Supplemental information for:

Non-methane organic gas emissions from biomass burning: identification, quantification, and emission factors from PTR-ToF during the FIREX 2016 laboratory experiment

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S1. Correction for reagent ion depletion.

In many fires, concentrations of NMOG were high and for some fires the primary reagent ion, H_3O^+, was depleted by up to 50% during the most intense stage of the fire. This leads to a non-linear sensitivity at those short time periods with the highest NMOG mixing ratios. Dilution of the sampled air can be used to avoid the primary ion depletion, but determining the dilution factor is not very accurate and mixing ratios in the diluted sample air at the later stage of the fire would be very small. Correcting for the non-linear NMOG sensitivity at very high mixing ratios results in a higher overall data quality.

We considered three effects of reagent ion depletion that could potentially contribute to inaccuracy in the reported NMOG concentration:

1) Change of relationship between ncps and ppb due to changes in sensitivity and H_3O^+ concentration

2) Inaccuracy of humidity correction based on H_3O^+ to $H_5O_2^+$ ratio

3) Secondary chemistry: proton donation from $NMOG_A \cdot H^+$ to $NMOG_B$

Variables used in the consideration of these effects and our correction are given below:

Variable	
$[H_3O^+]_0$	The initial concentration of H_3O^+ in the drift tube, before NMOG react
$[H_3O^+]_{meas}$	The measured concentration of H_3O^+ after reaction in the drift tube
k, k_{H3O+}	The rate constant between a NMOG and H_3O^+
k_{H5O2+}	The rate constant between a NMOG and the water cluster $H_5O_2^+$
$[VOC]$	The concentration of NMOG in the drift tube
$[VOC \cdot H^+]_{meas}$	The measured concentration of protonated NMOG after reaction in the drift tube
$[VOC \cdot H^+]_{linear}$	The concentration of protonated NMOG that would be measured, if there were no H_3O^+ depletion
Δt	Time available for H_3O^+ and a NMOG to react in the drift tube
$ncps_{meas}$	Measured normalized counts per second
$ncps_{linear}$	Normalized counts per second assuming a linear response with [NMOG]
$nhcps$	Normalized, humidity-corrected counts per second

In the following explanations, we use a simplified system in which there is only one NMOG reacting with H_3O^+. Of course, in reality, many hundreds of NMOG are reacting with H_3O^+ simultaneously. The technically accurate way to correct for reagent ion depletion effects would be to apply a separate correction to each NMOG ion species based on its rate constant with H_3O^+ and its fractional contribution to the H_3O^+ depletion. In practice, it is not possible to apply a separate correction to each ion, as this would

39   require *a priori* knowledge of the concentration of each NMOG. This means that *[NMOG]* is equivalent to

40   the weighted sum of all NMOG concentrations, k is the average rate constant, and so forth. The final derived

41   correction factor is an average correction factor. Some signals will be slightly overcorrected, others

42   undercorrected, but on average no bias is introduced into the total signal.

43   **S1.1 Effect 1: Changes in ncps/ppb**

44   It is usually assumed that the normalized protonated NMOG response (ncps/ppb) is linear with

45   NMOG concentration. However, when the reagent ion is depleted, NMOG sensitivity is no longer linear.

46   We applied a correction to the measured normalized NMOG signal (ncps) to account for this nonlinearity.

47   The correction factor is derived as follows:

48   The concentration of H_3O^+ in the drift tube decreases as it reacts with a NMOG:

49   $$[H_3O^+]_{meas} = [H_3O^+]_0 e^{-k[\text{NMOG}]\Delta t} \qquad (1)$$

50   The concentration of protonated NMOG mirrors this decrease:

51   $$[\text{NMOG} \cdot H^+]_{meas} = [H_3O^+]_0 (1 - e^{-k[\text{NMOG}]\Delta t}) \qquad (2)$$

52   When NMOG concentrations are small, we can approximate Eq. 2 as linear:

53   $$[VOC \cdot H^+]_{linear} = [H_3O^+]_0 k[NMOG]\Delta t \qquad (3)$$

54   The data used to calculate mixing ratios is the protonated NMOG signal normalized to the reagent ion

55   (ncps):

