Supporting Information

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Characterization of Gas-phase Organics Using Proton Transfer Reaction Time-of-Flight Mass Spectrometry: Aircraft Turbine Engines

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Table S1. Engine test parameters.

Engine model	Thrust rating (kN)	Ambient temperature (°C)	Ambient pressure (hPa)
Engine 1	111.2-155.7	~13.0	958
		16.0-18.0	972
		17.0-20.0	979
Engine 2	111.2-155.7	~15.0	965
		19.0-23	972
Engine 3	111.2-155.7	24.3-27.0	972
Engine 4	111.2-155.7	22.3-24.6	965
Engine 5	244.6-311.4	~20.0	965
Engine 6	244.6-311.4	~19.0	965
Engine 7	244.6-311.4	17.0-21.0	972

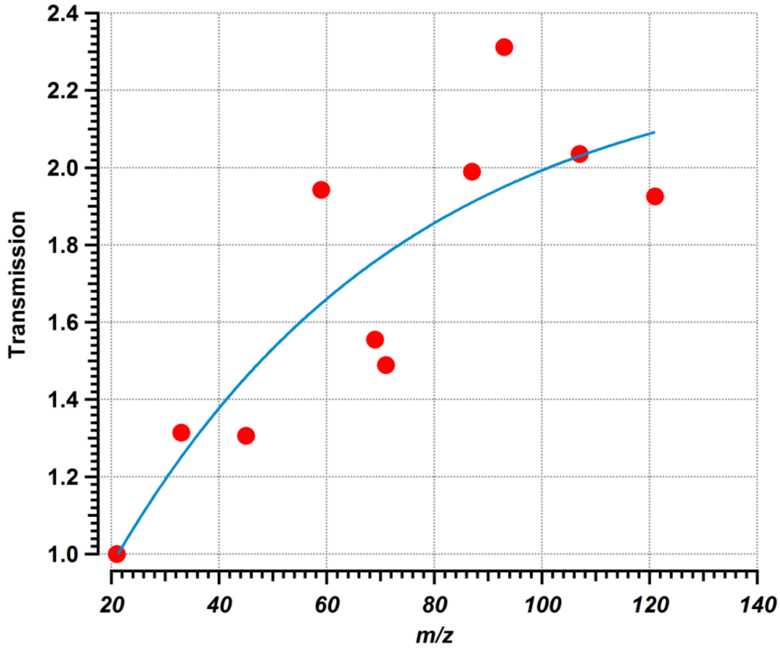

Figure S1. Transmission coefficient (TR_{OG^+}) of the reference compounds (red) and the fitted transmission function (blue line).

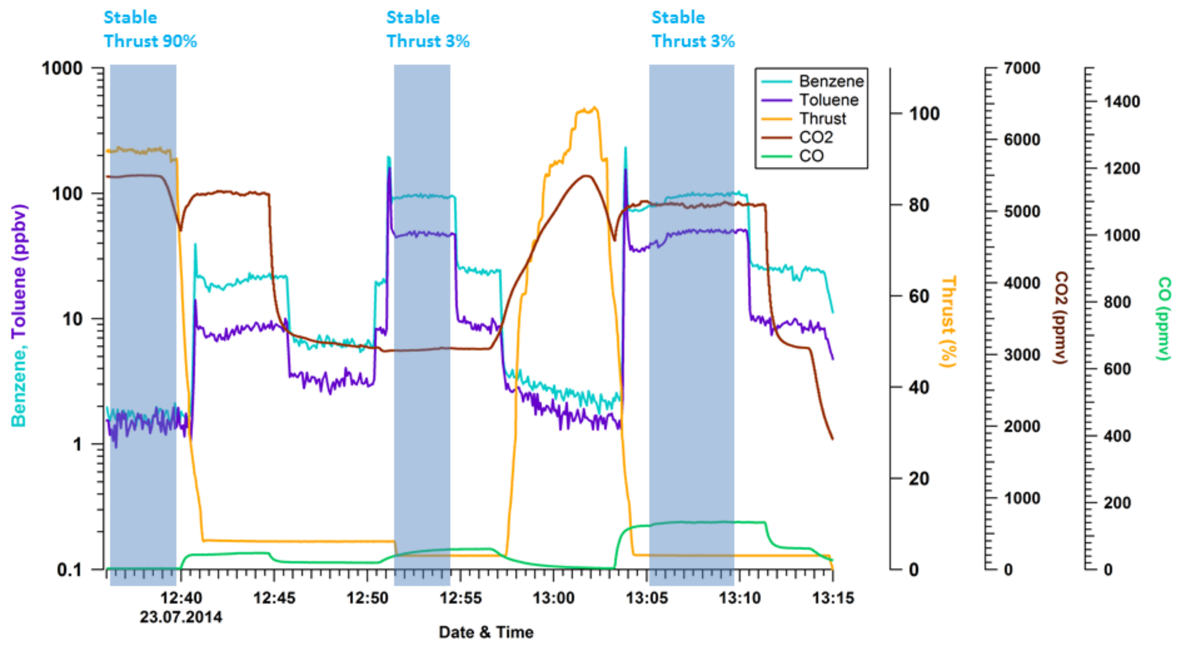

Figure S2. Time series data from the engine test performed on 23.07.2014 is given as an example. CO_2, CO (ppmC) measured from the raw gas line. Benzene and toluene mixing ratios (ppbv) were measured by the PTR-ToF-MS. The blue shaded regions highlight stable engine conditions (90% and 3% thrust). Only data from the stable periods (shaded areas) were used to estimate average EI. Such engine tests performed after maintenance services had shorter durations e.g. at most 10 minutes at a given thrust setting. Because of the short test durations, the NMOG signal was not stable in the unshaded regions. The durations of "dedicated engine tests", performed in September-October 2014, were longer (at least 10 minutes at given thrust setting) compared to these technical checks.

