

## **Supplemental material**

### **Semi-Continuous Measurements of Gas/Particle Partitioning of Organic Acids in a Ponderosa Pine Forest Using a MOVI-HRToF-CIMS**

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# 1. MOVI Cycle

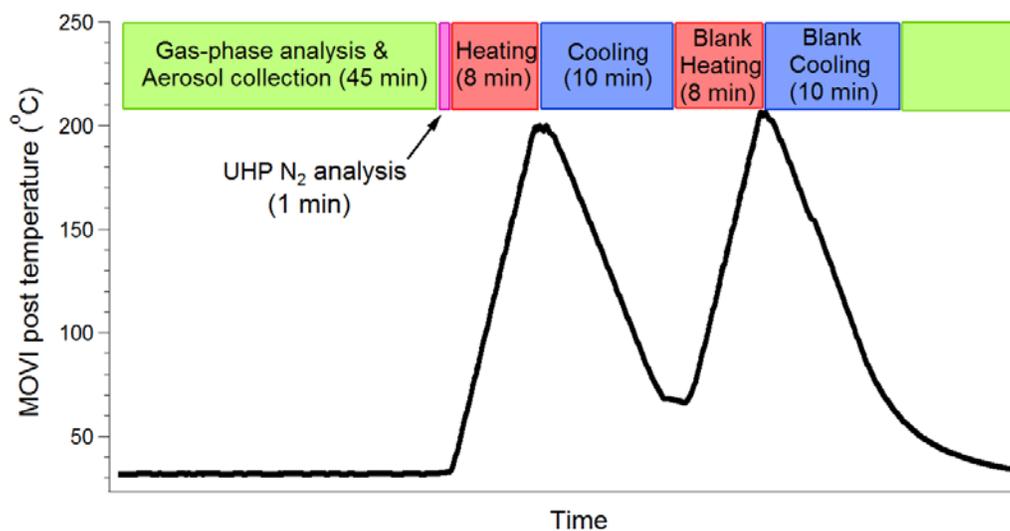


Figure S1. MOVI steps during BEACHON-RoMBAS field study

## 2. High-Resolution Peak Fitting of $^{183}\text{Th}$

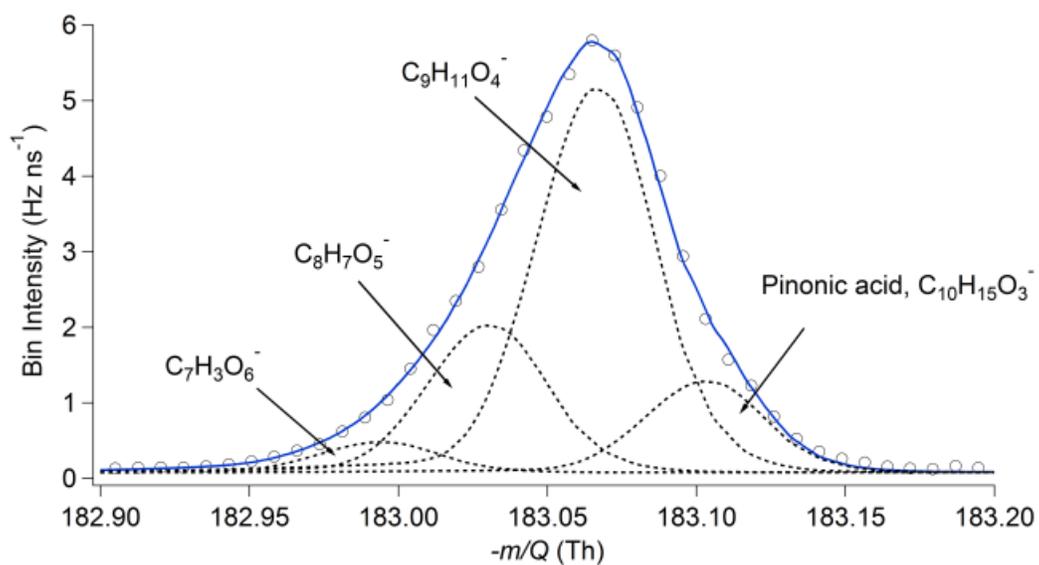


Figure S2. High resolution multi peak fitting result of  $^{183}\text{Th}$  showing several different isobaric compounds.