56   $$ncps_{meas} \propto \frac{[NMOG \cdot H^+]_{meas}}{[H_3O^+]_{meas}} \qquad (4)$$

57   From Eq. 3, we assume that the ncps signal is linear with NMOG concentration, and our sensitivity factors

58   are determined using this assumption:

59   $$ncps_{linear} \propto \frac{[NMOG \cdot H^+]_{linear}}{[H_3O^+]_0} = k[NMOG]\Delta t \qquad (5)$$

60   But, from Eqs. 1 and 2, the measured ncps signal is actually not linear with NMOG concentration:

61   $$\frac{[NMOG \cdot H^+]_{meas}}{[H_3O^+]_{meas}} = \frac{(1 - e^{-k[NMOG]\Delta t})}{e^{-k[NMOG]\Delta t}} \qquad (6)$$

62   To extrapolate the measured ratio to what it should be, if no reagent ion depletion occurred and the ncps

63   response were linear with NMOG concentration, we need to multiply $ncps_{meas}$ by:

64   $$correction\ factor = \frac{ncps_{linear}}{ncps_{meas}} = \frac{\frac{[NMOG \cdot H^+]_{linear}}{[H_3O^+]_0}}{\frac{[NMOG \cdot H^+]_{meas}}{[H_3O^+]_{meas}}} = \frac{k[NMOG]\Delta t}{\frac{(1 - e^{-k[NMOG]\Delta t})}{e^{-k[NMOG]\Delta t}}} \qquad (7)$$

65   From Eq. 1, we know that

66   $$e^{-k[NMOG]\Delta t} = \frac{[H_3O^+]_{meas}}{[H_3O^+]_0} \qquad (1a)$$

67   and

68 $$k[NMOG]\Delta t = -\ln\left(\frac{[H_3O^+]_{meas}}{[H_3O^+]_0}\right) \qquad (1b)$$

69 So:

70 $$correction\ factor = \frac{\ln\left(\frac{[H_3O^+]_{meas}}{[H_3O^+]_0}\right)\frac{[H_3O^+]_{meas}}{[H_3O^+]_0}}{\frac{[H_3O^+]_{meas}}{[H_3O^+]_0}-1} \qquad (8)$$

71 **S1.2 Effect 2: Humidity correction**

72 A secondary consideration is the depletion of the water cluster $H_5O_2^+$. Some NMOGs react with

73 H_3O^+ and $H_5O_2^+$ at different rates, or fragment in a way that is controlled by humidity. We use the ratio of

74 $H_5O_2^+$ to H_3O^+ to correct for this humidity dependence of NMOG sensitivity, but if this ratio changes as a

75 function of reagent ion depletion, the humidity correction will be inaccurate.

76 NMOG sensitivities are generally linear with the ratio "R" of $H_5O_2^+$ to H_3O^+. We experimentally

77 determined a humidity correction factor ("*Hfactor*") for each NMOG, and correct the normalized NMOG

78 signal by:

79 $$ncps_{corrected} = \frac{ncps_{uncorrected}}{1 + Hfactor \times R}$$

80 To determine if distortion of humidity correction is a significant issue, first we calculated how the

81 ratio R changes as a function of NMOG concentration:

82 $[H_3O^+]_{meas} = [H_3O^+]_0 e^{-k_{H3O+}[NMOG]\Delta t}$ (1)

83 And similarly:

84 $[H_5O_2^+]_{meas} = [H_5O_2^+]_0 e^{-k_{H5O2+}[NMOG]\Delta t}$ (10)

85 And the measured ratio is:

86 $\frac{[H_5O_2^+]_{meas}}{[H_3O^+]_{meas}} = R_{meas} = \frac{[H_5O_2^+]_0 e^{-k_{H5O2+}[NMOG]\Delta t}}{[H_3O^+]_0 e^{-k_{H3O+}[NMOG]\Delta t}}$ (11)

