Supplementary Material to Contributions to OH reactivity from unexplored volatile organic compounds measured by PTR-ToF-MS– A case study in a suburban forest of the Seoul Metropolitan Area during KORUS-AQ 2016

Methods

Limit of Detection Calculation

The limit of detection range of the PTR-ToF-MS during KORUS-AQ at 3σ over 30 seconds is in the range of tens of ppt. The limit of detection was assessed at a signal to noise ratio of 3.[1] The limit of detection of the calibration standards are tabulated below (Table S1).

OH Reactivity Estimations

Category I mass peaks masses for which a molecular formula had been assigned by the PTRwid software. We used the National Institute of Standards and Technology (NIST) gas kinetics database to find reaction rate coefficients for the individual peaks. For compounds without available gas kinetic information, we used the structure-reactivity relationship described in Kwok and colleagues[2] to obtain a rate coefficient and estimate the OH reactivity. This empirical estimation method uses four gas phase reaction pathways for OH and VOCs to estimate a reaction rate coefficient:

$$k_{total} = k_{(H\ atom\ abstraction)} + k_{(OH\ addition)} + k_{(OH\ addition\ to\ aromatic\ rings)} + k_{(OH\ interactions)} \quad \text{Eq. S1}$$

Equation S1 shows the calculation for the total rate constant (k_{total}) by adding four processes: (1) The abstraction of H atoms from C-H and O-H bonds, (2) the addition of OH to carbon double or triple bonds, (3) the addition of OH to aromatic rings, and (4) OH interactions with N, P, or S containing groups. The authors of Kwok and colleagues[2] demonstrated that this estimation method predicted 90% of 485 alkanes and alkenes within a factor of 2 of the experimental values. Category I included 18 peaks with reaction rate coefficients obtained from the NIST database and 63 calculated using the structure-reactivity relationship estimate.

Tables and Figures

Table S1. Limit of detection of select calibration standards.

Calibration Standard	**Limit of Detection (ppt)**
Isoprene	11
Benzene	6.8
Toluene	48
Xylenes	16
Monoterpenes	3.7

Table S2. PTR-ToF-MS NIST and structure-reactivity estimated compounds from Category I. The reaction rate coefficients correspond to a temperature of 298K.

Possible ID	**m/z**	**Molecular Formula**	**Estimated *k* (cm^3 $molecules^{-1}$ s^{-1})**	**NIST *k* (cm^3 $molecules^{-1}$ s^{-1})**
Formic acid	47.013	$CH_2O_2H^+$		4.50×10^{-13}
Methyl peroxide	49.027	$CH_4O_2H^+$		7.44×10^{-12}
	53.038	$C_4H_4H^+$		3.27×10^{-11}
Acetic Acid + Methyl Formate	61.028	$C_2H_4O_2H^+$		7.66×10^{-13} 1.83×10^{-13}

	65.022	$CH_4O_3H^+$	1.80×10^{-11}	
Cyclopentadiene	67.054	$C_5H_6H^+$		9.22×10^{-11}
	71.085	$C_5H_{10}H^+$	8.72×10^{-11}	
	72.089	$^{13}CC_4H_{10}H^+$	8.72×10^{-11}	
Methylglyoxal	73.029	$C_3H_4O_2H+$		1.26×10^{-11}
	75.043	$C_3H_6O_2H+$	1.20×10^{-12}	
	76.046	$^{13}CC_2H_6O_2H^+$	1.20×10^{-12}	
1,3-Propanedio propylene glycol	77.058	$C_3H_8O_2H^+$	8.95×10^{-12}	
	83.049	$C_5H_6OH^+$	1.11×10^{-10}	
	83.086	$C_6H_{10}H^+$	1.19×10^{-10}	
	84.086	$^{13}CC_5H_{10}H^+$	1.19×10^{-10}	
	85.028	$C_4H_4O_2H^+$	3.84×10^{-11}	
	85.065	$C_5H_8OH^+$	7.19×10^{-11}	
	85.101	$C_6H_{12}H^+$	9.40×10^{-11}	
	87.044	$C_4H_6O_2H^+$	2.49×10^{-11}	
	87.080	$C_5H_{10}OH^+$	2.48×10^{-11}	
Propene, 3-nitro-	88.042	$C_3H5O2NH^+$		1.22×10^{-11}
	89.060	$C_4H_8O_2H+$	1.14×10^{-11}	
	90.063	$^{13}CC_3H_8O_2H^+$	1.14×10^{-11}	
Methyl carbonate	91.040	$C_3H_6O_3H+$		3.20×10^{-13}
	95.085	$C_7H_{10}H^+$	1.21×10^{-10}	
	97.064	$C_6H_8OH^+$		2.00×10^{-10}
Cycloheptene	97.101	$C_7H_{12}H^+$		7.00×10^{-11}
Maleic anhydride	99.007	$C_4H_2O_3H^+$		
	99.044	$C_5H_6O_2H^+$	1.13×10^{-10}	
Trans-2-hexenal cis-3-hexenal	99.080	$C_6H_{10}OH^+$	5.30×10^{-11}	
Furandiones	101.023	$C_4H_4O_3H^+$	1×10^{-10}	
C_5 hydroxycarbonyl, 1,5-Pentanedial, Acetylacetone	101.06	$C_5H_8O_2H^+$	8.26×10^{-11}	
	101.096	$C_6H_{12}OH^+$	1.15×10^{-10}	
C_5 hydroxycarbonyl, 1,5-Pentanedial, Acetylacetone isotope	102.061	$^{13}CC_4H_8O_2H^+$	8.26×10^{-11}	
	102.098	$^{13}CC_5H_{12}OH^+$	1.15×10^{-10}	

