Supplement of

Real world observations of ultrafine particles and reduced nitrogen in commercial cooking organic aerosol emissions

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1. Sampling details

Figure S1. Example of mobile laboratory sampling from a restaurant exhaust plume. This photo shows the mobile laboratory parked near the restaurant location identified as “Pizza” in Table 1 and is collecting data on the plume source. As labeled, a sampling inlet is being used to sample the plume which is circled with a white dashed line. Upon entering the inlet, the contents of the plume are measured with equipment inside the mobile laboratory.

2. UFP measurements

For the duration of each sampling period, both the FMPS and CPC were co-located in the mobile laboratory. The FMPS integrated particle number consistently reported lower concentrations than the CPC number counts, though the two instruments were highly correlated. SI Figure 2 shows simultaneous FMPS and CPC number counts at each time resolution for data collected in an urban background location in Baltimore and Pittsburgh.

While sampling restaurant plumes, the concentrations often exceeded the upper detection concentration limit for the CPC. In these cases, an error flag was reported. Due to the frequency of these error flags, we developed a different method to reflect the concentration within the restaurant plumes. Thus, we used the integrated FMPS number and scaled this using the pre-established FMPS:CPC from SI Figure 2 to determine a reliable measure of PNC in the emission plumes.

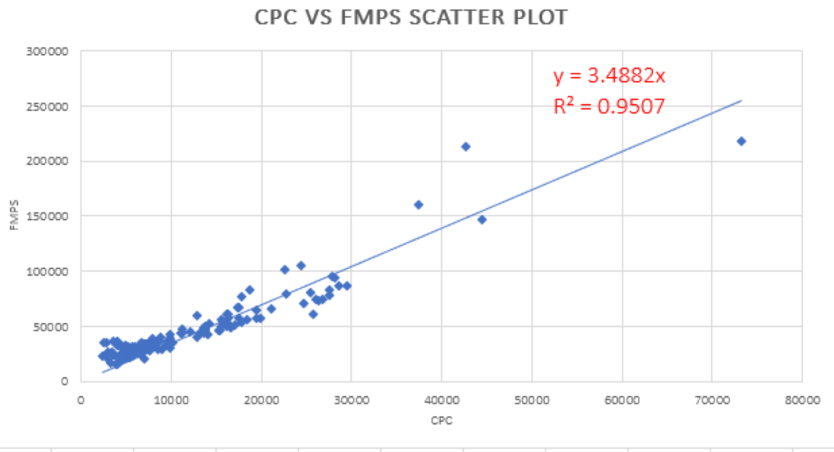


Figure S2. Scatter plot of CPC vs FMPS from the summer field campaign 2019.

Table S1. 5^{th} percentile background ($\mu g/m^3$) of OA and BC during the field campaign in this study the fifth percentile of each daily set of data was calculated and defined as the background concentration of OA and BC.

Background data pertaining to the day of measurement at the following sites	Background OA, 5^{th} percentile ($\mu g/m^3$)	Background BC, 5^{th} percentile ($\mu g/m^3$)
Island Cuisine	3.41	0.374
Pizza	3.95	0.428
BBQ	0.42	0.416
Café	3.35	0.820
Beef	2.41	0.352
Diner 1	3.41	0.374
Diner 2	3.95	0.428
Bakery 1	4.12	0.953
Bakery 2	3.06	0.757
Fast Food 1	0.42	0.416
Fast Food 2	3.06	0.757
Bar/Restaurant 1	5.88	1.31
Bar/Restaurant 2	3.35	0.820