87 The resulting error in the normalized, humidity-corrected counts per second is:

88 $\frac{nhcps_{meas}}{nhcps_0} = \frac{1 + Hfactor \times R_0}{1 + Hfactor \times R_0 e^{(k_{H5O2+} - k_{H3O+})[NMOG]\Delta t}}$ (12)

89 The difference between the measured ratio, and the "linear regime" ratio used to determine our humidity

90 correction values, is:

91 $ratio\ difference = \frac{R_{meas}}{R_0} = \frac{e^{-k_{H5O2+}[NMOG]\Delta t}}{e^{-k_{H3O+}[NMOG]\Delta t}} = e^{(k_{H5O2+} - k_{H3O+})[NMOG]\Delta t}$ (13)

92 If the rate constants of the NMOG with H_3O^+ and $H_5O_2^+$ are not equal, the measured ratio will decrease if

93 the NMOG concentration is very high. If we use the measured ratio for our humidity correction, then the

94 resulting measurements will be somewhat inaccurate. The largest inaccuracy will occur for a "worst case"

95 scenario where H_3O^+ is severely depleted, the relative humidity is very high, the NMOG reacts much more

96   with H_3O^+ than with $H_5O_2^+$ ($k_{H5O2+} \ll k_{H3O+}$), and the NMOG sensitivity has a very strong humidity

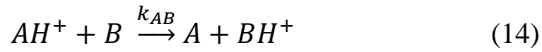97   dependence. An example scenario corresponds to the following values:

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Reagent ion depletion	$[H_3O^+]_{meas} = 0.5 \times [H_3O^+]_0$; [NMOG] = $1.6\text{x}10^{12}$ cm^{-3}		
Relative humidity	$[H_5O_2^+]_0 = 0.04 \times [H_3O^+]_0$		
Reaction rate	$k_{H5O2+} = 0$, $k_{H3O+} = 3.5 \times 10^{-9}$ cm^{-3} s^{-1}		
Strong humidity dependence	Humidity correction factor (Hfactor) = 4		
Δt	$1.2\text{x}10^{-4}$ s (from drift tube length, voltage, pressure; and typical ion mobility)		

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100   Using Eq. (12), the "worst-case" difference between measured and actual normalized, humidity-

101   corrected counts per second is 1.072 (7.2% positive error). Most NMOGs have a much smaller humidity
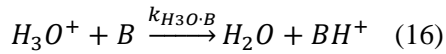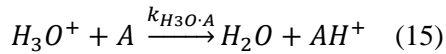
102   dependence.

103   A correction for this effect would need to address each NMOG individually. The humidity

104   correction factor and H_5O_2 rate constant for each NMOG are not available, but the error likely small (<7%)

105   and is accounted for in our overall error estimate.

106   **S1.3 Effect 3: Secondary chemistry**

107   If the concentration of a protonated NMOG, [AH+], becomes high enough, NMOG "A" may donate a

108   proton to a second NMOG, "B", with higher proton affinity:

109     $AH^+ + B \xrightarrow{k_{AB}} A + BH^+$ (14)

110   Additionally, direct proton transfer from H_3O^+ to A, and from H_3O^+ to B, is occurring:

111     $H_3O^+ + A \xrightarrow{k_{H3O\cdot A}} H_2O + AH^+$ (15)

112     $H_3O^+ + B \xrightarrow{k_{H3O\cdot B}} H_2O + BH^+$ (16)

113   The concentrations of [AH+] and [BH+] as a function of [A] and [B] can be solved through a set of

114   differential equations:

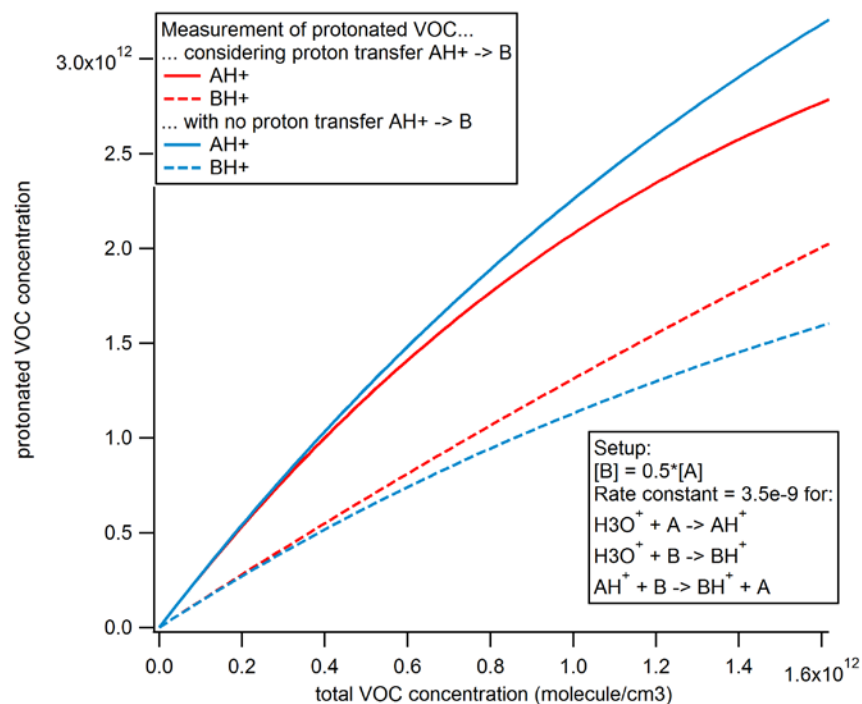115 $[B] = c[A]$ (17)

116     $\frac{d[AH^+]}{d[A]} = k_{H3O\cdot A}[A][H_3O^+] - k_{AB}[AH^+][B]$ (18)

117     $\frac{d[BH^+]}{d[A]} = k_{H3O\cdot B}[B][H_3O^+] + k_{AB}[AH^+][B]$ (19)

118     $\frac{d[H_3O^+]}{d[A]} = -k_{H3O\cdot A}[A][H_3O^+] - k_{H3O\cdot B}[B][H_3O^+]$ (20)

119 As an example, we solved this system for a case where [B] is a large fraction of [A] (c=0.5), and the rate

120 constant for proton transfer from AH^+ to B is high ($k_{AB} = k_{H3O·A} = k_{H3O·B} = 3.5 \times 10^{-9}$).

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122 Figure S1. Modelled NMOG·H+ ion concentrations with secondary proton-transfer-reaction.

123

124 In the "worst-case" scenario (a total NMOG concentration resulting in a 50% reagent ion

125 depletion), $[AH^+]$ is underestimated by about 15%, and $[BH^+]$ is overestimated by about 26%. This could

126 be a significant source of error. We note that this is the maximum possible error for a situation with severe

127 reagent ion depletion and a very high proton transfer rate from AH^+ to B, so error for most NMOGs in most

