

Supplementary Material

Simplifying emissions modelling from wildland fires: laboratory- scale emission factors are independent of fine woody debris fuel load

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Supplementary Material:

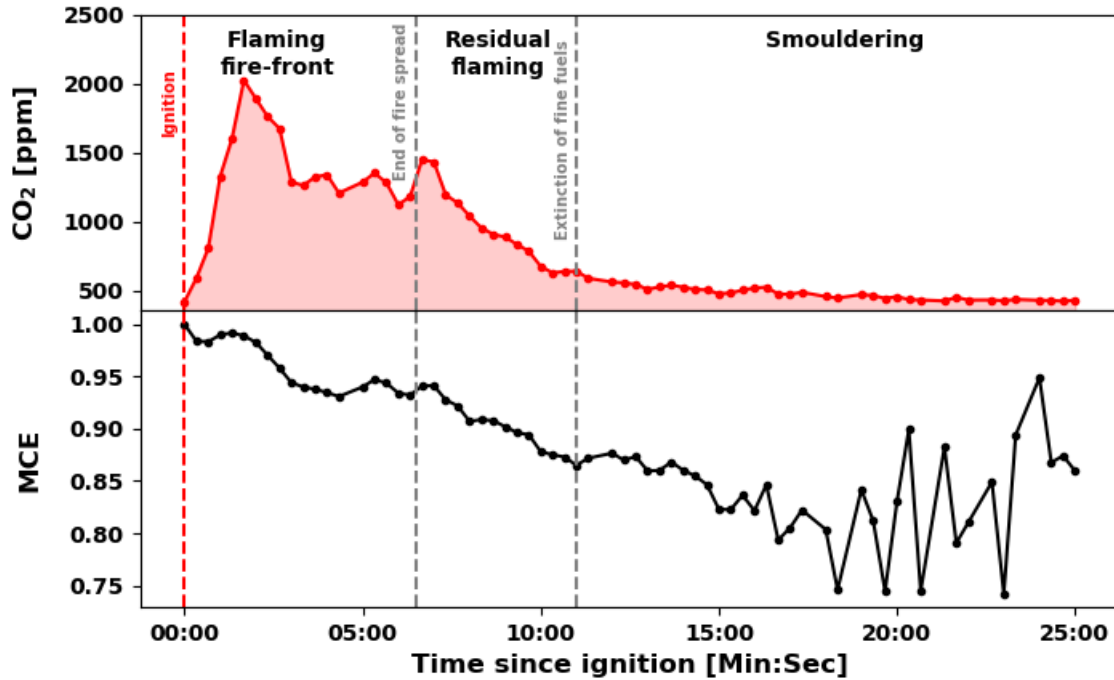


Figure S1: Upper panel repeats Figure 6, the time series of changing CO₂ from the first burn with load 2. The lower panel shows how MCE changes as this fire progresses. Note that large variation in MCE from about 18 minutes is a result of measurement uncertainty and sampling issues as very small enhancements of CO₂ and CO are detected as the fire is nearly extinguished.

Table S1: Emission factors for CO₂ and CO (in g.kg⁻¹ of fuel consumed) measured by open-path FTIR spectrometry, MCE, and % moisture for heading fires with different fuel loads along with the few backing fires from the Pyrotron experimental fire. [Note: Burns are labelled H for heading or B for backing, then load and replication number e.g. HL2-4 is thus the 4th replicate heading burn with load 2].

