

1 Supporting Information

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3 Commercial kitchen operations produce  
4 a diverse range of gas-phase reactive  
5 nitrogen species

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17

18 This supporting information contains 5 sections of text, three tables and 15 figures.

19

## 20 S1 Methods

### 21 S1.1 tN<sub>r</sub> instrument calibration, QA/QC and maintenance

22 The NO<sub>x</sub> analyser on the tN<sub>r</sub> instrument was calibrated with a gas-calibration system and a  
23 standard gas cylinder of NO (4.88 ppmv in N<sub>2</sub> ±5%, Linde Canada Inc., Toronto, ON) prior to the  
24 measurements, as per manufacturer specifications. The observed readings of NO<sub>x</sub> by the tN<sub>r</sub>  
25 instrument were found to agree well with a second co-located chemiluminescent NO<sub>x</sub> analyser.  
26 An intercompared linear regression for measurements by the two analyzers, while they were  
27 above the limit of detection has a slope of 0.96, indicating that the additional materials required  
28 for the tN<sub>r</sub> inlet were not affecting the quality of temporal response or accuracy of the NO<sub>x</sub>  
29 measurements. The Na<sub>2</sub>CO<sub>3</sub> and H<sub>3</sub>PO<sub>3</sub> annular denuders integrated into the inlet were changed  
30 every two days with ones freshly prepared. Their scrubbing efficacy was confirmed using known  
31 amounts of the target species HONO and NH<sub>3</sub> and confirmed to be greater than 95 % before and  
32 after each change. The tN<sub>r</sub> oven conversion efficiency to NO<sub>x</sub> was checked periodically  
33 throughout the campaign using the in-situ NH<sub>3</sub> calibration source and was observed to have a  
34 mean of 110±27% over the campaign. The observed levels of N<sub>r,base</sub> were found to agree well with  
35 co-located Ogawa NH<sub>3</sub> passive samplers measurements (Section S1.3) and suggest that the tN<sub>r</sub>  
36 instrument was quantitatively measuring this well-established indoor basic N<sub>r</sub> species. The  
37 uncertainty in the tN<sub>r</sub> measurement was estimated to be 20%, driven by uncertainty in the  
38 catalytic conversion of N<sub>r</sub> species like NH<sub>3</sub> to NO<sub>x</sub> in the oven and quantities being determined by  
39 difference.

### 40 S1.2 PTR-MS calibration, QA/QC and data processing

41 Data were collected every 30-seconds but are presented here as 1-minute averages. Every 5  
42 hours, the instrument was calibrated with ~10 ppb of select gases (listed below) and zeroed with  
43 VOC-free air generated using a heated catalyst acting as a combustion-based scrubber. During  
44 the campaign, the following subset of species were calibrated with a standard gas cylinder from  
45 Apel Reimer and mixing ratios used in this analysis: acetonitrile (C<sub>2</sub>H<sub>3</sub>N), acetone (C<sub>3</sub>H<sub>6</sub>O),  
46 acrylonitrile (C<sub>3</sub>H<sub>3</sub>N), benzene (C<sub>6</sub>H<sub>6</sub>), toluene (C<sub>7</sub>H<sub>8</sub>), o-xylene (C<sub>8</sub>H<sub>10</sub>), α-pinene (C<sub>10</sub>H<sub>16</sub>), and  
47 1,3,5-trimethylbenzene (C<sub>9</sub>H<sub>12</sub>). We calibrated additional species post-campaign that included:  
48 pyrrole (C<sub>4</sub>H<sub>5</sub>N), propionamide (C<sub>3</sub>H<sub>7</sub>NO), triethylamine (C<sub>6</sub>H<sub>15</sub>N), acetic acid (C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>),  
49 heptadienal (C<sub>7</sub>H<sub>10</sub>O), and nonanal (C<sub>9</sub>H<sub>18</sub>O). These calibrations were performed by evaporating  
50 liquid standards in to dry zero air, following the method described by Liu et al.<sup>1</sup>. Finally, several  
51 species were calibrated post-campaign with a different Apel Reimer cylinder: ethanol (C<sub>2</sub>H<sub>6</sub>O),  
52 acrolein (C<sub>3</sub>H<sub>4</sub>O), D4 siloxane (C<sub>8</sub>H<sub>24</sub>O<sub>4</sub>Si<sub>4</sub>), and hexanal (C<sub>6</sub>H<sub>12</sub>O). We report our PTR-MS's  
53 sensitivities for each of these calibrated chemicals in our companion paper (Figure S2 in<sup>2</sup>).

54 Data were processed in Tofware Version 3.2.5, based in Igor Pro. Detailed data processing steps  
55 are described in Ditto et al.<sup>2</sup> Non-targeted peak lists were generated for ions between m/z 30-  
56 500. Chemical formulas were assigned for lower molecular weight ions in the m/z 30-250 range,  
57 if a proposed formula within 10 ppm of the detected mass existed and had reasonable ratios of  
58 carbon, hydrogen, oxygen, nitrogen, sulfur, and chlorine atoms for small molecules, and if the  
59 proposed formula was the only one within 10 ppm or was clearly a better fit than other  
60 possibilities in this range. If there was no clear top formula choice, no formula was assigned. This  
61 m/z range was selected for confident peak identification given the mass resolution of the PTR-

62 MS instrument. In post-processing, signals were background subtracted and any signals below  
63 the limits of detection for a given ion were removed.

64 We acknowledge that with our 6.6 m long inlet, some VOCs may experience delays driven by gas-  
65 wall partitioning along the length of the PFA tubing. We observed a wide range of predominantly  
66 volatile organic compounds and intermediate volatility organic compounds in our  
67 measurements, whose observed estimated saturation concentration ranged from  $10^3$  to  $10^{10}$   
68  $\mu\text{g}/\text{m}^3$  (calculated using the molecular formula based approach in<sup>3</sup>), with most nitrogen-  
69 containing ions described in this paper falling in the range of  $10^5$  to  $10^8 \mu\text{g}/\text{m}^3$ . According to work  
70 by Deming et al.<sup>4</sup> and Pagonis et al.<sup>5</sup>, this could lead to variable delay times within the inlet tubing,  
71 e.g., approximately 2 min/m to  $<0.02 \text{ min}/\text{m}^5$  for the saturation concentration range of most N-  
72 containing species here. In our prior work with this inlet we see rapid transfer for a number of  
73 VOCs from cooking to the VOCUS without evidence for systematic tubing delays. Over the course  
74 of the cooking events described here (lasting minutes to hours), average N-containing ion signals  
75 at the estimated saturation concentration range, even if susceptible to a time delay on the order  
76 of 0.1-13 minutes based on the delay rates above, will not dramatically change observed plume  
77 analysis results<sup>2</sup>.

### 78 S1.3 Supporting instrument methodology

79 American Ecotech chemiluminescent  $\text{NO}_x$  (Mo-catalyst, EC9841), and UV-absorption  $\text{O}_3$   
80 analyzers (Serinus 10), passive samplers for gas-phase  $\text{NH}_3$  and amines. Two measurements  
of

81  $\text{CO}_2$  and air change rate (ACR) were made: one in the kitchen and the other from the exhaust duct  
82 in a mechanical room housing the dedicated exhaust system for the commercial kitchen.

83

84 The gas analyzers were operated at 1-minute time resolution throughout the campaign, using the  
85 shared inlet for the former and an identical, but independent inlet for the latter due to pressure  
86 drop restrictions, which also had a filter at the entry to prevent particle intrusion. Ogawa passive  
87 samplers with citric acid-coated reactive substrates were installed in the kitchen close to the  
88 sampling inlet for an intercomparison of measured gas-phase  $\text{NH}_3$  and amines levels. Citric acid  
89 coatings are standardized for volatile atmospheric base sampling, particularly for  $\text{NH}_3$  by  
90 monitoring networks such as the US EPA<sup>6,7</sup>. The passive samplers were deployed for two periods,  
91 7-13 and 13-17 Sept, and were extracted in 18.2  $\text{M}\Omega\text{-cm}$  deionised water followed by ion  
92 chromatography separation and conductivity detection, with full details available in Salehpour  
93 et al.<sup>8</sup>.