	103.039	$C_4H_6O_3H^+$	2.73×10^{-12}	
	103.075	$C_5H_{10}O_2H^+$	1.13×10^{-11}	
	105.034	$C_7H_4OH^+$	1.00×10^{-10}	
Styrene	105.069	$C_8H_8H^+$		6.08×10^{-11}
	111.044	$C_6H_6O_2H^+$	2.20×10^{-10}	
	111.08	$C_7H_{10}OH^+$	2.20×10^{-10}	
	111.117	$C_8H_{14}H^+$	3.00×10^{-11}	
	113.023	$C_5H_4O_3H^+$	1.00×10^{-10}	
	113.095	$C_7H_{12}OH^+$	1.10×10^{-10}	
	115.038	$C_5H_6O_3H^+$	1.00×10^{-10}	
2,5-hexanedione	115.075	$C_6H_{10}O_2H^+$		6.74×10^{-12}
	115.11	$C_7H_{14}OH^+$	2.60×10^{-12}	
	117.054	$C_5H_8O_3H^+$	2.98×10^{-10}	
	117.09	$C_6H_{12}O_2H^+$	3.00×10^{-12}	
Benzofuran, 2,3-dihydro	121.065			3.65×10^{-11}
Peroxyacetyl nitrate	122.006	$C_2H_3O_5NH^+$		3×10^{-14}
	123.044	$C_7H_6O_2H^+$	1.00×10^{-10}	
	123.116	$C_9H_{14}H^+$	6.16×10^{-12}	
	125.095	$C_8H_{12}OH^+$	2.39×10^{-10}	
	125.132	$C_9H_{16}H^+$	6.16×10^{-12}	
	127.037	$C_6H_6O_3H^+$	1.00×10^{-10}	
	127.075	$C_7H_{10}O_2H^+$	1.00×10^{-11}	
6-methyl-5-hepten-2-one	127.111	$C_8H_{14}OH^+$		4.29×10^{-12}
	129.056	$C_6H_8O_3H^+$	1.00×10^{-10}	
	129.126	$C_8H_{16}OH^+$	2.82×10^{-12}	
Pentyl acetate	131.105	$C_7H_{14}O_2H^+$		7.59×10^{-12}
	133.098	$C_{10}H_{12}H^+$	5.33×10^{-11}	
p-cymene	135.117	$C_{10}H_{14}H^+$		1.57×10^{-11}
	139.112	$C_9H_{14}OH^+$	6.16×10^{-12}	
	141.09	$C_8H_{12}O_2H^+$	3.69×10^{-10}	
	141.126	$C_9H_{16}OH^+$	2.32×10^{-10}	
	143.105	$C_8H_{14}O_2H^+$	1.20×10^{-10}	
	143.142	$C_9H_{18}OH^+$	3.08×10^{-12}	
Butyl butanoate	145.122	$C_8H_{16}O_2H^+$	9.33×10^{-12}	
	149.025	$C_8H_4O_3H^+$	1.00×10^{-10}	
	151.113	$C_{10}H_{14}OH^+$	5.33×10^{-11}	
	153.055	$C_8H_8O_3H^+$	1×10^{-10}	
	153.128	$C_{10}H_{16}OH^+$	5.33×10^{-11}	