| Fire ID | Load | Moisture % | EF CO ₂ | EF CO | Total MCE |
|---------------------------------------|-------|------------|--------------------|-----------------|--------------------|
| Burn 1 | HL1-1 | 11.5 | 1643 | 114 | 0.9 |
| Burn 13 | HL1-2 | 12.2 | 1688 | 74 | 0.94 |
| Burn 21 | HL1-3 | 10.7 | 1648 | 111 | 0.9 |
| | | | 1660 ± 25 | 100 ± 22 | 0.91 ± 0.02 |
| Burn 7 | HL2-1 | 14.5 | 1617 | 127 | 0.89 |
| Burn 11 | HL2-2 | 13.7 | 1654 | 104 | 0.91 |
| Burn 12 | HL2-3 | 12.2 | 1650 | 93 | 0.92 |
| Burn 14 | HL2-4 | 12 | 1698 | 78 | 0.93 |
| Burn 20 | HL2-5 | 12.7 | 1605 | 104 | 0.91 |
| | | | 1645 ± 36 | 101 ± 18 | 0.91 ± 0.01 |
| Burn 3 | HL3-1 | 17.1 | 1662 | 101 | 0.91 |
| Burn 8 | HL3-2 | 14.2 | 1663 | 99 | 0.91 |
| Burn 16 | HL3-3 | 12 | 1670 | 97 | 0.92 |
| Burn 17 | HL3-4 | 12.7 | 1681 | 89 | 0.92 |
| Burn 22 | HL3-5 | 10.9 | 1657 | 104 | 0.91 |
| | | | 1666 ± 9 | 98 ± 6 | 0.91 ± 0.01 |
| Burn 9 | HL4-1 | 13.7 | 1647 | 108 | 0.91 |
| Burn 10 | HL4-2 | 13.7 | 1665 | 98 | 0.92 |
| Burn 15 | HL4-3 | 12 | 1686 | 86 | 0.93 |
| Burn 18 | HL4-4 | 12.6 | 1682 | 87 | 0.93 |
| Burn 19 | HL4-5 | 12.7 | 1676 | 91 | 0.92 |
| | | | 1671 ± 16 | 94 ± 9 | 0.92 ± 0.01 |
| Mean ± stdev all heading fires | | | 1661 ± 24 | 98 ± 13 | 0.92 ± 0.01 |
| Burn 4 | BL1-1 | 10 | 1596 | 135 | 0.88 |
| Burn 2 | BL2-1 | 11.9 | 1520 | 172 | 0.85 |
| Burn 24 | BL3-1 | 11 | 1597 | 135 | 0.88 |
| Burn 23 | BL4-1 | 11.9 | 1558 | 153 | 0.87 |
| Mean ± stdev all backing fires | | | 1568 ± 37 | 149 ± 18 | 0.87 ± 0.01 |

Table S2: Emission ratios to CO for all emitted trace gases measured along with the square of the correlation coefficient (R^2) and the p -value for dependence on the amount of fine woody debris in the fuel load.

| Trace Gas from Open-Path FTS | Mean ER | R^2 | p-value |
|--|----------------|-------------------------|-----------------------------|
| C₂H₄ | 0.007 | 0.06 | 0.42 |
| CH₃OH | 0.007 | 0.07 | 0.31 |
| CH₄ | 0.048 | 0.04 | 0.42 |
| CH₂O | 0.014 | 0.09 | 0.26 |
| CH₃COOH | 0.009 | 0.09 | 0.24 |
| HCOOH | 0.0010 | 0.01 | 0.88 |
| NH₃ | 0.025 | 0.11 | 0.22 |
| Trace gas from Tedlar bag samples | | | |
| Acetaldehyde | 0.0030 | 0.01 | 0.72 |
| Acetone | 0.0018 | 0.06 | 0.34 |
| Acetonitrile | 0.0006 | 0.01 | 0.78 |
| Acetylene | 0.0022 | 0.00 | 1.00 |
| Benzene | 0.0011 | 0.00 | 0.99 |
| Butadiene | 0.0004 | 0.39 | 0.06 |
| HCN | 0.0014 | 0.01 | 0.63 |
| Isoprene | 0.0007 | 0.03 | 0.54 |
| Pyrrole | 0.0002 | 0.20 | 0.08 |
| TMB | 0.0002 | 0.06 | 0.32 |
| Toluene | 0.0019 | 0.01 | 0.78 |

There are two compounds that have p values that are close to the 0.05 significance threshold, including: butadiene (as measured by SIFT-MS) with a p -value of 0.06, and a potential trend of ~ -5 % per extra tonne of fine woody debris and pyrrole (as measured by SIFT-MS) with a p -value of 0.08, and a potential trend of ~ -5 % per extra tonne of fine woody debris. Whilst none of these trends are significant, it is worth noting that the measured emission ratios for each load are quite variable and so could hide small trends.

