Supplemental Material for *Elemental Composition and Oxidation of Chamber Organic Aerosol*

P. S. Chhabra[1], **N. L. Ng**[2], **M. R. Canagaratna**[2], **A. L. Corrigan**[3], **L. M. Russell**[3], **D. R. Worsnop**[2], **R. C. Flagan**[1,4], **and J. H. Seinfeld**[1,4]

[1]Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA
[2]Aerodyne Research, Inc. Billerica, MA
[3]Scripps Institution of Oceanography, University of California, San Diego, CA
[4]Division of Engineering and Applied Science, California Institute of Technology, Pasadena, CA

Correspondence to: J. H. Seinfeld
(seinfeld@caltech.edu)

1 Calculating FTIR O/C and H/C Elemental Ratios

Russell (2003) and Russell et al. (2009) provide standard methods used for quantifying ambient organic mass. This method relies on reference compounds that are appropriate for typical ambient mixtures measured in urban and rural conditions. In this study, we extend this approach to the specific organic mixtures generated in laboratory conditions, namely the smog chamber products of the oxidation of α-pinene and guaiacol.

FTIR absorption is proportional to the bonds present in organic functional groups. In order to relate bonds to atoms (and mass), we use rules to associate each bond with the atoms associated with that bond. Most of the atoms associated with each bond are specific to that bond, and their number of atoms per bond are invariant (in atmospheric aerosol conditions). However, carbon may have from two to four bonds associated with each atom. This results in some variability, which we quantify as ϕ, the number of carbon atoms per organic functional group (i.e. the reciprocal of the number of bonds that are not carbon-carbon). A lower bound of ϕ=0 represents a branched carbon bonded only to other carbon atoms, which are likely at most a small fraction of OM. Typically particle-phase ambient OM contains 1 carbon atom for every 2 non-carbon bonds, i.e. ϕ=0.5 (Russell, 2003). An upper bound of ϕ=1 represents only one non-carbon bond on each carbon atom. Since ϕ=1 means that every carbon atom is either branched or unsaturated, reaching a value this high is unlikely in particle OM. Table 1 summarizes the number of atoms for alcohol, alkane, amine, and organonitrate groups. (ϕ is not applied to acid, carbonyl, alkene, or aromatic groups as these groups always have one carbon atom per functional group.)

To evaluate ϕ for smog chamber products, we consider here two cases that illustrate the range of possible values: (1) the standard ambient case and (2) an precursor-specific case. For the ambient case, the elemental ratios calculated for α-pinene and guaiacol experiments used ϕ=0.5 to represent chamber products similar to ambient OM. Since both alkene and aromatic functional groups were below detection limit for α-pinene and guaiacol photooxidation experiments, contributions from these organic functional groups were excluded from the elemental calculations for the ambient case. As a precursor specific value for ϕ for the smog chamber products, we use the value for ϕ of the precursor molecules. Here ϕ is the ratio of carbon atoms to the number of FTIR-quantifiable groups, namely ϕ=0.63 for α-pinene and ϕ=0.88 for guaiacol. Since both α-pinene and guaiacol are less saturated and more branched than ambient VOC mixtures, for which ϕ=0.5 has been used, the resulting values of ϕ are greater than 0.5 and less than 1.0.

Maria et al. (2003) and Russell et al. (2009) have noted that an important trade-off of the quantification enabled by transmission through a Teflon filter is the overlap of the Teflon C-F absorption (1300-1150 cm^{-1}) with ether (C-O-C) bond absorption (1300-1000 cm^{-1}). Peroxide bonds are likely not observed for similar reasons. As a result, in smog chamber aerosol in which ether and peroxide bonds are likely a significant fraction of the products, it is important to correct for this missing functional group. On average, the guaiacol products identified in this work, produced under both low-$\mathrm{NO_x}$ and high-$\mathrm{NO_x}$ conditions, contain 3 oxygen atoms in ether, peroxide and nitro functional groups per 7-carbon ring structure. Therefore, we add 3/7 to the O/C for guaiacol smog aerosol (for both the ambient and extreme cases) to account for the missing O and C atoms.

Table 1. C, O, and H atom apportionment for each FTIR-measured functional group

X	Alcohol	Alkane	Carbonyl	Amine	Acid	Org. Nitrate	Alkene	Aromatic
C	ϕ	ϕ	1	ϕ	1	ϕ	1	1
O	1	0	1	0	2	3	0	0
H	1	1	0	2*	1	0	1	1

*The H atoms associated with amine groups are omitted for comparison with the AMS.

Table 2. Elemental Ratios determined by FTIR analysis

SOA System	O/C	H/C
	Ambient Case	
α-pinene high-NO_x	0.41	1.82
α-pinene low-NO_x	0.44	1.79
guaiacol high-NO_x 1	0.59	1.74
guaiacol high-NO_x 2	0.65	1.69
guaiacol low-NO_x	0.66	1.72
	Precursor-Specific Case	
α-pinene high-NO_x	0.32	1.46
α-pinene low-NO_x	0.34	1.44
guaiacol high-NO_x 1	0.73	1.08
guaiacol high-NO_x 2	0.76	1.07
guaiacol low-NO_x	0.78	1.08

Table 3. Average ratios of particle phase signals of CO^+ to $\mathrm{CO_2}^+$. Ratios were determined from high-resolution spectra that had adequate separation of the CO^+ and $\mathrm{N_2}^+$ ions, typically from experiments with high organic loadings. The average values found are close to the default value of 1.0 in the AMS High-Resolution Fragmentation Table and in agreement with other studies (Zhang et al., 2005; Takegawa et al., 2007) so this default value was used for all experiments in this study.