### 3. Alkanoic acid signals on August 26, 2011

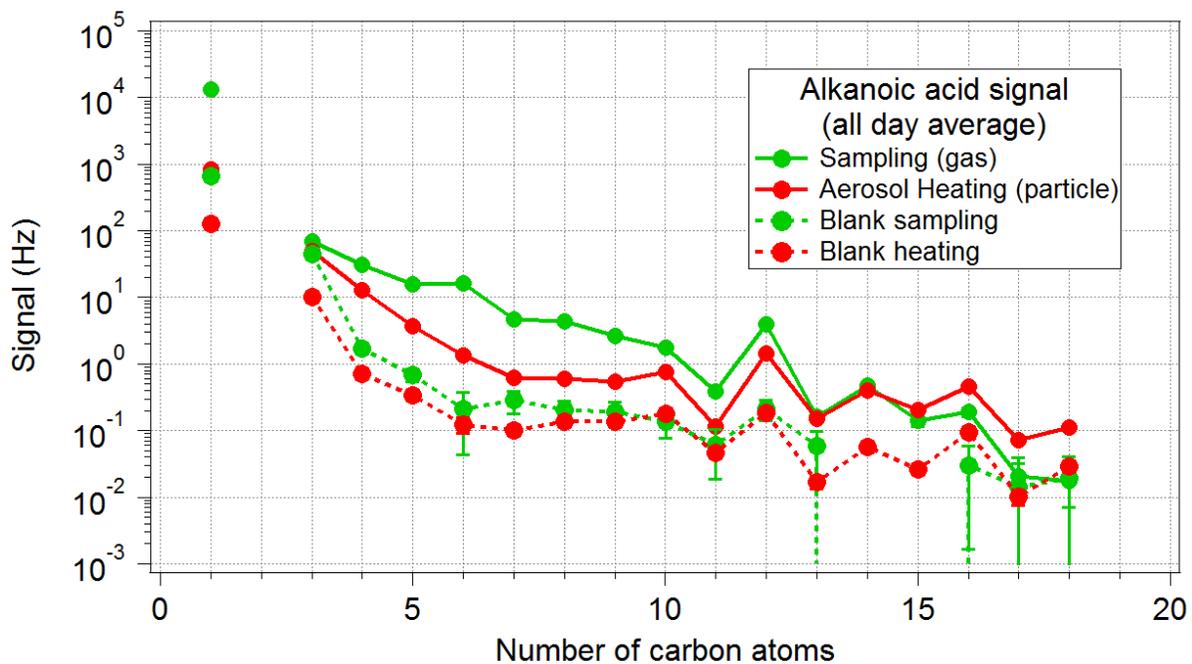


Figure S3. All-day average signals measured at each alkanoic acid during *Sampling* (gas), *Aerosol Heating* (particle), *Blank Sampling* and *Blank Heating* steps. Signals are from August 26, 2011.