94

95 Two measurements of  $\text{CO}_2$  and air change rate (ACR) were made: one in the kitchen and the other  
96 from the exhaust duct in a mechanical room housing the dedicated exhaust system for the  
97 commercial kitchen. Here, flows from the individual range hoods were combined to be vented  
98 outdoors. The measurements of  $\text{CO}_2$  were made by simple non-dispersive infrared absorption  
99 (K30, Sensair,  $\text{CO}_2$  Meter, Ormond Beach, FL, USA). These  $\text{CO}_2$  sensors were calibrated prior to  
100 the campaign and logged measurements at 1-minute intervals. The kitchen ACR was determined  
101 by recording current output on the exhaust fan controller via an Arduino datalogger. This exhaust  
102 fan controller provides an analog output of 4-20 milliamperes (mA) that corresponds to the active  
103 rotation rate, which spans 0-1750 rotations per minute (RPM). The accuracy of the fan controller  
104 signal output is  $\pm 10 \%$ , as specified by the manufacturer (AAHC-550-UH HVAC drive controller,

105 AAB Group). These observations were supported further by data logged through an automated  
106 control system (DCKV Cloud Panel, Ecoazur, Laser Controls Ltd., Brampton, ON) which also  
107 recorded temperature and steam/smoke detection through blue light sensors installed in the  
108 cooking area range hoods. Irradiance throughout the commercial kitchen was measured by a  
109 spectral radiometer (StellarNet Inc.) roughly at head height and ~2 m from the ceiling, which is  
110 most relevant to consider the exposure for occupants or to model the chemical reactivity in the  
111 space relevant to such exposure.

112

#### 113 S1.4 Details of production rate of HONO from NO<sub>2</sub> box model

114 The surface uptake coefficient of NO<sub>2</sub> ( $\gamma_{\text{NO}_2}$ ) describes the reaction probability of gaseous NO<sub>2</sub>  
115 when colliding with an indoor surface (e.g. to produce HONO) and was calculated using E2  
116 following prior approaches<sup>9,10</sup>.

$$117 \quad \gamma_{\text{NO}_2} = \frac{4 k_{\text{rem,NO}_2} V}{v_{\text{NO}_2} S} \quad (\text{E2})$$

118 where  $V$  is the geometric room volume (m<sup>3</sup>),  $v_{\text{NO}_2}$  is the thermal velocity of NO<sub>2</sub> at the average  
119 indoor temperature over the campaign (28.0 °C; m s<sup>-1</sup>),  $S$  is the geometric indoor surface area  
120 (m<sup>2</sup>), and  $k_{\text{rem,NO}_2}$  is the removal rate of gaseous NO<sub>2</sub> to surfaces (s<sup>-1</sup>) after accounting for loss by  
121 air exchange. Continuous measurements of NO<sub>2</sub>\* from the second chemiluminescence analyzer  
122 were used to find times when a peak in NO<sub>2</sub> levels was observed to decay exponentially,  
123 indicative of an isolated plume being removed. Twenty-three such events were observed (Table  
124 S1) and an exponential fit was applied to the decay from the maximum level of NO<sub>2</sub> to calculate  
125 the time constant ( $\tau$ ) and corresponding removal rate ( $k_{\text{rem,NO}_2} = 1/\tau$ ). An example event and the  
126 fit to the decrease in NO<sub>2</sub> levels is shown in Fig S1, demonstrating that its decay was slightly faster  
127 than ACR, as would be expected if there was additional loss via surface uptake. However, this  
128 was not the case for all 23 events, with only 6 events observed to have an NO<sub>2</sub> removal faster than  
129 ACR because the plume removal was happening very quickly (ACR=20-40 hr<sup>-1</sup>). The resulting  
130 uptake coefficients for NO<sub>2</sub>, therefore, likely represent upper limit on this potential chemistry and  
131 we consider additional uncertainties in the discussion below.

132 The HONO production rate ( $P_{\text{HONO}}$ ; molec cm<sup>-3</sup> s<sup>-1</sup>) from the heterogeneous hydrolysis of NO<sub>2</sub> on  
133 surfaces according to the mechanism of R1 was calculated using E3. Values of  $P_{\text{HONO}}$  calculated  
134 with this approach also represent the upper limit of HONO formation from NO<sub>2</sub> hydrolysis<sup>9</sup>, as  
135 retention of HONO on surfaces as nitrite from this reaction, or other NO<sub>2</sub> heterogeneous losses  
136 having a lower HONO yield, are possible<sup>11-14</sup>.

$$137 \quad P_{\text{HONO}} = 0.5 \times k_{\text{rem,NO}_2} \times [\text{NO}_2] \quad (\text{E3})$$

138 The loss rate of HONO via photolysis ( $L_{\text{HONO}}$ ; molec cm<sup>-3</sup> s<sup>-1</sup>) was calculated using the photolysis  
139 rate ( $J_{\text{HONO}}$ ; s<sup>-1</sup>) determined from the spectral radiometer measurements<sup>15</sup>.

$$140 \quad L_{\text{hv}} = J_{\text{HONO}}[\text{HONO}] \quad (\text{E4})$$

141 The other major loss process for HONO is removal by the ventilation system ( $L_{\text{ACR}}$ ; molec cm<sup>-3</sup> s<sup>-1</sup>)  
142 and was calculated based on the ACR (s<sup>-1</sup>).

143  $L_{ACR} = ACR \times [HONO]$  (E5)

144 Taken together, the production and loss terms were then used to approximate the HONO levels  
 145 (E6) for comparison to observations. Where there is a difference between these known  
 146 mechanisms and observations, the presence of other production and/or loss terms can be  
 147 inferred.

148  $[HONO]_{pred} = (P_{HONO} - (L_{hv} + L_{ACR})) dt$  (E6)

149 where  $[HONO]_{pred}$  represents the HONO generated in sum from E3 through E5. Consequently, in  
 150 the absence of direct emissions or outdoor air bringing HONO indoors, and based on the current  
 151 state of knowledge indoors, the difference between the measured and predicted HONO will be  
 152 equivalent to the HONO originating from or deposited onto surfaces, which act as reservoirs  
 153 ( $[HONO]_{sur}$ ; E7).

154  $[HONO]_{sur} = [HONO]_{meas} - [HONO]_{pred}$  (E7)

155 Due to its inlet duty cycle time, the tNr instrument did not capture the dynamic trends of the  
 156 HONO emitted in short pulses directly from gas stove fuel combustion in the kitchen<sup>16</sup> and so  
 157 the assumed mechanism inferred from E7 as reversible surface partitioning, when using  
 158 observations to drive this model, is likely to be true. Note that if other HONO production or loss  
 159 mechanisms are able to establish equilibrium on timescales similar to the ACR, that these would  
 160 be encapsulated in our  $[HONO]_{sur}$  term. Consequently, the calculated  $HONO_{sur}$  can be converted  
 161 to a flux from the room surfaces (E8) into the overlying air within the kitchen.

162  $\square\square\square\square_{sur\_flux} = \frac{[HONO]_{sur}}{(\frac{S}{V})dt}$  (E8)

163 where the  $HONO_{sur\_flux}$  is the flux from the surface in molec  $cm^{-2} s^{-1}$ , and  $S/V$  the geometric surface  
 164 area to volume ratio of the kitchen ( $0.032 cm^{-1}$ ), which dictates the surface in contact with the air  
 165 in which  $[HONO]_{sur}$  in molec  $cm^{-3}$  was measured, at a time resolution ( $dt$  in s) of the observations.  
 166 In sum, these combined equations allow for description of the chemistry governing the observed  
 167 HONO levels in the commercial kitchen which can be compared to observations in other indoor  
 168 environments, whether experimental or under normal use.