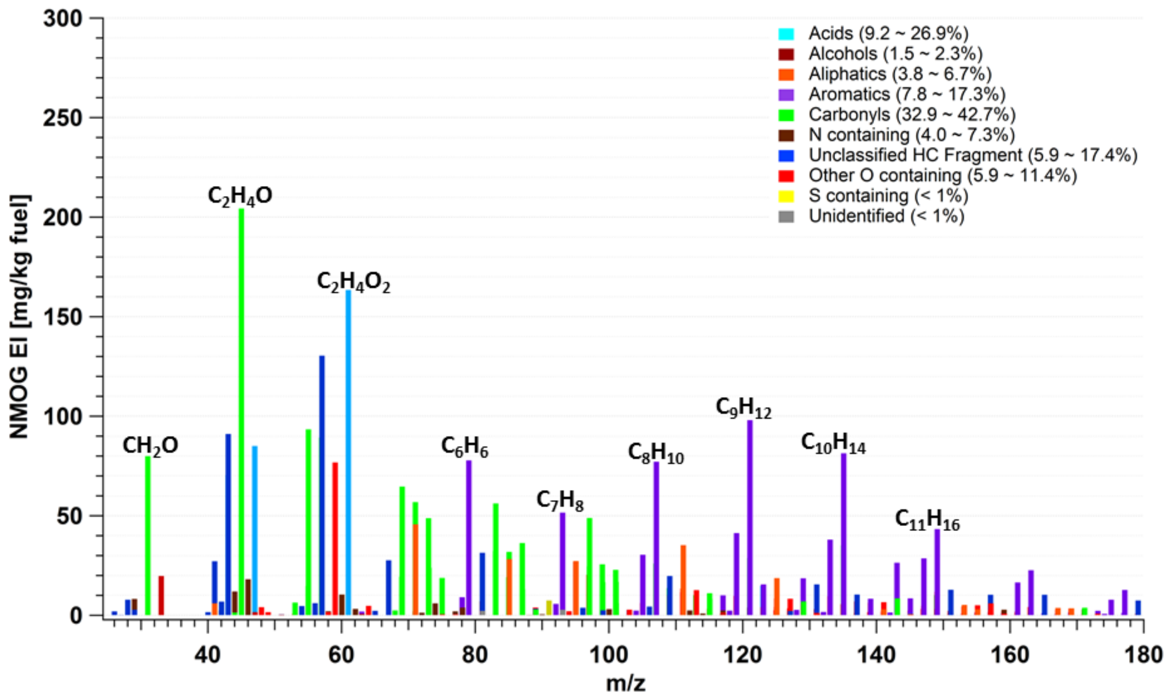

Figure S3. A sample PTR-ToF-MS mass spectrum at idling 5% for a turbine engine from July 2014.

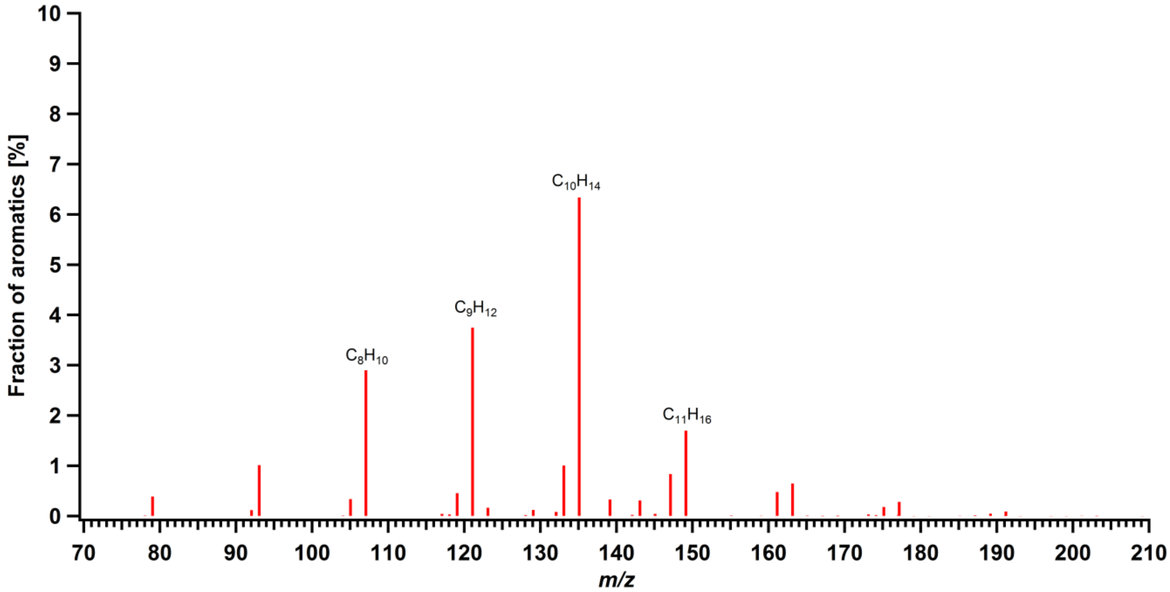

Figure S4. Molar fractions of aromatics during the fuel evaporation test at laboratory temperature (24°C). The four most abundant peaks were $C_{10}H_{14}$, C_9H_{12}, C_8H_{10} and $C_{11}H_{16}$ in JET-A1 fuel as shown by text on the mass spectrum.