Table S3: Emission ratios to CO for all emitted particulate phase components measured along with the square of the correlation coefficient (R^2) and the p -value for dependence on the amount of fine woody debris in the fuel load.

| Particle phase component | Mean ER | R^2 | p-value |
|--|----------------|-------------------------|-----------------------------|
| <i>PM_{2.5}</i> | <i>0.073</i> | <i>0.095</i> | <i>0.33</i> |
| <i>PM (gravimetric total suspended particles)</i> | <i>0.086</i> | <i>0.25</i> | <i>0.06</i> |
| <i>Na⁺</i> | <i>0.00014</i> | <i>0.04</i> | <i>0.47</i> |
| <i>NH₄⁺</i> | <i>0.00027</i> | <i>0.08</i> | <i>0.29</i> |
| <i>K⁺</i> | <i>0.00030</i> | <i>0.06</i> | <i>0.37</i> |
| <i>Mg²⁺</i> | <i>0.00009</i> | <i>0.05</i> | <i>0.43</i> |
| <i>Ca²⁺</i> | <i>0.00056</i> | <i>0.07</i> | <i>0.33</i> |
| <i>Cl⁻</i> | <i>0.00075</i> | <i>0.13</i> | <i>0.18</i> |
| <i>Br⁻</i> | <i>0.00002</i> | <i>0.07</i> | <i>0.34</i> |
| <i>NO₃⁻</i> | <i>0.00012</i> | <i>0.04</i> | <i>0.48</i> |
| <i>SO₄²⁻</i> | <i>0.00040</i> | <i>0.00</i> | <i>0.89</i> |
| <i>C₂O₄²⁻</i> | <i>0.00007</i> | <i>0.05</i> | <i>0.45</i> |
| <i>PO₄³⁻</i> | <i>0.00015</i> | <i>0.08</i> | <i>0.32</i> |
| <i>Acetic acid</i> | <i>0.00005</i> | <i>0.08</i> | <i>0.29</i> |
| <i>Formic acid</i> | <i>0.00020</i> | <i>0.04</i> | <i>0.48</i> |
| <i>Levogluconan</i> | <i>0.011</i> | <i>0.05</i> | <i>0.44</i> |
| <i>Mannosan</i> | <i>0.00058</i> | <i>0.17</i> | <i>0.13</i> |
| <i>Organic Carbon</i> | <i>0.046</i> | <i>0.13</i> | <i>0.18</i> |
| <i>Elemental Carbon</i> | <i>0.0088</i> | <i>0.09</i> | <i>0.29</i> |
| <i>Total Carbon</i> | <i>0.0550</i> | <i>0.13</i> | <i>0.19</i> |
| <i>Black Carbon</i> | <i>0.014</i> | <i>0.03</i> | <i>0.52</i> |

There is one compound that has a p value that is close to the 0.05 significance threshold which is total particulate matter (as measured from the filters) with a p -value of 0.06, and a potential trend of $\sim -4\%$ per extra tonne of fine woody debris.

Table S4: Mean and 1 sigma standard deviations of emission ratios to CO for trace gases for different fire stages.

| | Fire front | | Residual | | Smouldering | |
|-----------------------------------|------------|--------|----------|-------|-------------|--------|
| | Mean | Std | mean | std | mean | std |
| CH₄ | 0.037 | 0.009 | 0.06 | 0.05 | 0.06 | 0.01 |
| C₂H₄ | 0.011 | 0.004 | 0.016 | 0.005 | 0.008 | 0.002 |
| NH₃ | 0.014 | 0.004 | 0.03 | 0.02 | 0.018 | 0.003 |
| CH₃OH | 0.007 | 0.002 | 0.010 | 0.009 | 0.008 | 0.003 |
| CH₂O | 0.017 | 0.005 | 0.03 | 0.04 | 0.011 | 0.002 |
| HCOOH | 0.0017 | 0.0007 | 0.003 | 0.005 | 0.0018 | 0.0004 |
| CH₃COOH | 0.009 | 0.005 | 0.03 | 0.06 | 0.012 | 0.004 |
| PM_{2.5} | 0.11 | 0.07 | 0.12 | 0.05 | 0.08 | 0.02 |