SOA Precursor	$\mathrm{CO}^+/\mathrm{CO_2}^+$
glyoxal uptake	5.6[a]
α-pinene[b]	0.9
toluene	1.1
m-xylene	1.3
isoprene	1.3
naphthalene	1.2
phenol	0.9
guaiacol	1.0
syringol	1.1
acrolein	ND[c]
methacrolein	ND[c]
crotonaldehyde	ND[c]

[a] A value of 5.0 was used for $\mathrm{CO}^+/\mathrm{CO_2}^+$ in glyoxal uptake experiments presented in this study.

[b] Includes both ozonolysis and photooxidation experiments.

[c] Not Determined. CO^+ could not be adequately separated from $\mathrm{N_2}^+$ to determine a ratio accurately.

Table 4. Elemental composition of SOA system. Values represent the average ratio for each experiment at the time of maximum O/C.

VOC System	O/C (max)	H/C	N/C	OM/OC	ΔO/C	ΔH/C	$\Delta\overline{\mathrm{OS}_\mathrm{C}}$
glyoxal uptake[a]	1.13	1.54	0.01	2.68	0.13	0.54	0.72
α-pinene + O_3[a]	0.43	1.47	0.00	1.70	0.43	-0.13	0.99
α-pinene + OH	0.41	1.57	0.02	1.70	0.41	-0.03	0.85
low-NO_x	0.40	1.62	0.00	1.67	0.40	0.02	0.78
high-NO_x	0.42	1.51	0.03	1.73	0.42	-0.09	0.93
isoprene + OH[a]	0.61	1.55	0.02	1.96	0.61	-0.05	1.27
low-NO_x	0.59	1.64	0.00	1.92	0.59	0.04	1.14
high-NO_x	0.62	1.46	0.04	2.00	0.62	-0.14	1.38
aromatics + OH[a]	0.68	1.44	0.04	2.07	0.68		
m-xylene, high-NO_x	0.66	1.48	0.08	2.09	0.66	0.23	1.09
m-xylene, low-NO_x	0.60	1.54	0.00	1.93	0.60	0.29	0.91
toluene, high-NO_x	0.72	1.38	0.07	2.15	0.72	0.24	1.20
toluene, low-NO_x	0.74	1.39	0.00	2.10	0.74	0.25	1.23
naphthalene + OH[a]	0.62	0.89	0.02	1.93	0.62	0.09	1.15
low-NO_x	0.66	0.88	0.00	1.96	0.66	0.08	1.24
high-NO_x	0.57	0.90	0.04	1.89	0.57	0.10	1.04
phenol + OH	0.90	1.11	0.03	2.32	0.73	0.11	1.36
low-NO_x	0.88	1.10	0.00	2.26	0.71	0.10	1.33
high-NO_x	0.92	1.12	0.05	2.38	0.75	0.12	1.39
guaiacol + OH	0.92	1.28	0.03	2.37	0.63	0.14	1.13
low-NO_x	0.89	1.26	0.00	2.30	0.60	0.12	1.09
high-NO_x	0.94	1.30	0.06	2.43	0.65	0.16	1.15
syringol + OH	0.95	1.47	0.02	2.41	0.58	0.22	0.93
low-NO_x	0.97	1.41	0.00	2.41	0.60	0.16	1.03
high-NO_x	0.93	1.52	0.03	2.41	0.56	0.27	0.84
acrolein + OH	0.79	1.31	0.03	2.20	0.46	-0.02	0.94
methacrolein + OH	0.54	1.53	0.02	1.87	0.29	0.03	0.55
crotonaldehyde + OH	0.56	1.45	0.01	1.88	0.31	-0.05	0.67

[a] Values first reported in Chhabra et al. (2010).

