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Supplementary Information for Emissions from Agricultural Fires in India: Field Measurements of Climate Relevant Aerosol Chemical and Optical Properties

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S1 Ultimate Analysis

Carbon fractions of the fuel are needed to determine the emission factors using the carbon balance method. Here, the carbon fraction is determined using the ultimate analysis of crop residues collected on-field. A Carbon-Hydrogen-Nitrogen-Sulphur analyser (Thermo Finnigan Flash EA1112 series) using the Dumas method was used using the ASTM D3176-09 standard. From the analysis, the mean carbon fractions of wheat, cotton, pigeon pea, and banana residue were 39.6%, 44.5%, 44.1% and 42.05% respectively.

S2 Measured properties

The measurement of CO₂ and CO is crucial to determining emission factors using the carbon balance method. These were measured in real-time and had experiment averaged elevations of about two times above the background in case of CO_2 . During the background measurements, the CO concentration was below the instrument's detection limit, but concentrations of over 100 ppm were observed when the source was switched on. All the measured properties' averaged concentrations and background values are summarised in Table S1. Real-time measurements of scattering and absorption properties were also made during these periods. Absorption at 880 nm is dominated by black carbon particles, whereas the same at 370 nm may have a potential contribution by brown carbon aerosol as well. Large elevations in absorption coefficients, ranging from 50 times, have been observed. Time-series plots of a few selected experiments are shown Figure S2. The emission plume is not always captured because of the inlet being kept static in most cases and natural changes in wind direction. This causes large fluctuations in the concentrations of species, especially in the case of cotton and banana; the wheat residue burning measurements were done by following the fire front. We also observed lower concentrations, larger Angstrom exponents and lower CO₂ elevations during the latter periods for the piled experiments when the combustion reached a smouldering stage, which had lower efficiencies. The absorption data is missing for some data points because the Aethalometer filter reaches the set attenuation limit, initiating the tape

advance procedure, which causes data loss for a few minutes. To account for the entire combustion cycle of these emissions, the experiment averaged values of all the real-time data were used for further calculations.

As expected, the concentrations of PM species during source emission measurements were substantially higher than those measured in the ambient background, reaching up to 350, 530, and 450 times higher than ambient for $PM_{2.5}$, EC, and OC, respectively. (Table S1). While these elevations are much higher than those seen in CO₂ and CO, the overall concentrations of carbon in these gaseous species are much higher in comparison (PM species are in $\mu g m^{-3}$ while CO₂ and CO in ppm). The absolute concentrations of the source measurements depend on how well the inlet is able to capture the smoke plumes. Hence, these concentrations alone cannot be used to make any inferences about the emissions. Their relative concentrations are more useful and have been discussed in the Results section. Meanwhile, the ratios of these emissions can help us understand combustion emission characteristics. The OC/EC ratio during the fire experiments is lower than the ambient for wheat, oilseed, and cotton burning experiments but higher for the banana experiments. This is likely due to the low efficiency of the banana experiments that have inefficient combustion conditions (MCE of 0.73 \pm 0.18). It also has led to higher OC_{HV}/OC_{LV} ratios compared to emissions from other crops. The combustion efficiencies reported for the other crops are within the ranges of those reported by 1 . Inorganic ions and elemental species in PM_{2.5} are also measured. Potassium, chlorine, and sodium are found to be the dominant species, similar to what has been reported by previous studies also^{2–5}. The overall contribution of PM constituents is shown in Figure S3. Most experiments have large contributions of chloride (Cl^{-}), potassium (K^{+}) and organic carbon (OC). The reconstructed $PM_{2.5}$ are found to be higher than those of measured $PM_{2.5}$, which is likely because of the positive filter sampling artefacts. All constituent species' concentrations are used to estimate the emission factors.