#### 4. Estimated partitioning to the aerosol aqueous phase on August 26, 2011

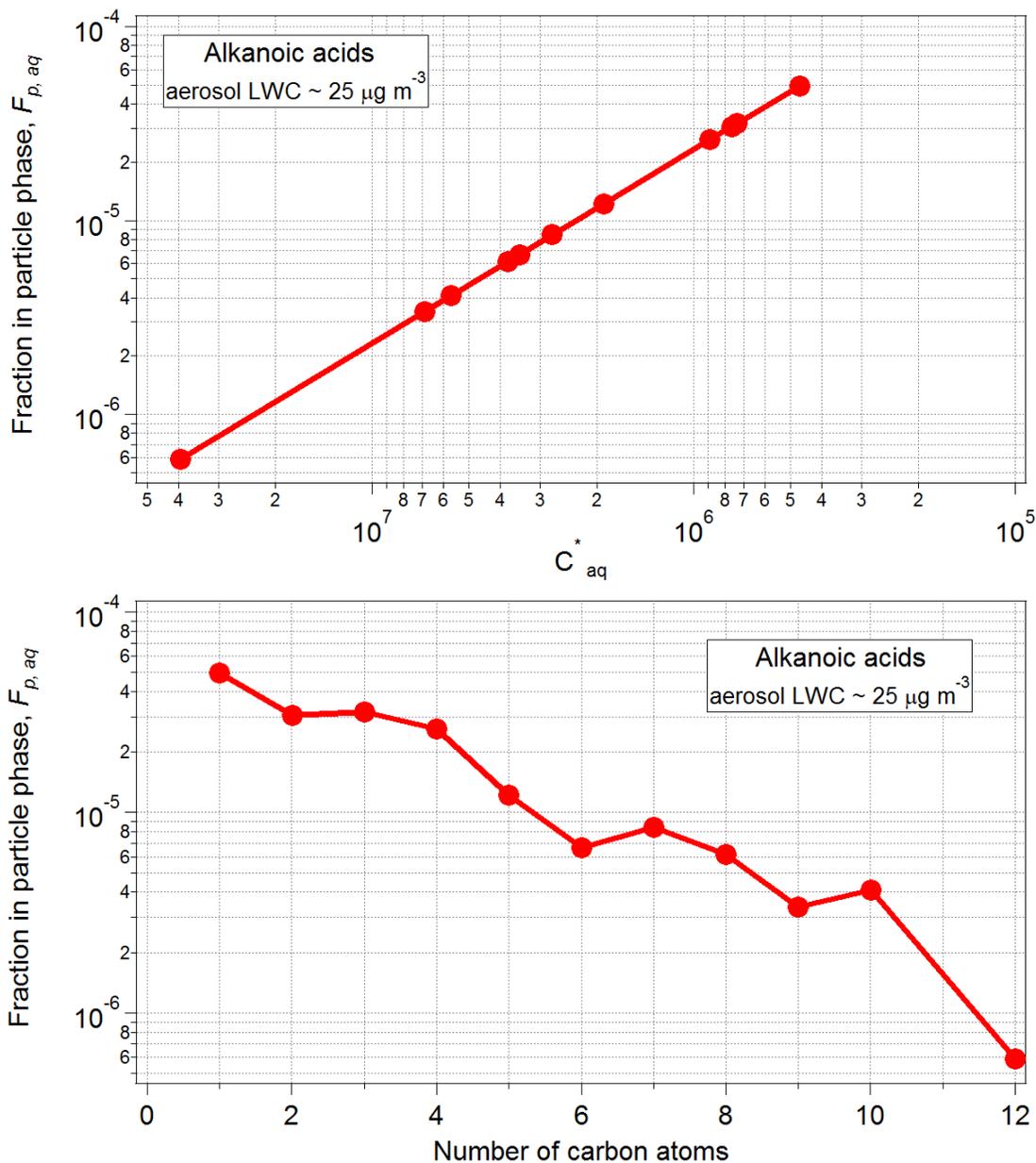


Figure S4. Calculated partitioning to aerosol aqueous phase using Henry's law coefficients for C<sub>1</sub>-C<sub>12</sub> alkanolic acids. Maximum aerosol liquid water content (LWC) was calculated at 10:45 pm (local time) on August 26, 2011. Aerosol LWC is calculated using the E-AIM II (Clegg et al., 1998; E-AIM, <http://www.aim.env.uea.ac.uk/aim/aim.php>). Aerosol ionic composition as measured by the AMS was  $\text{SO}_4^{2-} = 4.2 \times 10^{-9} \text{ mol m}^{-3}$ ,  $\text{NO}_3^- = 2.97 \times 10^{-9} \text{ mol m}^{-3}$  and  $\text{NH}_4^+ = 1 \times 10^{-8} \text{ mol m}^{-3}$ . Ambient temperature = 15.5 °C and RH = 99%. Henry's law constants for C<sub>1</sub>-C<sub>12</sub> alkanolic acids are from NIST Chemistry WebBook (Sander, 2011), and National Institutes of Health TOXNET database (ChemIDplus, 1986).

### 5. Relative humidity and ambient temperature from Aug 20 – 30, 2011

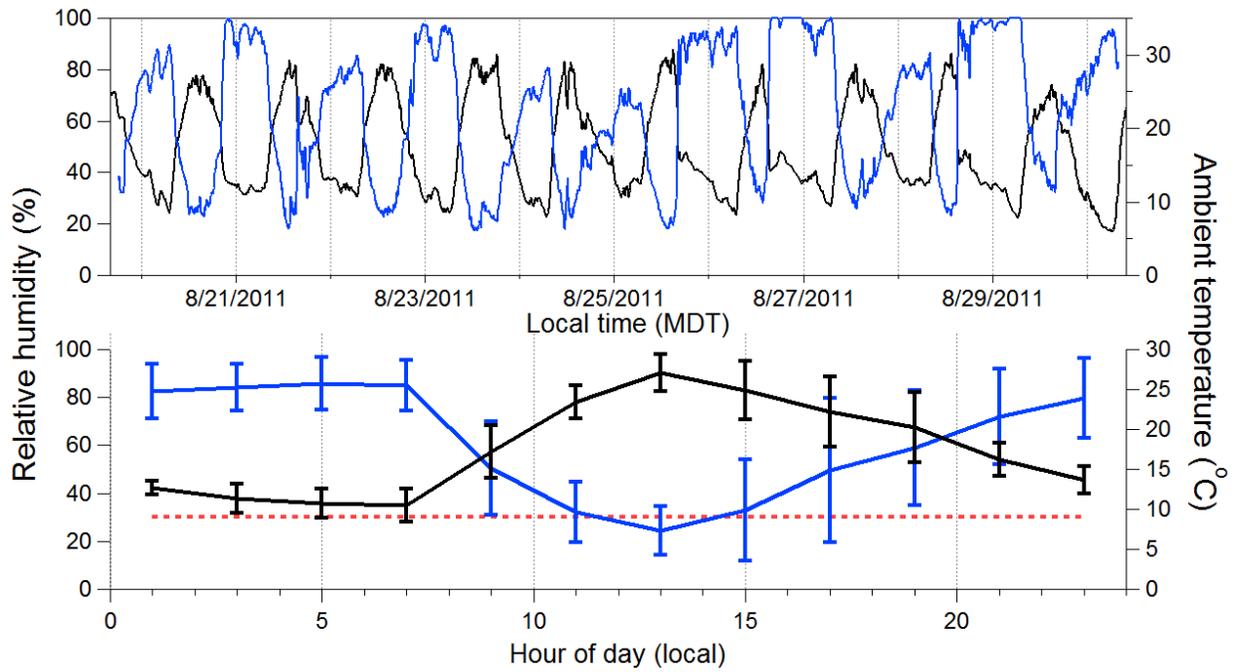


Figure S5. Relative humidity and ambient temperature during the measurement period. Dotted red line indicated RH = 30%. Error bars in the diurnal cycle represent day-to-day variability.