	154.051	$C_7H_7O_3NH^+$	2×10^{-10}	
	157.12	$C_9H_{16}O_2H^+$	1.90×10^{-10}	
	157.157	$C_{10}H_{20}OH^+$	1.24×10^{-10}	
	159.137	$C_9H_{18}O_2H^+$	1.93×10^{-11}	
	173.152	$C_{10}H_{20}O_2H^+$	1.94×10^{-10}	
	179.179	$C_{13}H_{22}H+$	1.53×10^{-10}	
	183.174	$C_{12}H_{22}OH+$	2.32×10^{-10}	
	199.171	$C_{12}H_{22}O_2H+$	3.05×10^{-10}	

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42 Table S3. PTR-ToF-MS compounds in Category II

Category II					
m/z	**Correlation**	**m/z**	**Correlation**	**m/z**	**Correlation**
42.009	Benzene	92.062	Toluene	139.032	MVK + MACR
43.017	Benzene	93.036	Toluene	139.074	MVK + MACR
45.992	MVK + MACR	94.99	MVK + MACR	141.053	MVK + MACR
47.022	MVK + MACR	98.027	MVK + MACR	143.071	MVK + MACR
62.03	Benzene	102.023	MVK + MACR	147.043	MVK + MACR
63.025	Benzene	113.059	MVK + MACR	147.106	Toluene
63.041	Benzene	114.055	MVK + MACR	149.132	Toluene
68.06	Isoprene	116.036	MVK + MACR	154.131	MT
70.04	Benzene	116.078	MVK + MACR	157.084	MVK + MACR
74.025	MVK + MACR	118.062	Benzene	163.038	MVK + MACR
74.063	Toluene	125.059	MVK + MACR	185.022	MVK + MACR
82.945	Benzene	129.018	MVK + MACR	199.037	MVK + MACR
82.987	Toluene	131.033	MVK + MACR	225.016	MVK + MACR
83.012	MVK + MACR	135.042	MVK + MACR		
84.942	Benzene	137.059	MVK + MACR		

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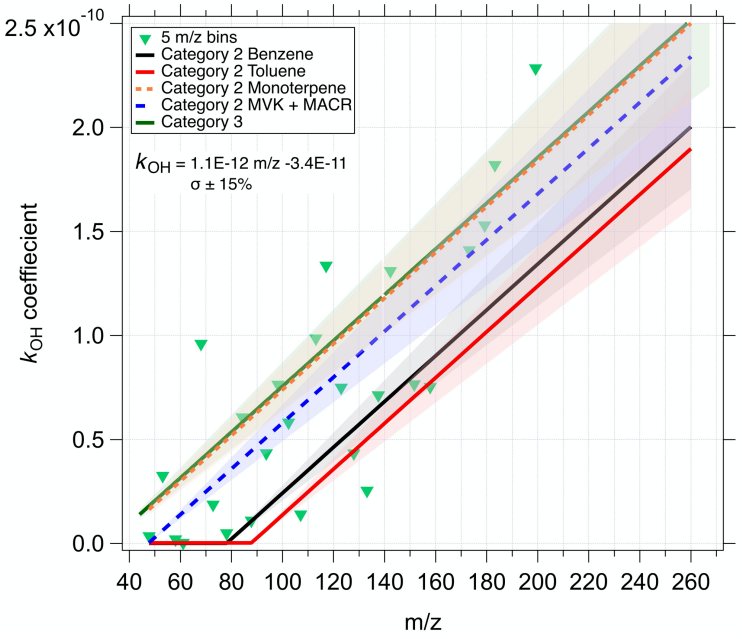
47 Table S4. PTR-ToF-MS compounds in Category III

m/z	**m/z**	**m/z**	**m/z**	**m/z**
44.000	88.077	123.945	155.106	197.893
44.014	88.953	124.948	157.032	198.113
44.997	89.951	125.022	159.023	198.898
48.007	90.019	125.96	160.914	201.172
48.983	90.948	126.966	161.001	203.180
49.014	91.948	127.944	161.058	204.183
49.999	93.956	127.96	161.131	206.199
51.007	94.951	128.075	163	207.011
51.043	95.014	128.965	163.146	209.019
51.940	95.048	129.089	164.016	207.208
52.940	95.951	129.913	164.907	211.008
53.001	96.959	130.054	165.004	212.995
53.939	96.995	130.921	165.09	213.889
55.037	97.949	130.991	165.163	214.894
55.934	98.069	131.069	167.06	215.901
56.934	98.104	131.91	167.106	217.192
57.041	98.953	132.026	168.065	219.208
57.935	99.948	132.918	168.985	223.063
59.930	99.993	133.012	169.081	225.885
60.051	100.041	134.106	169.122	226.008
59.966	100.081	134.914	170.046	227.012
61.928	100.939	134.951	171.025	227.234
62.929	101.941	135.08	171.065	233.225
63.006	102.947	136.034	171.099	235.240
63.927	103.953	136.121	171.137	239.012
63.978	104.049	135.945	173.004	239.238
64.001	104.953	136.953	173.035	241.021
64.018	105.935	137.959	174.034	242.038
64.928	106.962	138.959	175.018	243.013
65.059	107.951	139.019	175.147	245.002
66.016	108.958	139.967	176.007	247.015
68.994	109.956	140.034	177.015	248.948
69.996	110.959	140.114	177.163	250.95
73.945	111.953	141.021	178.895	252.953
75.946	112.043	141.954	179.026	259.013

