



## Short communication

## Organic aerosol characterization by complementary measurements of chemical bonds and molecular fragments

Lynn M. Russell<sup>a,\*</sup>, Ranjit Bahadur<sup>a</sup>, Lelia N. Hawkins<sup>a</sup>, James Allan<sup>b</sup>, Darrel Baumgardner<sup>c</sup>, Patricia K. Quinn<sup>d</sup>, Timothy S. Bates<sup>d</sup><sup>a</sup> Scripps Institution of Oceanography, University of California, San Diego, La Jolla, CA 92093-0221, USA<sup>b</sup> School of Earth, Atmospheric, and Environmental Sciences, University of Manchester, Manchester, UK<sup>c</sup> Center for Atmospheric Sciences, National Autonomous University of Mexico, Mexico City, Mexico<sup>d</sup> Pacific Marine Environmental Laboratory, National Oceanic and Atmospheric Administration, Seattle, WA, USA

## ARTICLE INFO

## Article history:

Received 29 June 2009

Received in revised form

22 September 2009

Accepted 25 September 2009

## Keywords:

Organic aerosols

Aerosol mass spectrometry

Infrared spectroscopy

Chemical composition

## ABSTRACT

Organic aerosol chemical markers from normalized concentrations of independent measurements of mass fragments (using Aerosol Mass Spectrometry, AMS) are compared to bond-based functional groups (from Fourier Transform Infrared spectroscopy, FTIR) during eight field projects in the western hemisphere. Several field projects show weak correlations between alcohol group fractions and  $m/z$  60 fractions, consistent with the organic hydroxyl groups and the fragmentation of saccharides, but the weakness of the correlations indicate chemical differences among the relationships for ambient aerosols in different regions. Carboxylic acid group fractions and  $m/z$  44 fractions are correlated weakly for three projects, with correlations expected for aerosols dominated by di-acid compounds since their fragmentation is typically dominated by  $m/z$  44. Despite differences for three projects with ratios of  $m/z$  44 to  $m/z$  57 fragments less than 10, five projects showed a linear trend between the project-average  $m/z$  44 to  $m/z$  57 ratio and the ratio of acid and alkane functional groups. While this correlation explains only a fraction of the fragment and bond variability measured, the consistency of this relationship at multiple sites indicates a general agreement with the interpretation of the relative amount of  $m/z$  44 as a carboxylic acid group marker and  $m/z$  57 as an alkane group marker.

© 2009 Elsevier Ltd. All rights reserved.

## 1. Background

The limitations in our ability to measure and model the quantity, size distribution, and chemical composition of particles in the atmosphere are among the largest uncertainties in quantifying human impacts on climate change. Organic components typically account for 10–50% of the fine particle mass of aerosol in the atmosphere, with some regions having as much as 80% (Jacobson et al., 2000; Turpin and Lim, 2001). Quantifying the thousands of molecules present in these complex and variable particle types remains an important but elusive goal for instrument development, as this ability would help us to improve our descriptions of the properties and chemical reactivity of organic particles. Current gas chromatographic techniques can identify and quantify only a small fraction of the total organic mass (OM) (Fuzzi et al., 2006). Measurements of the organic chemical composition of total particle OM thus are limited to

measurements of components (such as atoms, bonds, fragments, and ions) rather than specific compounds. Given these limitations, improving our understanding of the organic composition of atmospheric particles in the decades before new instruments are developed is aided by comparing multiple simultaneous measurements of organic properties.

Comparisons of complementary measurement techniques on real atmospheric particles can improve our understanding of instrument-specific operational definitions of “organic aerosol” or “organic mass” (OM). The purpose of the comparative approach in this work is to go beyond these operational metrics to gain insight into the organic composition itself, as opposed to exercises that either compare nominally identical measurements (such as sulfate) or adjust calibration parameters for “validation.” This approach recognizes the individual strengths of different techniques and the limitation that none of the methods are complete. Comparisons of independent methods can yield a more complete picture of particle composition, moving us one step closer to understanding the organic chemical composition rather than just identifying particles as method-dependent organic types.

\* Corresponding author. Tel.: +1 858 534 4852; fax: +1 858 534 4851.  
E-mail address: [lmrussell@ucsd.edu](mailto:lmrussell@ucsd.edu) (L.M. Russell).