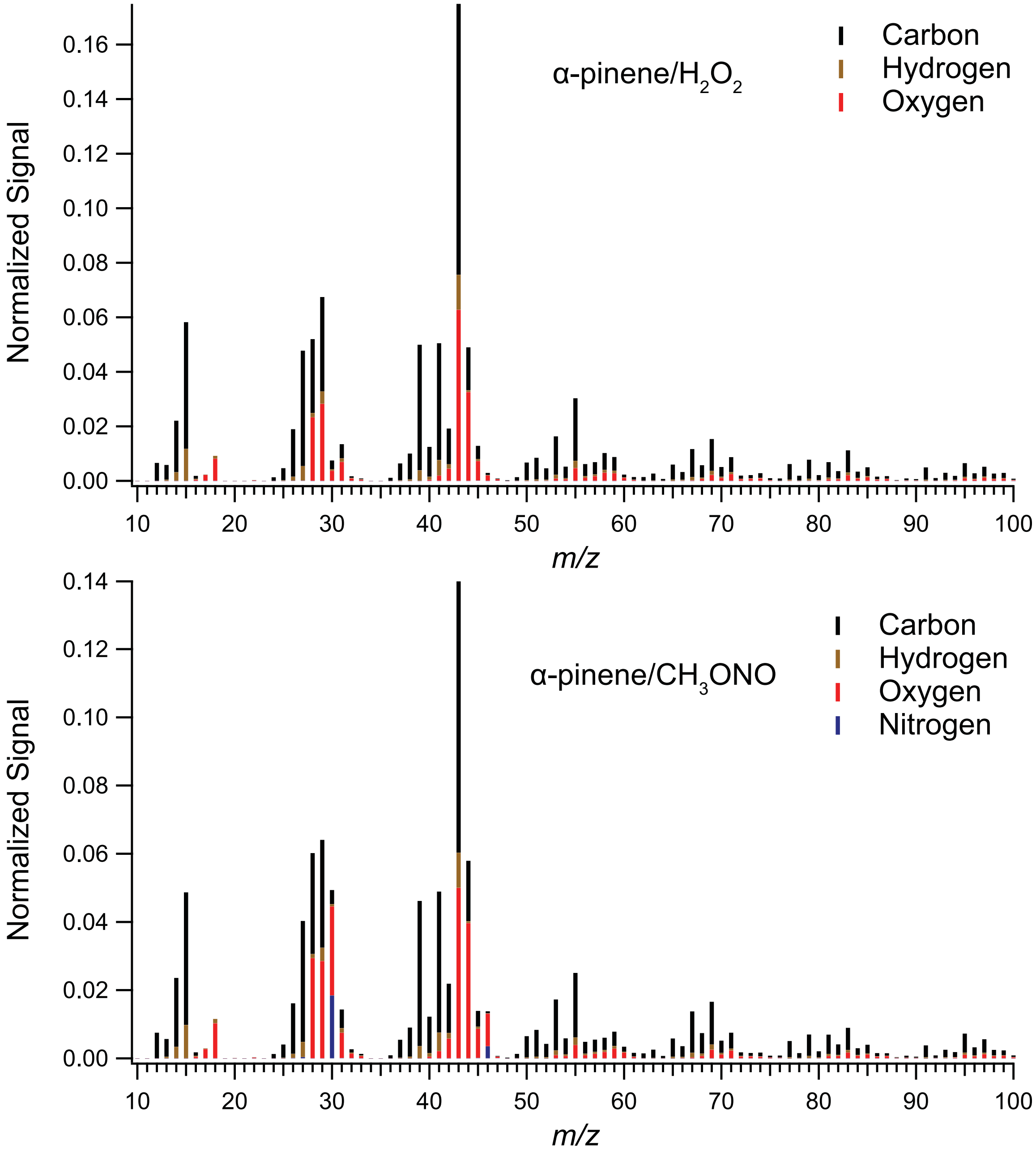

Fig. 1. Elemental spectra of α-pinene photooxidation SOA formed under high- and low-NO_x conditions.

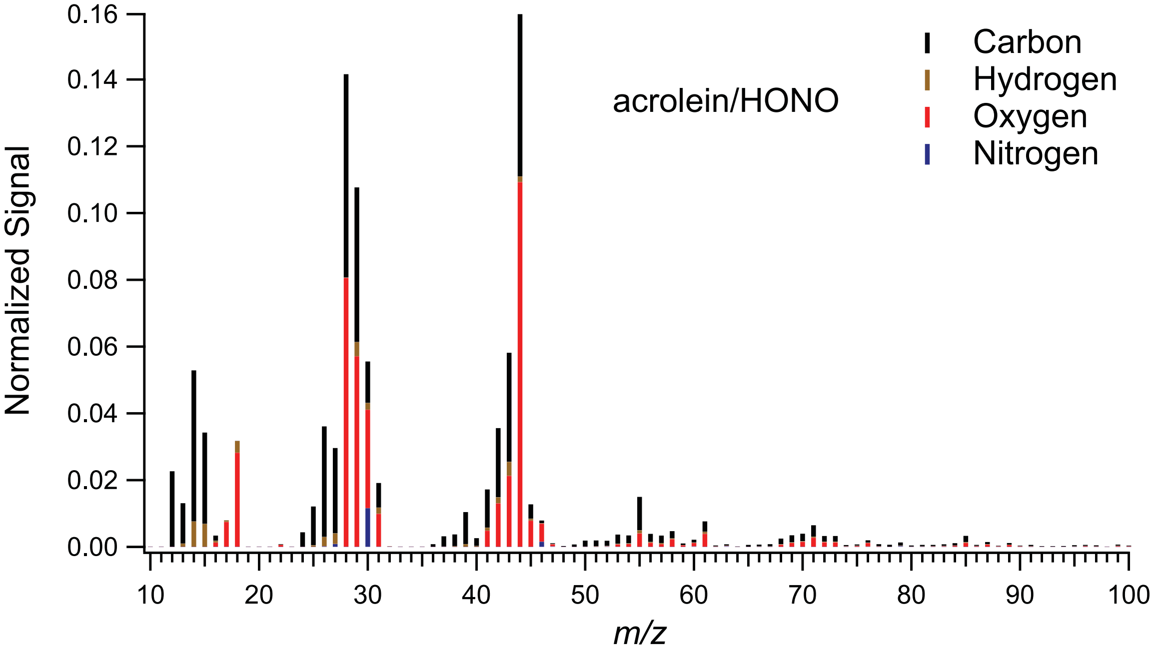

Fig. 2. Elemental spectra of acrolein photooxidation SOA.