77.021	112.12	143.033	179.895	262.989
77.941	112.953	143.967	180.89	267.268
78.046	114.016	144.071	180.990	
79.939	115.007	144.108	183.013	
80.990	116.906	144.145	183.100	
81.035	116.948	145.028	185.117	
82.038	117.937	146.977	187.019	
83.930	117.954	147.994	191.179	
84.051	118.903	148.039	189.018	
84.964	118.943	148.974	191.023	
85.944	119.95	149.990	193.015	
86.029	120.9	152.021	193.195	
86.066	120.955	152.118	195.005	
86.104	121.957	155.024	196.008	
87.925	122.963	155.068	197.018	

Figure S1. Correlation plot between OH reaction rate coefficients and molecular mass of identified compounds. The green triangles represent the averaged 5 m/z bins of identified compounds plotted against their averaged OH rate coefficients. The dark green line is the best-fit line of the green triangles with a y-intercept adjusted to the m/z of acetaldehyde. The Category II regressions have a y-intercept adjusted to the m/z of either benzene, toluene, monoterpene, or MVK + MACR. The shaded areas represent 1σ sigma uncertainty.



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79 Figure S2. Mixing ratios of select compounds measured at TRF a) NO and NO_2, b) CO and SO_2,

80 c) isoprene and MVK+MACR, and d) benzene and toluene.