## 6. Sampling and Aerosol Heating signals in the C<sub>12</sub> bin on August 26, 2011

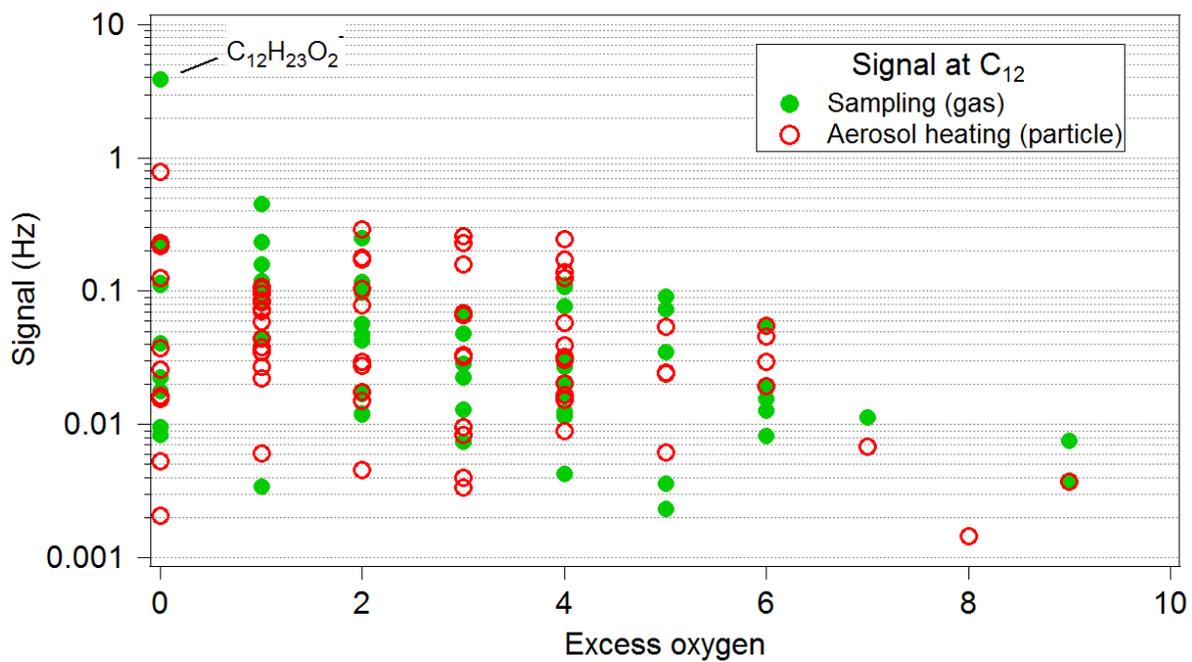


Figure S6. All day averaged *Sampling* and *Aerosol Heating* signals measured for various ions with 12 carbons.

## 7. Meteorology and OA on August 26, 2011

Fig. S6 shows the time series of ambient temperature, RH, OA, and photosynthetically-active radiation (PAR) on 26 Aug 2011. Temperature and RH varied between 8 – 29 °C and 24 – 100 %, respectively, with an average temperature of 15.8 °C. During brief rain showers from 3 – 5 PM (local time, UTC-6:00) temperature decreased by 10 - 15 °C and RH increased from 30 to 100 %. Total precipitation for this day was 7.1 mm. OA mass concentration did not show any clear diurnal pattern on this day (nor typically throughout the campaign) with an average OA mass concentration of  $2.4 \mu\text{g m}^{-3}$ .

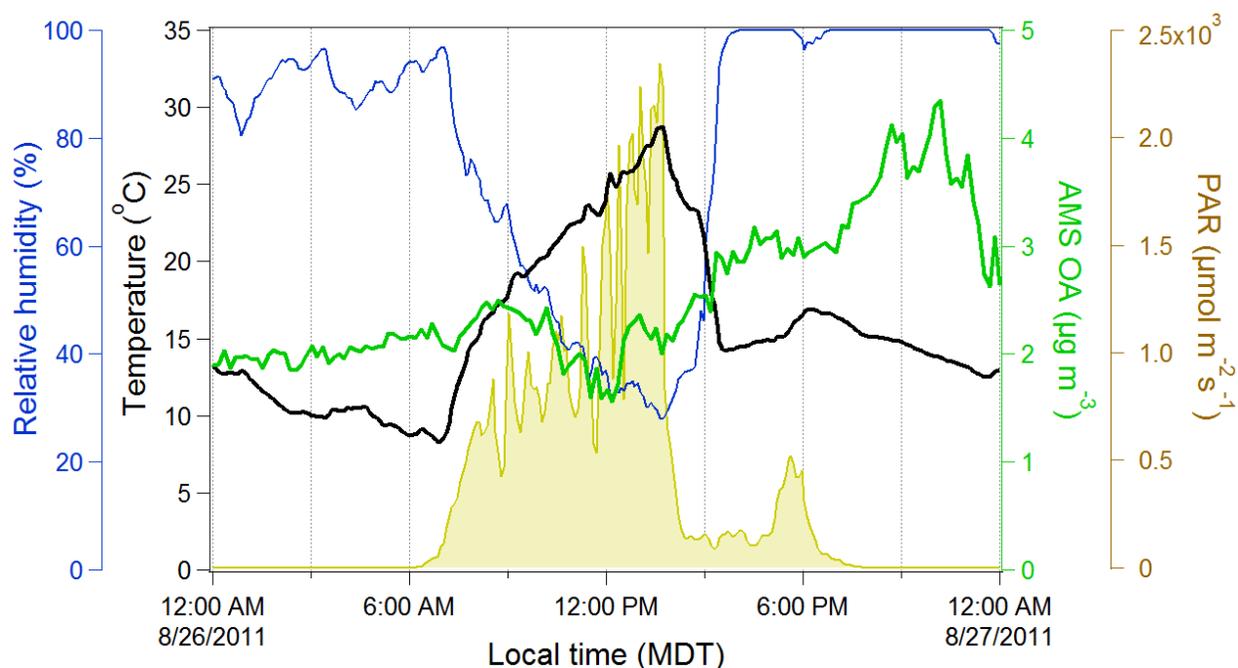


Figure S7. Time series of temperature, RH, OA and PAR on August 26, 2011. No precipitation was observed on this day.

