fixed	
	SP	AML	SP	AML	SP	AML
CO_2	91.4 (2)		88.9 (2)		88.1 (2)	
CO	2.57 (1.)	3.78 (3.)	2.94 (1.)	3.8 (2.5)	5.56 (1.3)	5.57 (1.9)
TOC[2]	0.12 (0.1)		0.29 (0.3)		0.77 (0.1)	
CH_4		0.14 (0.1)		0.19 (0.2)		0.31 (0.1)
NO		0.06 (0.1)		0.06 (0.1)		0.04 (0.02)
NO_2		0.1 (0.1)		0.05 (0.1)		0.05 (0.03)
SO_2		0.058 (0.08)		0.016 (0.02)		0.007 (0.003)
$PM_{2.5}$[3]	0.11 (0.04)	0.1 (0.05)	0.27 (0.2)	0.13 (0.1)	0.07 (0.1)	0.07 (0.1)
BC	0.01 (0.01)	0.04 (0.03)	0.02 (0.01)	0.04 (0.03)	0.03 (0.04)	0.05 (0.12)
OC	0.002 (0.002)	0.03 (0.034)	0.018 (0.04)	0.069 (0.1)	0.007 (0.006)	0.009 (0.009)
Fullerene ($x10^{-3}$)		1.8 (2)		1.6 (2)		0.4 (1)
Ammonium ($x10^{-3}$)	14.2 (6)	5.6 (4)	54.9 (62)	3.9 (4)	0.2 (0.1)	0.3 (0.3)
Nitrate ($x10^{-3}$)	0.1 (0)	1.4 (2)	0.6 (1)	0.7 (1)	0.2 (0.1)	0.3 (0.3)
Sulfate ($x10^{-3}$)	7.8 (6)	7.01 (12)	5.4 (2)	4.01 (6)	2.6 (3)	1.1 (1)
Chloride ($x10^{-3}$)	35.7 (12)	13.5 (9)	113.9 (122)	13.2 (13)	1.1 (1)	0.6 (0.2)
Sodium ($x10^{-3}$)	1.6 (1)		1.3 (0.5)		0.8 (1)	
Magnesium ($x10^{-3}$)	0.04 (0.02)		0.08 (0.05)		0.06 (0.04)	
Potassium ($x10^{-3}$)	10.9 (8)		6.7 (4)		2.3 (3)	
Calcium ($x10^{-3}$)	0.3 (0.2)		0.5 (0.3)		0.3 (0.2)	
Fluoride ($x10^{-3}$)	0.1 (0.04)		0.1 (0.1)		0.1 (0.04)	
Chloride ($x10^{-3}$)	35.7 (12)		113.9 (122)		1.1 (1)	
Bromide ($x10^{-3}$)	0.3 (0.1)		1.4 (2)		0.1 (0.1)	
Ethane		0.009 (0.01)		0.012 (0.01)		0.023 (0.01)
Methanol		0.115 (0.12)		0.069 (0.14)		0.172 (0.06)
Acetonitrile		0.014 (0.01)		0.009 (0.01)		0.024 (0.01)
Acetaldehyde		0.065 (0.07)		0.031 (0.02)		0.115 (0.03)
Acetone		0.074 (0.09)		0.036 (0.11)		0.048 (0.02)
Acetic acid		0.153 (0.18)		0.052 (0.15)		0.055 (0.04)
Benzene		0.048 (0.05)		0.038 (0.04)		0.026 (0.02)
Toluene		0.054 (0.05)		0.025 (0.05)		0.015 (0.01)
C2Benzenes		0.059 (0.07)		0.031 (0.09)		0.01 (0.01)
C3Benzenes		0.05 (0.06)		0.026 (0.07)		0.007 (0.01)

[1] Values in parenthesis are 1 standard deviation.
[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. Mechanical resistance of bricks

Tables SM8 shows the average mechanical resistance measured for each of the three levels (bottom, middle and top) for a random sample of 60 bricks at each kiln following the NMX-CC-404-ONNCCE-2012 Mexican standard.

Table SM8. Mechanical resistance [kg/cm^2] of bricks produced.

Level[1]	MK2 kiln	Traditional-campaign kiln	Traditional-fixed kiln
Bottom level	112.3	142.5	57.5
Middle level	98.8	138.8	78.0
Top level	78.9	118.1	87.5
Average	96.7	133.1	74.3

[1] Bottom level: 0.4 m above the combustion chamber; Top level: 0.3 m below the last layer of bricks at the top of the kiln; Middle level: half the distance between bottom and top levels.

5. Additional figures

The following figures are discussed in the text of the manuscript.