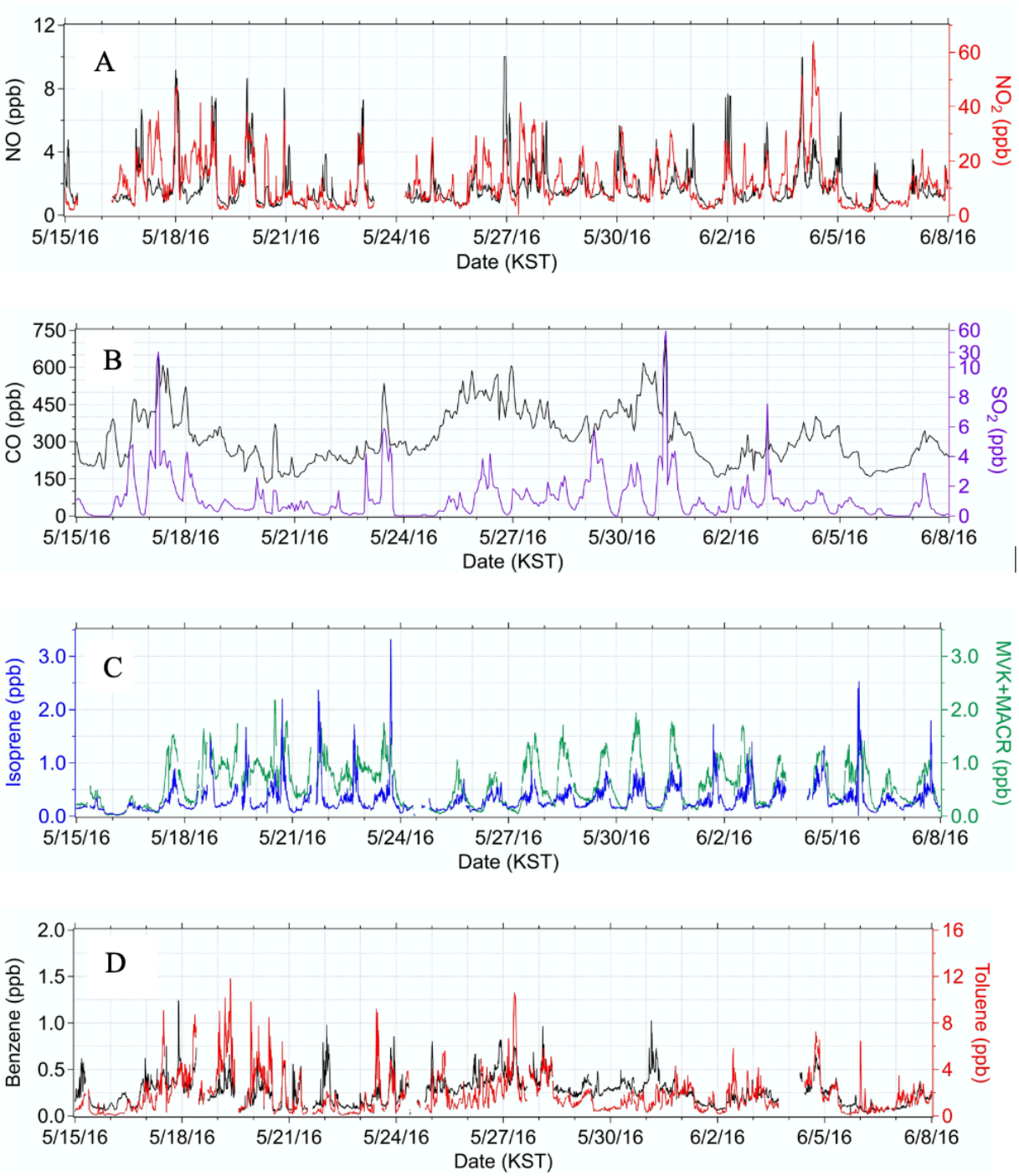

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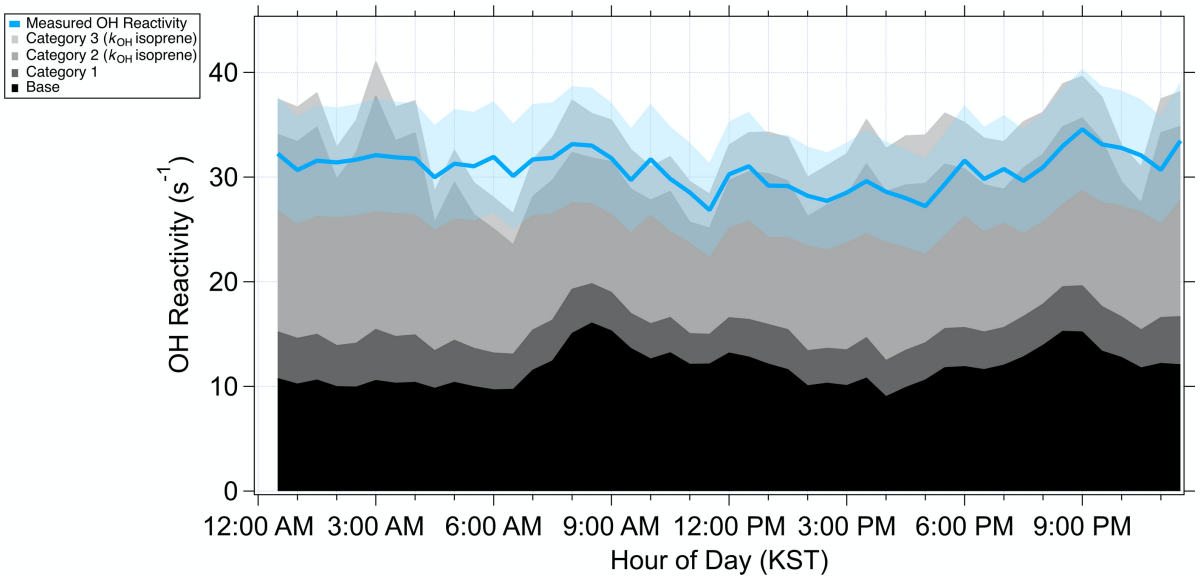
Figure S3. The diel average of OH reactivity from 15 May – 7 June 2016. The OH reactivity was calculated from the base compounds (black) and Categories I – III (shades of grey). The blue line represents the measured OH reactivity with the shading representing 1σ of uncertainty.



References

1. Koss, A.; Yuan, B.; Warneke, C.; Gilman, J. B.; Lerner, B. M.; Veres, P. R.; Peischl, J.; Eilerman, S.; Wild, R.; Brown, S. S.; Thompson, C. R.; Ryerson, T.; Hanisco, T.; Wolfe, G. M.; Clair, J. M. S.; Thayer, M.; Keutsch, F. N.; Murphy, S.; de Gouw, J., Observations of VOC emissions and photochemical products over US oil- and gas-producing regions using high-resolution H3O+ CIMS (PTR-ToF-MS). *Atmos. Meas. Tech.* **2017,** *10*, (8), 2941-2968.
2. Kwok, E. S. C.; Atkinson, R., Estimation of hydroxyl radical reaction rate constants for gas-phase organic compounds using a structure-reactivity relationship: An update. *Atmospheric Environment* **1995,** *29*, (14), 1685-1695.