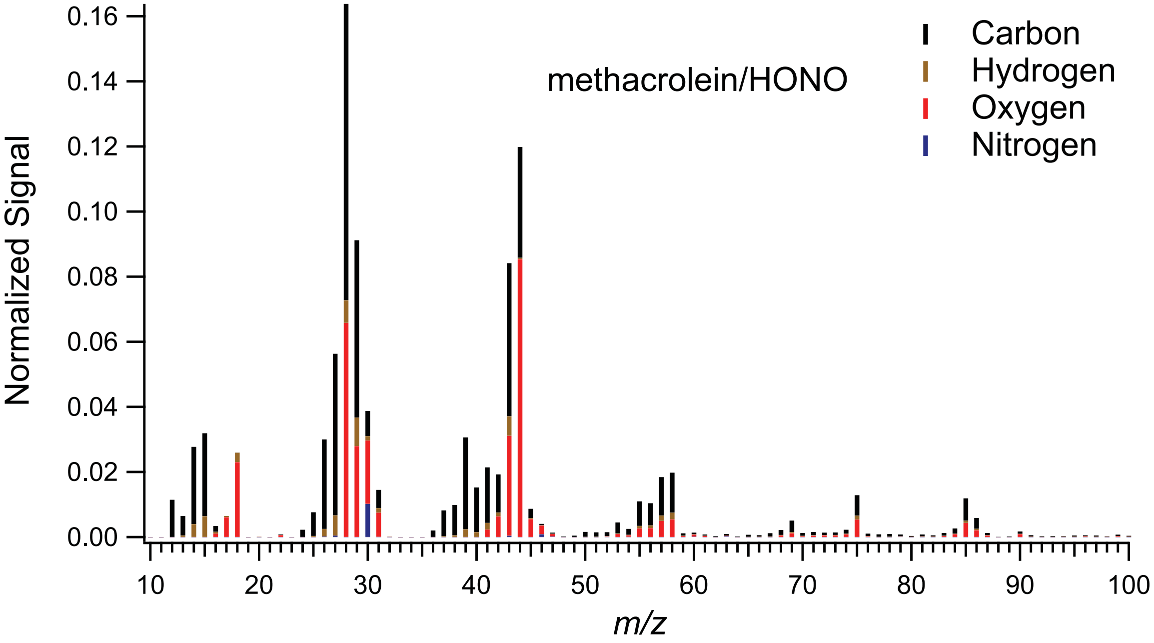

Fig. 3. Elemental spectra of methacrolein photooxidation SOA.

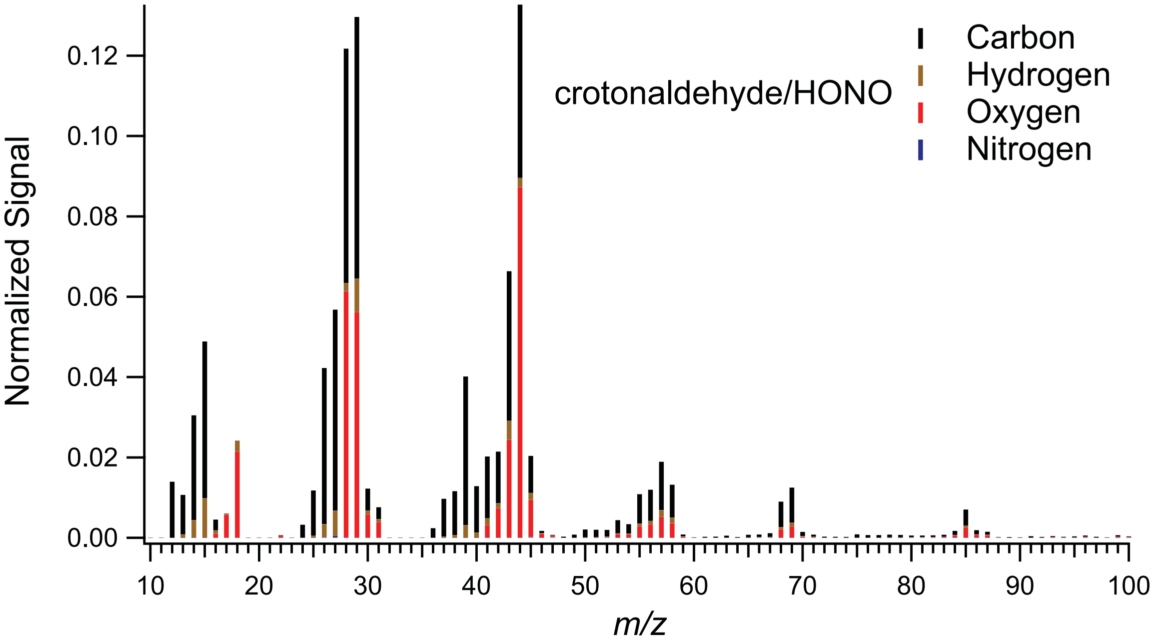

Fig. 4. Elemental spectra of crotonaldehyde photooxidation SOA.