Kilns sampled

Figure 1 in the main text shows the kilns sampled. In the MK2 an active kiln is connected at the base with a second identical loaded kiln that acts as a filter of the combustion products while drying the raw material (Bruce et al., 2007). However, many parameters are involved in a semi-controlled burning process that difficult the standardization of the kiln design and thus there may be important differences in the resulting energy efficiency. Therefore, MK2 kilns should be carefully designed and properly operated to better obtain environmental and energy efficiency benefits.

Traditional-campaign kilns are built with the bricks to be cooked and sealing the sides of the formed kiln with clay to reduce heating losses. Bricks are arranged internally in a way to form the combustion chamber at the bottom of the kiln and subsequently in a gridded form to allow the releasing of the exhaust at the top of the kiln. They are called campaign kilns because they can be built in different locations and sizes, as needed by the kiln operator. In contrary, traditional-fixed kilns have already built-in walls and combustion chambers and thus are permanently stationed. Typically, special care is put to cover any leaks along the walls of the kiln, and the arrangement of the bricks inside kiln is also designed to force the combustion gases upward through the interior and minimize heating loses.

Figures SM1-SM3 show the temporal distributions of fuel-based emission factors (g/kg-fuel) measured with both the tracer ratio and the sampling probe techniques for the MK2 kiln, the traditional-campaign kiln, and the traditional-fixed kiln, respectivetly, as described in the manuscript.