## 2. Measurement campaigns

Quadrupole Aerosol Mass Spectrometers (Q-AMS from Aerodyne Inc.) collect near real-time, in situ measurements of molecular fragments (Jimenez et al., 2003; Allan et al., 2004) that provide a contrasting perspective to a more traditional filter-based “offline” technique that measures chemical bonds, such as Fourier Transform Infrared (FTIR) spectroscopy (Maria et al., 2003; Russell, 2003). Both techniques, as deployed here, nominally measure submicron particles. The components measured by the Q-AMS are referred to as non-refractory (NR) and are defined as all chemical components that vaporize at the operating temperature of 550–600 °C. This vaporization temperature includes some inorganic compounds such as ammonium nitrate and ammonium sulfate (but not mineral dust, elemental carbon, or sea salts) and most organic reference compounds that have been calibrated in the laboratory (Quinn et al., 2006; Matthew et al., 2008). Organic compounds associated with refractory and solid particles may not fully vaporize in the AMS, because substrate effects such as particle bounce may affect the detection of these compounds disproportionately. In addition, the transmission efficiency of the AMS aerodynamic lens is less than 100% for particles with diameters greater than 500 nm. Compounds present on particles larger than 500 nm diameter may be under-sampled, although collection efficiencies can be applied to address this shortcoming.

FTIR analysis is performed on Teflon filters downstream of a 1 µm impactor (SCC 2.229PM1, BGI Inc., Waltham, Massachusetts), with nominal 50% cut-off corresponding to the reported transmission efficiency of the aerodynamic lens (Jayne et al., 2000). FTIR spectroscopy measures the absorption of organic functional groups associated with the frequency of a particular type of bond, including saturated aliphatic C–CH (abbreviated here as “alkane”), carboxylic COH with associated C=O in an acid group COOH (abbreviated here as “acid”), non-acidic carbonyl C=O groups (abbreviated as “carbonyl” and including ketone), non-acidic hydroxyl COH (abbreviated here as “alcohol” which we have specified to include non-acidic organic hydroxyl groups such as straight chain and fatty

alcohols, polyols such as triols and tetrols, and saccharides such as sugars, cellulose and starches), primary amine C–NH<sub>2</sub> groups, and organosulfate groups characterized by C–OSO<sub>3</sub>. Aromatic and unsaturated aliphatic (or “alkene”) groups were below detection for more than 80% of samples and are omitted from this discussion, recognizing that these groups may account for 2–5% of OM depending on sample duration. Bond absorption is measured by transmission, automated algorithms for peak fitting and integration are employed to minimize bias (Russell et al., 2009), and absorption is converted to mass by reference to calibration standards that have been shown to represent atmospheric organic composition with uncertainties of up to 20% (Maria et al., 2003; Russell, 2003; Gilardoni et al., 2007).

Despite the potential sampling differences, the general agreement of these two independent techniques in quantifying organic mass for many ambient and laboratory aerosols has been demonstrated for a series of campaigns. A few cases also have highlighted some important differences. Table 1 summarizes the comparisons for atmospheric measurement campaigns. The correlations between the techniques are typically mild ( $0.5 < r < 0.75$ ), with two exceptions for the Scripps pier in winter (2009) and TexAQS with slightly stronger correlations ( $r = 0.83$  and  $r = 0.79$ , respectively). For all projects taken together, the correlation is strong at  $r = 0.80$ , and the fitted slopes vary from 0.38 to 1.26. For campaigns dominated by small, water or organic-containing particles, the AMS technique reports up to 40% more OM than quantified by FTIR absorption, after corrections to account for the AMS collection efficiencies are applied. Such discrepancies are within the conservative 20–30% uncertainties of each technique and suggest that losses of OM due to both volatilization in sample collection and omission of organic groups not resolved by FTIR or AMS are typically less than 20% (Russell et al., 2009). Larger discrepancies in which FTIR exceeds AMS occur in campaigns with larger concentrations of dust or other non-refractory particles (such as VOCALS where the linear slope is 0.38), as these solid particles may not be efficiently sampled by the AMS (even though they can serve as a condensational sink for a significant fraction of the organic mass).