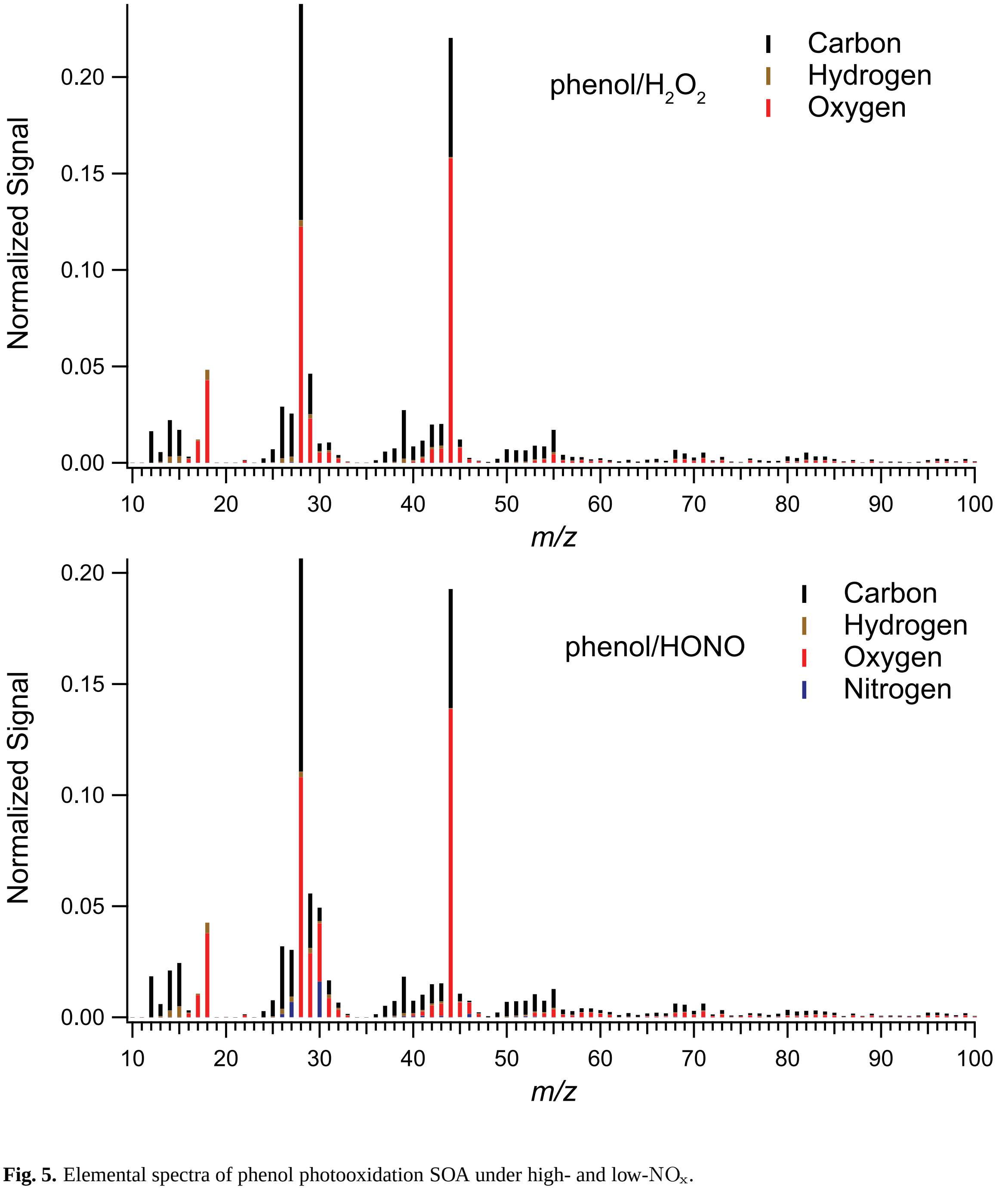

Fig. 5. Elemental spectra of phenol photooxidation SOA under high- and low-NO_x.