### 169 S1.5: Comparison of TMA measured by PTR-MS and passive samplers

170 The ambient levels were below the co-deployed passive sampler detection limits for TEA (LOD =  
 171 2.59 ppbv for 5 days of collection), while the PTR-MS detected it at levels above its detection  
 172 limits (on average 25 pptv). This would therefore indicate that TEA comprised a minor part of  $N_{r,base}$   
 173 as its quantitative conversion by the tNr oven<sup>16</sup> would generate less than 100 pptv of signal, which  
 174 is less than 2% of the total  $N_{r,base}$ . In contrast, the trimethylamine (TMA) levels measured by the  
 175 passive samplers were a factor of 35 larger than TEA observed by the PTR-MS (1.45 ppbv of TMA  
 176 and 25 pptv of TEA, respectively), but unfortunately TMA was not calibrated directly for the PTR-  
 177 MS. A theoretical estimate using the proton transfer reaction rate constant methods in Sekimoto  
 178 et al.<sup>17</sup> of the campaign-wide TMA mixing ratio observed by the PTR-MS was calculated by scaling  
 179 the TEA sensitivity down by 20% to account for the relative theoretical difference between the  
 180 sensitivity of these two analytes. Note that this assumes that both compounds have the same  
 181 degree of fragmentation in the PTR-MS ion-molecule reaction region, which is a reasonable  
 182 estimate based on past measurements of both of these compounds with different instruments,

183 though TMA might fragment slightly less<sup>5</sup>. The resulting TMA mixing ratio from this sensitivity  
184 estimation is 0.28 ppb. This adjustment remains insufficient to resolve the difference between  
185 the passive sampler and PTR-MS observations. The difference remains substantial between the  
186 two techniques despite the passive sampler being within 2 m of the PTR-MS inlet and at  
187 approximately the same height. It is possible that a point source of TMA was located close to the  
188 passive samplers during this period, while the NH<sub>3</sub> measurements used for intercomparison to  
189 the N<sub>r,base</sub> represent kitchen-wide values. Also, there could be fragmentation of protonated TMA  
190 in the PTR-MS, which is not accounted for here. These issues make intercomparison of TMA and  
191 assessment of its role as a component of tN<sub>r</sub> instrument measurements unexpectedly difficult.

192

193

194 **Table S1.** NO<sub>2</sub> decay events observed in the main kitchen during periods when the air exchange  
 195 rate was stable.

Event	Background d NO <sub>2</sub> (ppbv)	Peak NO <sub>2</sub> (ppbv)	τ (s)
1	13.9 ± 0.15	16.1 ± 0.65	279
2	12.1 ± 0.59	80.4 ± 2.8	777
3	20.6 ± 1.0	71.9 ± 4.5	148
4	19.8 ± 0.27	30.3 ± 1.0	79
5	6.5 ± 0.3	27.6 ± 0.55	418
6	17.6 ± 2.4	115.9 ± 7.6	136
7	13.6 ± 0.8	69.8 ± 3.8	123
8	8.9 ± 0.37	62.5 ± 2.1	171
9	7.6 ± 0.21	25.4 ± 0.65	240
10	8.5 ± 0.38	42.1 ± 1.1	53
11	9.2 ± 0.31	12.8 ± 0.82	130
12	11.8 ± 0.24	17.5 ± 0.8	160
13	11.7 ± 2.7	84.6 ± 3.5	389
14	15.4 ± 0.37	27.2 ± 1.8	78
15	7.8 ± 0.21	7.8 ± 0.59	345
16	12.8 ± 0.73	64.8 ± 2.1	62
17	10.7 ± 0.39	18.6 ± 1.1	73
18	8.9 ± 0.54	36.9 ± 2.2	40
19	9.6 ± 0.29	32.1 ± 1.3	313
20	7.9 ± 0.12	26.3 ± 0.5	483
21	15.1 ± 5.5	49.2 ± 5.9	163
22	19.0 ± 0.24	14.4 ± 0.84	124
23	7.7 ± 0.17	43.5 ± 1.1	152

196

197

198 **Table S2.** Model results from HONO production and loss calculations to infer surface source  
 199 strengths, at hourly time resolution. The estimates range from a low to high role for NO<sub>2</sub>  
 200 heterogeneous conversion ( $\gamma_{\text{NO}_2}$ ) with matching impacts from air change rates estimated at  
 201 night ( $\text{ACR}_{\text{night}}$ ) to provide upper and lower limits on the inversely-related level of importance for  
 202 HONO surface sources. Number density equivalent values of the daily and nighttime only  
 203 (22:00-06:00) contributions from the dominant terms are provided with one standard deviation  
 204 in the hourly variability from the observations.

NO <sub>2</sub> Importance Scenario	Outcome Period	NO <sub>2</sub> to HONO Production (molec cm <sup>-3</sup> hr <sup>-1</sup> )	HONO ACR Loss (molec cm <sup>-3</sup> hr <sup>-1</sup> )	HONO from Surfaces (molec cm <sup>-3</sup> hr <sup>-1</sup> )
Low ( $\gamma_{\text{NO}_2}=1 \times 10^{-6}$ ; $\text{ACR}_{\text{night}}=1.0$ )	Daily			
	Average	$1.8 \pm 0.3 \times 10^9$	$1.9 \pm 1.4 \times 10^{10}$	$7.5 \pm 1.9 \times 10^{10}$
	Night Only	$1.8 \pm 0.1 \times 10^9$	$2.0 \pm 3.1 \times 10^9$	$5.6 \pm 0.3 \times 10^{10}$
Medium ( $\gamma_{\text{NO}_2}=2 \times 10^{-6}$ ; $\text{ACR}_{\text{night}}=0.5$ )	Daily			
	Average	$3.5 \pm 0.6 \times 10^9$	$1.9 \pm 1.4 \times 10^{10}$	$7.3 \pm 1.9 \times 10^{10}$
	Night Only	$3.5 \pm 0.1 \times 10^9$	$1.6 \pm 3.2 \times 10^9$	$5.6 \pm 0.6 \times 10^{10}$
High ( $\gamma_{\text{NO}_2}=1.4 \times 10^{-5}$ ; $\text{ACR}_{\text{night}}=0.$ )	Daily			
	Average	$2.5 \pm 0.5 \times 10^{10}$	$1.8 \pm 1.4 \times 10^{10}$	$5.3 \pm 1.9 \times 10^{10}$
	Night Only	$2.5 \pm 0.2 \times 10^{10}$	$1.3 \pm 3.3 \times 10^9$	$3.3 \pm 0.3 \times 10^{10}$