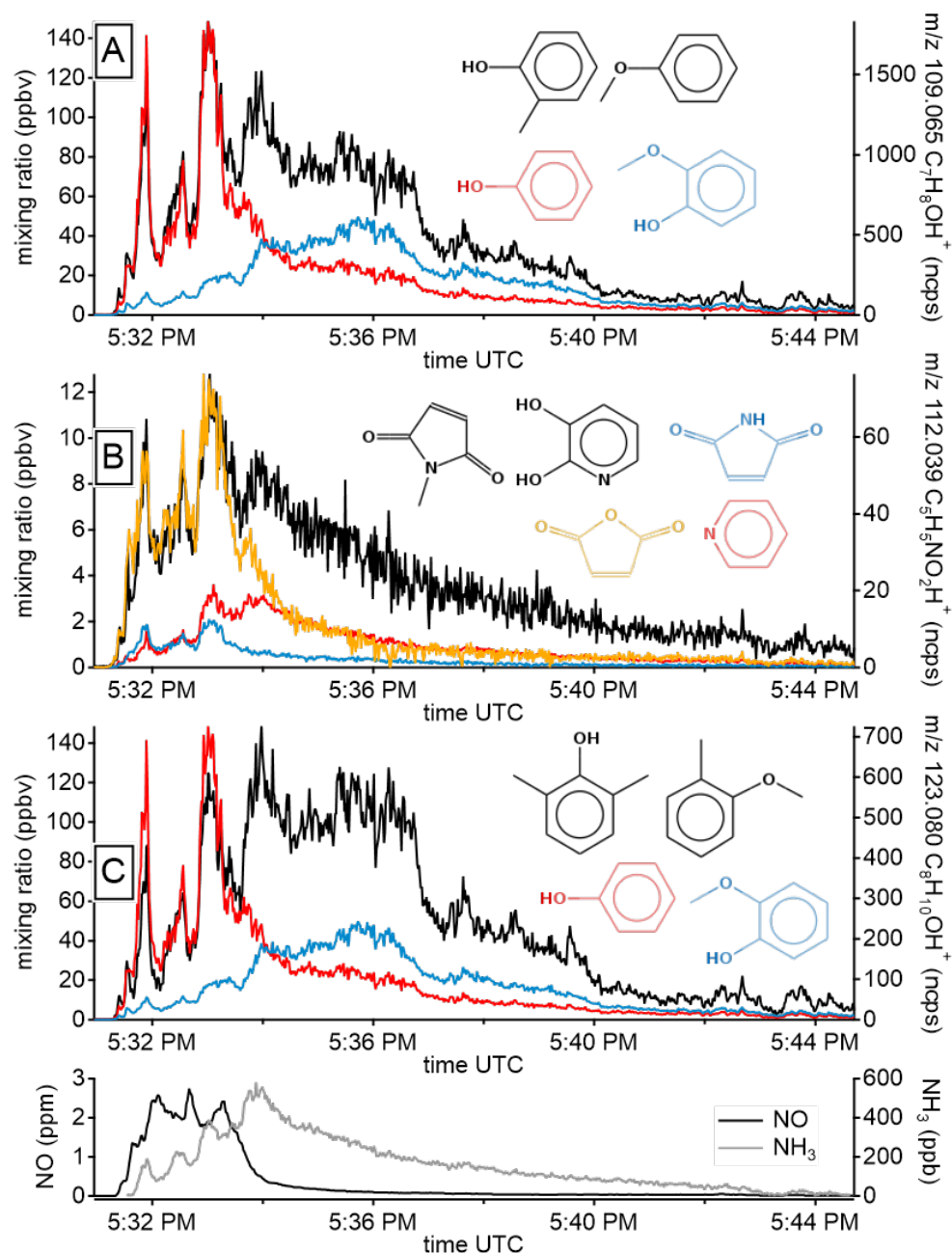128 situations will be smaller than this.

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Figure S2.