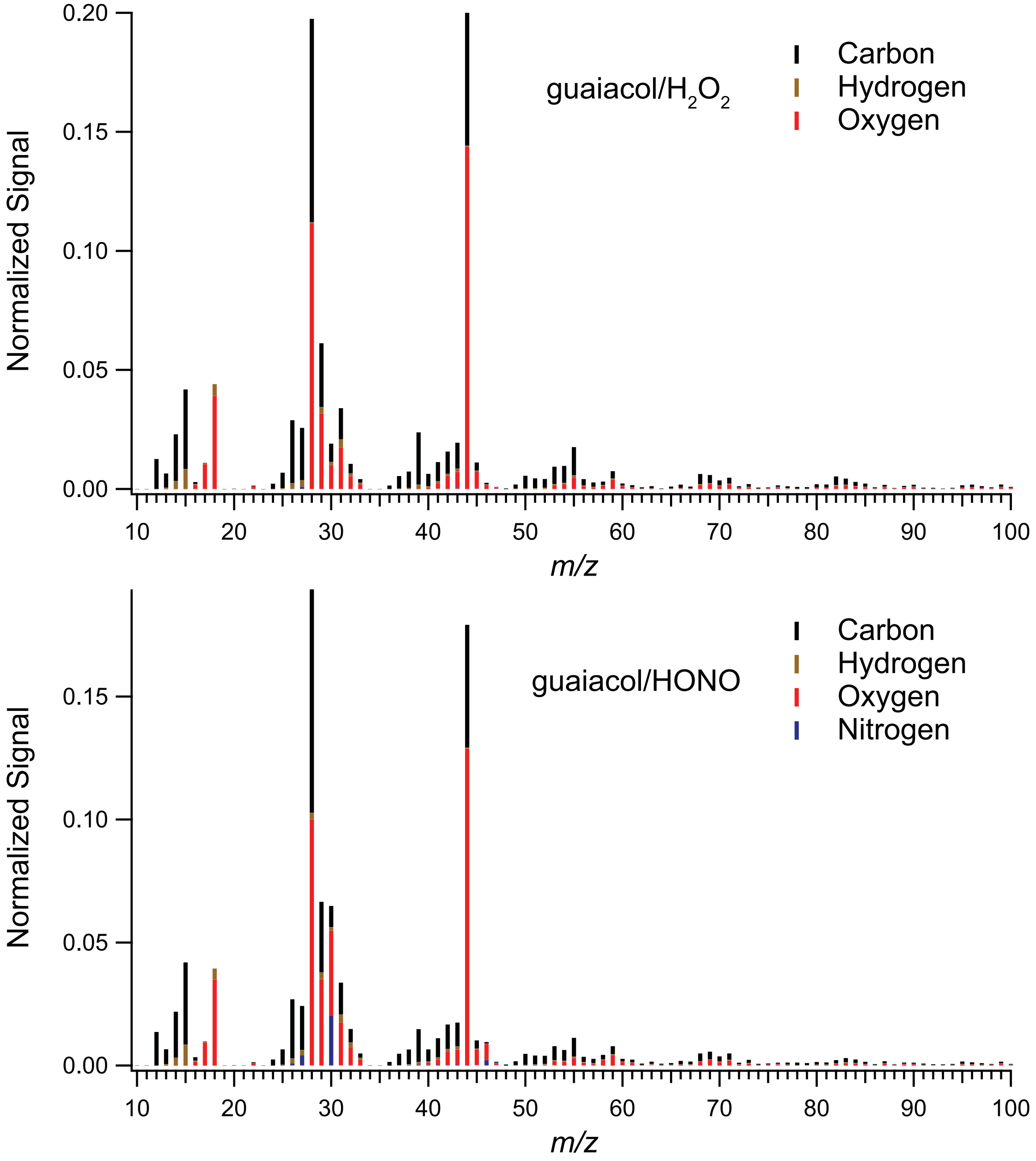

Fig. 6. Elemental spectra of guaiacol photooxidation SOA under high- and low-NO_x.

