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Source Apportionment of Atmospheric Fine Particulate Matter Collected at the Seney National Wildlife Refuge

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Abstract. The trends in secondary organic aerosol at a remote location are studied using atmospheric fine particulate matter samples collected at Seney National Wildlife Refuge (NWR) in Northern Michigan. Detailed organic analysis by gas chromatography-mass spectrometry (GC-MS) reveals tracers for primary anthropogenic emissions at low concentrations compared to relatively high levels of organic di- tri- and tetra-carboxylic acids thought to be indicators of secondary organic aerosols. Seasonal changes in these organic compounds are tracked using monthly composites. The concentration of aromatic and aliphatic dicarboxylic acids peak in July and taper off in the fall, which coincides with fine particle organic carbon concentration. In contrast, a chemical mass balance model used to quantify primary sources of particulate matter shows higher contributions from primary emissions in the winter. Complementing the monthly average concentrations, event-based composites of high volume samples were used to track the different species of secondary organic aerosols at the Seney NWR location. The distribution of aliphatic diacids and the aromatic di- and triacids varied across different atmospheric conditions, which suggests different precursor gases for these secondary organic aerosol components. The aliphatic diacid concentrations track with ambient concentrations of particle-phase pinonic acid. In addition, back trajectories for the 8 event-based composites are compared to the organic acid concentrations, and source regions were linked to the distribution of organic acid present in the composites.

Introduction.

Secondary organic aerosol (SOA) is formed in the atmosphere from the oxidation of volatile and semi-volatile organic precursors emitted by a variety of sources. Quantitative tracers have yet to be determined for secondary processing of aerosols, but insight into possible tracers can be gained by studying particulate matter (PM) from a location with high SOA relative to primary sources. The advantage of studying SOA produced in the natural atmosphere, as opposed to laboratory smog chambers [1-6], is that the relative distribution of SOA components under real atmospheric reaction conditions can be investigated. Since the dynamics of how anthropogenically- and biogenically-derived SOA are processed and transported in the atmosphere are not fully understood, it is very difficult to realistically simulate these processes in smog chambers. Stable end-products need to be identified which can account for these dynamic conditions in order to accurately track SOA under a variety of circumstances.

Recent advances in the measurement of high molecular weight, polymeric components of SOA have come nearer to closing the organic mass balance for SOA [7-9]. Samples collected at SOA-impacted sites have measured these oligomers and other secondary species in ambient aerosol [7,10]. However, these species, including carbonyl and multi-functional carbonyl, alcohol, and acid compounds, require more complicated derivatization techniques or instrumentation and cannot all be quantified readily by standard GC-MS techniques [3,4,7,8]. As a result, a need remains for identifying SOA tracers that can be readily incorporated into the existing framework for organic aerosol analysis by GC-MS and that can support source attribution efforts [11-16]. Aliphatic diacids and aromatic di-, tri- and tetra acids are often reported as indicators of SOA in urban atmospheres, as they can be quantified readily using standard GC-MS techniques [17-19]. However, in aerosol samples containing a mixture of both SOA and primary source emissions, the origins of these compounds have not yet been definitively identified. To address this, the present study exploits aerosol samples collected in Seney National Wildlife Refuge (NWR) from November 2001 to December 2002 to investigate the potential of these organic acids for tracking SOA using standard GC-MS techniques.