Table S5: As Table S4 except with outlier removed.

| | Fire front | | Residual | | Smouldering | |
|-----------------------------------|------------|--------|----------|-------|-------------|--------|
| | mean | Std | mean | std | mean | std |
| CH₄ | 0.037 | 0.009 | 0.05 | 0.02 | 0.06 | 0.01 |
| C₂H₄ | 0.011 | 0.004 | 0.016 | 0.005 | 0.008 | 0.002 |
| NH₃ | 0.014 | 0.004 | 0.02 | 0.01 | 0.018 | 0.003 |
| CH₃OH | 0.007 | 0.002 | 0.008 | 0.002 | 0.008 | 0.003 |
| CH₂O | 0.017 | 0.005 | 0.02 | 0.01 | 0.011 | 0.002 |
| HCOOH | 0.0017 | 0.0007 | 0.002 | 0.002 | 0.0018 | 0.0004 |
| CH₃COOH | 0.009 | 0.005 | 0.02 | 0.01 | 0.012 | 0.004 |
| PM_{2.5} | 0.11 | 0.07 | 0.10 | 0.04 | 0.08 | 0.02 |

Table S6: Mean emission factors for particle phase chemical components and trace gases averaged from all experimental fires.

| Particle phase component | Mean EF in g kg ⁻¹ | Trace Gas from Open-Path FTS | Mean EF in g kg ⁻¹ |
|---|-------------------------------|--|-------------------------------|
| PM _{2.5} | 2.7 ± 0.7 | C ₂ H ₄ | 0.6 ± 0.3 |
| PM _{TSP} | 6.2 ± 2.1 | CH ₃ OH | 0.8 ± 0.6 |
| Na ⁺ | 0.010 ± 0.005 | CH ₄ | 2.7 ± 1.2 |
| NH ₄ ⁺ | 0.019 ± 0.007 | CH ₂ O | 1.4 ± 0.9 |
| K ⁺ | 0.021 ± 0.008 | CH ₃ COOH | 1.9 ± 1.5 |
| Mg ²⁺ | 0.008 ± 0.013 | HCOOH | 0.2 ± 0.1 |
| Ca ²⁺ | 0.05 ± 0.07 | NH ₃ | 1.4 ± 0.7 |
| Cl ⁻ | 0.05 ± 0.02 | | |
| Br ⁻ | 0.0016 ± 0.0004 | | |
| NO ₃ ⁻ | 0.008 ± 0.003 | Trace gas from Tedlar bag samples | |
| SO ₄ ²⁻ | 0.03 ± 0.01 | Acetaldehyde | 0.0030 ± 0.0005 |
| C ₂ O ₄ ²⁻ | 0.005 ± 0.002 | Acetone | 0.0018 ± 0.0003 |
| PO ₄ ³⁻ | 0.011 ± 0.007 | Acetonitrile | 0.0006 ± 0.0002 |
| Acetic acid | 0.005 ± 0.002 | Acetylene | 0.0020 ± 0.0006 |
| Formic acid | 0.02 ± 0.02 | Benzene | 0.0011 ± 0.0002 |
| Levogluconan | 0.8 ± 0.2 | Butadiene | 0.0004 ± 0.0001 |
| Mannosan | 0.04 ± 0.01 | Hydrogen | 0.0014 ± 0.0009 |
| Organic Carbon | 3 ± 1 | Cyanide | 0.0007 ± 0.0002 |
| Elemental Carbon | 0.6 ± 0.2 | Isoprene | 0.0007 ± 0.0002 |
| Total Carbon | 3.8 ± 1.2 | Pyrrole | 0.00015 ± 0.00008 |
| Black Carbon | 0.9 ± 0.4 | Tri methyl benzene | 0.0002 ± 0.0001 |
| | | Toluene | 0.0019 ± 0.0006 |