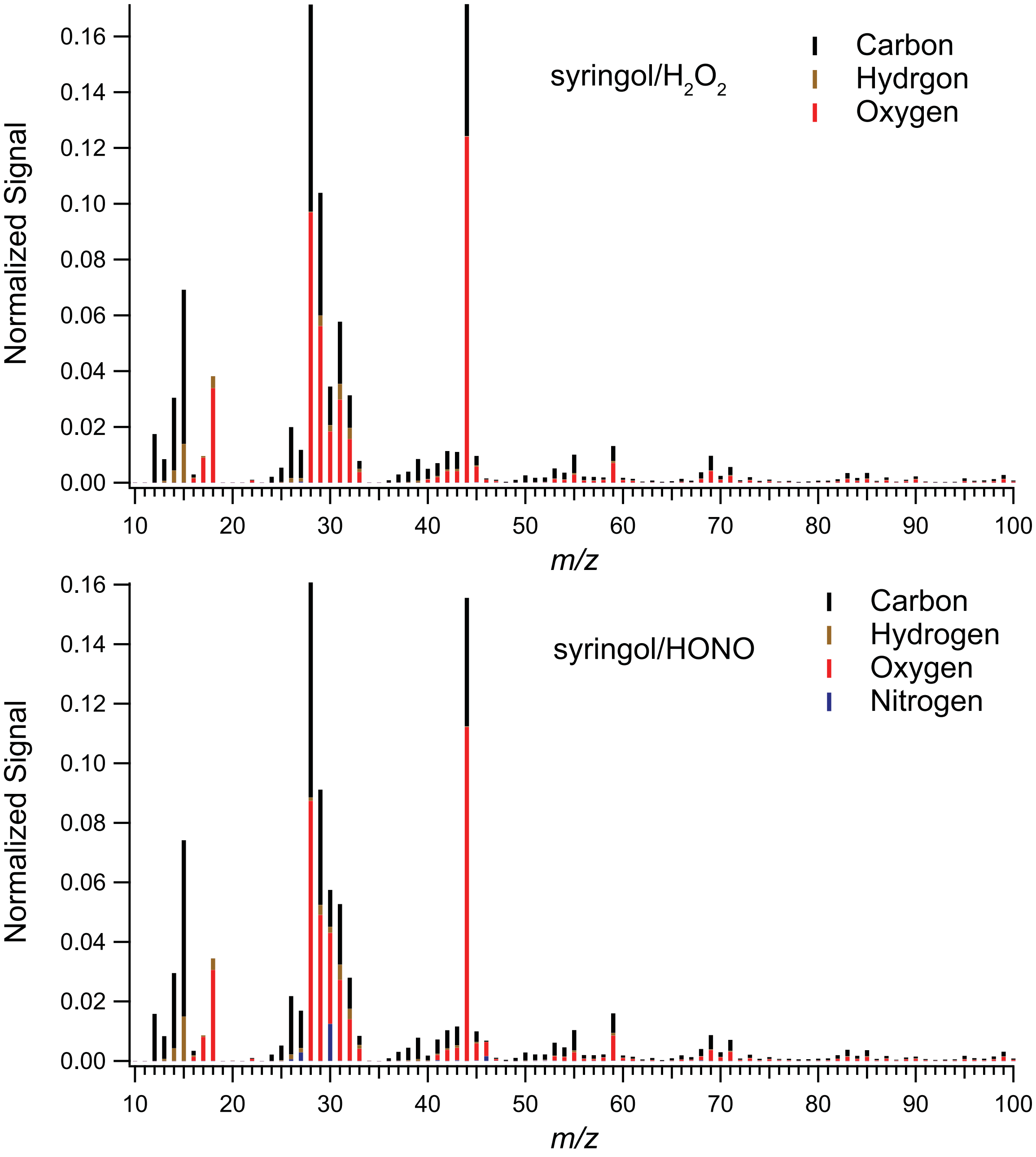

Fig. 7. Elemental spectra of syringol photooxidation SOA under high- and low-NO_x.

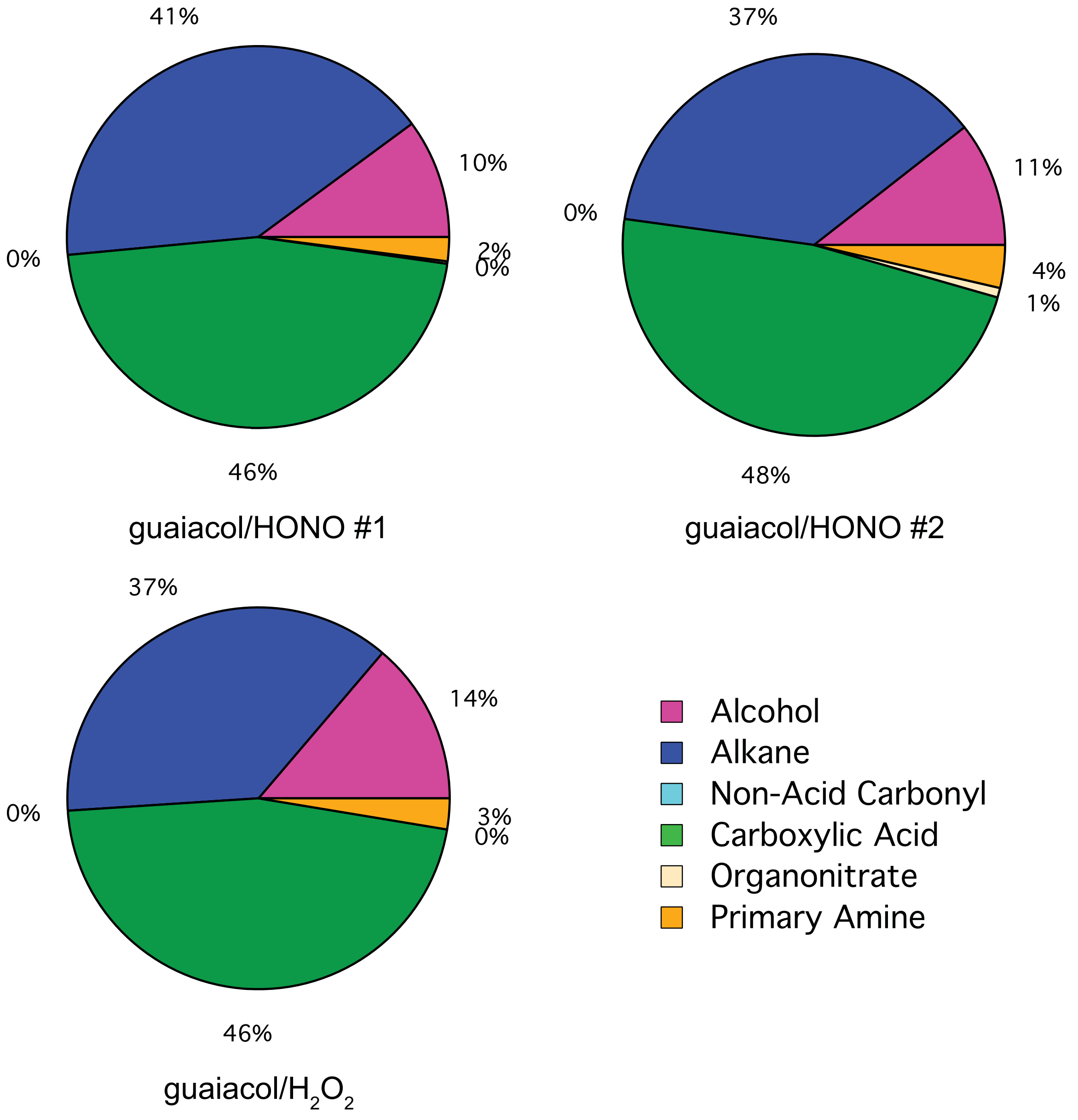

Fig. 8. Average composition by mass of guaiacol photooxidation SOA as measured by FTIR analysis.