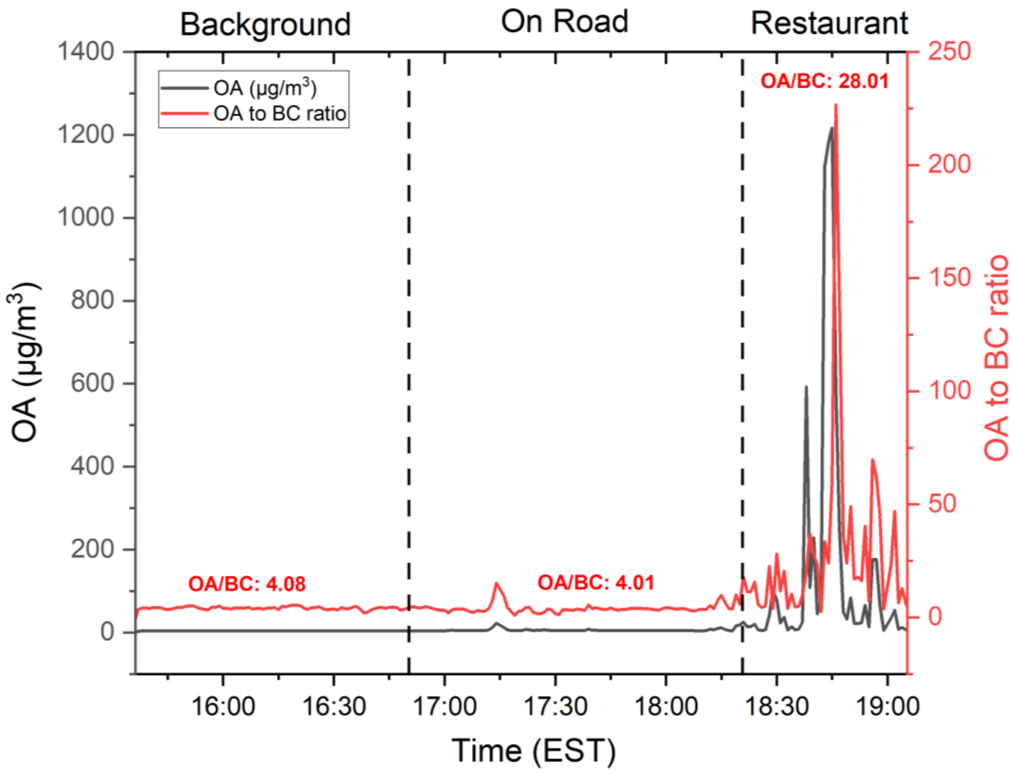
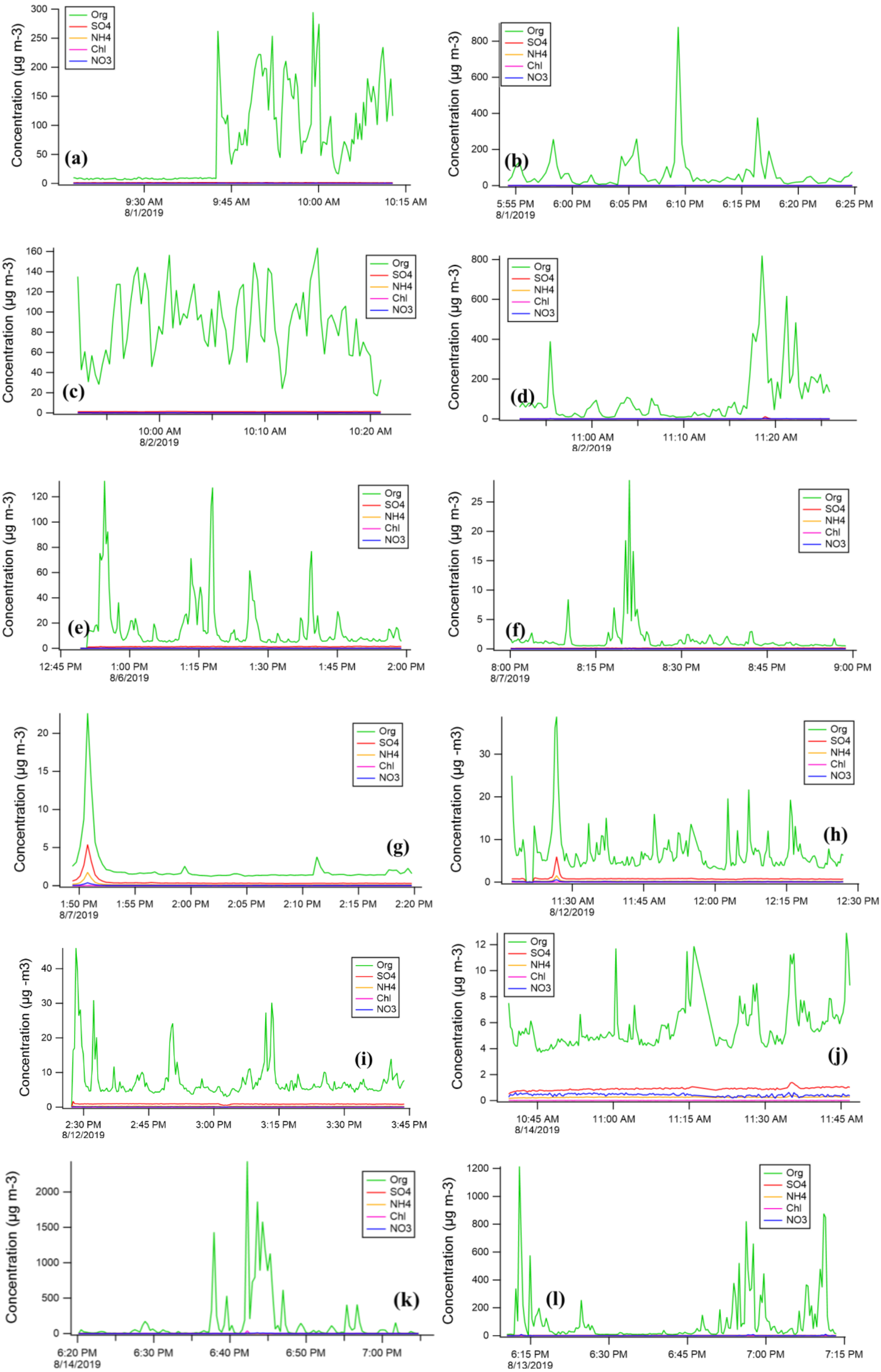


Figure S3. OA/BC time series at Bar/Restaurant 2 sample (background, on-road, and restaurant sampling period). The respective OA/BC ratios in the urban background and on-road sampling periods were both ~4. In contrast, the OA/BC ratio was significantly higher in the restaurant plume at 28.


(a)
Concentration (µg m-3)
300
250
200
150
100
50
0
Org
SO4
NH4
Chl
NO3
9:30 AM
8/1/2019
9:45 AM
10:00 AM
10:15 AM
(b)
Concentration (µg m-3)
800
600
400
200
0
Org
SO4
NH4
Chl
NO3
5:55 PM
8/1/2019
6:00 PM
6:05 PM
6:10 PM
6:15 PM
6:20 PM
6:25 PM
(c)
Concentration (µg m-3)
160
140
120
100
80
60
40
20
0
Org
SO4
NH4
Chl
NO3
10:00 AM
8/2/2019
10:10 AM
10:20 AM
(d)
Concentration (µg m-3)
800
600
400
200
0
Org
SO4
NH4
Chl
NO3
11:00 AM
8/2/2019
11:10 AM
11:20 AM
(e)
Concentration (µg m-3)
120
100
80
60
40
20
0
Org
SO4
NH4
Chl
NO3
12:45 PM
1:00 PM
8/6/2019
1:15 PM
1:30 PM
1:45 PM
2:00 PM
(f)
Concentration (µg m-3)
25
20
15
10
5
0
Org
SO4
NH4
Chl
NO3
8:00 PM
8/7/2019
8:15 PM
8:30 PM
8:45 PM
9:00 PM
(g)
Concentration (µg m-3)
20
15
10
5
0
Org
SO4
NH4
Chl
NO3
1:50 PM
8/7/2019
1:55 PM
2:00 PM
2:05 PM
2:10 PM
2:15 PM
2:20 PM
(h)
Concentration (µg -m3)
30
20
10
0
Org
SO4
NH4
Chl
NO3
11:30 AM
8/12/2019
11:45 AM
12:00 PM
12:15 PM
12:30 PM
(i)
Concentration (µg -m3)
40
30
20
10
0
Org
SO4
NH4
Chl
NO3
2:30 PM
8/12/2019
2:45 PM
3:00 PM
3:15 PM
3:30 PM
3:45 PM
(j)
Concentration (µg m-3)
12
10
8
6
4
2
0
Org
SO4
NH4
Chl
NO3
10:45 AM
8/14/2019
11:00 AM
11:15 AM
11:30 AM
11:45 AM
(k)
Concentration (µg m-3)
2000
1500
1000
500
0
Org
SO4
NH4
Chl
NO3
6:20 PM
8/14/2019
6:30 PM
6:40 PM
6:50 PM
7:00 PM
(l)
Concentration (µg m-3)
1200
1000
800
600
400
200
0
Org
SO4
NH4
Chl
NO3
6:15 PM
8/13/2019
6:30 PM
6:45 PM
7:00 PM
7:15 PM