8. Time series, diurnal average and scatter plot of measured and modeled  $F_p$  for bulk-averaged acids.

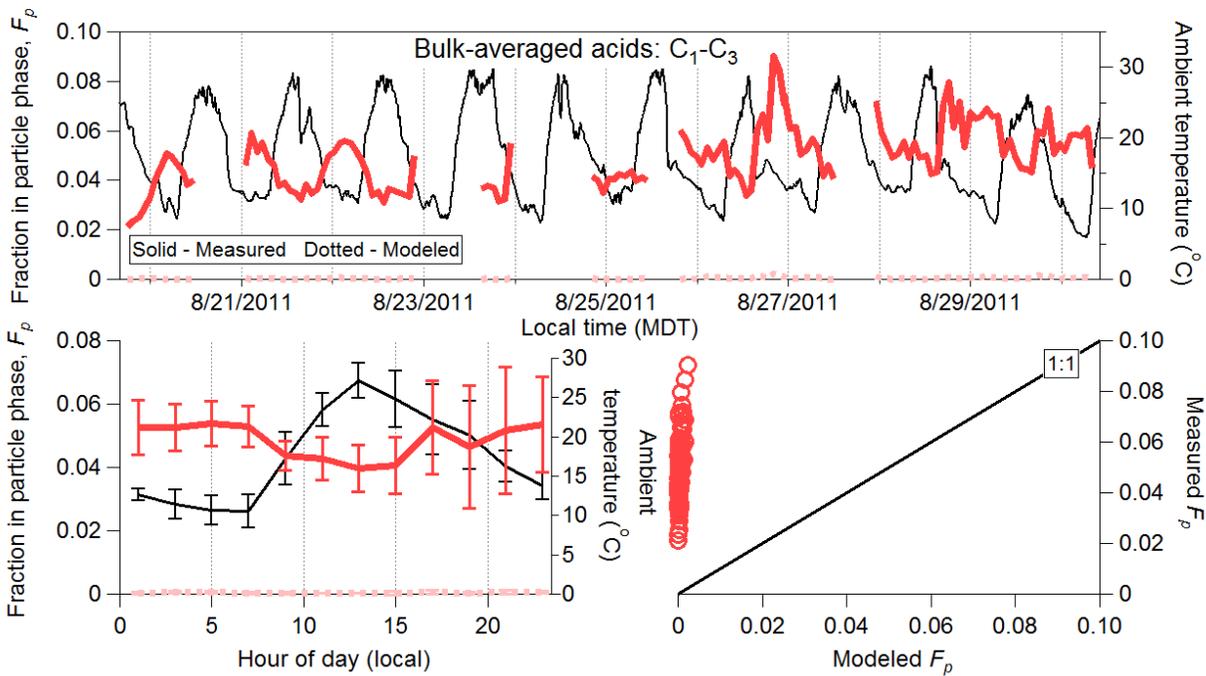


Figure S8. Time series, diurnal cycle and scatter plot of measured and modeled  $F_p$  for  $C_1-C_3$  averaged bulk acids. Model uses excess oxygen as a hydroxyl group.

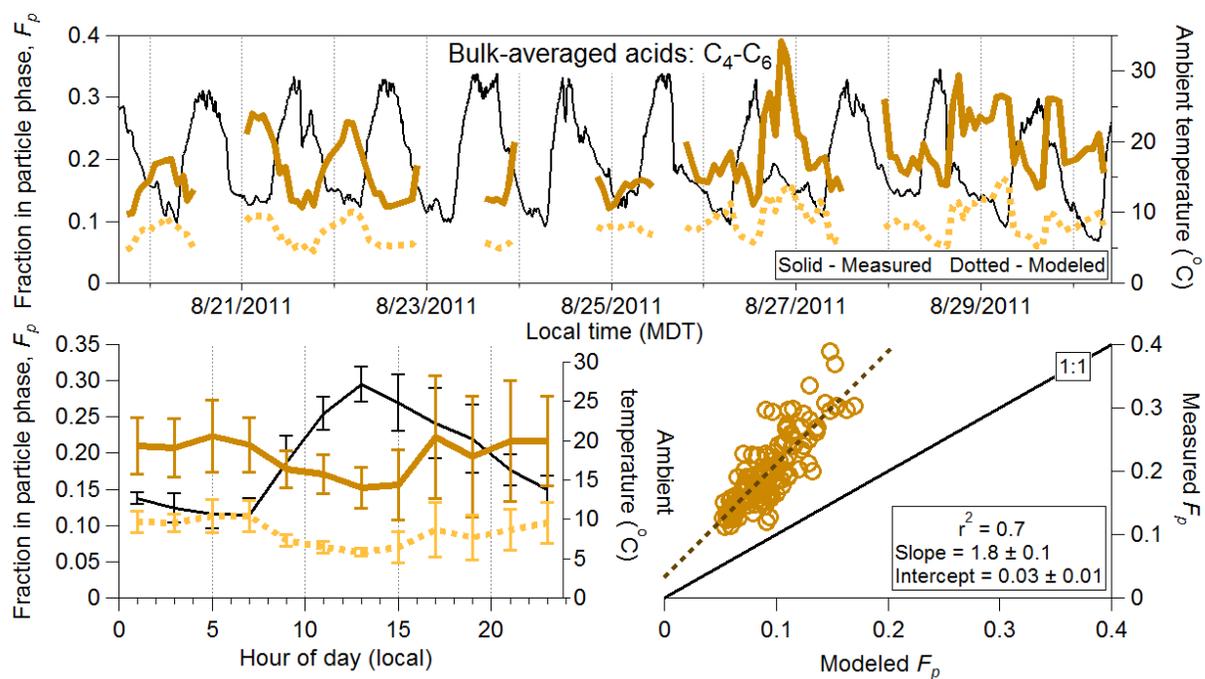


Figure S9. Time series, diurnal cycle and scatter plot of measured and modeled  $F_p$  for C<sub>4</sub>-C<sub>6</sub> averaged bulk acids. Model uses excess oxygen as a hydroxyl group.