To characterize the organic aerosol at Seney NWR, two different sets of fine particulate matter (PM2.5) samples were analyzed as part of the present study. The first set of samples was collected as a supplement to the IMPROVE monitoring network. Twenty-four hour samples were collected at a frequency of 2-in-3 days to provide composites of roughly 20 filters per month. These composites were analyzed for detailed organics using GC-MS, resulting in average monthly concentrations for organic species. The second set of 24-hour, PM2.5, high-volume samples were collected every third day in a summer intensive study. These high-volume PM2.5 samples were composited into groups of 3-4 samples based upon bulk chemical composition. Compositing by month and aerosol composition allowed for a more thorough look at the impact of SOA and the distribution of potential SOA tracers without requiring analysis of single samples. The monthly composites showed seasonal changes in local sources, while the summer intensive composites provided a more detailed look at different SOA events. The contribution of unaltered primary sources was ascertained using molecular markers, which were analyzed by GC-MS [20,21]. Although the total SOA could not be directly quantified, its relative importance was estimated by calculating the organic aerosol that could not be attributed to motor vehicles, biomass burning, meat cooking, resuspended road dust, vegetative detritus, and other fossil fuel combustion. Strong correlation existed between the organic carbon not attributed to primary sources and the measured diacids. In addition, the distribution of the aliphatic and aromatic diacid indicators (in the high-volume PM2.5 composites) clustered into 3 distinct patterns, which suggested different sources for the SOA precursors (i.e. anthropogenic versus biogenic). The relationships between these potential SOA tracers and precursor sources were further supported by back trajectories.

Experimental Methods

Sampling and Chemical Analysis. Fine particulate matter samples were collected every day from November 2001 through December 2002 at the Seney NWR. Samples were collected every 2-in-3 days using an EPA Speciation Trends Network (STN) sampler by Met One and were analyzed in accordance with the EPA fine particle network by RTI (Research Triangle Park, NC). The 47mm quartz fiber filters were analyzed by RTI for elemental and organic carbon (ECOC) analysis (NIOSH 5040) by

removing a 1.5 cm square punch, leaving approximately 85 percent of the samples for further analysis. The remaining portions of these filters were composited by month for analysis of organic compounds using GC-MS techniques at the University of Wisconsin-Madison.

Supplemental measurements from co-located filters including mass, ammonium, nitrate, sodium, sulfate, aluminum, potassium, and silicon has been provided by RTI for this set of samples. Blank subtraction was not performed by RTI, so the raw data provided for field and trip blanks was averaged and subtracted from the reported values.

A high volume PM2.5 sampler built by the UW-Madison was also deployed at Seney NWR mid-June to mid-September 2002 for a summer intensive study. Sampling at 92 Lpm, 24 hour fine particle samples were collected on pre-baked 90mm quartz fiber filters (Pall-Life Sciences). A portion of each filter was analyzed for ECOC by thermal evolution and combustion (NIOSH 5040), and for sulfate, nitrate, ammonium and chloride by ion chromatography at the University of Wisconsin-Madison. Based on the results of the bulk chemistry analysis, one third of each of up to four filters were composited for GC-MS analysis, except for the filter from July 15, 2002 which was analyzed separately.

The organic analysis method used for both the monthly composites and the high-volume PM2.5 composites has been described previously [22]; however, modifications were made specifically for this study. The 47mm quartz filters from RTI were composited by month (approximately 20 samples per month), spiked with internal standard and extracted by sonication, twice with dicholormethane (DCM) and twice with methanol. These extracts were combined and then concentrated first by rotory evaporation, and then under nitrogen. Extractions were conducted in two sets: November 2001-August 2002 and September – December 2002. Due to matrix effects associated with the high filter blanks (contamination from filter cassettes is discussed in Appendix A), the GC-MS total ion chromatograph for the monthly composites was dominated by a large hump of synthetic organic contaminants. The contamination was very different from the organic complex mixture present in atmospheric aerosols. The contaminant was mitigated, in part, for the second set of monthly composite extractions by filtering the September 2002 through December 2002 extracts through a 0.2µm Acrodisc PTFE syringe filter

(Pall Life Sciences), which reduced the insoluble contaminants but not the target analytes. An extended GC run time was used for both sets of monthly composites to minimize the instrument noise associated with the contamination. Recovery of target analytes was monitored by deuterated internal standards. The summer intensive samples were composited based upon bulk chemical composition and then spiked with internal standard. The composites were soxhlet extracted first with DCM, then with methanol and then concentrated by rotary evaporation and nitrogen blow-down.