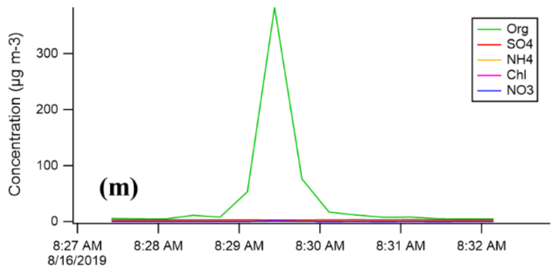


Figure S4. High-resolution time series of organics, sulfate, ammonium, chloride, and nitrate observed by HR-ToF-AMS while measuring restaurant plumes. (a) Diner 1, (b) Island Cuisine, (c) Diner 2, (d) Pizza, (e) Bakery 1, (f) BBQ, (g) Fast Food 1, (h) Fast Food 2, (i) Bakery 2, (j) Café, (k) Bar/Restaurant 2, (l) Bar/Restaurant 1, (m) Beef

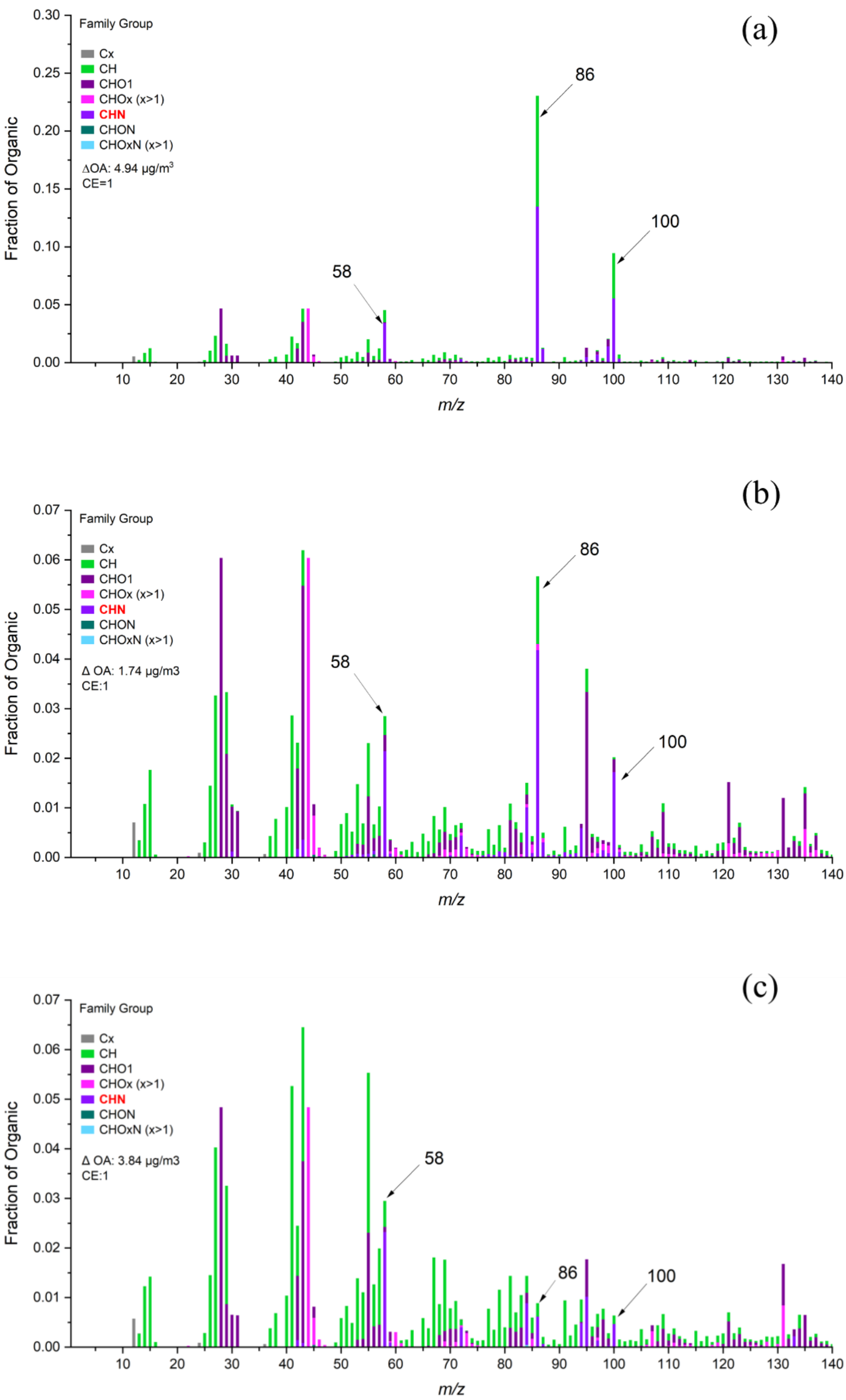


Figure S5. Average AMS mass spectra from three other restaurant sites in this study. (a) Bakery 2, (b) Fast Food 1, and (c) Fast Food 2.