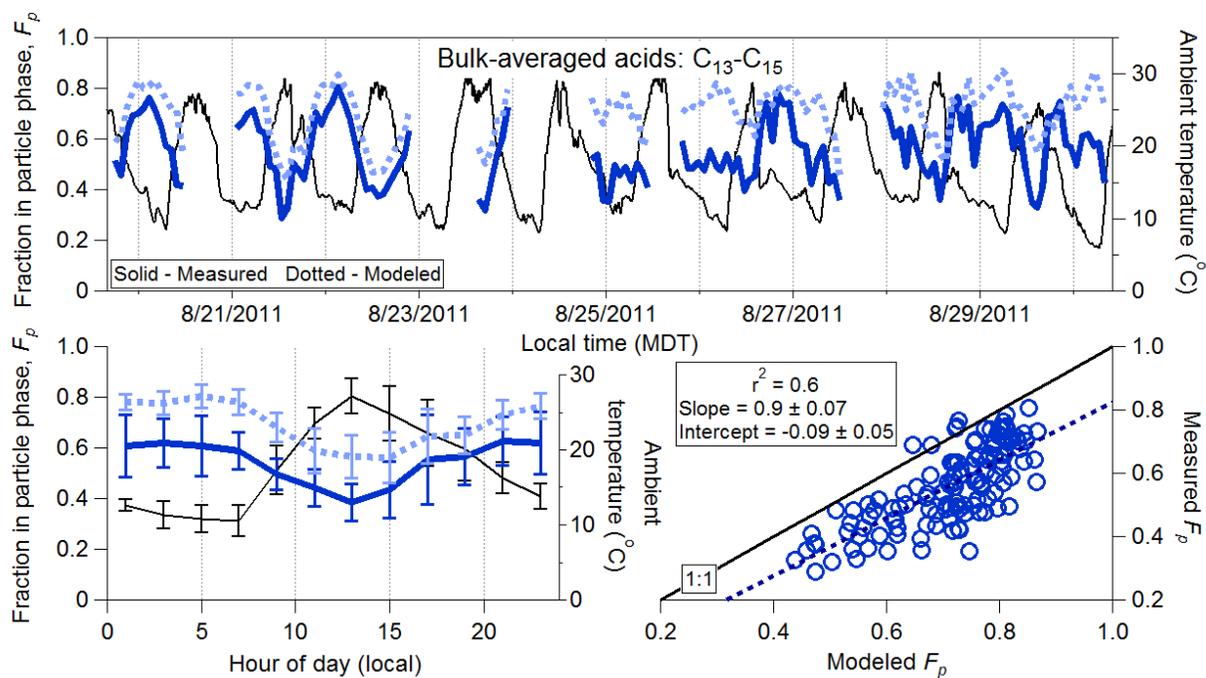


Figure S10. Time series, diurnal cycle and scatter plot of measured and modeled  $F_p$  for  $C_{13}$ - $C_{15}$  averaged bulk acids. Model uses excess oxygen as a hydroxyl group.

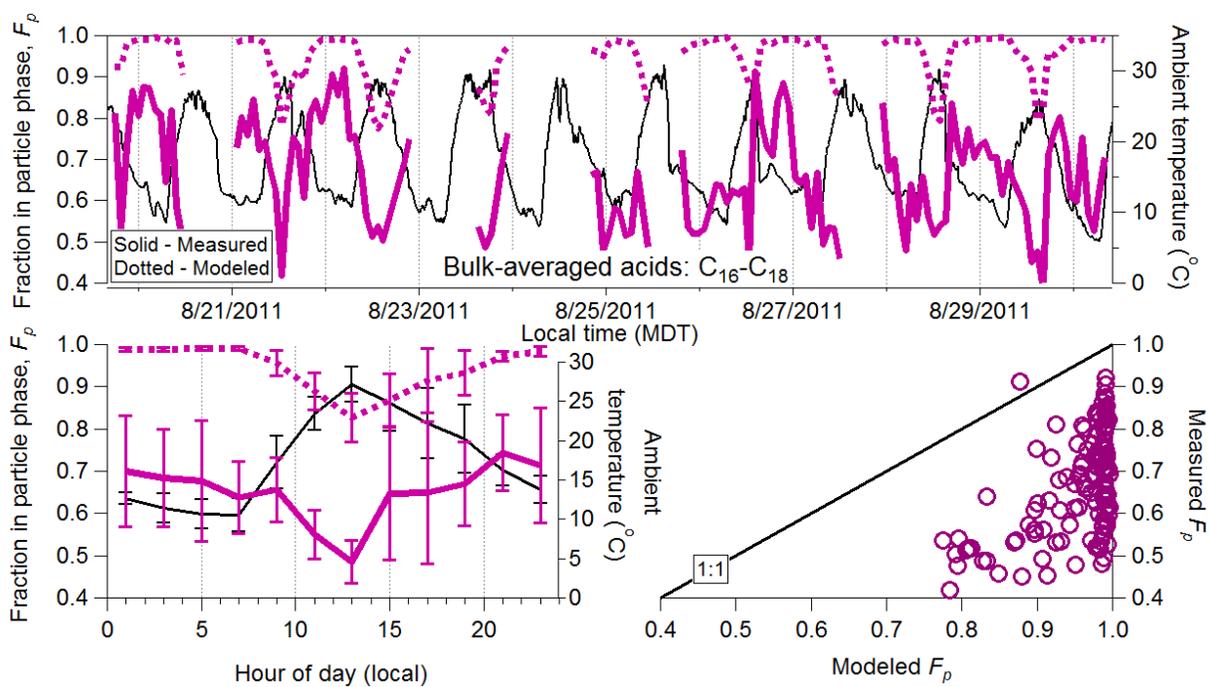


Figure S11. Time series, diurnal cycle and scatter plot of measured and modeled  $F_p$  for  $C_{16}$ - $C_{18}$  averaged bulk acids. Model uses excess oxygen as a hydroxyl group.