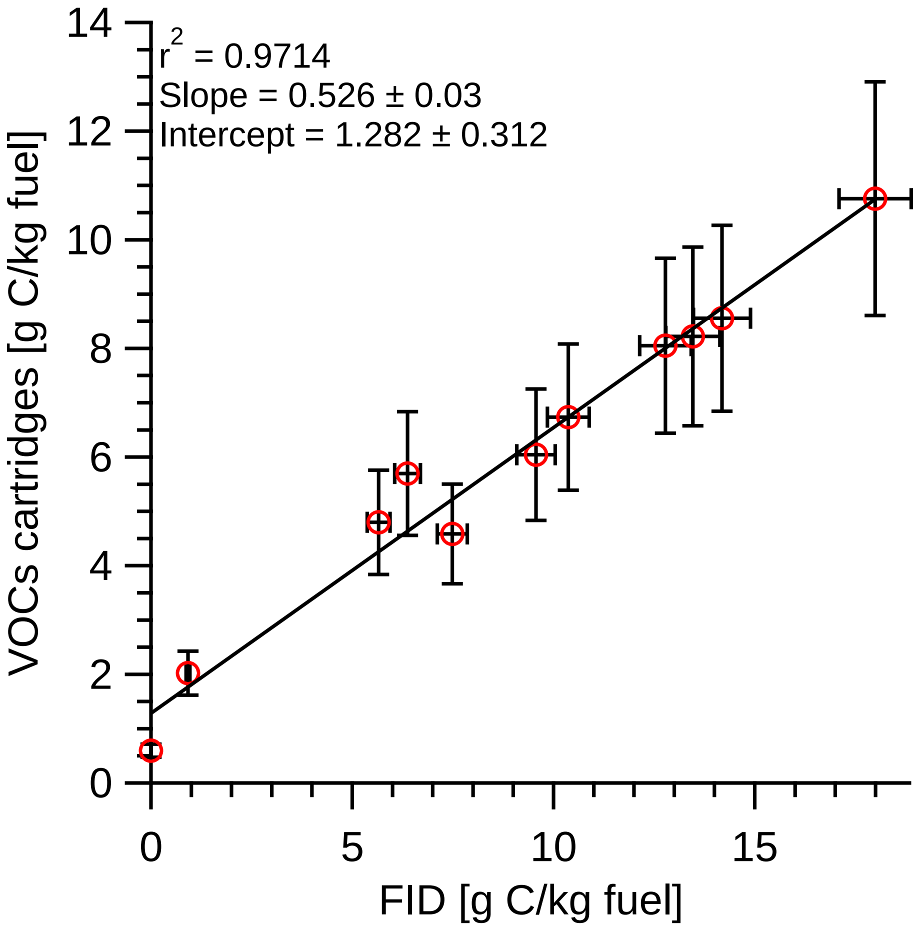

Figure S5. Scatter plot of total VOCs measured during idle by gas-chromatography (y-axis) and FID (x-axis).

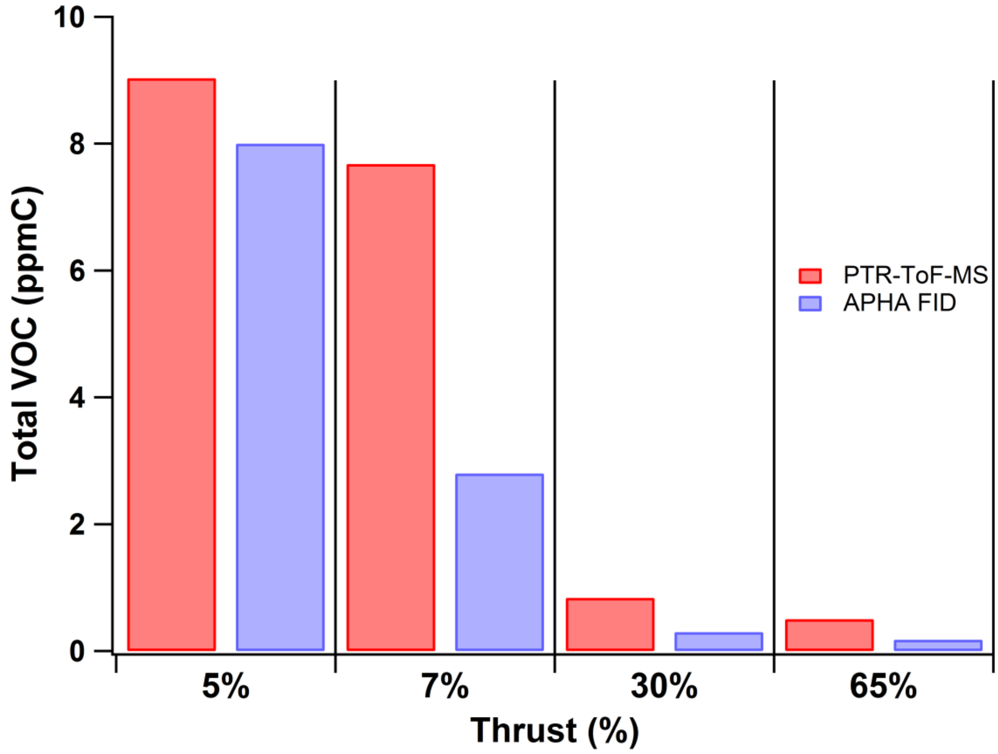

Figure S6. Total VOC mixing ratios (ppmC) measured by a hydrogen flame ionization hydrocarbon detector (FID) and a PTR-ToF-MS. Engine tests from July 2014 are presented as an example. PTR-ToF-MS and FID monitor measurements are similar with a ratio of about 0.9 at thrust 5%. This ratio decreases with thrust by increasing oxygen content due to the sensitivity of flame ionization detectors for oxygenated compounds e.g. acids, aldehydes.

Table S2. PTR-ToF-MS peak list (accounts for 95% of the total NMOG mass) including compound formula, molecular mass, corresponding functional group, the reaction rate constant for "NMOG + H_3O^+" reaction from Cappelin et al. (2012),[1] and the average emission indices with the standard deviation (+/-) for varying thrust settings.