S3 Emission factor calculations

During the post-harvest months, large quantities of banana leaves and some stems are burned off (efficiently); but in the proceeding months, scattered (inefficient) burning of stems is carried out. The measurements in the present study include both these kinds of burns during the average of both types (1 measurement for leaves dominated and 2 for stem dominated), which have been reported in this study. From surveys, we find⁶ that most of the burns (80%) of the burns are during the post-harvest months and the remaining during the other months (20%); hence, these weights are used to calculate the mean and standard deviation of the emission factors (equations below).

$$EF_{p,mean} = \Sigma(w_x \times EF_{x,p}) \tag{1}$$

$$EF_{p,std} = \Sigma[w_x \times (EF_{x,p} - EF_{p,mean})^2]$$
⁽²⁾

S4 Uncertainty Calculations

Uncertainty in emission factor for each experiment was calculated by propagating uncertainties in each term of the carbon balance equation (Equation 6 in the main text). Uncertainty was propagated in quadrature; when two terms are added or subtracted, their absolute uncertainties are used (Equation 3), and when they are multiplied or divided, the relative uncertainties are used (Equation 4). The uncertainties in CO₂ and CO measurements reported by manufacturers is $\pm 5\%$. The uncertainty in temperature measurements is $\pm 2\%$, which leads to an equivalent uncertainty in $\rho_{C,air}$. Uncertainty in carbon fraction (CF) is $\pm 10\%$, based on measured standard deviations. The uncertainties in measured concentrations of different species for which emission factors need to be calculated depend on the measurement methods. For the present analysis, we assume an uncertainty of $\pm 20\%$ as a conservative estimate for all the species. Plugging in these values for typical concentrations of CO₂ observed during the burn measurements, we obtain a relative uncertainty of 25% in the emission factors.

This estimate of 25% is the uncertainty for a single experiment. In the present study, we report the emission factors for each crop type by averaging the emission factors for all the experiments for that crop type. The uncertainty in the emission factor for each crop is reported as the standard deviation around the reported average emission factor. The standard deviation is chosen over the propagated uncertainty (which would also be around 25%), as the standard deviation leads to larger uncertainty values. This is evident in Table 1, where uncertainties in CO (32%), PM_{2.5} (44%), OC (38%), and EC (11-48%) are almost always greater than the propagated 25% uncertainty. The larger standard deviation likely arises from differences in combustion conditions and fuel composition at different locations (farms), providing a more conservative estimate for uncertainties in emission factors.

$$UNC_Y = \sqrt{UNC_{X1}^2 + UNC_{X2}^2 + UNC_{X3}^2 + \dots}$$
(3)

$$\frac{UNC_Y}{Y} = \sqrt{\left(\frac{UNC_{X1}}{X1}\right)^2 + \left(\frac{UNC_{X2}}{X2}\right)^2 + \left(\frac{UNC_{X3}}{X3}\right)^2 + \dots}$$
(4)

S5 Figures and Tables

Table S1: Measured (mean \pm standard deviation) concentrations of species, ratios, and optical properties during ambient and source emission measurement periods.*

Pollutant	Unit	Background	Straw	Stalks	Stem & Leaves
CO_2	ppm	280 ± 70	685 ± 294	651 ± 152	539 ± 13
CO	ppm	ND	42 ± 19	31 ± 20	90 ± 74
$b_{abs,880}$	Mm^{-1}	26 ± 5	12012 ± 6435	7238 ± 5865	4859 ± 4222
AAE _{370/660}		1.52 ± 0.1	1.41 ± 0.19	1.84 ± 0.35	3.12 ± 1.29
$AAE_{660/880}$		1.25 ± 0.08	1.29 ± 0.1	1.51 ± 0.23	1.79 ± 0.45
SSA ₅₃₂		0.68 ± 0.1	0.41 ± 0.09	0.53 ± 0.15	0.53 ± 0.2
MCE			0.89 ± 0.03	0.92 ± 0.05	0.81 ± 0.12
$PM_{2.5}$	$\mu g m^{-3}$	72 ± 47	5403 ± 3760	2129 ± 1568	26093 ± 22384
EC	$\mu g m^{-3}$	2.31 ± 0.17	945 ± 673	935 ± 634	454 ± 294
OC	$\mu g m^{-3}$	26 ± 16	1035 ± 539	552 ± 493	11465 ± 9930
OC/EC		11.75 ± 8.18	1.24 ± 0.33	0.7 ± 0.46	19 ± 14
$OC_{HV}/OC_{LV} **$		1.43 ± 0.95	0.48 ± 0.2	0.68 ± 0.27	1.18 ± 0.78
Potassium	$\mu g m^{-3}$	ND	1616 ± 191	292 ± 199	930 ± 806
Sodium	$\mu g m^{-3}$	0.54	466 ± 140	83 ± 69	87 ± 30
Ammonium	$\mu g m^{-3}$	9.38	258 ± 83	33 ± 15	1453 ± 1334
Chloride	$\mu g m^{-3}$	33.68 ± 0.32	4079 ± 538	801 ± 463	7600 ± 6278
Al	$\mu g m^{-3}$	0.54 ± 0.18	135 ± 19	54 ± 29	208 ± 78
Si	$\mu g m^{-3}$	0.55 ± 0.16	76 ± 14	38 ± 19	121 ± 43