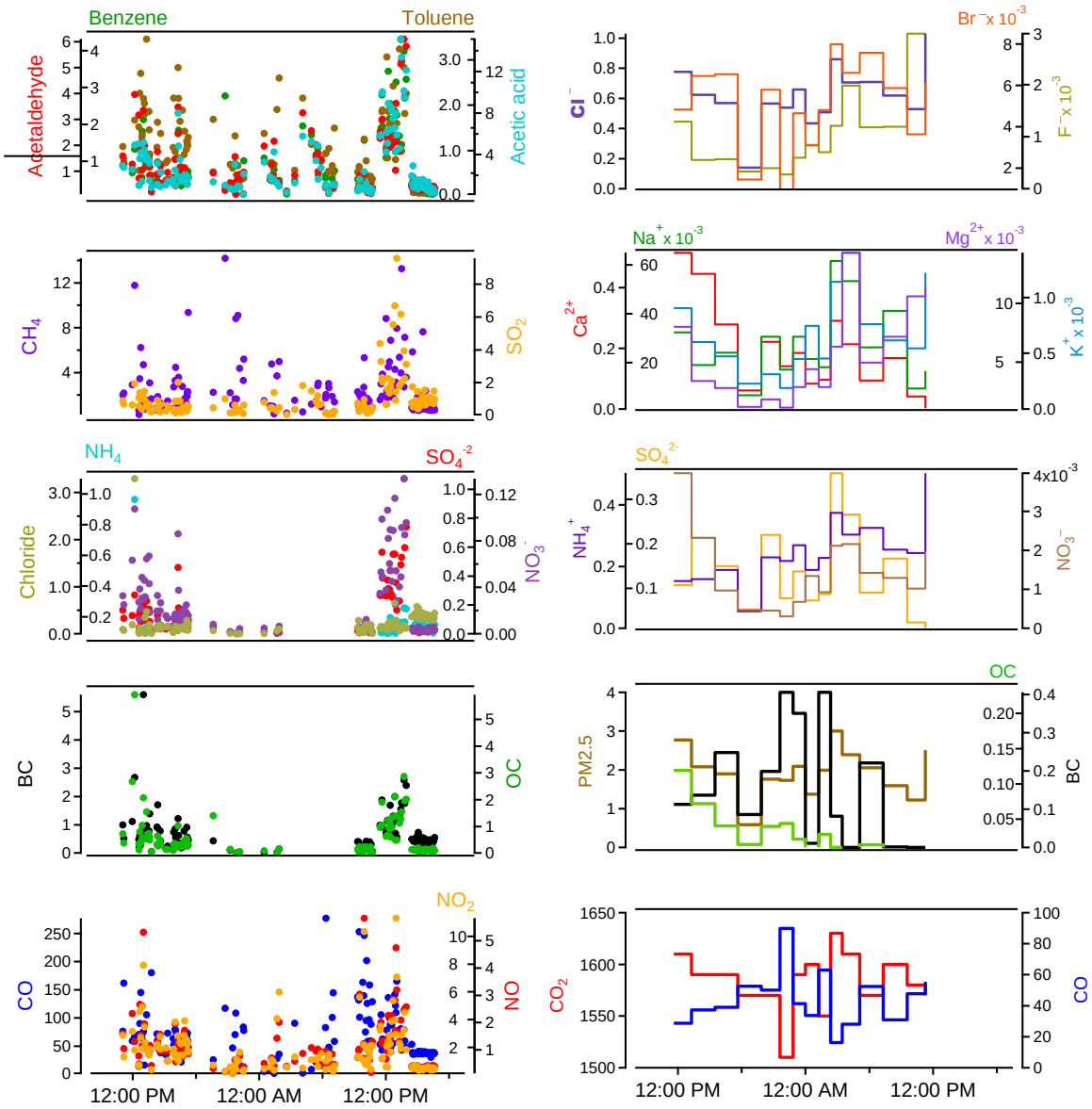

Figure SM1. Temporal distributions of fuel-based emission factors (g/kg-fuel) measured with the tracer ratio technique (left panels) and the sampling probe (right panels) techniques for the MK2 kiln. Labels located on the top of the plots correspond to the inner –scaled axis.

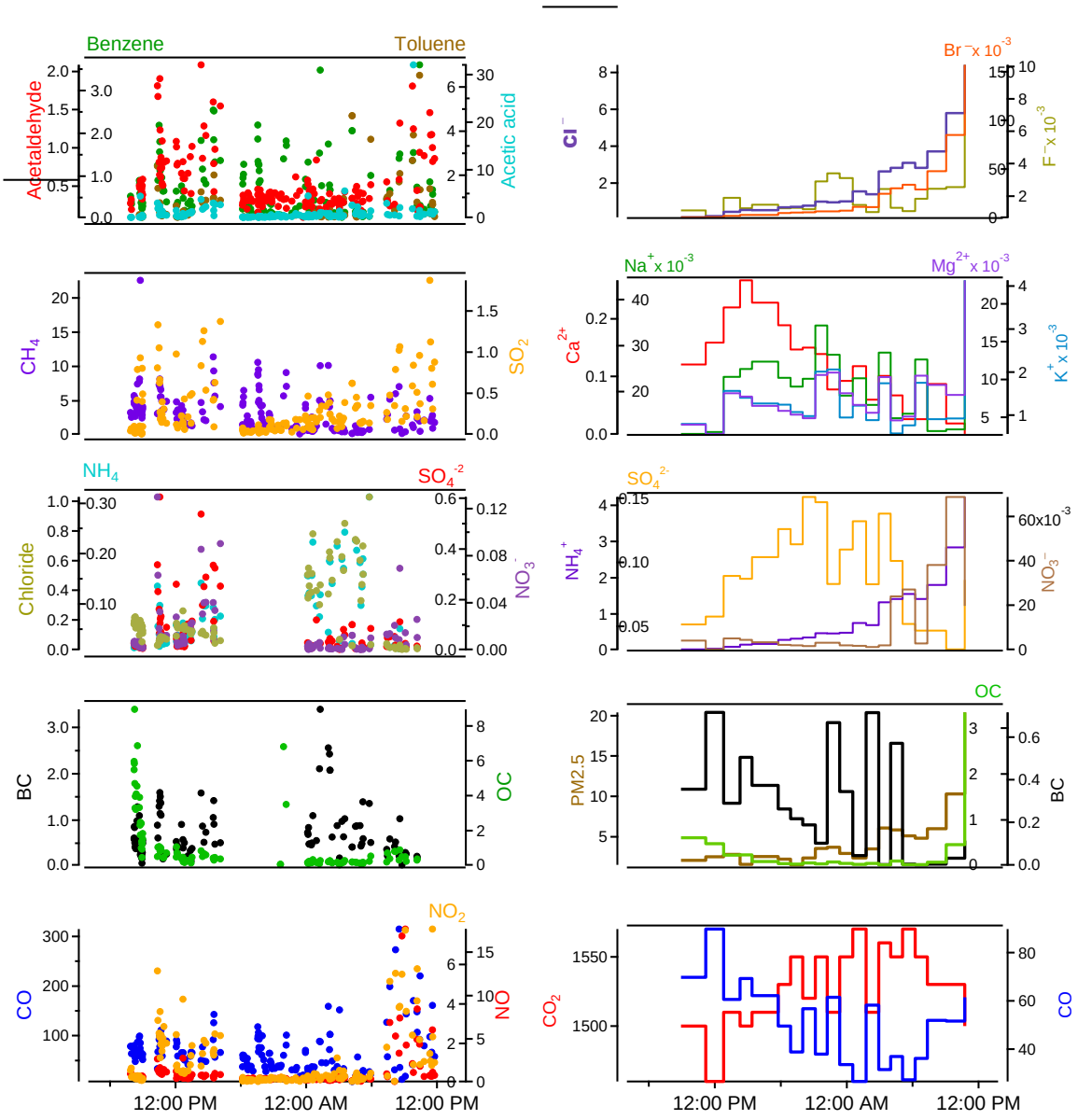

Figure SM2. Temporal distributions of fuel-based emission factors (g/kg-fuel) measured with the tracer ratio technique (left panels) and the sampling probe (right panels) techniques for the Traditional-campaign kiln. Labels located on the top of the plots correspond to the inner–scaled axis.