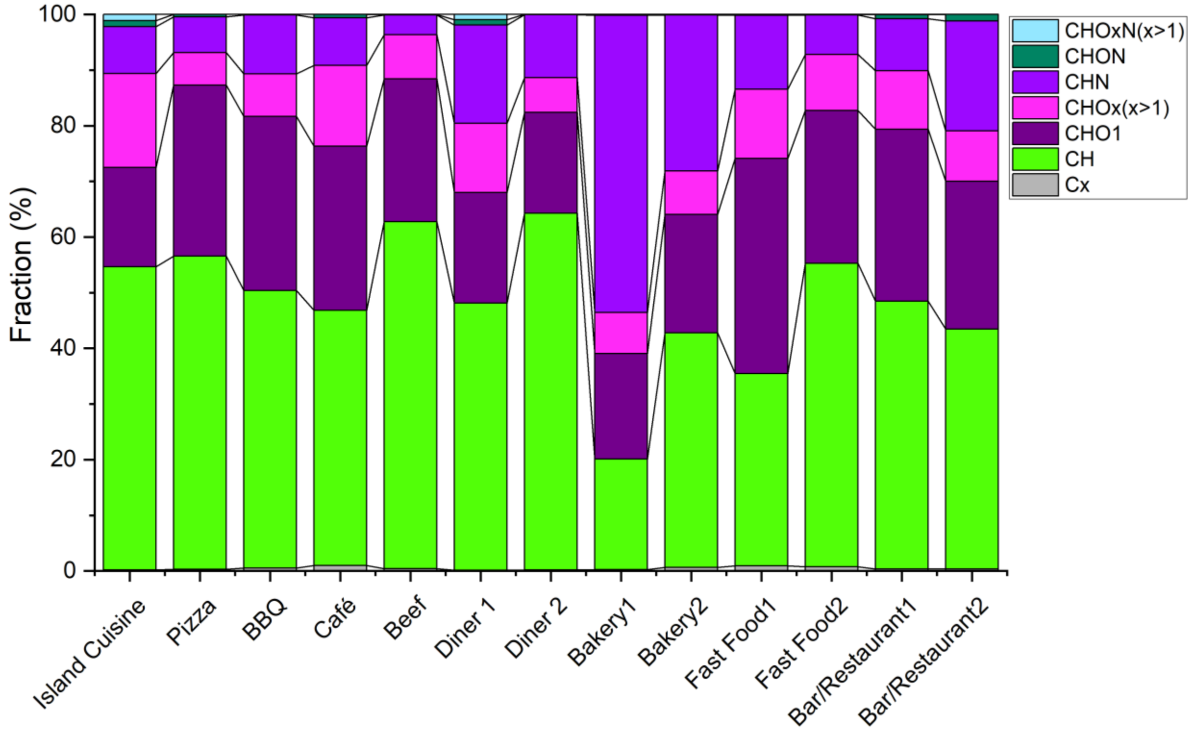


Figure S6. Fractions of CHO_XN, CHON, CHN, CHO_X, CHO1, CH, and C_X families across cooking sites. Within the distribution of the CHN family group, Bakery 1 and Bakery 2 were observed to have predominant proportions of CHN.

Table S2. Fractions of ions by family group (%) and from three significant nitrogen-containing fragments (%) at *m/z* 58 ($C_3H_8N^+$), 86 ($C_5H_{12}N^+$), and 100 ($C_6H_{14}N^+$). These reduced nitrogen peaks are the largest in the bakery mass spectra but are not present in the emissions from the majority of the restaurants.

	Cx	CH	CHO1	CHOx(x>1)	CHN	CHON	CHOxN(x>1)	$fC_3H_8N^+$	$fC_5H_{12}N^+$	$fC_6H_{14}N^+$
Island Cuisine	0.196	54.5	17.9	16.88	8.41	1.10	1.11	3.27	0.00	0.00
Pizza	0.284	56.3	30.7	5.88	6.41	0.417	0.009	2.57	0.57	0.23
BBQ	0.538	49.9	31.3	7.65	10.6	0.114	0	2.78	1.66	0.55
Café	0.952	45.9	29.5	14.5	8.60	0.579	0	1.36	0.96	0.55
Beef	0.406	62.3	25.7	7.93	3.56	0.077	0.026	1.51	0.18	0.00
Diner 1	0.138	48.0	19.9	12.5	17.6	0.958	0.958	9.40	0.64	0.00
Diner 2	0.205	64.1	18.1	6.26	11.3	0.020	0	5.30	1.11	0.38
Bakery1	0.265	19.8	19.0	7.37	53.4	0.067	0.082	31.4	17.3	1.63
Bakery2	0.653	42.2	21.3	7.80	28.0	0.049	0.048	3.42	13.5	5.55
Fast Food1	0.889	34.6	38.7	12.4	13.3	0.152	0	2.15	4.18	1.72
Fast Food2	0.742	54.5	27.5	10.1	7.06	0.066	0.047	2.33	0.62	0.47
Bar/Restaurant1	0.365	48.1	31.0	10.5	9.33	0.717	0.043	0.35	0.30	0.11
Bar/Restaurant2	0.342	43.1	26.6	9.02	19.7	1.19	0	0.14	0.05	0.01