*Elevations of dominants species are shown here; calculated emission factors for all measured species are shown in Table 1 in the main text

 $**OC_{HV}/OC_{LV} = (OC1+OC2)/(OC3+OC4)$

Table S2: Ranges of AAE, MAC, and SSA compared to previous measurements and those calculated from empirical equations using predictor variables (measured range) MCE (0.73-0.98), EC/OC (0.03-4.98), and OA/EC (0.36-59).

Study	Equation/Measured	Variable	Range
Present Study	Measured	SSA_532 MAC_PM,532 MAC_EC,532	0.29-0.83 0.03-29 0.33-44
Stockwell et al., 2016 ⁷	Measured	AAE_405/870 SSA_870	1.58-3.53 0.579–0.981
Holder et al., 2017 ⁸	Measured	AAE_405/780 AAE_405/532 SSA_532	1.6-3.1 1.48-4 0.67-0.96
Liu et al., 2014 ⁹	$1-0.762 \times (MCE)^{23.003}$	SSA_532	0.51-1
Pokhrel et al., 2016 ¹⁰	$\begin{array}{l} 0.933-1.637\times(\text{MCE})^{58.492}\\ 2.454\times(\text{MCE})^{-3.292}\\ 1.802\times(\text{EC/OC})^{-0.232}\\ 1-0.469\times(\text{EC/OC})^{0.576} \end{array}$	SSA_532 AAE_405/660 SSA_532 AAE_405/660	0.43-0.93 2.62-6.92 1.24-4.07 -0.18-0.94'
Cheng et al., 2019 ¹¹	$1.21 \times (EC/OC)^{-0.4155} + 1$ $1.21 \times \log(EC/OC) + 4.13$	AAE_422/780 MAC_532_TC	1.62-6.19 2.29-4.97
McClure et al., 2020 ¹²	$\begin{array}{l} 9.124\text{-}7.476/(1+\exp((0.884-\text{MCE})/0.0236))\\ \exp(4.949\text{-}5.073/(1+\exp((0.882\text{-}\text{MCE})/0.0705)))\\ 0.954\text{-}0.88\times\text{MCE}^{22.76}\\ 1.25\text{+}7.81/(1+\exp((2.298\text{-}\log10(\text{OA/BC}))/0.554))\\ 10^{(0.94+2.56/(1+\exp((3.721-\log10(\text{OA/BC}))/0.9)))}\\ 0.085\text{+}0.91/(1+\exp((0.623\text{-}\log10(\text{OA/BC}))/0.52))\end{array}$	$\begin{array}{l} AAE_{405-532} \\ MAC_BC,405 \\ SSA_405 \\ AAE_{405-532} \\ MAC_BC,405 \\ SSA_405 \end{array}$	1.77-9.11 2.43-83.31 0.4-0.95 1.3-3.43 9.22-15.96 0.19-0.9

Table S3: Emission factors (g/kg_{fuel}) of select species used by emissions inventories. A comparison of emissions is shown in Figure S8.