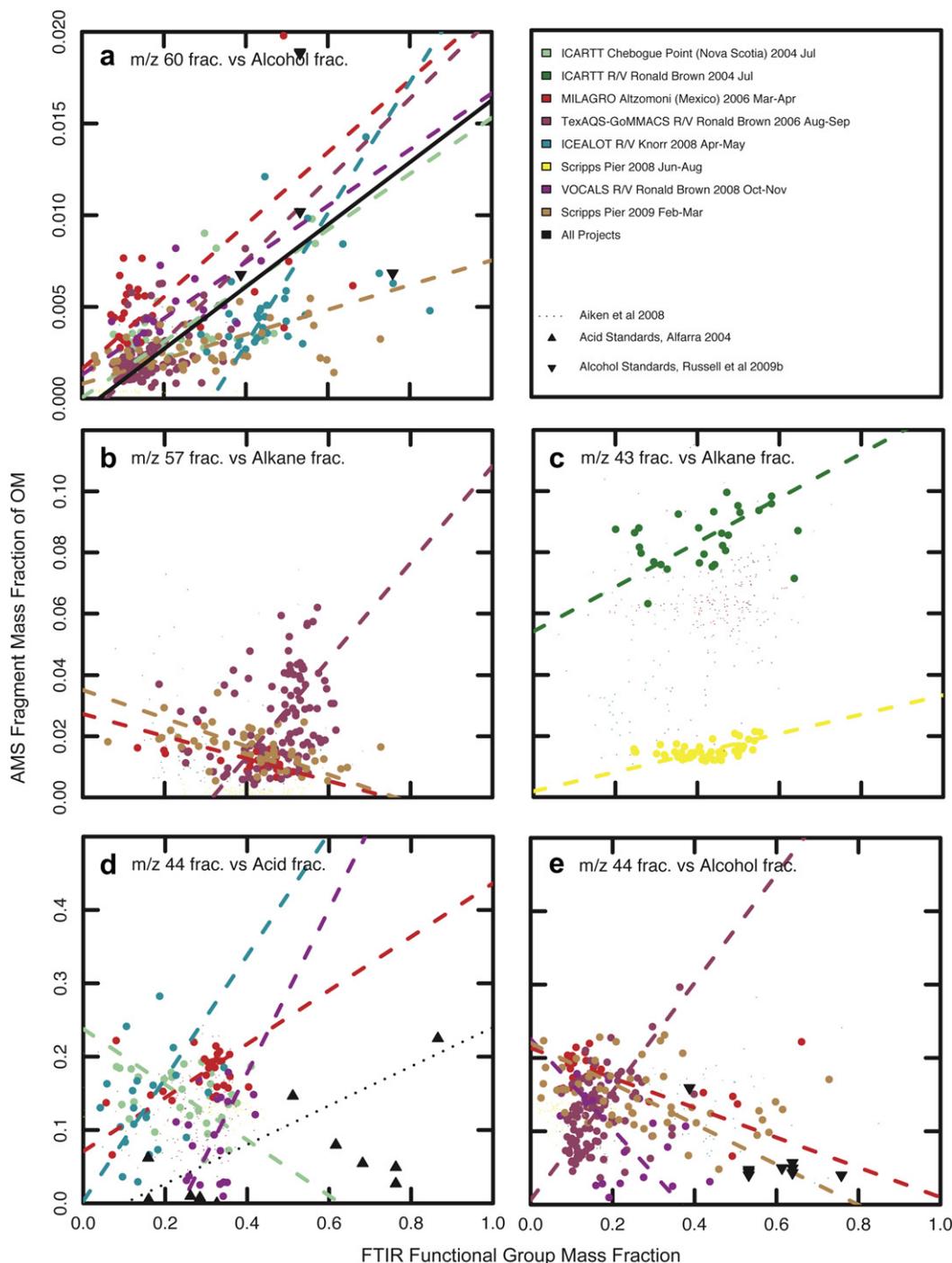
**Table 1**  
Projects with complementary organic aerosol measurements by FTIR and Q-AMS.