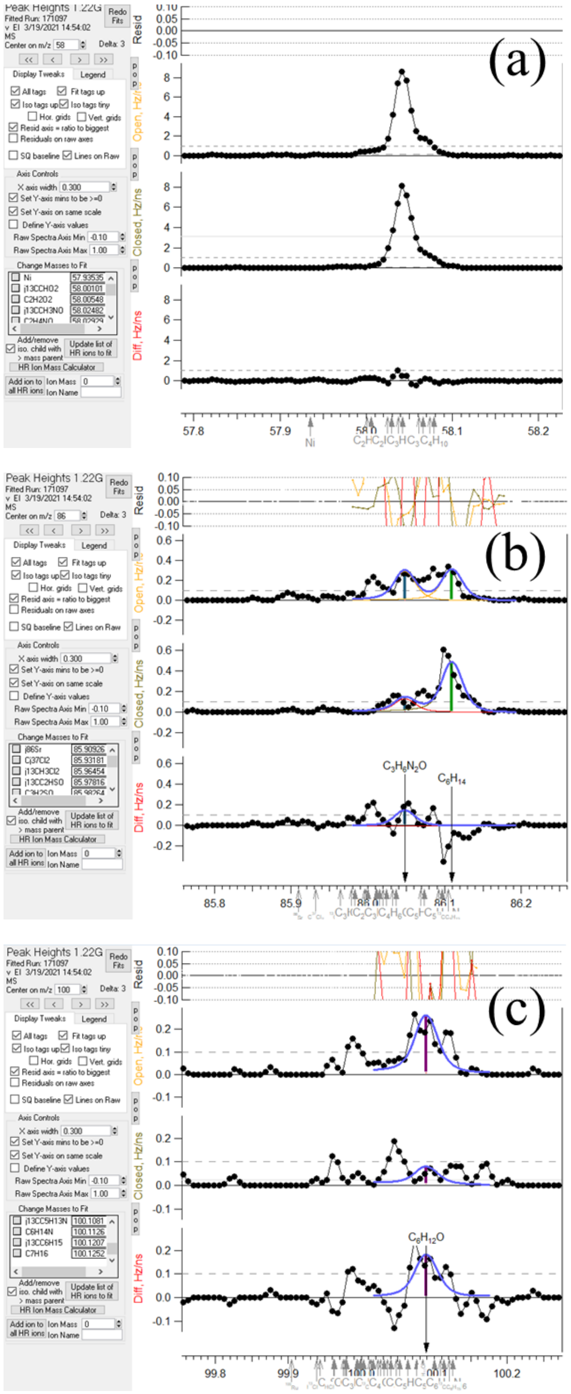


Figure S7. Peak fittings of (a) *m/z* 58, (b) *m/z* 86, and (c) *m/z* 100 from bread baking experiments using Azodicarbonamide ($C_2H_4N_4O_2$, ADA).

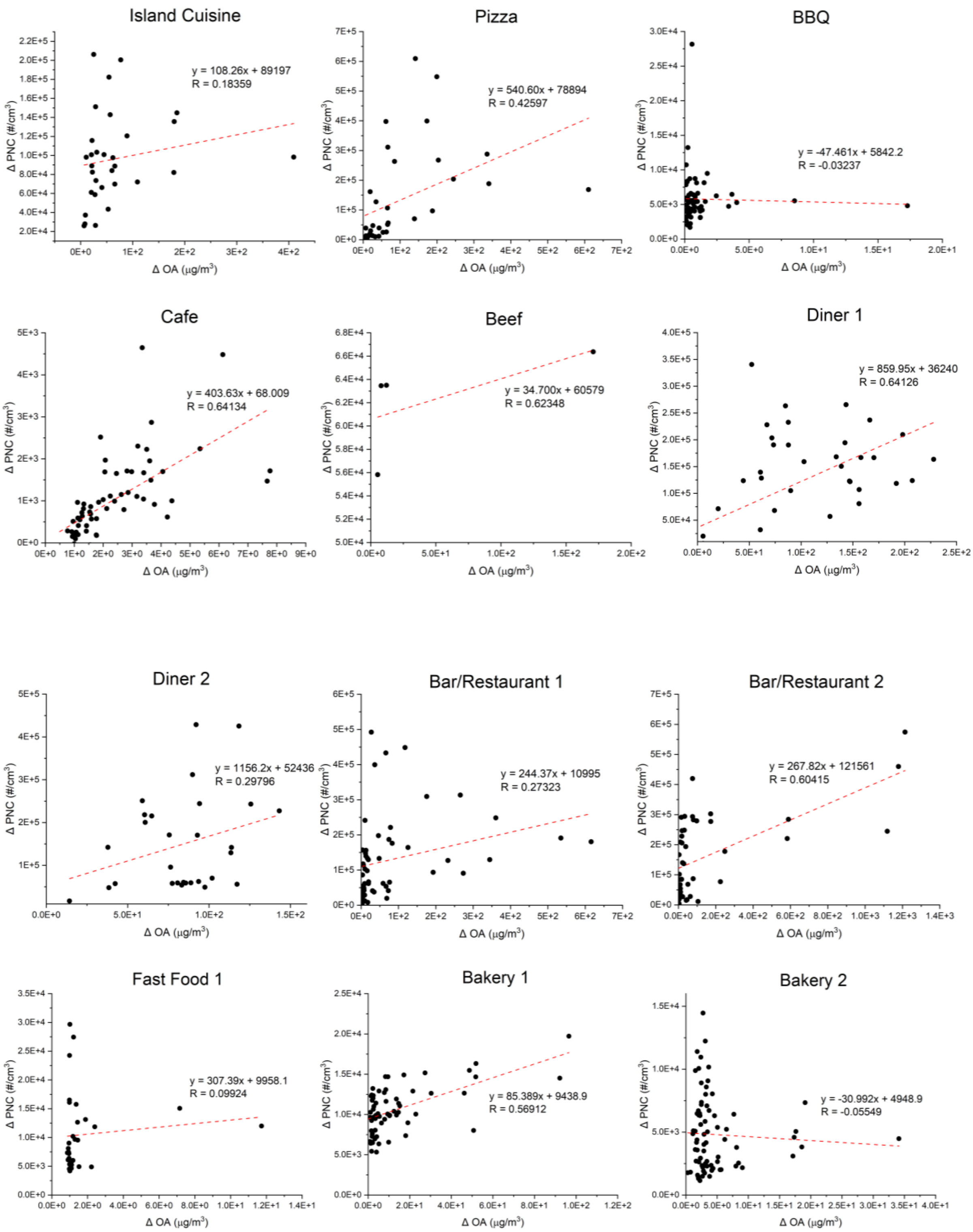


Figure S8. Scatter plot and correlation coefficient of ΔPNC (#/cm^3) vs ΔOA (μg/m^3) across 13 cooking sites in this study. There is no strong linear correlation between ΔPNC and ΔOA with R (<0.7).