Species	СО	PM _{2.5}	OC	EC
Andreae and Merlet, 2001 ^{#13}	92 ± 84	3.9	3.3	0.69 ± 0.13
Akagi et al., 2011 ^{\$14}	102 ± 33	6.3 ± 2.4	2.3	0.75
Andreae, 2019 ¹⁴	76.3 ± 55.3	8.2 ± 4.4	4.9 ± 3.6	0.42 ± 0.28
Pandey et al., 2014^{15} – cereals	76 ± 45	8.8 ± 2.9	2.9 ± 0.9	0.55 ± 0.37
Pandey et al., 2014^{15} – sugarcane	82 ± 40	3.92 ± 0.08	0.6 ± 0.12	1.5 ± 0.12
Present study – straw	97 ± 32	7.5 ± 4.9	2.1 ± 0.8	1.9 ± 1.0
Present study – stalks	74 ± 43	4.6 ± 2.2	1.1 ± 0.9	2.1 ± 1.0
Present study – stem & leaves	86 ± 98	19.3 ± 27.7	7.6 ± 12.7	0.9 ± 0.1

[#]Jain et al., 2014 used emission factors from Andreae and Mertlet, 2001

^{\$}GFED use emission factors from Akagi et al., 2011

State	CO	$PM_{2.5}$	OC	EC
Madhya Pradesh	1474	117.3	33.4	29.4
Punjab	1151	88.8	24.8	22.6
Uttar Pradesh	1024	81.2	23.1	23.2
Gujarat	459	39.6	11.8	9.8
Andhra Pradesh	266	35.4	12.5	4.9
Telangana	467	34.7	9.5	10.1
Tamil Nadu	298	31.5	10.3	5.7
Maharashtra	459	31.5	8.2	11.3
Haryana	348	26.5	7.3	7.1
Karnataka	342	24.7	6.6	7.7
Rajasthan	217	15.9	4.3	4.7
Bihar	155	11.7	3.2	3.2
West Bengal	109	8.2	2.3	2.2
Odisha	76	5.7	1.6	1.6
Assam	29	3.9	1.4	0.5
Jharkhand	43	3.3	0.9	0.9
Uttarakhand	27	2.1	0.6	0.6
Kerala	12	1.7	0.6	0.2
Total	6990	566	163	146

Table S4: Emissions contributions from major states (descending order of $PM_{2.5}$ emissions). These states contribute to more than 99.5% of the total emissions of these pollutants.

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Figure S1: Schematic showing measurement locations.



Figure S2: Samples of measured real-time concentrations of CO_2 , CO and optical properties. Three sample experiments are shown for (A1-3) Cotton, (B1-3) Banana, and (C1-3) Wheat. Missing data points in the absorption (and AAE) correspond to periods of tape advance in the Aethalometer.



Figure S3: Source profiles of agricultural residue burning emissions of different crop residue types.



Figure S4: Correlation coefficient plot between all measured and calculated properties. Colours indicate the spearman-r correlation coefficient, and the dots indicate significance at p<0.1.



Figure S5: Emissions of carbonaceous aerosols from burning different crop residues. Emissions are calculated using activity from Kapoor et al.⁶ and emission factors from the present study. Cereal emission factors are used for rice, wheat, maize, and millets; stalks factors for oilseeds, groundnut, cotton, and sugarcane; and stem and leaves factors for banana residue burning.



Figure S6: (a) Gridded $(0.05^{\circ} \times 0.05^{\circ})$ emissions of PM_{2.5} (Mg year⁻¹) from crop residue burning in India (b) Monthly (Gg month⁻¹, left y-axis) and daily (Gg day⁻¹, right y-axis) variation of PM_{2.5} emissions across the year. Daily emissions are presented as 10-day running means for clarity.



Figure S7: (a) Gridded $(0.05^{\circ} \times 0.05^{\circ})$ emissions of OC (Mg year⁻¹) from crop residue burning in India (b) Montly (Gg month⁻¹, left y-axis) and daily (Gg day⁻¹, right y-axis) variation of OC emissions across the year. Daily emissions are presented as 10-day running means for clarity.

Figure S8: Emissions from crop residue burning in India estimated from different emissions inventories. Jain et al. (2014)¹⁶ and Pandey et al. (2014)¹⁵ report emissions only from India; meanwhile, EDGAR¹⁷ and GFED¹⁸ are global emissions inventories. GFED is a top-down (satellite-derived) estimate, while the other three are bottom-up estimates.

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