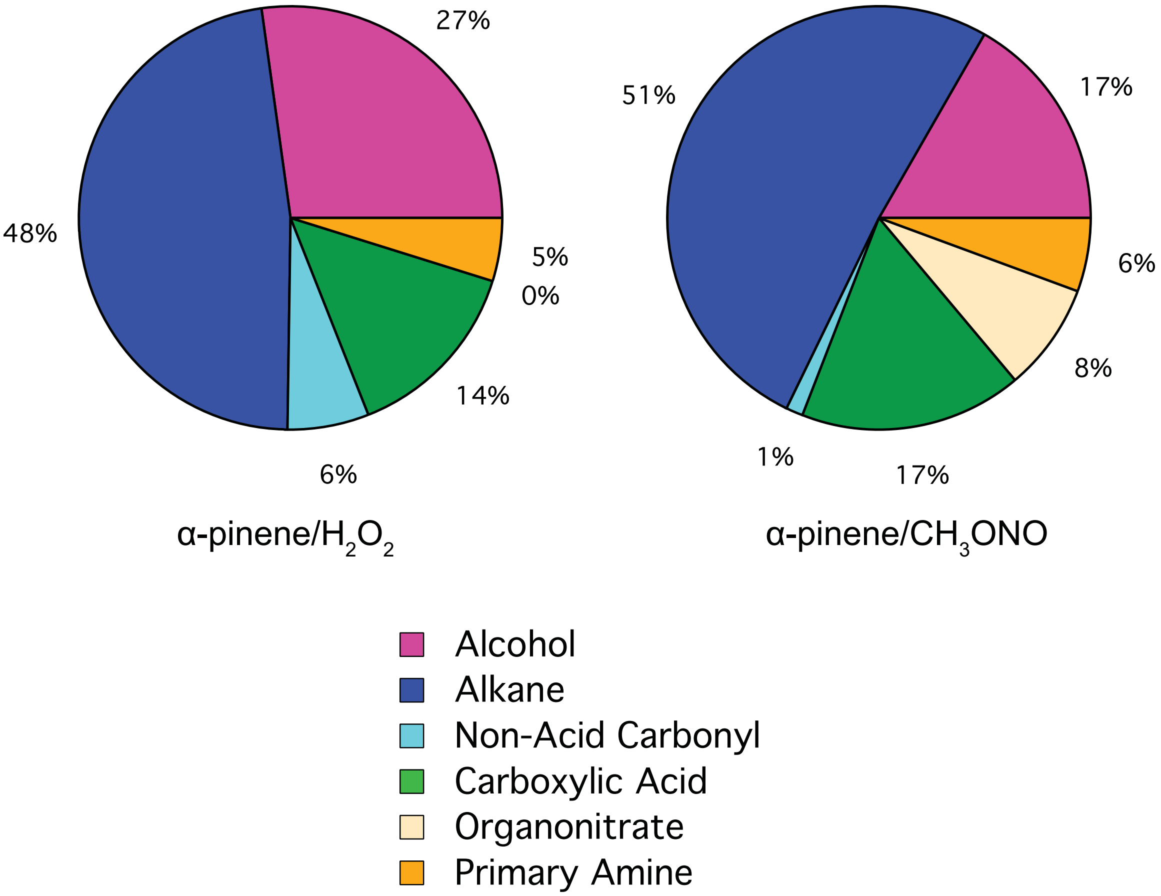

Fig. 9. Average composition by mass of α-pinene photooxidation SOA as measured by FTIR analysis.

References

Chhabra, P. S., Flagan, R. C., and Seinfeld, J. H.: Elemental analysis of chamber organic aerosol using an aerodyne high-resolution aerosol mass spectrometer, Atmos. Chem. Phys., 10, 4111–4131, doi:10.5194/acp-10-4111-2010, 2010.

Maria, S. F., Russell, L. M., Turpin, B. J., Porcja, R. J., Campos, T. L., Weber, R. J., and Huebert, B. J.: Source signatures of carbon monoxide and organic functional groups in Asian Pacific Regional Aerosol Characterization Experiment (ACE-Asia) submicron aerosol types, J. Geophys. Res., 108, 8637, doi:10.1029/2003JD003703, 2003.

Russell, L. M.: Aerosol organic-mass-to-organic-carbon ratio measurements, Environ. Sci. Technol., 37, 2982–2987, doi:10.1021/Es026123w, 2003.

Russell, L. M., Takahama, S., Liu, S., Hawkins, L. N., Covert, D. S., Quinn, P. K., and Bates, T. S.: Oxygenated fraction and mass of organic aerosol from direct emission and atmospheric processing measured on the R/V Ronald Brown during TEXAQS/GoMACCS 2006, J. Geophys. Res.-Atmos., 114, doi:10.1029/2008jd011275, 2009.

Takegawa, N., Miyakawa, T., Kawamura, K., and Kondo, Y.: Contribution of selected dicarboxylic and omega-oxocarboxylic acids in ambient aerosol to the m/z 44 signal of an aerodyne aerosol mass spectrometer, Aerosol Sci. Technol., 41, 418–437, doi:10.1080/02786820701203215, 2007.

Zhang, Q., Alfarra, M. R., Worsnop, D. R., Allan, J. D., Coe, H., Canagaratna, M. R., and Jimenez, J. L.: Deconvolution and quantification of hydrocarbon-like and oxygenated organic aerosols based on aerosol mass spectrometry, Environ. Sci. Technol., 39, 4938–4952, doi:10.1021/Es048568l, 2005.