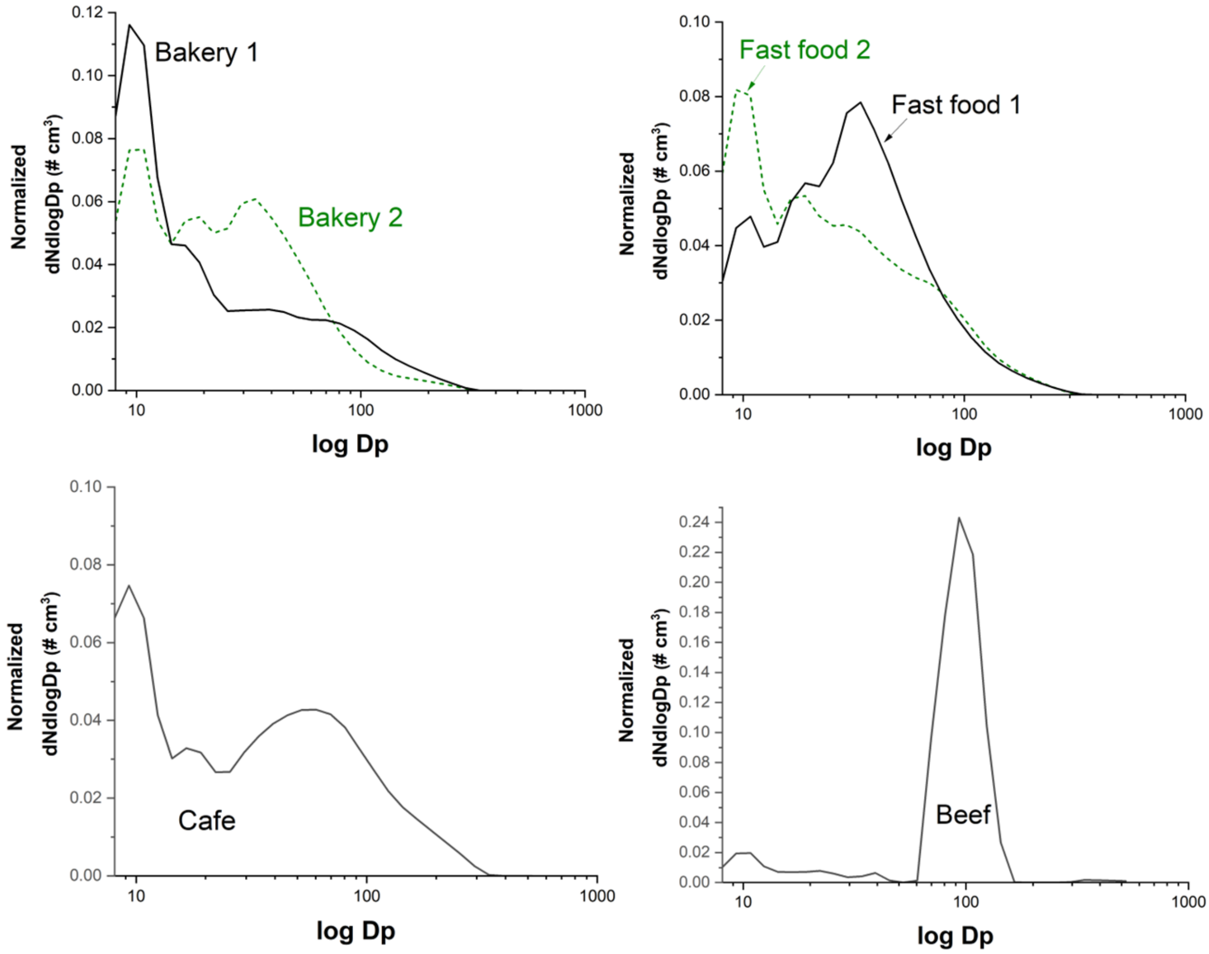


Figure S9. Particle size and total particle number distributions of cooking samples with lower PNC concentrations.

3. Offline sample preparation and analysis

After MS compound formulas were generated from high mass resolution (within 2 ppm) data, and underwent QC/QA, including background subtraction and formula composition checks, target lists were created for each sample and used to analyze the compounds of interest with tandem mass spectrometry. As there were less than 200 compounds of interest for each sample, all MS compounds which passed QC/QA were included in the target lists.

SIRIUS 5.6.3 was used to analyze the LC-MS/MS samples, and an updated version of the R code that formats the updated exported SIRIUS results to work with the Python APPI code can be provided for MS/MS analysis if requested. SIRIUS was used with a free academic/non-commercial user account, and more information can be found at https://bio.informatik.uni-jena.de/software/sirius/ for future updates and information on SIRIUS 5.

Table S3. Offline filter sample volumes and sampling times.

Date	Day of Week	Location	Sample Volume (L)	Sample Start Time (EST)	Sample End Time (EST)
8/1/19	Thursday	Diner 1	2,250	9:42:00	10:12:00
8/1/19	Thursday	Island Cuisine	1,890	17:54:00	18:24:00
8/2/19	Friday	Urban Background 1	2,624	14:16:00	17:00:00
8/2/19	Friday	Diner 2	1,764	9:52:00	10:20:00
8/2/19	Friday	Pizza	2,079	10:52:00	11:25:00
8/5/19	Monday	Field Blank			
8/5/19	Monday	Urban Background 2	2,898	5:39:00	6:25:00
8/6/19	Tuesday	Urban Background 3	5,607	9:48:00	11:17:00
8/6/19	Tuesday	Bakery 1	4,095	12:49:00	13:54:00
8/7/19	Wednesday	Fast Food 1	2,520	1:34:00	2:14:00
8/9/19	Friday	Urban Background 4	4,860	13:37:00	14:58:00
8/9/19	Friday	Linwood Asphalt	3,840	10:00:00	11:04:00
8/12/19	Monday	Fast Food 2	3,840	11:22:00	12:26:00
8/12/19	Monday	Bakery 2	4,560	14:27:00	15:43:00
8/13/19	Tuesday	Bar/Restaurant 1	3,304	18:14:00	19:10:00
8/13/19	Tuesday	Field Blank			
8/14/19	Wednesday	Cafe	3,953	10:39:00	11:46:00
8/14/19	Wednesday	Urban Background 5	4,307	15:36:00	16:49:00
8/14/19	Wednesday	Bar/Restaurant 1	2,596	18:20:00	19:04:00