The internal standard was also included in the quantification standards that were run at three dilutions dispersed through each set of sample runs on the GC-MS. Calibration curves for each compound in the standards were calculated using the internal standard that most closely mimics the compound based upon structure, polarity, molecular weight and retention time. Compounds in the samples are quantified using the response curves calculated from the quantification standard and the same internal standard reference. Compounds that are not represented in the quantification standards are calculated by estimating the response curve from the compound in the standard that is most similar in structure, polarity, molecular weight and retention time. Ambient concentrations for each individual compound quantified in both the monthly STN composites and the summer intensive study are in Appendix B.

In order to quantitatively apportion the contribution from major primary emission sources to ambient organic carbon concentrations in Seney NWR, a chemical mass balance (CMB) model was used to apportion source contribution for the monthly STN composites [20]. The detailed chemical profiles for non-catalyst gasoline-powered motor vehicles and medium-duty diesel trucks were used to approximate the contribution from on-road and off-road gasoline-powered motor vehicles and diesel vehicles [13,23]. To apportion meat charbroiling, Schauer et al.'s (1999) profile was used [12]. An average profile was calculated for pine and oak wood smoke emissions [24]. Finally, a road dust profile was averaged from 6 samples reported for southern California [25]. Although these profiles were not generated in the same region as the ambient samples, they are used to illustrate that the primary source contributions in the study are very small. Development of a local source profile is clearly not warranted as can be seen from the results presented below.

Back trajectories were calculated for all of the summer intensive sampling days using the HYSPLIT program from NOAA [26]. Four 96-hour back trajectories, every 6 hours, were modeled for each midnight-to-midnight sampling day. The complete set of back trajectories has been included in Appendix C.

Results and Discussion

Monthly composites. The bulk chemistry results from RTI for the 2-in-3 day samples have been averaged by month and plotted in Figure 1 with a conversion factor of 1.7 to convert organic carbon to organic compound mass. Significant uncertainty is associated with this organic carbon conversion factor [27,28]. Turpin and Lim recommend a value of 1.6 ± 0.2 for urban aerosols and 2.1 ± 0.2 for non-urban aerosols [27], while Russell found that FTIR measurements of northeastern Asian and Caribbean aerosol to have 90% of ratios ranging from 1.2 to 1.6 [28]. To address the concerns raised by both of these studies, a ratio of 1.7 was chosen to account for any impact of non-urban aerosols. Very low concentrations of organic fine particulate matter was present in the winter and spring months. In Table 1, uncertainties of the monthly averages are included with organic and elemental carbon concentrations. The uncertainty for the STN monitors is based upon the monthly average standard error of the blanks. For March 2002, the organic carbon concentration is not statistically different from zero for the composite used in this study.

The summer months (June-September) have the largest monthly average concentration of organic mass with a corresponding, though not as large, increase in sulfate concentrations. The elemental carbon monthly averages are generally quite low with June being the highest at 0.27 $\mu g/m^3$ and no measurable elemental carbon in August after blank subtraction. There is no seasonal trend for the ammonium concentrations, however, nitrate concentrations are highest in the winter and lowest in July through October.

Figures 2 and 3 show the select primary source molecular markers and organic acids which are present in the monthly composites. A complete table of quantified compounds is included in Appendix B. The line marks the detection limit for a given class of compounds. There is good agreement

between the November and December 2001 concentrations and the November and December 2002 concentrations for PAH and levoglucosan, considering that the measured concentrations are close to the detection limit. Seasonal trends are evident in the different compound classes. For example, PAH concentrations are higher in the winter months, corresponding to detection of hopanes and steranes (Figure 2), all of which are emited by motor vehicles, fuel oil combustion and low temperature coal combustion [13,23,29,30]. Hopanes and steranes are not detected in the November and December 2002 samples, however, if the ratio of PAH to hopanes and steranes was considered similar for all these months, then the levels in 2002 would be below the detection limit. Although it may be that different, combustion sources are dominating the PAH concentrations in late 2002 and 2001. The biomass burning marker, levoglucosan, is also higher in the November to January samples (Figure 2). There is also a second, smaller seasonal peak for levoglucosan in the summer months. This seasonal fluctuation in levoglucosan corresponds, in part, to the trends seen in the monthly resin acid concentrations (dehydroabietic acid and 7-oxodehydroabietic acid), which are present in emissions from wood smoke as well as tire wear. In general, the primary emission markers are highest in the winter months (November to February), although these are still present in very low concentrations compared to past studies [19,31]. The highest concentration of resolvable organics and total organic carbon, is in the summer months, especially July.