Compound Formula	m/z detected	Category	k rates [10^{-9} cm^3/s]	Thrust Setting							
				3-5%		6-7%		30-45%		95-100%	
				Average EI [mg / kg fuel]	+/-	Average EI [mg / kg fuel]	+/-	Average EI [mg / kg fuel]	+/-	Average EI [mg / kg fuel]	+/-
$C_2H_5O^+$	45.034	Carbonyl	2	**446**	571.5	**236.4**	149.4	**6.7**	2.2	**8.4**	7.6
$C_2H_5O_2^+$	61.028	Acid	2.25	**356.2**	591.2	**206.8**	181.5	**10.7**	3	**15.1**	10.3
$C_4H_9^+$	57.070	Non-arom HC	1.8	**282.9**	456.3	**101.7**	92.4	**20.4**	15.5	**4.2**	1.6
$C_9H_{13}^+$	121.101	Aromatic	2.4	**212.5**	431.6	**36.4**	26.7	**1.9**	1.5	**1.2**	0.8
$C_4H_7^+$	55.054	Non-arom HC	1.76	**202.5**	348.7	**55.7**	36.9	**1.9**	1.2	**2.8**	1.5
$C_3H_7^+$	43.054	Non-arom HC	1.62	**197.4**	292.4	**60.9**	48.7	**1.8**	1.1	**1.5**	1.5
$C_3H_5O^+$	57.034	Carbonyl	3.55	**193.6**	335.3	**80.3**	70.6	**0.7**	0.1	**0.9**	0.6
$CH_3O_2^+$	47.013	Acid	1.99	**184.3**	255.5	**147.3**	134.3	**11.2**	1.1	**15.9**	13.1
$C_{10}H_{15}^+$	135.117	Aromatic	2	**176.4**	344.3	**29.3**	22.2	**1.7**	1.3	**1.4**	0.6

$C_3H_7O^+$	59.049	Carbonyl	3.32	**173.5**	240.2	**90.7**	70.3	**9.7**	6.4	**7.6**	7.7
CH_3O^+	31.018	Carbonyl	2.73	**173.3**	162.35	**127.5**	107.8	**2.6**	0.7	**1.8**	2.9
$C_6H_7^+$	79.054	Aromatic	1.93	**188.3**	349.1	**46.6**	33	**0.5**	0.3	**0.5**	0.4
$C_8H_{11}^+$	107.086	Aromatic	2.26	**167.4**	339.7	**31.2**	23.8	**1.7**	1.4	**0.9**	0.7
$C_2H_3O^+$	43.018	O-containing	3.12	**152.7**	194.1	**83.3**	54.2	**4.1**	1	**6.6**	6.4
$C_5H_9^+$	69.070	Non-arom HC	2.06	**140.1**	255.8	**31.2**	21.1	**1.4**	0.9	**1.7**	1
$C_4H_7O^+$	71.049	Carbonyl	3.3	**123.2**	220.2	**44.2**	36.6	**0.7**	0.2	**1**	0.6
$C_6H_{11}^+$	83.086	Non-arom HC	2.08	**121.8**	227.2	**25.6**	17.3	**2.5**	1.8	**2.5**	1.1
$C_7H_{13}^+$	97.101	Non-arom HC	2.09	**114.2**	216.8	**26.2**	24.4	**2.3**	1.9	**1.4**	0.8
$C_7H_9^+$	93.070	Aromatic	2.08	**111.9**	217.5	**27.6**	20.6	**2.1**	1.7	**1.5**	2
$C_3H_5O_2^+$	73.029	Carbonyl	2	**105.8**	159.8	**56**	60.6	**2.2**	0.5	**3.3**	1.8
$C_5H_{11}^+$	71.086	Alkene	1.9	**99.1**	179.6	**17.9**	11.3	**1.4**	1	**1**	0.6
$C_{11}H_{17}^+$	149.133	Aromatic	2	**93.8**	180.7	**15.9**	11.5	**1.1**	0.8	**0.8**	0.4
$C_9H_{11}^+$	119.086	Aromatic	2	**89.4**	187.6	**15.9**	9.5	**0.4**	0.3	**0.5**	0.2
$C_{10}H_{13}^+$	133.101	Aromatic	2	**82.4**	171.3	**12.8**	8	**0.5**	0.4	**0.5**	0.3
$C_4H_7O_2^+$	87.044	Carbonyl	1.7	**78.7**	117.8	**37.5**	40.7	**1.9**	0.7	**2.8**	1.4
$C_8H_{15}^+$	111.117	Alkyne	2	**76.4**	148.4	**12.4**	9	**1.5**	1.2	**0.9**	0.5
$C_9H_{11}O^+$	135.080	Carbonyl	2	**76.1**	174.1	**19.3**	14.6	**0.6**	0.4	**0.6**	0.6
$C_3H_5^+$	41.039	Alkene	2	**71.6**	47.5	**59.2**	44.3	**1.9**	1.1	**2.1**	2.7
$C_5H_7O^+$	83.049	Carbonyl	2	**69.9**	140.2	**20.8**	15.7	**0.3**	0.2	**0.5**	0.3
$C_5H_9O^+$	85.065	Carbonyl	2.2	**69**	125.6	**19.9**	16.1	**0.6**	0.3	**1.4**	0.9
C_6H_9+	81.070	Non-arom HC	2	**67.9**	127.2	**12.4**	7.7	**0.8**	0.6	**0.8**	0.6
$C_8H_9^+$	105.070	Aromatic	2.27	**65.9**	136.5	**13.4**	8.4	**0.3**	0.2	**0.4**	0.3
$C_6H_7O^+$	95.049	Alcohol	2	**62.9**	142.9	**20.3**	13.6	**0.9**	0.6	**1**	0.9
$C_8H_9O^+$	121.065	Carbonyl	3.48	**62.3**	138.6	**19.6**	14.7	**0.4**	0.2	**0.4**	0.4
$C_{11}H_{15}^+$	147.117	Aromatic	2	**61.9**	124.5	**9.6**	6.4	**0.7**	0.5	**0.5**	0.3
$C_6H_{13}^+$	85.101	Alkene	2.04	**61.1**	114	**10**	6.4	**0.8**	0.6	**0.6**	0.3
$C_5H_7^+$	67.054	Non-arom HC	1.83	**59.8**	112.9	**11.4**	7.6	**0.2**	0.2	**0.3**	0.3
$C_7H_{11}^+$	95.086	Alkane (fragment)	2	**59**	107.7	**10.7**	6.5	**0.9**	0.7	**0.6**	0.4
$C_{11}H_{11}^+$	143.086	Aromatic	2	**57.2**	114.5	**16**	16.7	**0.8**	0.5	**0.8**	0.6
$C_7H_7O^+$	107.049	Carbonyl	3.82	**56.3**	111.9	**22.2**	17.9	**0.8**	0.3	**0.7**	0.4
$C_4H_3O_3^+$	99.008	Carbonyl	2	**55.5**	71.6	**47.7**	78.7	**2**	0.6	**4.1**	3.8
$C_6H_9O^+$	97.065	Carbonyl	2	**53.1**	110.1	**13.2**	10.2	**0.3**	0.2	**0.5**	0.3
$C_4H_9O^+$	73.065	Carbonyl	3.2	**51.8**	77.2	**27.5**	25.8	**2**	1.2	**5.4**	7.5
$C_4H_5O_3^+$	101.023	Carbonyl	2	**49.5**	70.9	**31.6**	48	**2**	0.3	**3.6**	1.6
$C_{12}H_{19}^+$	163.148	Aromatic	2	**49**	93.7	**8.6**	6.6	**0.7**	0.5	**0.5**	0.4
$C_4H_5O^+$	69.034	Carbonyl	1.7	**47.1**	84.5	**17.3**	12.3	**0.3**	0.1	**0.5**	0.3
$C_5H_5O_2^+$	97.028	O-containing	2	**44**	85.4	**22.3**	22.6	**0.5**	0.2	**1.2**	0.9
$C_8H_{13}^+$	109.101	Non-arom HC	2	**42.8**	79.1	**7.3**	4.7	**0.5**	0.4	**0.4**	0.3
CH_5O^+	33.034	Alcohol	2.22	**42.7**	40	**32**	26.4	**1.2**	0.3	**0.8**	1.2
$C_4H_5O_2^+$	85.028	O-containing	2	**41.6**	79.5	**19.3**	18.4	**0.5**	0.2	**1**	0.6