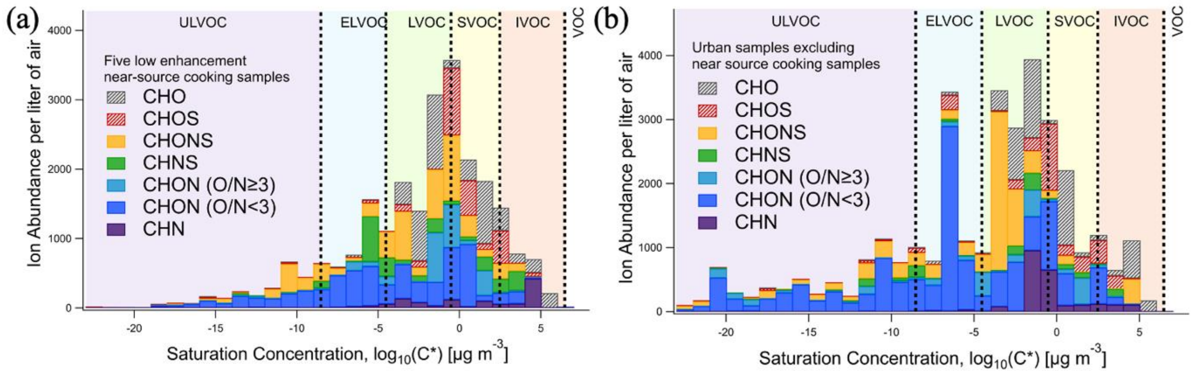


Figure S10. Averaged chemical composition of particle-phase functionalized organic compounds from (a) five lower enhanced near-source cooking samples (bakery 1, bakery 2, fast food 1, fast food 2, café), (b) other urban samples excluding near-source cooking samples. In Table S3, the five urban background samples are all included in (b). Supplementary figures are provided to accompany Figure 7.

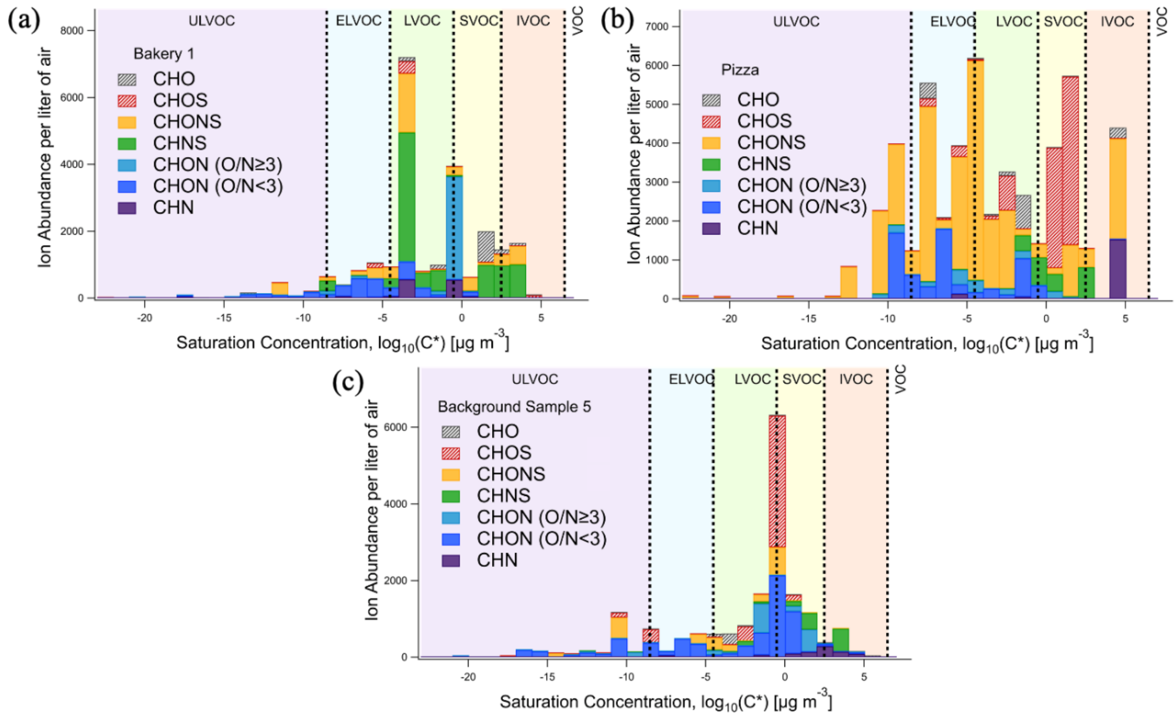


Figure S11. LC-TOF speciation of Bakery 1, Pizza, and Urban Background 5 samples, shown as compound class volatility distributions. Supplemental figures are provided as they are the samples selected for MS/MS analysis.