Project	OM (µg m <sup>-3</sup> ):	Fraction:	Fraction:	Fraction:	Fraction:	Fraction:
AMS (y)	AMS <sup>a</sup> OM	m/z 60	m/z 57	m/z 43	m/z 44	m/z 44
FTIR (x)	FTIR OM	Alcohol	Alkane	Alkane	Acid	Alcohol
Slope (m), intercept (c)	m	m, c	m, c	m, c	m, c	m, c
Correlation coefficient (r)	(r)	(r)	(r)	(r)	(r)	(r)
ICARTT Chebogue Point (Nova Scotia) 2004: July (Gilardoni et al., 2007)	0.56 (0.75)	0.015, 0.00 (0.54)				-0.38, 0.2 (-0.25)
ICARTT-NEAQS R/V Ronald Brown 2004: July (Gilardoni et al., 2007)	1.26 (0.55)			0.07, 0.0 (0.34)		
MILAGRO Altzomoni (Mexico) 2006: Mar–Apr (Gilardoni et al., 2009; Liu et al., 2009)	0.83 (0.65)	0.020, 0.00 (0.44)	-0.04, 0.0 (-0.54)		0.37, 0.1 (0.41)	-0.20, 0.2 (-0.36)
TexAQS-GoMACCS R/V Ronald Brown 2006: Aug–Sep (Russell et al., 2009)	1.02 (0.79)	0.022, 0.00 (0.39)	0.16, -0.1 (0.28)			0.74, 0.0 (0.35)
ICEALOT R/V Knorr 2008: Apr–May (Russell et al., submitted for publication)	0.91 (0.57)	0.036, -0.01 (0.26)			0.84, 0.0 (0.24)	
Scripps Pier 2008: Jun–Aug	0.99 (0.51)			0.04, 0.0 (0.49)		
VOCALS R/V Ronald Brown 2008: Oct–Nov (Hawkins et al., submitted for publication)	0.38 (0.70)	0.015, 0.00 (0.46)			1.12, -0.3 (0.29)	-0.61, 0.2 (-0.35)
Scripps Pier 2009: Feb–Mar	1.22 (0.83)	0.007, 0.00 (0.26)	-0.05, 0.0 (-0.28)			-0.30, 0.2 (-0.30)
Linear Fits for Projects Above 2004–2009	0.99 (0.80)	0.017, 0.00 (0.48)				

<sup>a</sup> AMS collection efficiencies used for this comparison were calculated according to Quinn et al. (2006), except for VOCALS where 1.0 was used based on co-sampling of sulfate by ion chromatography (Hawkins et al., submitted for publication). Each project data set contains approximately 60 samples, each typically between 6 and 12 h duration.

Of greater value is a comparison of the specific fragments and groups that are detected by each technique. Here our scope is limited to existing campaigns, 1-*amu*-resolution AMS, and a normalized, single-component approach. The normalization as a fraction of OM is used to remove the inherent correlation due to collocated or co-emitted sources, in order to identify relationships in the organic composition itself. Fig. 1 shows a comparison of the atmospheric Q-AMS fragment fractions *m/z* 43, 44, 57, and 60 to the FTIR carboxylic acid, alcohol (including sugars, other saccharides, and other polyols), and alkane

group fractions, with these three FTIR groups typically constituting more than 80% of the OM. In general, weak ( $0.25 < r < 0.5$ ) to mild ( $0.5 < r < 0.75$ ) correlations appear for the limited project durations and their specific regions of measurement, which are illustrated here by grouping the comparisons by project. The variety of comparisons were chosen to show the different mixtures and compounds that dominate the range of organic compounds in aerosol particles, with specific fragment-group comparisons selected on the basis of previously observed laboratory or ambient relationships (Alfarra, 2004;



**Fig. 1.** Comparison of AMS and FTIR organic metrics for the projects identified in Table 1 (using the color scheme shown in the legend): (a) AMS *m/z* 60 fraction of OM and FTIR alcohol fraction of OM, (b) AMS *m/z* 57 fraction of OM and FTIR alkane fraction of OM, (c) AMS *m/z* 43 and FTIR alkane fraction, (d) AMS *m/z* 44 and FTIR carboxylic acid fraction, and (e) AMS *m/z* 44 and FTIR alcohol fraction. Solid circles show measurements for projects with  $|r| > 0.24$  and small dots show measurements for all other projects. Legend gives the correlation coefficient ( $r$ ), slope ( $m$ ) and non-zero intercept ( $c$ ) of best linear fit for the form  $y = mx + c$ , for correlations with  $|r| > 0.24$ .

Allan et al., 2004; Aiken et al., 2008). The stronger correlations may indicate either that the fragment and bond belong to the same organic compound or that the compounds associated with the fragment and the bond co-vary in the mixture for the location and duration of the project. The variation in slopes between projects for the correlated bonds and fragments reflect both differences in detection efficiencies and in the location-specific mixtures.