$C_3H_7O_2^+$	75.044	Carbonyl	2.41	**40.7**	70.1	**17.9**	14	**1.1**	0.2	**2**	1.1
$C_9H_{17}^+$	125.133	Alkyne	2	**40.5**	79.6	**6.1**	4.5	**0.7**	0.5	**0.4**	0.2
$C_{10}H_9^+$	129.070	Aromatic	2.45	**40.2**	76.4	**12.8**	11.6	**0.3**	0.1	**0.3**	0.1
CH_4NO^+	46.029	N-containing	2	**39.3**	58.5	**19.6**	28.7	**1.2**	0.3	**1.2**	0.5
$C_5H_9O_2^+$	101.060	Carbonyl	2.2	**36.3**	60.5	**16.1**	16.1	**1.1**	0.5	**1.9**	1.2
$C_6H_{11}O^+$	99.080	Carbonyl	3.8	**35.8**	68.1	**15.7**	12	**1.6**	0.9	**3.9**	2.3
$C_{12}H_{17}^+$	161.133	Aromatic	2	**35.7**	70.7	**6.1**	4.6	**0.5**	0.4	**0.4**	0.3
$C_9H_{15}^+$	123.117	Non-arom HC	2	**33.7**	62.6	**5.4**	3.7	**0.3**	0.2	**0.3**	0.2
$C_{10}H_{11}^+$	131.086	Non-arom HC	2	**33.6**	74.5	**4.4**	2.6	**0.1**	0.1	**0.1**	0.1
$C_7H_7O_2^+$	123.044	Acid	2	**32**	74	**10.1**	7	**0.3**	0	**0.4**	0.2
$C_3H_3O^+$	55.018	Carbonyl	2	**32**	47.7	**12**	8.1	**0.1**	0	**0.3**	0.3
$C_6H_5O_2^+$	109.028	Carbonyl	2	**29.5**	53.4	**11**	11	**0.2**	0.1	**0.4**	0.2
$C_7H_{11}O^+$	111.080	O-containing	2	**29**	61.4	**6.6**	5.5	**0.1**	0.1	**0.2**	0.1
$C_5H_{11}O^+$	87.080	Carbonyl	2.3	**28.3**	45.5	**10.4**	9.5	**0.8**	0.6	**1.1**	0.5
$C_{11}H_{19}^+$	151.148	Non-arom HC	2	**27.7**	51.6	**4.8**	3.4	**1**	0.9	**0.4**	0.3
$C_{13}H_{21}^+$	177.164	Aromatic	2	**27.6**	53	**5.7**	5.1	**0.5**	0.4	**0.4**	0.3
$C_7H_{13}O^+$	113.096	Carbonyl	2	**27.2**	52.4	**6.2**	5	**0.3**	0.2	**0.4**	0.2
CH_2NO^+	44.014	N-containing	2	**25.8**	38.6	**14.6**	19.4	**0.7**	0.1	**1.1**	1
$C_{10}H_{13}O^+$	149.096	Carbonyl	2	**25.6**	57.1	**7.3**	6.2	**0.3**	0.2	**0.4**	0.3
$C_6H_7O_2^+$	111.044	O-containing	2	**24.9**	53.3	**9.1**	8.7	**0.2**	0.1	**0.3**	0.2
$C_6H_{11}O_2^+$	115.075	Carbonyl	2	**24.1**	42.2	**8.7**	8.7	**0.5**	0.2	**0.8**	0.4
$C_2H_6NO^+$	60.044	N-containing	2	**22.6**	39.3	**9.1**	16.3	**0.3**	0.1	**0.5**	0.4
$C_{10}H_{17}^+$	137.133	Non-arom HC	2.44	**22.4**	41.2	**4**	2.6	**0.5**	0.4	**0.2**	0.2
$C_{12}H_{21}^+$	165.164	Non-arom HC	2	**22.4**	41.2	**3.9**	2.8	**0.7**	0.6	**0.4**	0.2
$C_{12}H_{13}^+$	157.101	Aromatic	2	**22.3**	44.7	**6.1**	6.2	**0.4**	0.2	**0.5**	0.4
$C_7H_9O^+$	109.065	Alcohol	2.3	**22**	50.7	**5.9**	4	**0.3**	0.2	**0.4**	0.4
$C_5H_5O_3^+$	113.023	Carbonyl	2	**22**	31.8	**13.3**	19	**0.4**	0.1	**0.8**	0.4
$C_8H_5O_3^+$	149.023	O-containing	2	**21.9**	41.7	**16.8**	22.8	**0.9**	0.9	**2.1**	2
$C_9H_9^+$	117.070	Aromatic	2.43	**21.6**	47.4	**3.5**	2.1	**0.1**	0	**0.1**	0
$C_8H_7O^+$	119.049	O-containing	2	**21.1**	40.8	**6.1**	4.2	**0.1**	0.1	**0.1**	0.1
$C_9H_9O^+$	133.065	O-containing	2	**20.6**	46.1	**5.4**	3.9	**0.2**	0.1	**0.2**	0.1
$C_8H_{13}O^+$	125.096	O-containing	2	**18.4**	38.9	**4.2**	3.5	**0.1**	0.1	**0.2**	0.1
$C_9H_{19}O^+$	143.143	Carbonyl	2	**18.4**	37.4	**5.4**	5.2	**0.3**	0.2	**0.5**	0.3
$C_{11}H_{13}^+$	145.101	Aromatic	2	**18.4**	37	**2.9**	2.2	**0.2**	0.1	**0.1**	0.1
$C_8H_{15}O^+$	127.112	O-containing	2	**18**	36.2	**4**	3.3	**0.2**	0.1	**0.3**	0.1
$C_{10}H_{19}^+$	139.148	Non-arom HC	2	**18**	34.6	**2.9**	2.2	**0.5**	0.5	**0.2**	0.1
CH_3N^+	29.026	N-containing	2	**17.8**	20.3	**17.1**	21.2	**1.3**	0.1	**1.6**	1.5
$C_7H_{15}O^+$	115.112	Carbonyl	2	**17.7**	31.8	**5.9**	4.9	**0.6**	0.4	**0.8**	0.4
$C_2H_4^+$	28.031	Non-arom HC	2	**16.9**	14	**11.8**	9.6	**0.1**	0	**0.1**	0.1
$C_{13}H_{19}^+$	175.148	Aromatic	2	**16.9**	33.1	**3.5**	3	**0.4**	0.3	**0.3**	0.3
$C_8H_{11}N^+$	121.089	N-containing	2	**16.6**	21.6	**4.9**	6.4	**0.2**	0.1	**0.3**	0.2