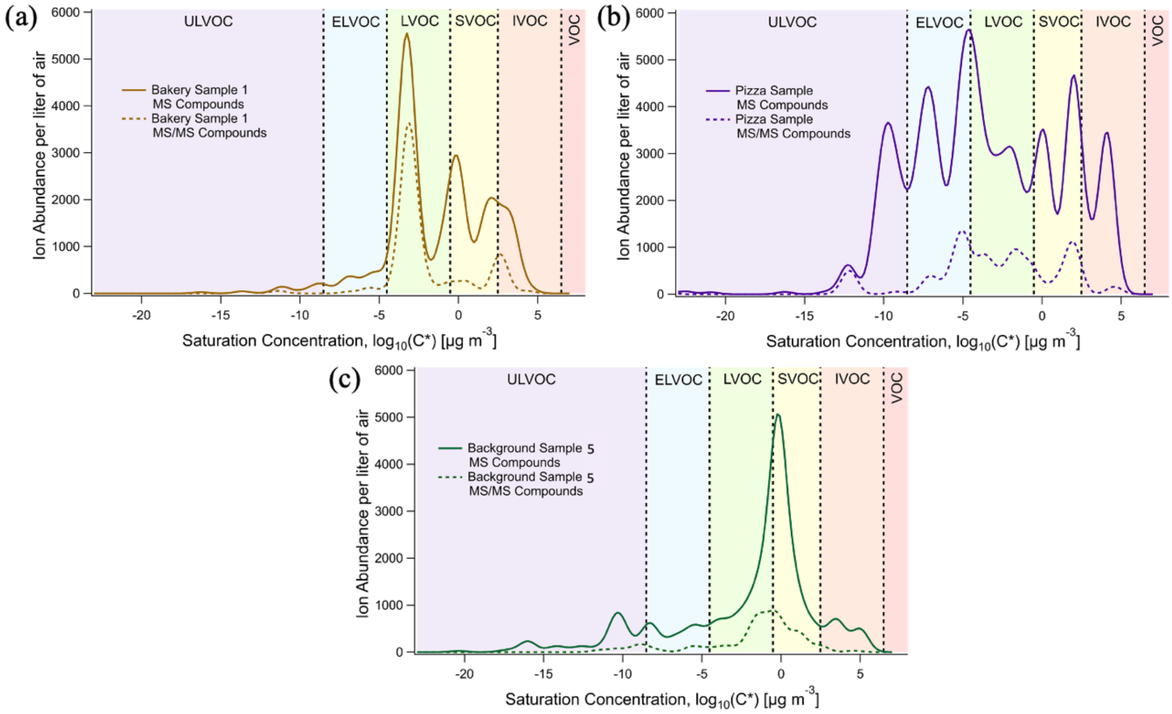


Figure S12. Ion abundance volatility distributions of compounds characterized with LC-MS/MS compared to LC-TOF compounds, for **(a)** Bakery sample 1, **(b)** Pizza sample, and **(c)** urban background sample 5. Notes: For the three samples selected for MS/MS analysis, on average, 24.8% of targeted compounds were observed via MS/MS and assigned functionalities, with an average of 21.4% of the total MS abundance observed via MS/MS. This figure shows the compound class volatility distribution of MS/MS observed compounds for each sample compared to the abundance from all MS compounds. While not all compounds were observed, the MS/MS compounds were from a range of volatilities and compound classes. The volatility distributions of the particle-phase organic compounds' chemical composition at each of these three sites can be found in Figure S11.

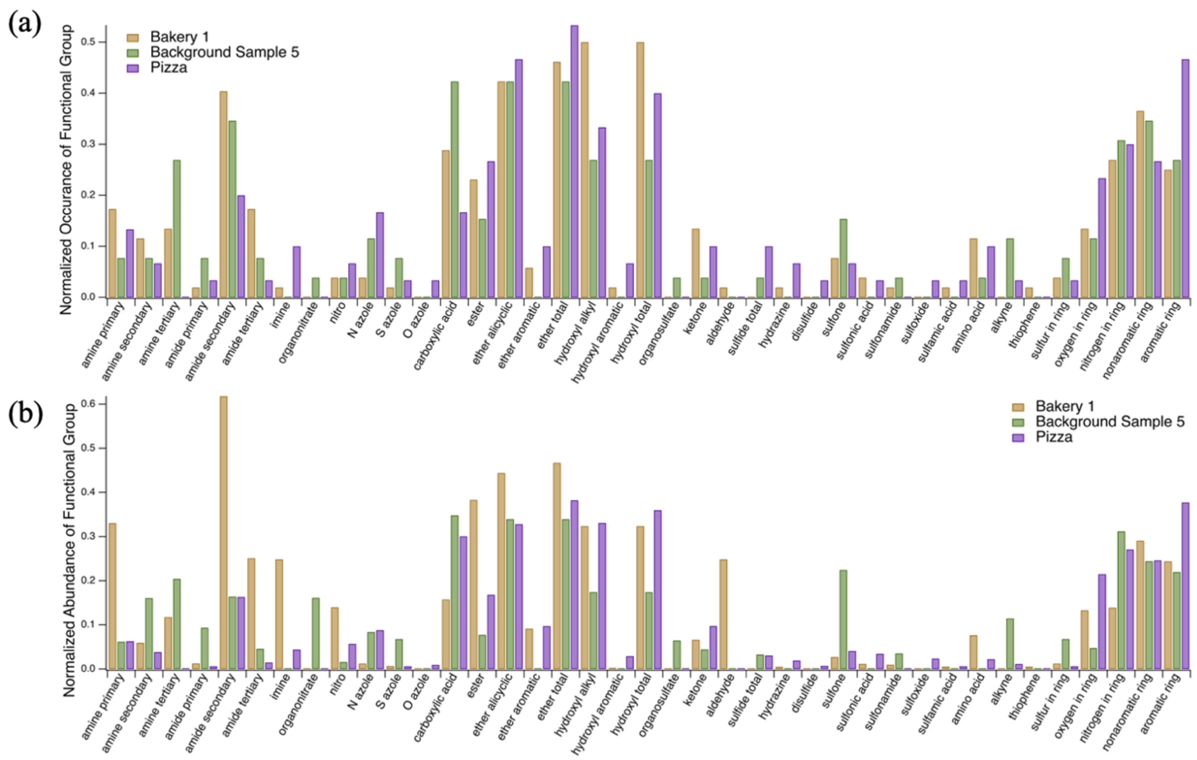


Figure S13. The functional groups and structural features observed in Bakery 1 (gold), Pizza (purple), and urban background sample 5 (green) by the (a) number of occurrences and (b) relative abundance of each functional group or structural features. The structural features are on the far right (i.e., ringed species), and the nitrogen-containing functional groups are on the left. The distributions represent the relative occurrence or abundance of a functional group within that sample's MS/MS analyzed compounds. Similar to prior work, the occurrence of organonitrates is lower than expected due to potential losses and poor ionization of organonitrates (Ditto et al., 2020); however, there are additional CHON functional groups observed, such as nitro, and some oxygen-containing azoles (grouped into azoles in Figure 8).

Other functional groups searched for but not seen in these samples are listed below.

1. peroxide
2. hydroperoxide
3. carbonylperoxynitrate
4. carbonylperoxyacid
5. peroxy nitrate
6. nitroester
7. nitrophenol
8. nitrile
9. anhydride
10. isocyanate
11. isothiocyanate
12. oxime
13. enamine
14. azide
15. hyrazone
16. nitroso
17. carbothioester

18. thiol
19. thioamide
20. sulfinate
21. sulfinic_acid
22. sulfonate
23. carboazosulfone
24. alt_sulfoxide
25. sulfuric acid diester
26. sulfamate
27. sulfenic acid
28. sulfenate
29. thioketone
30. thial
31. diazene
32. azoxy nitrogen
33. diazo nitrogen
34. azo
35. isonitrile
36. carbothiocarboxylate