### 3. Results and discussion

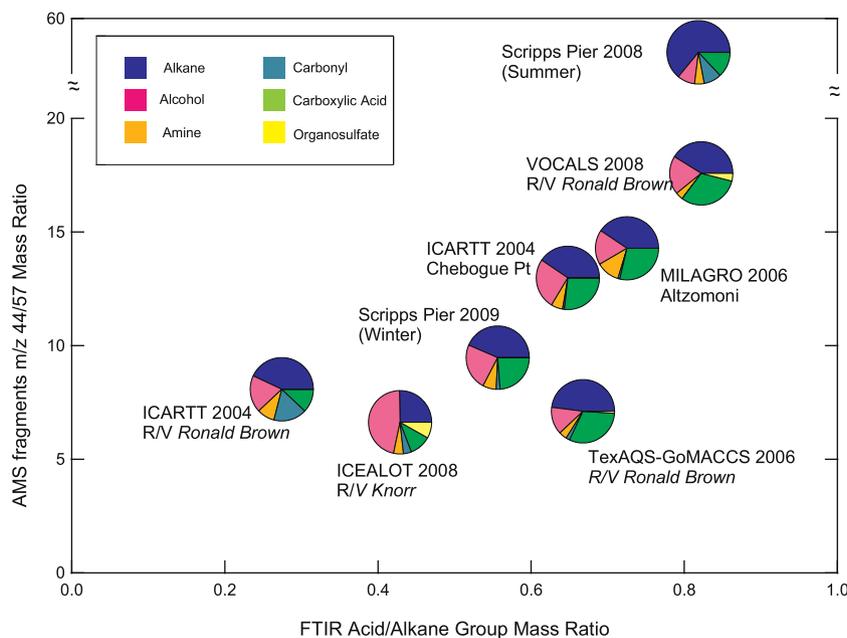
The fragment-to-group fraction correlations use concentrations normalized by the respective OM concentrations and are at most weak ( $0.25 < r < 0.5$ ) or mild ( $0.5 < r < 0.75$ ) for each project, as shown in Fig. 1a. The correlations observed in the largest number of projects were between  $m/z$  60 (representing  $C_2H_4O_2$  fragments) and the alcohol (or organic hydroxyl) groups. The correlation coefficients for six of the eight projects ranged from 0.26 to 0.54, with linear slopes varying by a factor of 5 from 0.007 to 0.036 for the AMS mass fragment as the dependent variable and FTIR functional group as the independent variable. One interesting aspect of the variation in the ratio is that the highest slope and largest offset from zero for the intercept corresponds to the recent ship-based polar ICEALOT project, where marine saccharides that typically have a large number of hydroxyl groups were associated with sea salt (Russell et al., submitted for publication). The lower slope may indicate chemical differences in the relative frequencies of  $m/z$  60 fragments and hydroxyl groups in the molecules as well as differences in collection efficiencies. Higher ratios of  $m/z$  60 fractions to alcohol fractions were measured in projects with alcohol fractions associated with non-marine sources (Russell et al., 2009; Liu et al., 2009), including Altzomoni near Mexico City (0.02) and TexAQS near Houston (0.02).

A weak and infrequent correlation was seen for two mass fragments with the alkane fraction. AMS  $m/z$  43 fractions (representing  $C_3H_7$  and  $C_2H_3O$  fragments) showed a weak correlation with alkane fractions aboard the ship during ICARTT and at the Scripps pier in summer 2008, which both measured frequently in air masses that were directly downwind of a large number of urban combustion

emissions. The slope of the best-fit line of  $m/z$  43 fractions to alkane fractions was 0.07 for ICARTT on the R/V Ronald Brown. A lower slope of the two markers was found for the Scripps pier. One marker found to be associated with hydrocarbon-like organic aerosol (HOA) is  $m/z$  57 (Zhang et al., 2005). The only positive correlation between  $m/z$  57 fractions and alkane fractions was found for another project dominated by proximate urban emissions – TexAQS, a result mirrored by the finding of  $m/z$  57 associated strongly only with fresh combustion exhaust during NEAQS (Marcolli et al., 2006). Two projects showed a mild-to-weak negative correlation, which may indicate that  $m/z$  57 and alkane groups had sources located in different directions so that they were anti-correlated. However, these negative correlations could also reflect the fact that the Q-AMS  $m/z$  57 includes both non-oxygenated ( $C_4H_9$ ) and oxygenated ( $C_3H_5O$ ) fragments.

Perhaps the most frequently discussed individual mass fragment that has been linked most strongly to a semi-specific chemical structure is  $m/z$  44 (representing  $CO_2$  fragments), a marker of oxidized organic aerosol (OOA) and typically associated with fragmentation of mono and di-carboxylic acids (Alfarra, 2004; Zhang et al., 2005). Three projects showed a weak positive correlation ( $r > 0.24$ ) with a range of slopes – Altzomoni (0.37), ICEALOT (0.84), and VOCALS (1.12) – and one project showed a weak negative correlation (Chebogue Point). The slopes of the line fits differ from the carboxylic acid standards reported to date (Alfarra, 2004) and from ambient relationships reported (Aiken et al., 2008), but may reflect the variability of atmospheric mixtures in different regions. There is a weak positive correlation between  $m/z$  44 fractions and alcohol fractions ( $r = 0.35$ ) for TexAQS, which may result from the fragmentation of polyols such as saccharides. The more frequent negative correlations between  $m/z$  44 and alcohol fractions indicates that the relationship cannot be generalized to a wider variety of particle compositions.