205

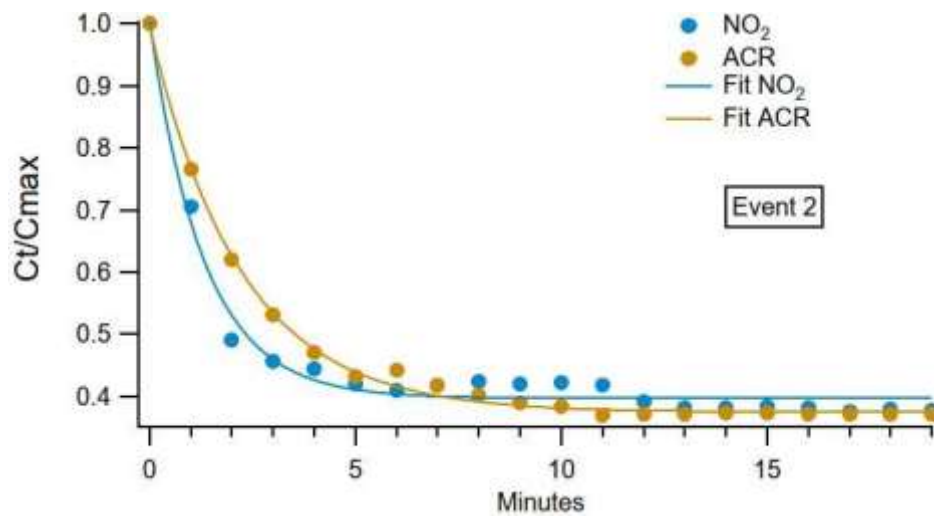
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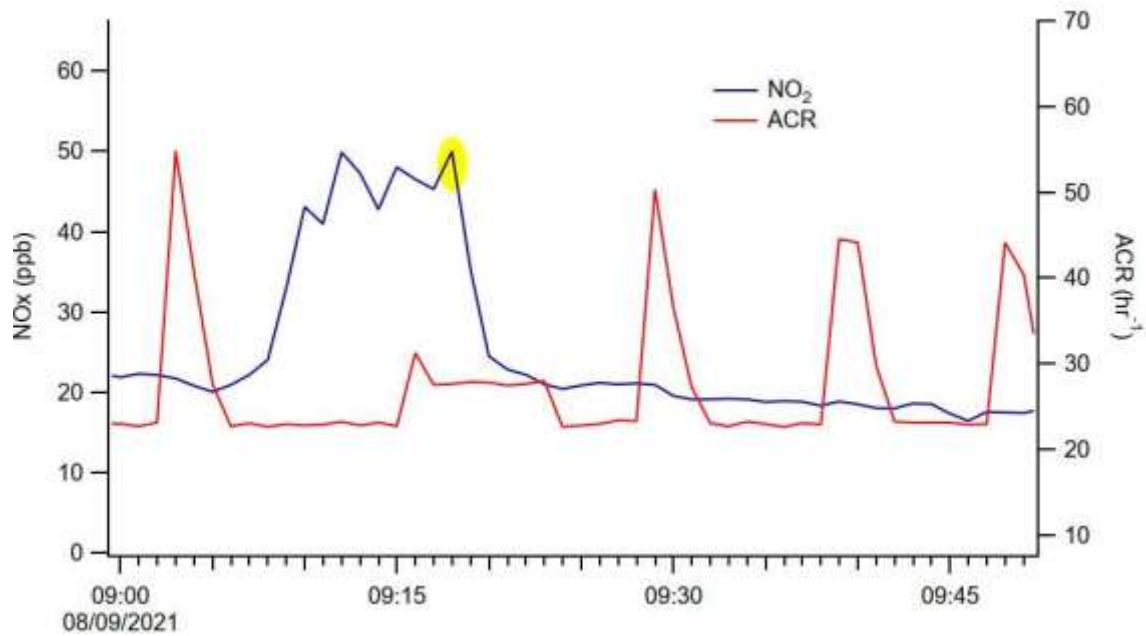
207 **Table S3.** Estimated surface emissions for calibrated VOCs from PTR-MS measurements.

Ion	$\mu\text{g hr}^{-1}\text{m}^{-2}$
$\text{NH}_2\text{CH}^+$	8.71E-01
$\text{C}_2\text{H}_3\text{NH}^+$	5.16E+00
$\text{C}_2\text{H}_6\text{OH}^+$	5.84E+02
$\text{C}_3\text{H}_3\text{NH}^+$	1.66E-01
$\text{C}_3\text{H}_4\text{OH}^+$	1.23E+01
$\text{C}_3\text{H}_6\text{OH}^+$	3.52E+01
$\text{C}_2\text{H}_4\text{O}_2\text{H}^+$	8.96E+01
$\text{C}_4\text{H}_5\text{NH}^+$	3.79E-01
$\text{C}_3\text{H}_7\text{NOH}^+$	5.90E+00
$\text{C}_6\text{H}_7^+$	3.86E+01
$\text{C}_7\text{H}_9^+$	1.61E+01
$\text{C}_6\text{H}_{12}\text{OH}^+$	7.88E+00
$\text{C}_6\text{H}_{15}\text{NH}^+$	3.55E-01
$\text{C}_8\text{H}_{11}^+$	1.05E+01
$\text{C}_7\text{H}_{10}\text{OH}^+$	2.82E+00
$\text{C}_9\text{H}_{13}^+$	4.16E+00
$\text{C}_{10}\text{H}_{17}^+$	1.20E+01
$\text{C}_9\text{H}_{18}\text{OH}^+$	1.18E+01
$\text{C}_{10}\text{H}_{30}\text{O}_5\text{Si}_5\text{H}^+$	3.54E+02

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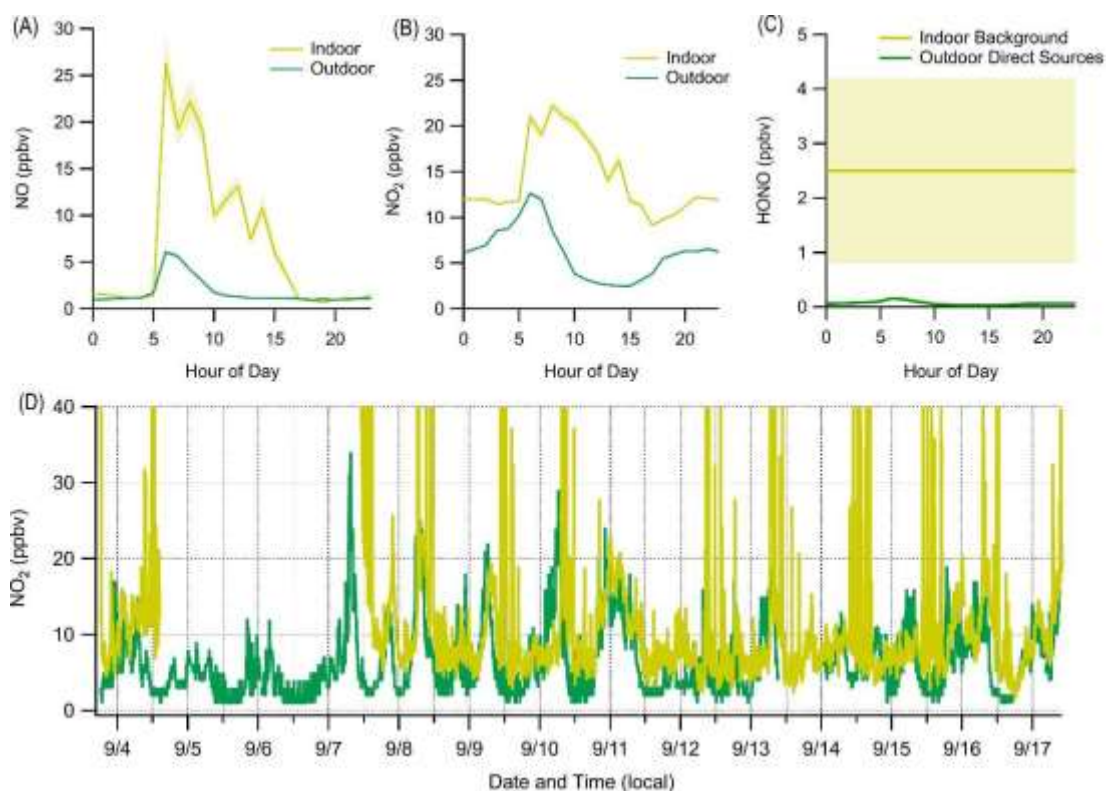


210

211 **Fig S1.** (Top) Normalised decay in NO<sub>2</sub> over time (blue circles) for a representative event starting  
 212 at ~9:20 AM in bottom panel (yellow highlighted circle around 9:20), equivalent to t = 0 minutes  
 213 here. The expected loss of NO<sub>2</sub> as calculated from the measured ACR alone (orange), which was  
 214 also fast, but slower than the observed NO<sub>2</sub> decay (blue). Note that NO<sub>2</sub> never decays to zero due  
 215 to a reservoir present in the kitchen. (Bottom) Time series of measured NO<sub>2</sub> mixing ratio and ACR  
 216 logged from the ventilation system for this event.