Additional time-series correlations. (A) m/z 109.065 (methylphenol or anisole, black) compared to phenol (red) and guaiacol (blue). (B) m/z 112.039 (methylmaleimide or dihydroxypyridine, black) compared to maleimide (blue), furandione (blue), and pyridine (red). (C) m/z 123.080 (dimethylphenol or methylanisole, black) compared to phenol (red) and guaiacol (blue). NO and NH_3 are shown as a reference for higher- and lower- temperature fire processes, respectively.
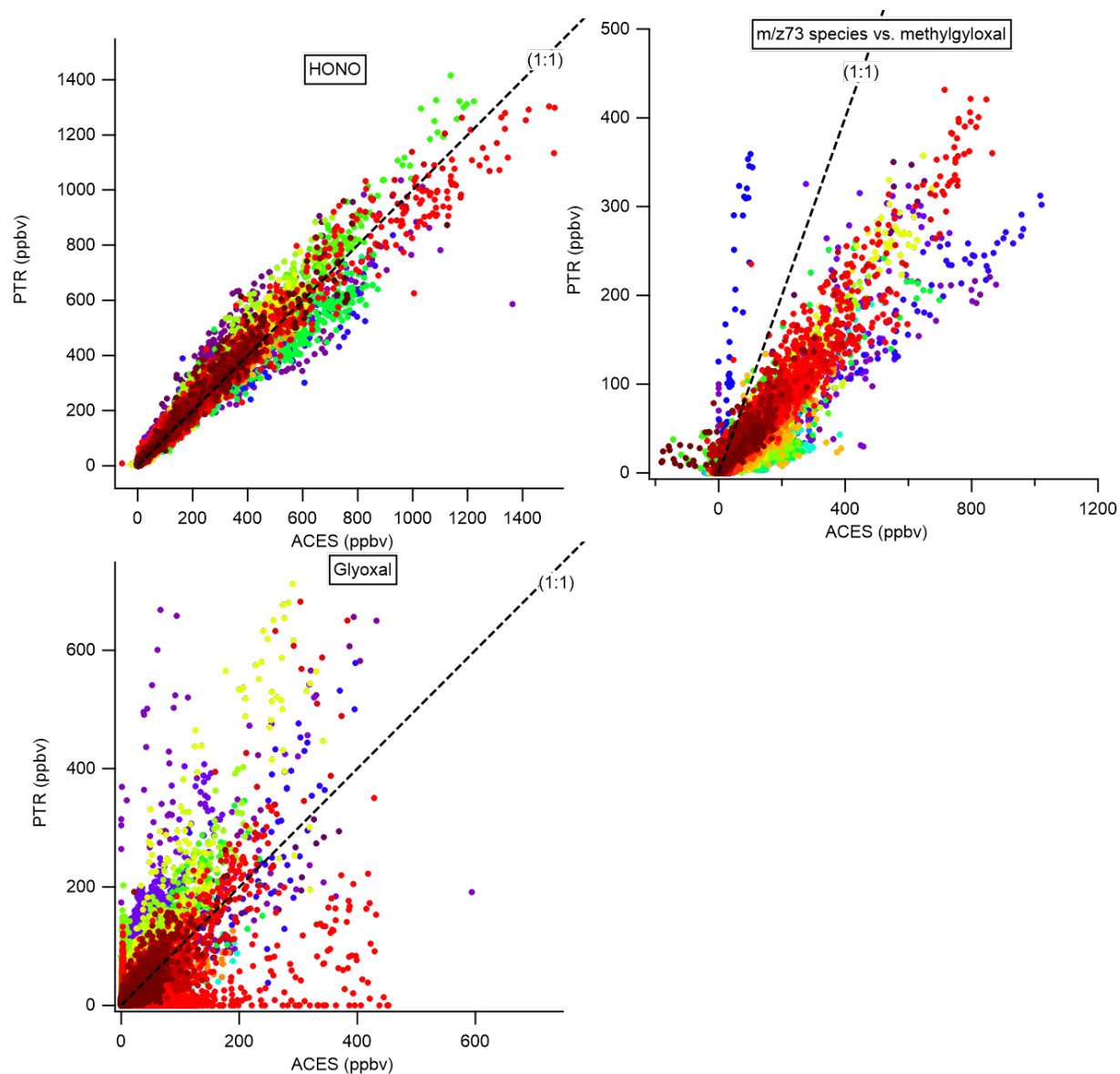
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138 **Figure S3.**