A clear trend is seen in comparing the relative fractions of oxygenated and hydrocarbon-like organic compounds for many of the project averages, as shown in Fig. 2. Most of the projects fall near a single linear relationship between the acid/alkane ratio for 44/57 ratios of 10 and above. The exception is the 2008 Scripps pier measurements, which had near-detection values of  $m/z$  57 making



**Fig. 2.** Comparison of AMS and FTIR organic ratios of oxidized and non-oxidized markers for the projects identified in Table 1. Markers for each project are labeled and show the average FTIR composition with FTIR functional group contributions given by the colors in the legend shown. Note that the y-axis is broken to include the Scripps Pier (2008 Jun–Aug), as it has an AMS  $m/z$  44 to 57 ratio of 48. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the ratio very large at 48. For AMS  $m/z$  44 to  $m/z$  57 ratios under 10, there is significantly more variability, suggesting that in these conditions these two markers have influence from functional groups other than carboxylic acid and alkane groups. This interpretation is consistent with the significant carbonyl contribution in the ICARTT measurements on the R/V *Ronald Brown* and the significant alcohol contribution in the ICEALOT measurements on the R/V *Knorr*. Text-AQS measurements on the R/V *Ronald Brown* also show a different trend, resulting either from the large contribution of the relatively unique sources of emissions related to oil refining or from differences in collection efficiencies indicated by the larger than usual slope and intercept of the measured OM between the AMS and FTIR.

An analogous approach for organic aerosols from a different region has already been investigated for AMS and water-soluble organic components by proton Nuclear Magnetic Resonance spectroscopy (HNMR) (McFiggans et al., 2005). The relationships presented here reveal a similar range and complexity and go beyond the limitations of water-soluble extraction, with the higher sampling frequency of FTIR with respect to HNMR providing some preliminary metrics characteristic of alcohol groups from biomass burning and marine production, carboxylic acid groups from atmospheric oxidation of fossil fuel combustion products, and alkane groups in urban areas. As additional measurements are collected to allow us to identify specific source signatures, multivariate techniques can be used to build on these underlying primary relationships.

#### 4. Conclusions

By using more chemically-specific techniques, such as FTIR, to interpret the chemical functionality associated with specific AMS mass fragments in different aerosol organic mixtures, we can then use the size and time resolution of the AMS to improve quantification of the chemical properties and reactions that occur in the atmosphere. Here we have shown the occasional correspondence of the AMS markers to FTIR functional groups such as carboxylic acid, alkane, and alcohol groups in specific regions for local emission sources and their mixtures. The relationships of alcohol group fractions and  $m/z$  60 fractions show that a significant fraction of the OM in these samples can be identified with sugar-type compositions. The differences in the slopes of the relationships provide a way to identify the fragmentation of the organic hydroxyl compounds produced from sources such as marine saccharides. The correlations of carboxylic acid group fractions and  $m/z$  44 fractions show consistency with the trend expected based on di-acid fragmentation patterns, but significant differences among the projects studied show that in some regions  $m/z$  44 fraction is dominated by mono-acids that have a weaker  $m/z$  44 signal or by components other than carboxylic acid groups.

In summary, the correlations of mass fragments with functional groups provide support for their use as markers of chemical functionality in some conditions. The weakness of correlations is consistent with the multitude of variables that control aerosol composition in the atmosphere. Nonetheless, in regions where sufficient  $m/z$  44 and  $m/z$  57 fragments are both present, the  $m/z$  44 to  $m/z$  57 ratio is indicative of the ratio of carboxylic acid and alkane functional groups.