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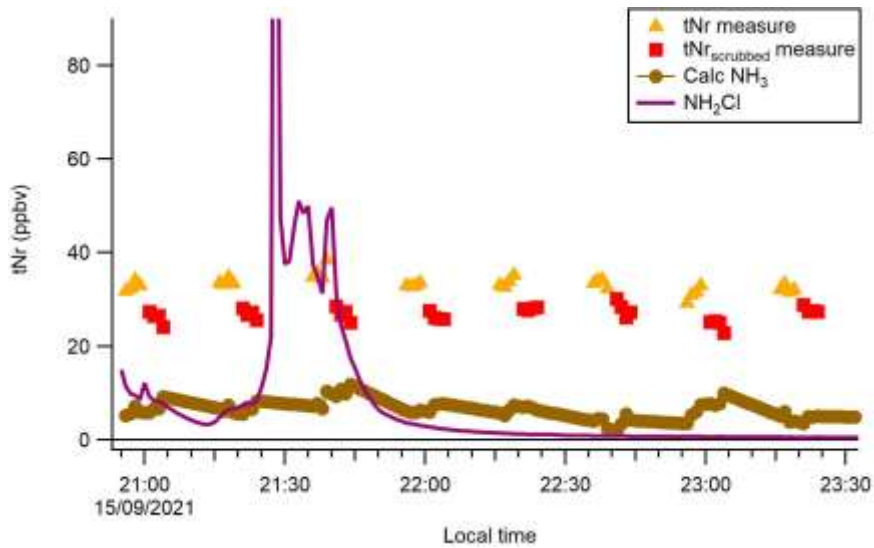
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220

221 **Fig S2:** Diurnal averages of (A) NO and (B) NO<sub>2</sub> from within the kitchen (yellow) and the local  
 222 Environment Canada – Downsview air quality monitoring station (green) during the KOCENA  
 223 campaign. Shaded regions denote the standard error of the mean. (C) Mean HONO observed in  
 224 the kitchen (error of one standard deviation) and estimated outdoor values based solely on a  
 225 HONO/NO<sub>x</sub> emission ratio of 0.85% recently observed from a UK road tunnel<sup>18</sup>. The indoor  
 226 kitchen time series of NO<sub>2</sub> (D) was often elevated at different times of day (axis limited to 40  
 227 ppbv; see Figure 1 for full range) compared to outdoors, especially during cooking.

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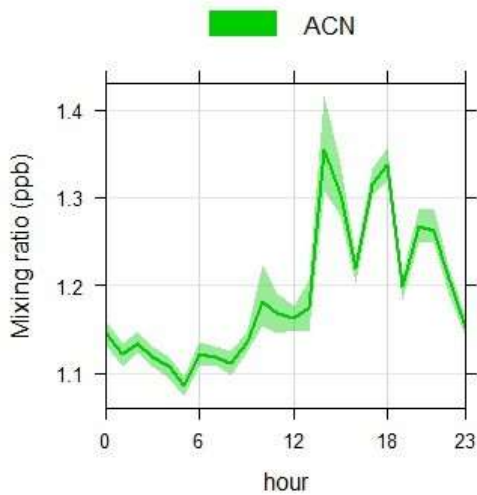


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230 **Fig S3:** Time series of measured  $tN_r$  and  $tN_r$  scrubbed only (without interpolation) compared to  
 231 the measured  $NH_2Cl$  by PTR-MS.

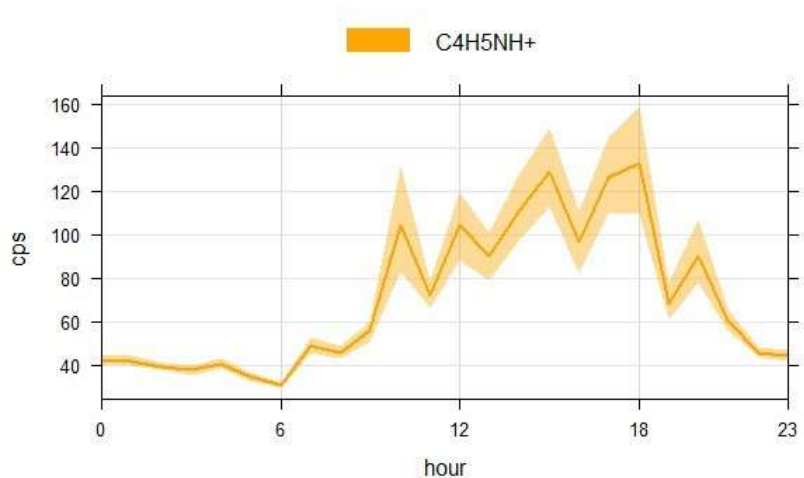
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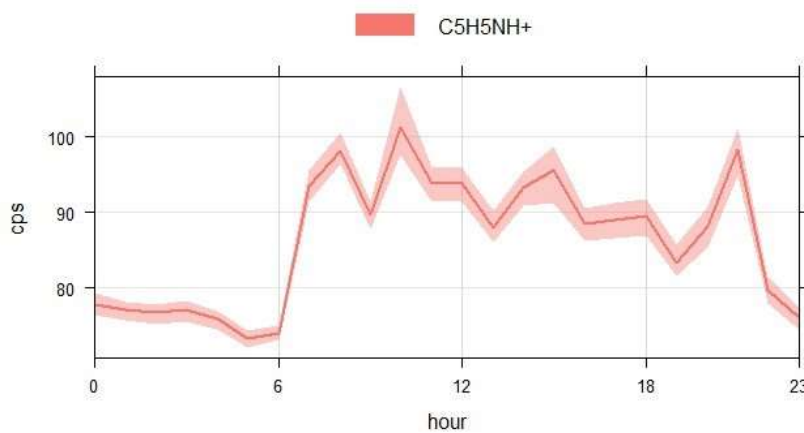
234

235 **Fig S4:** Mean diurnal trends in acetonitrile (ACN) as measured by the PTR-MS over the whole  
 236 campaign<sup>19</sup>.



237

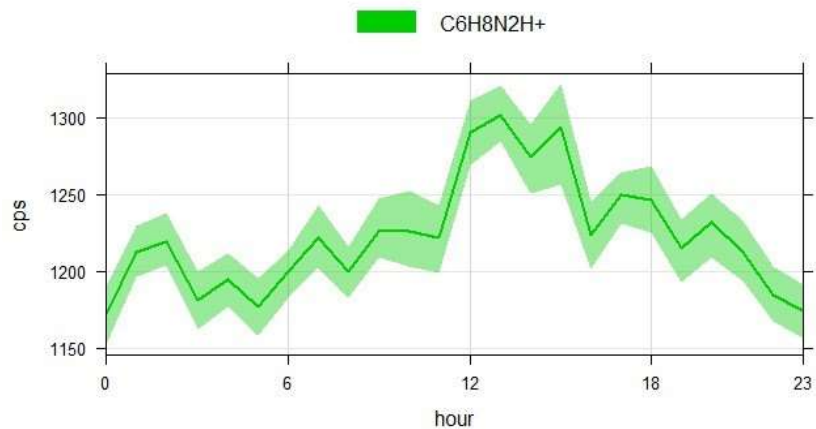
238 **Fig S5:** Mean diurnal trends in ion C<sub>4</sub>H<sub>5</sub>NH<sup>+</sup>, nominally assigned to pyrrole (and  
 239 isomers/fragments of higher molecular weight ions), as measured by the PTR-MS over the  
 240 whole campaign.



241

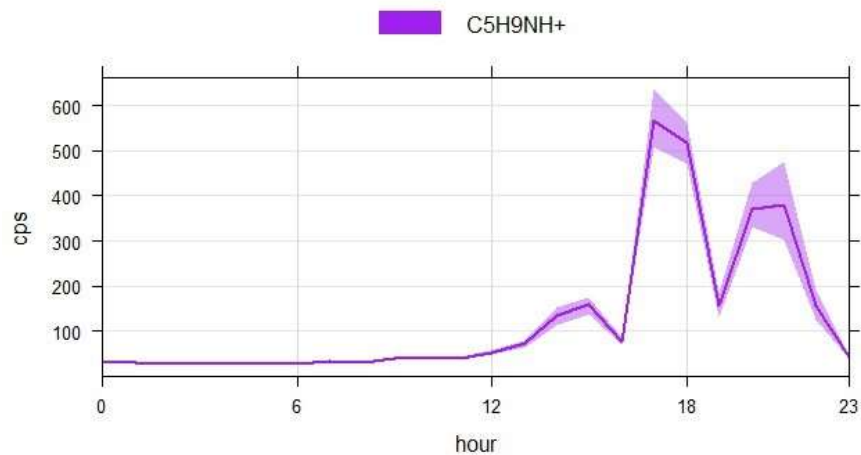
242 **Fig S6:** Mean diurnal trends in ion C<sub>5</sub>H<sub>5</sub>NH<sup>+</sup>, nominally assigned to pyridine (and  
 243 isomers/fragments of higher molecular weight ions), as measured by the PTR-MS over the  
 244 whole campaign.