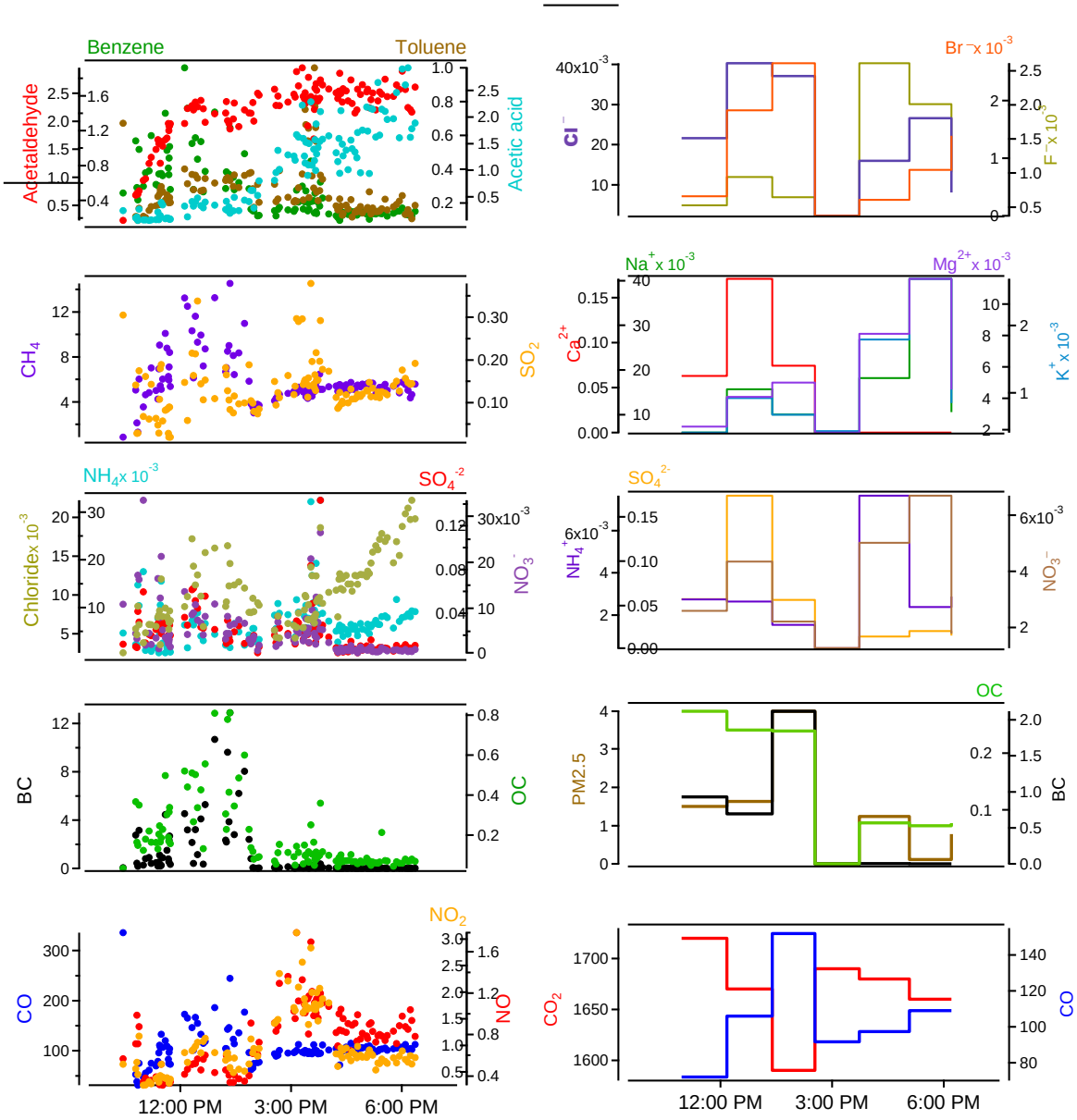

Figure SM3. Temporal distributions of fuel-based emission factors (g/kg-fuel) measured with the tracer technique (left panels) and the sampling probe (right panels) techniques for the Traditional-fixed kiln. Labels located on the top of the plots correspond to the inner –scaled axis.