$C_6H_9O_2^+$	113.060	Carbonyl	2	**16.6**	31.6	**5.8**	5.6	**0.2**	0.1	**0.4**	0.2
$C_4H_{11}S^+$	91.058	S-containing	2	**16**	33.2	**6.3**	4.5	**0.8**	0.5	**0.7**	0.6
$C_{13}H_{23}^+$	179.179	Non-arom HC	2	**16**	29.1	**3**	2.5	**0.4**	0.3	**0.2**	0.1
$C_5H_5O^+$	81.034	O-containing	2	**15.1**	30.1	**4.2**	3	**0.1**	0	**0.2**	0.1
$C_8H_9O_2^+$	137.060	O-containing	2	**15.1**	36.5	**4**	2.8	**0.1**	0	**0.2**	0.1
$C_8H_{17}O^+$	129.127	Carbonyl	2	**15**	28.7	**4.7**	3.9	**0.4**	0.2	**0.5**	0.2
$C_3H_6^+$	42.046	Non-arom HC	1.62	**14.9**	17.7	**4.4**	2.8	**0.1**	0	**0.1**	0.1
$C_9H_{17}O^+$	141.127	Carbonyl	2	**14.2**	29.5	**3**	2.6	**0.1**	0.1	**0.1**	0.1
$C_3H_5N^+/C_2H_3N_2^+$	55.039	N-containing	2	**13.9**	42.2	**4.7**	3.9	**1.6**	0.8	**1.5**	1
$C_4H_5^+$	53.039	Carbonyl	2	**13.7**	23.7	**3.9**	2.8	**0**	0	**0**	0
$C_9H_{15}O^+$	139.112	Carbonyl	2	**13.5**	28.2	**2.9**	2.4	**0.1**	0.1	**0.2**	0.1
$C_7H_5O^+$	105.034	O-containing	2	**13.4**	22.1	**4.8**	4.4	**0.1**	0.1	**0.2**	0.2
$C_6H_{13}O^+$	101.096	Carbonyl	3.35	**13.2**	22.5	**5.2**	4.1	**0.6**	0.4	**0.7**	0.3
$C_4H_8^+$	56.062	Non-arom HC	1.8	**13.1**	14.3	**4.4**	2.3	**1**	0.8	**0.6**	0.8
$C_7H_7^+$	91.050	Aromatic	2	**12.9**	22	**4.4**	3.8	**0.6**	0.4	**0.6**	0.5
$C_{10}H_{21}O^+$	157.159	O-containing	2	**12.9**	28.1	**2.8**	2.8	**0.1**	0.1	**0.2**	0.1
$C_2H_4NO_2^+$	74.024	N-containing	2	**12.9**	20.1	**6.5**	9.3	**0.5**	0.1	**0.8**	0.4
$C_7H_{13}O_2^+$	129.091	Acid	2	**12.7**	23.1	**4.3**	4.4	**0.2**	0.1	**0.4**	0.3

Table S3. Calibration gases and their abundance in the gas bottle.