245



246

247 **Fig S7:** Mean diurnal trends in ion  $C_6H_8N_2H^+$ , nominally assigned to alkyprazine (and  
 248 isomers/fragments of higher molecular weight ions), as measured by the PTR-MS over the  
 249 whole campaign.

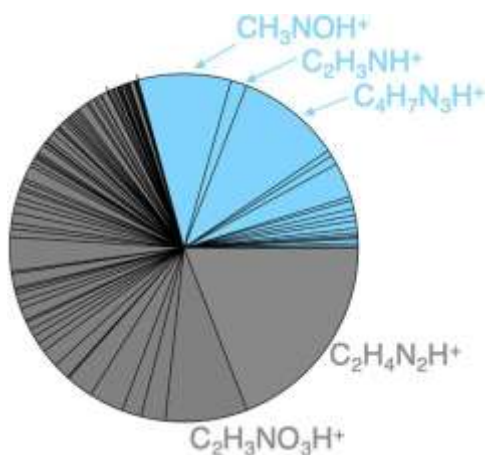


250

251 **Fig S8:** Mean diurnal trends in ion  $C_5H_9NH^+$ , as measured by the PTR-MS over the whole  
 252 campaign.

253

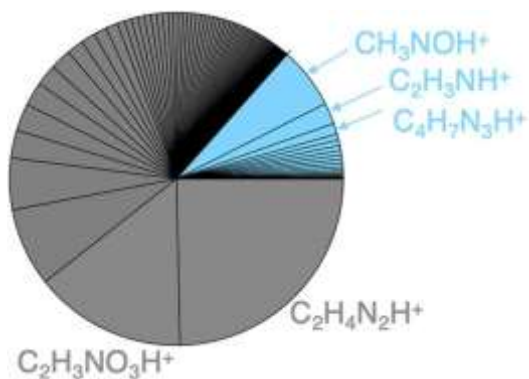
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255

256 **Fig S9:** Pie chart of detected N-containing ions by PTR-MS during a chicken, salmon, and  
 257 vegetable cooking event (event #49-51). Blue coloured regions indicate ions detected during a  
 258 cooking oil + amino acid lab study<sup>20</sup>.

259



260

261 **Fig S10:** Pie chart of detected N-containing ions by PTR-MS during a pork and vegetable cooking  
 262 event (event #55). Blue coloured regions indicate ions detected during a cooking oil + amino acid  
 263 lab study<sup>20</sup>.

264

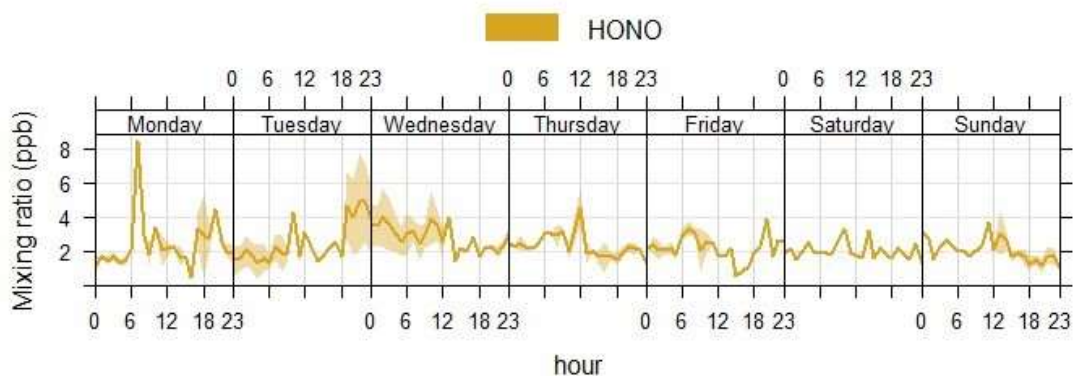
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## 266 S2. Reservoirs and partitioning fluxes of nitrous acid (HONO)

267 It is worth commenting that the observed very high  $\text{NO}_2$  loss rates may reflect substantial  
268 heterogeneity in the kitchen originating from point sources near ventilation locations (i.e. stove  
269 under the range hood) diluting into the room volume beyond our inlets, while simultaneously  
270 being removed. Some portion of these higher values may also stem from our inability to capture  
271 the true S/V in this space, as we opted to use the common approximation method based on  
272 geometric room dimensions<sup>21</sup>. This does not capture the hidden spaces above the drop ceiling,  
273 behind walls, nor the porosity of room materials. Further, an in-use commercial kitchen has  
274 many added surfaces including storage racks, appliances, preparation equipment and tables,  
275 among many other supplies and apparatus. Therefore, the value of  $\gamma_{\text{NO}_2}$  in this commercial  
276 kitchen could range from  $1 \times 10^{-6}$  up to  $1.4 \times 10^{-5}$ , with  $2 \times 10^{-6}$  reflective of a reasonable  
277 approximation based on the best direct comparison in the literature from a residential kitchen  
278 with a similar geometric S/V. In the following discussion, we present the results of simulations  
279 using this  $\gamma_{\text{NO}_2}$  value and a nighttime unventilated  $\text{ACR}_{\text{night}}$  of 0.5 when the HVAC is off. In Table  
280 S2, we provide model outcomes at the upper ( $\gamma_{\text{NO}_2}=1.4 \times 10^{-5}$ ;  $\text{ACR}_{\text{night}}=0.1$ ) and lower ( $\gamma_{\text{NO}_2}=1 \times 10^{-6}$ ;  
281  $\text{ACR}_{\text{night}}=1.0$ ) boundaries of the importance of  $\text{NO}_2$  and our best estimate to compare the model  
282 to existing observations from the literature (Fig 6;  $\gamma_{\text{NO}_2}=2 \times 10^{-6}$ ;  $\text{ACR}_{\text{night}}=0.5$ ).

### 283 S2.1 Role of transport and photochemistry on HONO levels in the kitchen

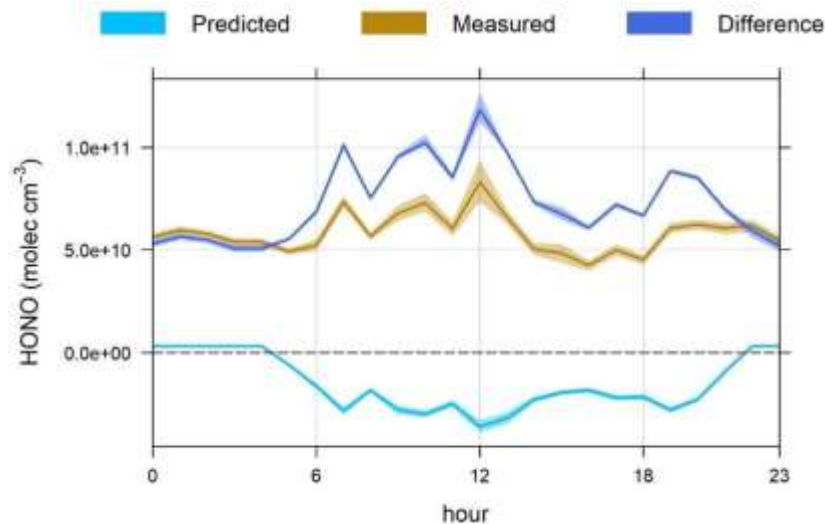
284 The first source we consider is outdoor to indoor transport. While it may be possible for HONO  
285 produced outdoors at night to be brought indoors in the morning, kitchen activities and  
286 ventilation of this space start at 7 am, just following sunrise at 6 am, at which time substantial  
287 losses of HONO in the outdoor atmosphere by photolysis and planetary boundary layer mixing  
288 disrupting the nocturnal boundary layer would be expected. We were not able to measure HONO  
289 in the air supply duct and in the room during this work but can approximate its impact. During  
290 this brief period of the day ~50% of the HONO observed in the kitchen could be originating from  
291 outdoors if mixing ratios were on the order of 1 ppbv ( $2.5 \times 10^{10} \text{ molec cm}^{-3}$ )<sup>22</sup>. Next, many studies  
292 have proposed indoor photochemical HONO production mechanisms<sup>23–26</sup>, but the kitchen has  
293 no penetration of sunlight into its space, which negates their relevance to this indoor space. This  
294 makes the final option that surface reservoirs are the dominant and controlling driver of observed  
295 indoor HONO mixing ratios the most likely explanation, consistent with prior reports.