139 Intercomparison data between PTR-TOF (y-axis, "PTR") and ACES (x-axis). Each color is a separate fire.
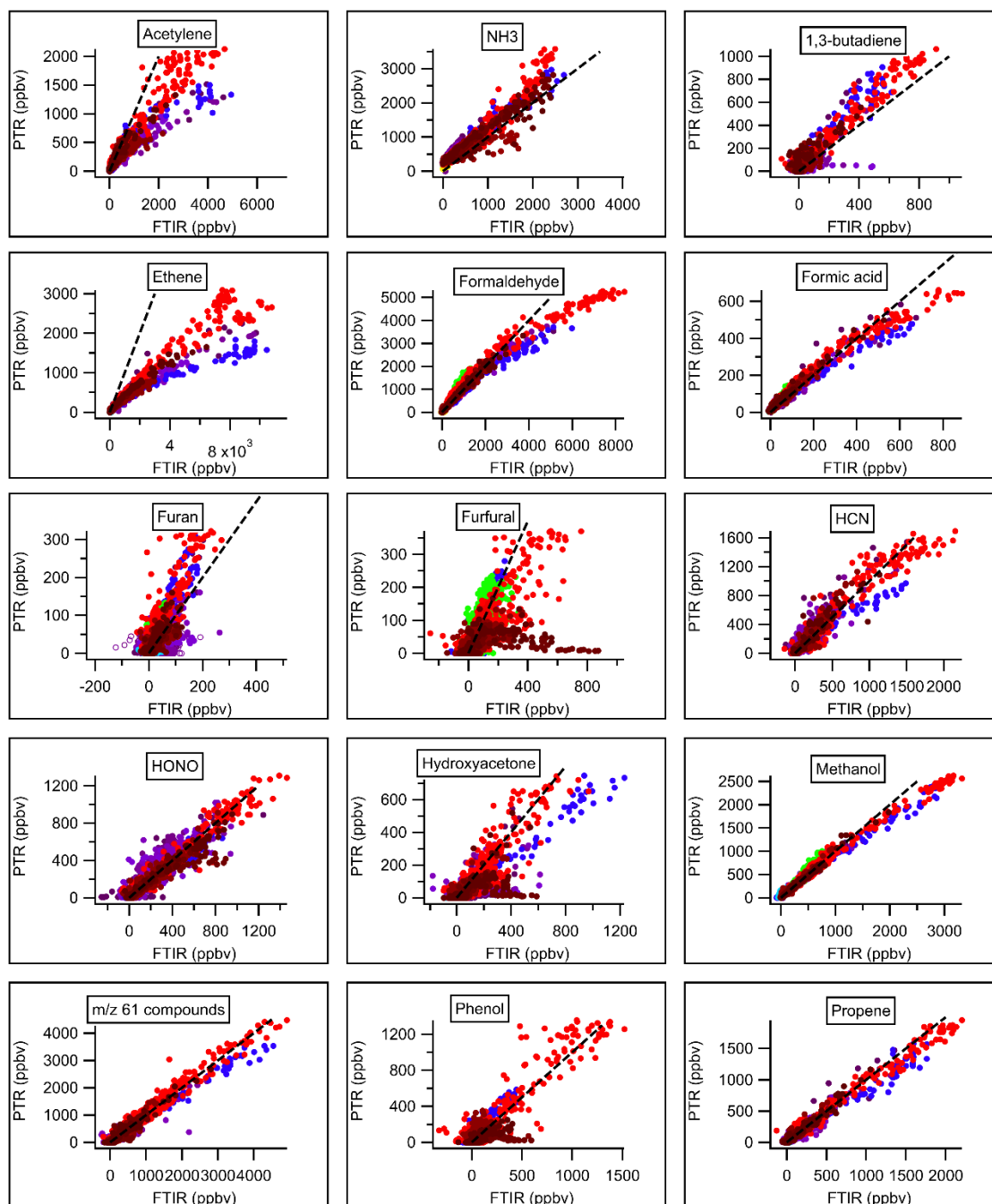
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Figure S4.