Gas	Formula	*m/z* (protonated)	Mixing ratio (ppbv)
Methanol	CH_4O	33.034	100.3
Acetaldehyde	C_2H_4O	45.034	100.3
Acetone	C_3H_6O	59.049	100.0
Isoprene	C_5H_8	69.070	99.3
Methacrolein	C_4H_6O	71.049	100.3
3-Pentanone	$C_5H_{10}O$	87.080	100.0
Toluene	C_7H_8	93.070	100.3
p-Xylene	C_8H_{10}	107.086	100.2
α-Pinene	$C_{10}H_{16}$	137.132	99.9
1,3,5-Trimethylbenzene	C_9H_{12}	121.101	99.9
1,2,4-Trichlorobenzene	$C_6H_3Cl_3$	180.937	100.0

Table S4. Thrust levels and average fuel consumption per engine at different operating modes.

Operating Mode	Thrust Setting (%)	Fuel Consumed (kg/sec)	EI (g/kg fuel)	Emission/LTO (kg/LTO)
Take-off	100	0.946	0.13	0.005
Climb	85	0.792	0.05	0.005
Approach	30	0.29	0.13	0.01
Taxi-Idle	6-7 / 3-5	0.114 / 0.09	2.9 / 7.8	0.52 / 1.22
	Total NMOG per LTO for Twinjet (idling 3-5%):			**2.23**
	Total NMOG per LTO by single-engine use at idle 3-5%:			**1.26**
	Total NMOG per LTO by single-engine use at idle 6-7%:			**0.56**

Thrust setting (% of the take-off thrust), average fuel consumption at each thrust setting and NMOG EI measured were measured during experiments. To estimate NMOG emissions per LTO cycle, ICAO-suggested durations[2] of the operating modes were used.

Table S5. Annual NMOG emissions by aircraft in 2010 in Zurich Airport.

Operation Mode	Thrust setting (%)	Annual fuel consumed (tons)	NMOG EI (g/kg fuel)	Annual NMOG emission (tons)
Take-off	100	10321	0.13	1.34
Climb	85	18349	0.05	0.92
Approach	30	20951	0.13	2.72
Taxi-Idle (I)	6-7	29717	2.9	86.18
Taxi-Idle (II)	3-5	23461	7.8	182.99
	Annual NMOG based on Taxi-idle 6-7% (I)			**91.16**
	Annual NMOG based on Taxi-idle 3-5% (II)			**187.98**

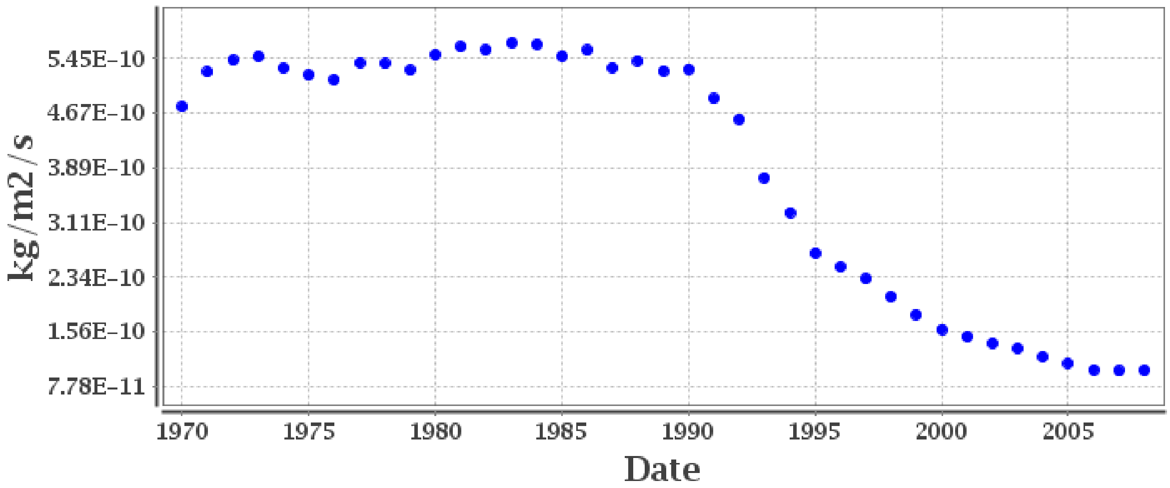

Figure S7. Annual NMVOC emission from road transportation per m^2 per second is shown for the years from 1970 to 2009. The annual NMVOC emission from road vehicles was ~1.1E-10 kg/m^2/sec in Zurich (@ 47.25^O North, 8.75^O East) in 2009. Multiplying this EI of 1.1E-10 kg/m2/sec by the Zurich surface area of ~90km^2, average annual NMVOC emission by road transportation is calculated as 312 tons/year according to EDGARv4.2 emission inventory.[3]