296

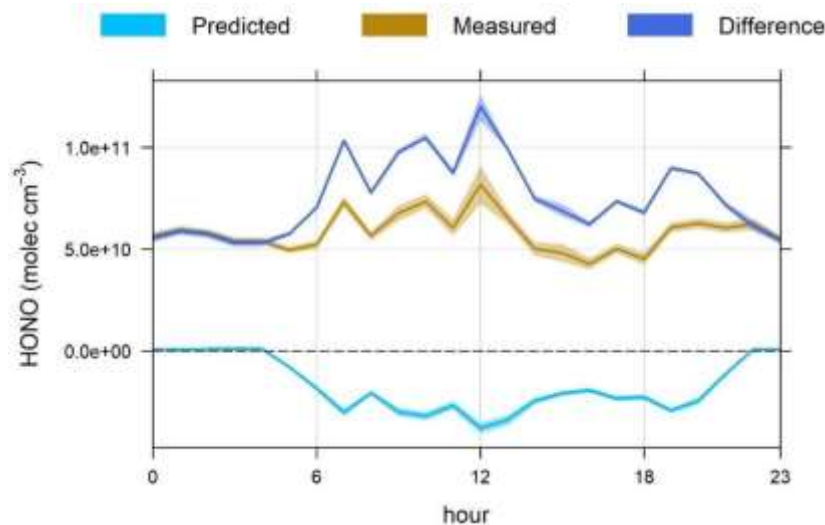
297 **Fig S11:** Mean diurnal trends of HONO as function of day of week.





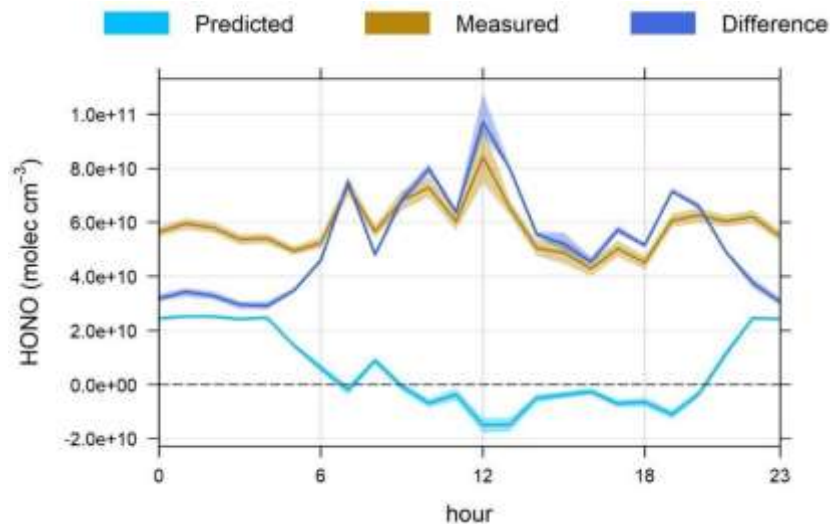
298

299 **Fig S12:** Mean diurnal trends in predicted HONO levels calculated from production of HONO  
 300 from NO<sub>2</sub> uptake on surfaces and loss by photolysis and ventilation compared to measured  
 301 HONO by day of week. The difference in predicted and measured HONO is also plotted. This is  
 302 using  $\gamma_{\text{NO}_2}=2 \times 10^{-6}$ ;  $\text{ACR}_{\text{night}}=0.5$  (See Table S2).



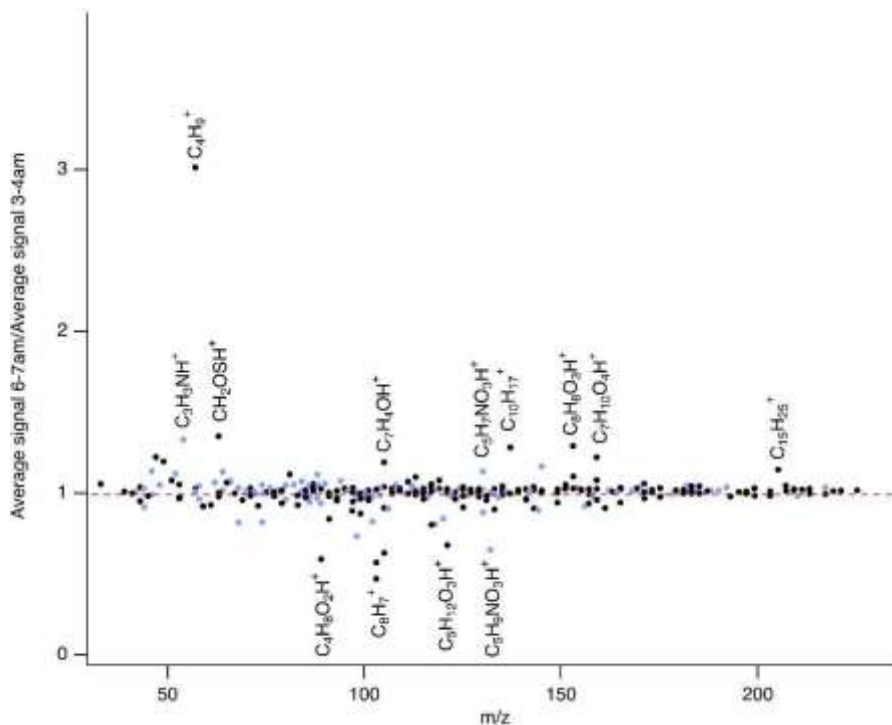
303

304 **Fig S13:** Mean diurnal trends in predicted HONO levels calculated from production of HONO  
 305 from NO<sub>2</sub> uptake on surfaces and loss by photolysis and ventilation compared to measured  
 306 HONO by day of week. The difference in predicted and measured HONO is also plotted. This is  
 307 using  $\gamma_{\text{NO}_2}=1 \times 10^{-6}$ ;  $\text{ACR}_{\text{night}}=1.0$  (See Table S2).



308

309 **Fig S14:** Mean diurnal trends in predicted HONO levels calculated from production of HONO  
 310 from  $\text{NO}_2$  uptake on surfaces and loss by photolysis and ventilation compared to measured  
 311 HONO by day of week. The difference in predicted and measured HONO is also plotted. This is  
 312 using  $\gamma_{\text{NO}_2}=1.4 \times 10^{-5}$ ;  $\text{ACR}_{\text{night}}=0.1$  (See Table S2).



313

314 **Fig S15:** Mean PTR-MS ion signals averaged daily from 6-7 am (during ventilation ramp-up but  
 315 prior to cooking/cleaning emissions) divided by mean ion signals averaged daily from 3-4 am  
 316 (overnight, with no mechanical ventilation or emissions sources). The red dashed line shows a  
 317 1:1 ratio, indicating no change in signal with ventilation ramp up. Blue-shaded points represent  
 318 nitrogen-containing ions.