Intercomparison between PTR-TOF ("PTR", y-axis) and OP-FTIR ("FTIR", x-axis). Each fire is a different color. Data excluded from the intercomparison due to instrument issues are shown as open circles. In each scatterplot, a black dashed 1:1 line is shown. For "hydroxyacetone", PTR-ToF sum of hydroxyacetone, ethyl formate, and methyl acetate is shown. Uncorrected effects from reagent ion depletion can be seen in formaldehyde, formic acid, and methanol at the highest mixing ratios, where the PTR-ToF measures lower than FTIR.
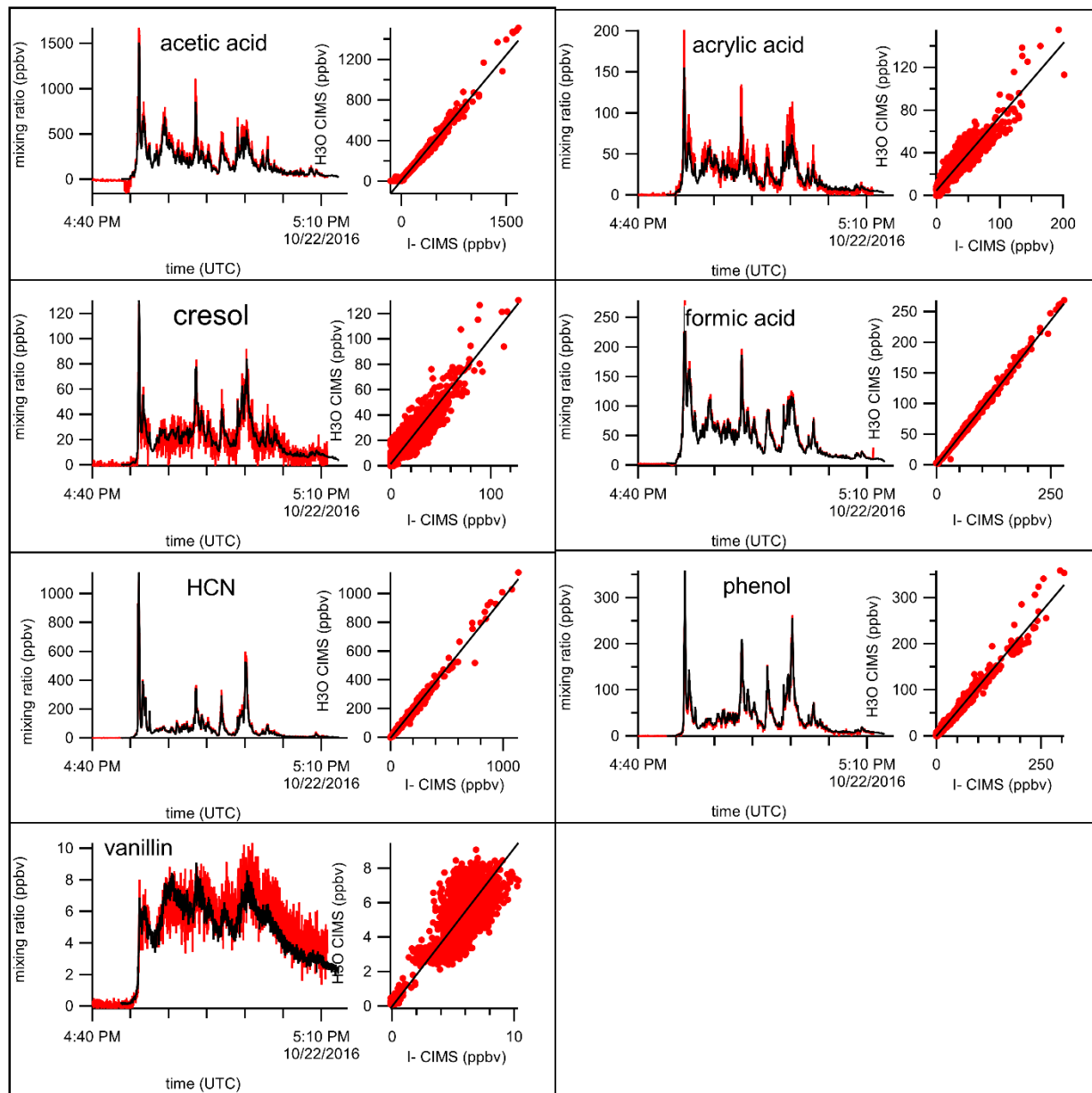
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149 **Figure S5.**

150 Intercomparison plots between PTR-TOF (y-axis in scatterplots) and I⁻ CIMS (x-axis in scatterplots). The

151 black line in the scatterplots is an ODR best-fit. The time series in Fire 72 are also shown. The PTR-TOF

152 is the black trace and the I⁻ CIMS is the red trace.