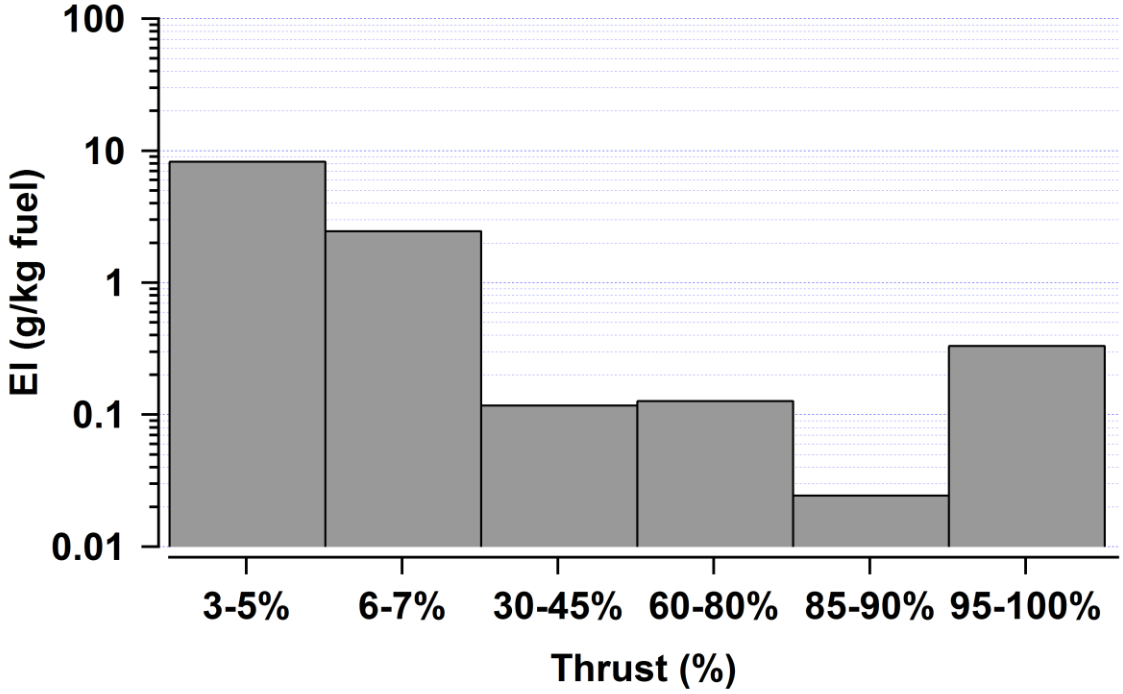

Figure S8. Mean total OG emission index (EI') as a function of thrust.

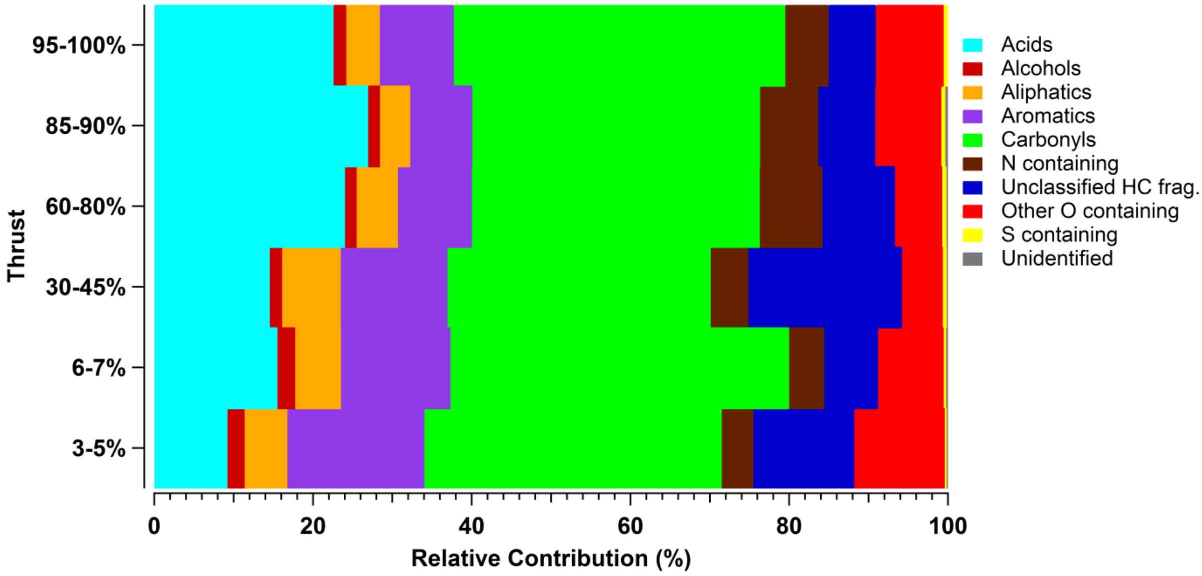

Figure S9. Top panel (based on group EI's) shows the OG group fractions (mass) for different thrust bins.

These newly determined EIs (denoted EI') for Figs.S8 and S9 are calculated as follows:

$$EI'_{engine\ i} = EI_{engine\ i} \times \frac{Idle\ EI_{engine\ i}}{Average\ Idle\ EI}$$

References

(1) Cappellin, L.; Karl, T.; Probst, M.; Ismailova, O.; Winkler, P. M.; Soukoulis, C.; Aprea, E.; Märk, T. D.; Gasperi, F.; Biasioli, F. On quantitative determination of volatile organic compound concentrations using proton transfer reaction time-of-flight mass spectrometry. *Environ. Sci. Technol.* ***2012,*** *46*, 2283–2290.

(2) *Airport Air Quality Manual*, First Edition; International Civil Aviation Organization; Doc 9889; Appendix 1 to Chapter 3, Montreal 2011.

(3) Emissions of atmospheric compounds & compilation of ancillary data, available on (02.02.2016): http://eccad.sedoo.fr/eccad_extract_interface/JSF/page_login.jsf