319 **References**

- 320 1 Q. Liu and J. P. D. Abbatt, Liquid crystal display screens as a source for indoor volatile  
321 organic compounds, *Proc. Natl. Acad. Sci.*, 2021, **118**, e2105067118.
- 322 2 J. C. Ditto, L. R. Crilley, M. Lao, T. C. VandenBoer, J. P. D. Abbatt and A. W. H. Chan,  
323 Indoor and outdoor air quality impacts of cooking and cleaning emissions from a  
324 commercial kitchen, *Environ. Sci. Process. Impacts*, 2023, **25**, 964–979.
- 325 3 Y. Li, U. Pöschl and M. Shiraiwa, Molecular corridors and parameterizations of volatility  
326 in the chemical evolution of organic aerosols, *Atmos. Chem. Phys.*, 2016, **16**, 3327–  
327 3344.
- 328 4 B. Deming, D. Pagonis, X. Liu, D. Day, R. Talukdar, J. Krechmer, J. A. de Gouw, J. L.  
329 Jimenez and P. J. Ziemann, Measurements of Delays of Gas-Phase Compounds in a Wide  
330 Variety of Tubing Materials due to Gas-Wall Interactions, *Atmos. Meas. Tech. Discuss.*,  
331 2019, 1–19.
- 332 5 D. Pagonis, K. Sekimoto and J. de Gouw, A Library of Proton-Transfer Reactions of H<sub>3</sub>O<sup>+</sup>  
333 Ions Used for Trace Gas Detection, *J. Am. Soc. Mass Spectrom.*, 2019, **30**, 1330–1335.
- 334 6 D. Key, J. Stihle, J.-E. Petit, C. Bonnet, L. Depernon, O. Liu, S. Kennedy, R. Latimer, M.  
335 Burgoyne, D. Wanger, A. Webster, S. Casunuran, S. Hidalgo, M. Thomas, J. A. Moss and  
336 M. M. Baum, Integrated method for the measurement of trace nitrogenous atmospheric  
337 bases, *Atmos. Meas. Tech.*, 2011, **4**, 2795–2807.
- 338 7 W. Winberry Jr, T. Ellestad and B. Stevens, *DETERMINATION OF REACTIVE ACIDIC AND*  
339 *BASIC GASES AND STRONG ACIDITY OF ATMOSPHERIC FINE PARTICLES*, 1999.
- 340 8 L. Salehpoor and T. C. Vandenboer, A highly selective, sensitive, and accurate ion  
341 chromatographic method with a conductivity detection for quantitative analysis of  
342 alkylamines in the aerosol and gas phases, *Anal. Methods*.
- 343 9 D. B. Collins, R. F. Hems, S. Zhou, C. Wang, E. Grignon, M. Alavy, J. A. Siegel and J. P. D.  
344 Abbatt, Evidence for Gas-Surface Equilibrium Control of Indoor Nitrous Acid, *Environ.*  
345 *Sci. Technol.*, 2018, **52**, 12419–12427.
- 346 10 M. Mendez, N. Blond, D. Amedro, D. A. Hauglustaine, P. Blondeau, C. Afif, C. Fittschen  
347 and C. Schoemaeker, Assessment of indoor HONO formation mechanisms based on  
348 situ measurements and modeling, *Indoor Air*, 2017, **27**, 443–451.
- 349 11 T. C. VandenBoer, M. Z. Markovic, J. E. Sanders, X. Ren, S. E. Pusede, E. C. Browne, R. C.  
350 Cohen, L. Zhang, J. Thomas and W. H. Brune, Evidence for a nitrous acid (HONO)  
351 reservoir at the ground surface in Bakersfield, CA, during CalNex 2010, *J. Geophys. Res.*  
352 *Atmos.*, 2014, **119**, 9093–9106.
- 353 12 T. C. VandenBoer, C. J. Young, R. K. Talukdar, M. Z. Markovic, S. S. Brown, J. M. Roberts  
354 and J. G. Murphy, Nocturnal loss and daytime source of nitrous acid through reactive  
355 uptake and displacement, *Nat. Geosci.*, 2015, **8**, 55–60.
- 356 13 M. E. Monge, B. D'Anna and C. George, Nitrogen dioxide removal and nitrous acid  
357 formation on titanium oxide surfaces-an air quality remediation process?, *Phys. Chem.*  
358 *Chem. Phys.*, 2010, **12**, 8991–8998.
- 359 14 R. Ammar, M. E. Monge, C. George and B. D'Anna, Photoenhanced NO<sub>2</sub> Loss on  
360 Simulated Urban Grime, *ChemPhysChem*, 2010, **11**, 3956–3961.

- 361 15 S. F. Kowal, S. R. Allen and T. F. Kahan, Wavelength-Resolved Photon Fluxes of Indoor  
362 Light Sources: Implications for HOx Production, *Environ. Sci. Technol.*, 2017, **51**, 10423–  
363 10430.
- 364 16 L. R. Crilley, M. Lao, L. Salehpoor and T. C. VandenBoer, Emerging investigator series: an  
365 instrument to measure and speciate the total reactive nitrogen budget indoors:  
366 description and field measurements, *Environ. Sci. Process. Impacts*, 2023.
- 367 17 K. Sekimoto, S.-M. Li, B. Yuan, A. Koss, M. Coggon, C. Warneke and J. de Gouw,  
368 Calculation of the sensitivity of proton-transfer-reaction mass spectrometry (PTR-MS) for  
369 organic trace gases using molecular properties, *Int. J. Mass Spectrom.*, 2017, **421**, 71–  
370 94.
- 371 18 L. J. Kramer, L. R. Crilley, T. J. Adams, S. M. Ball, F. D. Pope and W. J. Bloss, Nitrous acid  
372 (HONO) emissions under real-world driving conditions from vehicles in a UK road tunnel,  
373 *Atmos. Chem. Phys.*, 2020, **20**, 5231–5248.
- 374 19 W. D. Fahy, F. Wania and J. P. D. Abbatt, When Does Multiphase Chemistry Influence  
375 Indoor Chemical Fate?, *Environ. Sci. Technol.*, 2024, **58**, 4257–4267.
- 376 20 J. C. Ditto, J. P. D. Abbatt and A. W. H. Chan, Gas- and Particle-Phase Amide Emissions  
377 from Cooking: Mechanisms and Air Quality Impacts, *Environ. Sci. Technol.*, 2022, **56**,  
378 7741–7750.
- 379 21 A. T. Hodgson, K. Y. Ming and B. C. Singer, *Quantifying object and material surface areas*  
380 *in residences*, Lawrence Berkeley National Lab.(LBNL), Berkeley, CA (United States),  
381 2005.
- 382 22 C. L. Schiller, S. Locquiao, T. J. Johnson and G. W. Harris, Atmospheric measurements of  
383 HONO by tunable diode laser absorption spectroscopy, *J. Atmos. Chem.*, 2001, **40**, 275–  
384 293.
- 385 23 A. Depoorter, C. Kalalian, C. Emmelin, C. Lorentz and C. George, Indoor heterogeneous  
386 photochemistry of furfural drives emissions of nitrous acid, *Indoor Air*, 2021, **31**, 682–  
387 692.
- 388 24 J. Liu, H. Deng, P. S. J. Lakey, H. Jiang, M. Mekic, X. Wang, M. Shiraiwa and S. Gligorovski,  
389 Unexpectedly High Indoor HONO Concentrations Associated with Photochemical NO2  
390 Transformation on Glass Windows, *Environ. Sci. Technol.*, 2020, **54**, 15680–15688.
- 391 25 S. Pandit, S. L. Mora Garcia and V. H. Grassian, HONO Production from Gypsum  
392 Surfaces Following Exposure to NO2 and HNO3: Roles of Relative Humidity and Light  
393 Source, *Environ. Sci. Technol.*, 2021, **55**, 9761–9772.
- 394 26 H. Schwartz-Narbonne, S. H. Jones and D. J. Donaldson, Indoor lighting releases gas  
395 phase nitrogen oxides from indoor painted surfaces, *Environ. Sci. Technol. Lett.*, 2019, **6**,  
396 92–97.
- 397