## 9. Model simulation of pinic acid with constant ambient temp and constant OA

To investigate the effect of changing ambient temperature and OA on phase partitioning of organic acids we performed two simulations in which we either held the ambient temperature or ambient OA constant in the model. Fig. S7 shows the observed and modeled  $F_p$  along with model results when ambient temperature is held constant of 16 °C and ambient OA is held constant at  $2.4 \mu\text{g m}^{-3}$  and for simplicity, we only show results for pinic acid. The model with changing OA and constant ambient temperature results in much smaller variations in  $F_p$ . On the other hand, the model with changing ambient temperature and constant OA shows a pronounced variation in  $F_p$  that is more similar to the observed  $F_p$ . It is interesting to note the similarity in both the modeled (with changing ambient temperature) and observed  $F_p$  when the ambient temperature is highest and with the rapid temperature decrease that follows. These results clearly indicate that temperature is the major driver of phase partitioning at this site.

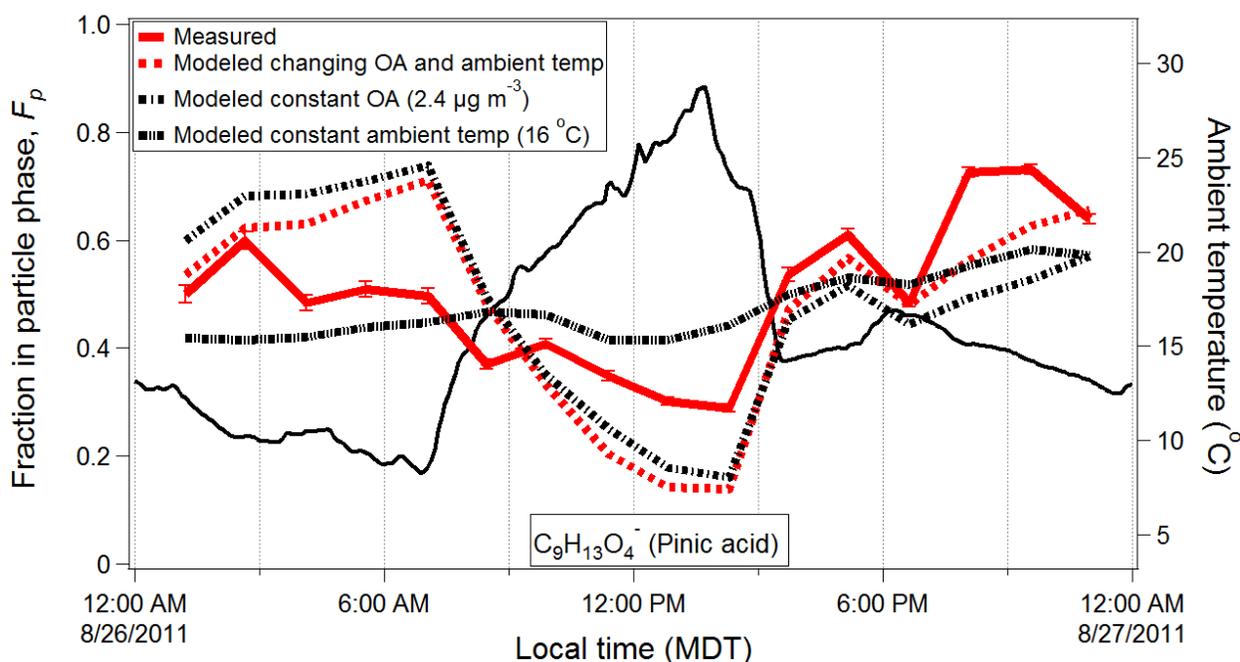


Figure S12. Measured and modeled time series of  $F_p$  for pinic acid on August 26, 2011. Model simulations are also shown with (a) changing ambient OA and temperature (b) ambient OA held constant at  $2.4 \mu\text{g m}^{-3}$ , (c) ambient temperature held constant at 16 °C.

**Table S1:**  $VP$  and  $\Delta H_{vap}$  used for phase-partitioning of alkanolic acids.  $P_v$  and  $C^*$  values are corrected for average ambient temperatures of 289 K on August 26, 2011 from that reported in the literature.

Acid	$n_C$	$P_v$ (torr)	$C^*$ ( $\mu\text{g m}^{-3}$ )	$\Delta H_{vap}$ ( $\text{kJ mol}^{-1}$ )	Ref
Methanoic	1	25.37	$6.4 \times 10^7$	46	a
		14.88	$3.78 \times 10^7$		e
		9.95	$2.53 \times 10^7$		f
Ethanoic	2	8.66	$2.9 \times 10^7$	52.3	a
		7.51	$2.49 \times 10^7$		e
		5.97	$1.98 \times 10^7$		f
Propanoic	3	2.06	$8.4 \times 10^6$	57.3	a
		1.86	$7.59 \times 10^6$		e
		1.67	$6.83 \times 10^6$		f
Butanoic	4	$3.91 \times 10^{-1}$	$1.9 \times 10^6$	63.6	a
		$4.83 \times 10^{-1}$	$2.34 \times 10^6$		e
		$4.94 \times 10^{-1}$	$2.4 \times 10^6$		f
Pentanoic	5	$1.08 \times 10^{-1}$	$6.0 \times 10^5$	62.4	a
		$1.4 \times 10^{-1}$	$7.89 \times 10^5$		e
		$1.65 \times 10^{-1}$	$9.26 \times 10^5$		f
Hexanoic	6	$2.36 \times 10^{-2}$	$1.5 \times 10^5$	73.2	a
		$3.8 \times 10^{-2}$	$2.43 \times 10^5$		e
		$5.14 \times 10^{-2}$	$3.29 \times 10^5$		f
Heptanoic	7	$7.1 \times 10^{-3}$	$5.1 \times 10^4$	72	a
		$1.18 \times 10^{-2}$	$8.41 \times 10^4$		e
		$1.84 \times 10^{-2}$	$1.32 \times 10^5$		f
Octanoic	8	$2.16 \times 10^{-3}$	$1.7 \times 10^4$	82.9	a
		$3.37 \times 10^{-3}$	$2.66 \times 10^4$		e
		$6.12 \times 10^{-3}$	$4.85 \times 10^4$		f
Nonanoic	9	$6.52 \times 10^{-4}$	$5.7 \times 10^3$	85.7	a
		$1.05 \times 10^{-3}$	$9.1 \times 10^3$		e
		$2.22 \times 10^{-3}$	$1.93 \times 10^4$		f
Decanoic	10	$1.87 \times 10^{-4}$	$1.8 \times 10^3$	101.8	b
		$3.02 \times 10^{-4}$	$2.85 \times 10^3$		e
		$7.5 \times 10^{-4}$	$7.07 \times 10^3$		f
Undecanoic	11	$6.75 \times 10^{-5}$	$6.9 \times 10^2$	93.65	a
		$1.03 \times 10^{-4}$	$1.06 \times 10^3$		e
		$3.03 \times 10^{-4}$	$3.09 \times 10^3$		f
Dodecanoic	12	$1.40 \times 10^{-5}$	$1.5 \times 10^2$	111.8	b
		$3.04 \times 10^{-5}$	$3.33 \times 10^2$		e
		$1.05 \times 10^{-4}$	$1.14 \times 10^3$		f
Tridecanoic	13	$3.73 \times 10^{-6}$	44	117.65	d
		$9.7 \times 10^{-6}$	$1.14 \times 10^2$	78.76	c
		$9.72 \times 10^{-6}$	$1.14 \times 10^2$		e
		$3.96 \times 10^{-5}$	$4.63 \times 10^2$		f