In many cases, the sophistication of climate model representation of aerosol properties and reactions of organic compounds exceeds the available observations, in that models predict changes in the hydrophobic character of organic-containing mixtures without the benefit of observational data sets for comparison. The consequence is that models rely on extrapolations and interpolations from available data, and this practice increases the uncertainty of their predictions. By using both characteristic fragmentation patterns and functional groups, we improve the measurements collected by quantifying the contribution of carboxylic acid and hydroxyl group

containing compounds of a majority of the OM, providing information with which appropriate model compounds can be constrained. As an example, the significant variability in the contributions of  $m/z$  44 and carboxylic acid groups suggests that aerosol particles contain a regionally-dependent mixture of compounds. While factorization approaches are beyond the scope of this work, we can extend similar caveats to factors that are strongly reliant on single mass fragment markers. This synthesis of multiple complementary techniques can be used to reduce the uncertainties associated with organic water uptake and reactivity, providing additional information that may help diagnose problems in sub-grid and other chemically-relevant model parameterizations.

#### Acknowledgments

Several of the field measurement campaigns reported here were supported by the National Science Foundation and the National Oceanic and Atmospheric Administration through a variety of grants, with the help of many science teams and collaborators who are too numerous to mention here. This retrospective work was made possible by the financial support of the James S. McDonnell Foundation and BP. We thank Doug Worsnop, John Jayne, and Jose Jimenez for technical advice and encouragement over the years required for this multi-project compilation.

#### References

- Aiken, A.C., DeCarlo, P.F., Kroll, J.H., Worsnop, D.R., Huffman, J.A., Docherty, K., Ulbrich, I.M., Mohr, C., Kimmel, J.R., Sueper, D., Zhang, Q., Sun, Y., Trimborn, A., Northway, M., Ziemann, P.J., Canagaratna, M.R., Onasch, T.B., Alfarra, R., Prevot, A.S.H., Dommen, J., Duplissy, J., Metzger, A., Baltensperger, U., Jimenez, J.L., 2008. O/C and OM/OC ratios of primary, secondary, and ambient organic aerosols with high resolution time-of-flight aerosol mass spectrometry. *Environmental Science and Technology* 42, 4478–4485. doi:10.1021/es703009q.
- Alfarra, R., 2004. Insights into Atmospheric Organic Aerosols Using an Aerosol Mass Spectrometer. Ph.D. thesis at the University of Manchester.
- Allan, J.D., Coe, H., Bower, K.N., Alfarra, M.R., Delia, A.E., Jimenez, J.L., Middlebrook, A.M., Drewnick, F., Onasch, T.B., Canagaratna, M.R., Jayne, J.T., Worsnop, D.R., 2004. Technical note: extraction of chemically resolved mass spectra from aerodyne aerosol mass spectrometer data. *Journal of Aerosol Science* 35, 909–922.
- Fuzzi, S., Andreae, M.O., Huebert, B.J., Kulmala, M., Bond, T.C., Boy, M., Doherty, S.J., Guenther, A., Kanakidou, M., Kawamura, K., Kerminen, V.M., Lohmann, U., Russell, L.M., Poschl, U., 2006. Critical assessment of the current state of scientific knowledge, terminology, and research needs concerning the role of organic aerosols in the atmosphere, climate, and global change. *Atmospheric Chemistry and Physics* 6, 2017–2038.
- Gilardoni, S., Russell, L.M., Sorooshian, A., Flagan, R.C., Seinfeld, J.H., Bates, T.B., Onasch, T., Quinn, P.K., Allan, J., Worsnop, D., Williams, B., Goldstein, A., 2007. Regional variation of oxygenated functional groups in aerosol particles on four east coast sampling platforms during ICARTT 2004. *Journal of Geophysical Research-Atmospheres* 12. doi:10.101029/2006JD007737.
- Gilardoni, S., Liu, S., Takahama, S., Russell, L.M., Allan, J.D., Steinbrecher, R., Jimenez, J.L., Decarlo, P.F., Dunlea, E.J., Baumgardner, D., 2009. Characterization of organic ambient aerosol during MIRAGE 2006 on three platforms. *Atmospheric Chemistry and Physics* 9, 5417–5432.
- Hawkins, L.N., Russell, L.M., Covert, D., Quinn, P., Bates, T. Carboxylic acids, sulfates, and organosulfates in processed continental organic aerosol over the Southeast Pacific Ocean during VOCALS-REx 2009, submitted for publication and available at <http://aerosols.ucsd.edu/publications.html>.
- Jacobson, M.C., et al., 2000. The surface tension and can make particles more CCN. *Reviews of Geophysics* 38, 267–294.
- Jayne, J.T., Leard, D.C., Zhang, X., Davidovits, P., Smith, K.A., Kolb, C.E., Worsnop, D.R., 2000. Development of an aerosol mass spectrometer for size and composition analysis of submicron particles. *Aerosol Science and Technology* 33, 49–70.
- Jimenez, J.L., Jayne, J.T., Shi, Q., Kolb, C.E., Worsnop, D.R., Yourshaw, I., Seinfeld, J.H., Flagan, R.C., Zhang, X., Smith, K.A., Morris, J., Davidovits, P., 2003. Ambient aerosol sampling with an aerosol mass spectrometer. *Journal of Geophysical Research-Atmospheres* 108 (D7), 8425. doi:10.1029/2001JD001213.
- Liu, S., Takahama, S., Russell, L.M., Gilardoni, S., Baumgardner, D., 2009. Oxygenated organic functional groups and their sources in single and submicron organic particles in MILAGRO 2006 campaign. *Atmospheric Chemistry and Physics* 9, 6849–6863.
- Maria, S.F., Russell, L.M., Turpin, B.J., Porcjan, R.J., Campos, T.L., Weber, R.J., Huebert, B.J., 2003. Source signatures of carbon monoxide and organic functional groups in Asian Pacific Regional aerosol characterization experiment