Acid	$n_c$	$P_{Li}^o$ (torr)	$C^*$ ( $\mu\text{g m}^{-3}$ )	$\Delta H_{vap}$ ( $\text{kJ mol}^{-1}$ )	Ref
Tetradecanoic	14	$8.38 \times 10^{-7}$	10	123.5	b
		$5.23 \times 10^{-6}$	65.6	80.5	c
		$3.13 \times 10^{-6}$	39		e
		$1.52 \times 10^{-5}$	$1.89 \times 10^2$		f
Pentadecanoic	15	$1.63 \times 10^{-7}$	2.2	131.8	d
		$2.02 \times 10^{-6}$	26.8	102.77	c
		$1.0 \times 10^{-6}$	13.2		e
		$5.79 \times 10^{-6}$	76.5		f
Hexadecanoic	16	$3.19 \times 10^{-8}$	$4.5 \times 10^{-1}$	140.1	b
		$9.9 \times 10^{-7}$	13.9	80.29	c
		$3.22 \times 10^{-7}$	4.59		e
		$2.23 \times 10^{-6}$	31.2		f
Heptadecanoic	17	$1.26 \times 10^{-8}$	$1.8 \times 10^{-1}$	141.6	d
		$5.52 \times 10^{-7}$	8.17	99.65	c
		$1.07 \times 10^{-7}$	1.57		e
		$8.93 \times 10^{-7}$	13.1		f
Octadecanoic	18	$4.95 \times 10^{-9}$	$7.7 \times 10^{-2}$	143.1	b
		$2 \times 10^{-7}$	3.1	97.5	c
		$3.54 \times 10^{-8}$	$5.48 \times 10^{-1}$		e
		$3.58 \times 10^{-7}$	5.55		f

a – Reaxys database (2012), b – Cappa et al. (2008), c – Chattopadhyaya and Ziemann (2005), d – linear interpolation, e – Nannoolal et al. (2008), f – Marydal and Yalkowsky (1997).

**Table S2:**  $P_v$ ,  $C^*$  and  $\Delta H_{vap}$  used for estimating phase partitioning of terpenoic acids.  $P_v$  values are for 298 K.

Acid	Elemental Comp	$P_{Li}^o$ (torr)	$C^*$ ( $\mu\text{g m}^{-3}$ )	$\Delta H_{vap}$ ( $\text{kJ mol}^{-1}$ )	Ref
OH-Glutaric	$\text{C}_5\text{H}_8\text{O}_5$	$2.65 \times 10^{-8}$	$2.1 \times 10^{-1}$	101	b,c
Terpenylic	$\text{C}_8\text{H}_{12}\text{O}_4$	$9.75 \times 10^{-7}$	9.03	42	a
Pinonic	$\text{C}_{10}\text{H}_{16}\text{O}_3$	$1.0 \times 10^{-4}$	$1 \times 10^3$	98	d,e
Pinic	$\text{C}_9\text{H}_{14}\text{O}_4$	$9.97 \times 10^{-7}$	10	109	a
OH-Pinonic	$\text{C}_{10}\text{H}_{16}\text{O}_4$	$5.7 \times 10^{-7}$	6.14	122	e,f
MBTCA	$\text{C}_8\text{H}_{12}\text{O}_6$	$9.09 \times 10^{-11}$	$1 \times 10^{-3}$	164	e,g

a – Bilde and Pandis (2001), b –  $P_v$  estimated by reducing glutaric acid  $P_v$  measured by Bilde and Pandis (2001) by  $5.7 \times 10^{-3}$  due to addition of hydroxyl group. c –  $\Delta H_{vap}$  from Salo et al. (2010) for glutaric acid. d – assumed  $P_v$  for pinonic acid similar to Muller et al. (2012). e –  $\Delta H_{vap}$  estimated using Eq. (12) of Epstein et al. (2010). f -  $P_v$  estimated by reducing pinonic acid  $P_v$  assumed by Muller et al. (2012) by  $5.7 \times 10^{-3}$  due to addition of hydroxyl group. g – assumed  $P_v$  for MBTCA similar to Muller et al. (2012).

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