- (ACE-Asia) submicron aerosol types. *Journal of Geophysical Research-Atmospheres* 108. doi:10.1029/2003JD003703.
- Matthew, B.M., Middlebrook, A.M., Onasch, T.B., 2008. Collection efficiencies in an aerodyne aerosol mass spectrometer as a function of particle phase for laboratory generated aerosols. *Aerosol Science and Technology* 42 (11), 884–898. doi:10.1080/02786820802356797.
- Marcolli, C., Canagaratna, M.R., Worsnop, D.R., Bahreini, R., de Gouw, J.A., Warneke, C., Goldan, P.D., Kuster, W.C., Williams, E.J., Lerner, B.M., Roberts, J.M., Meagher, J.F., Fehsenfeld, F.C., Marchewka, M., Bertman, S.B., Middlebrook, A.M., 2006. Cluster analysis of the organic peaks in bulk mass spectra obtained during the 2002 New England air quality study with an aerodyne aerosol mass spectrometer. *Atmospheric Chemistry and Physics* 6, 5649–5666.
- McFiggans, Gordon, Alfarra, M. Rami, Allan, James, Bower, Keith, Coe, Hugh, Cubison, Mike, Topping, Dave, Williams, Paul, Decesari, Stefano, Facchini, Cristina, Fuzzi, Sandro, 2005. Simplification of the representation of the organic component of atmospheric particulates. *Faraday Discussions* 130, 341–362.
- Quinn, P.K., Bates, T.S., Coffman, D., Onasch, T.B., Worsnop, D., Baynard, T., de Gouw, J.A., Goldan, P.D., Custer, W.C., Williams, E., Roberts, J.M., Lerner, B., Stohl, A., Pettersson, A., Lovejoy, E.R., 2006. Impacts of sources and aging on submicrometer aerosol properties in the marine boundary layer across the Gulf of Maine. *Journal of Geophysical Research-Atmospheres* 111, D23S36. doi:10.1029/2006JD007582.
- Russell, L.M., 2003. Aerosol organic-mass-to-organic-carbon ratio measurements. *Environmental Science and Technology* 37, 2982–2987.
- Russell, L.M., Takahama, S., Liu, S., Hawkins, L.N., Covert, D.S., Quinn, P.K., Bates, T.S., 2009. Oxygenated fraction and mass of organic aerosol from direct emission and atmospheric processing measured on the R/V *Ronald Brown* during TEX-AQS/GoMACCS 2006. *Journal of Geophysical Research-Atmospheres* 114 (D00F05). doi:10.1029/2008JD011275.
- Russell, L.M., Hawkins, L.N., Frossard, A., Day, D.A., Quinn, P.K., Bates, T.S. Composition and abundance of primary marine organic aerosol particles, submitted for publication and available at <http://aerosols.ucsd.edu/publications.html>.
- Turpin, B.J., Lim, H.-J., 2001. Species contributions to PM<sub>2.5</sub> mass concentrations: revisiting common assumptions for estimating organic mass. *Aerosol Science and Technology* 35, 602–610.
- Zhang, Q., Alfarra, M.R., Worsnop, D.R., Allan, J.D., Coe, H., Canagaratna, M.R., Jimenez, J.L., 2005. Deconvolution and quantification of hydrocarbon-like and oxygenated organic aerosols based on aerosol mass spectrometry. *Environmental Science and Technology* 39, 4938–4952. doi:10.1021/es048568l.