The highest concentrations for all the organic acids is measured in the summer months (July-September), peaking in July (Figure 3). The higher molecular weight alkanoic acids parallel the silicon and aluminum monthly average concentrations; all three are components of soil dust (Figure 3). Monthly averages of fine particulate Aluminum and Silicon concentrations have different relationships when plotted against the sum of even carbon number alkanoic acids, but both are roughly correlated (Figure 4). The idea that aromatic and aliphatic di- and tri-acids are indicators of SOA is supported in this data set by the lack of primary emission markers present in the summer composites and good agreement with pinonic acid monthly variations (Figures 2 & 3). Pinonic acid is known to be a

secondary, particle-phase, product of pinene, which is emitted from plants, particularly conifers [32]. This is a fairly quick reaction, and has been documented in reaction chambers experiments [33].

A chemical mass balance model [20] was run to quantitate the impact of predominant primary sources including motor vehicles, biomass burning, meat charbroiling, and soil dust on organic carbon in Seney NWR (Figure 5 & Table 2). The November 2001 and January 2002 monthly composites have the most organic carbon apportioned to primary emissions, with the highest contributions from meat charbroiling, non-catalyst gasoline exhaust, and diesel exhaust and minimal contributions (<0.04 $\mu g/m^3$) from road dust and wood smoke. The contribution from diesel exhaust varies throughout the year, but never exceeds 0.17 $\mu g/m^3$. The large increase in organic carbon for the summer months (June-September), however, cannot be accounted for by the predominant primary sources of organic aerosol. In addition, an exploratory analysis of the GC-MS results provided no evidence of additional primary sources not included in this model. This gives further credence to the idea of SOA as a major source in Seney NWR in the summer season.

The source apportionment result that appears erroneous in the model is meat charbroiling. The resulting OC contribution from meat charbroiling November 2001 and January 2002 comprises over 200% and 50% of the measured organic carbon, respectively. The cholesterol and hopane concentrations in the samples are not far above the detection limit, which increases the uncertainty, but this should not cause such a large over-prediction for these months. The minimum detection limits (MDL) for cholesterol and the hopanes were put into the model, resulting in an OC contribution for meat charbroiling and non-catalyst gasoline-powered motor vehicle exhaust of less than 0.37 and 0.15 $\mu g/m^3$, respectively. Due to the fact that it is unreasonable that all of the OC at this site is from meat charbroiling in November 2001, it would appear that an additional source of cholesterol is impacting the Seney NWR samples. The Seney NWR sampling site is located in a large wetland, so any emissions of sterols from aquatic organisms could potentially impact the cholesterol concentration seen in the monthly composites [34]. Nonetheless, the impact of meat cooking, or this additional source of

cholesterol, is not the predominant source or organic carbon in the spring, summer, or early fall monthly averages.

Summer intensive study. In order to study these SOA-indicator acid species in more detail, a high-volume PM2.5 sampler was deployed for summer intensive sampling in 2002. Daily samples were composited for GC-MS analysis based upon the type of particulate matter event, as determined by bulk chemistry (Figure 6a). This compositing format results in a non-chronological grouping of sampling days sorted first by bulk ionic loadings (sulfate, nitrate and ammonium) and then organic mass in the order shown in Fig 6a. The September sampling days in composite 1 are very distinctive, with high sulfate and ammonium concentrations compared to the rest of the sampling days. The organic mass concentration is not as variable as the bulk ion concentrations, if one excludes the July 15th event. The July 15th sample has a very distinctive bulk profile with high organic mass and was therefore analyzed individually.

In Figure 6b, primary emission tracers for the six composites and July 15th are shown. As seen with the monthly STN summer composites, these tracers are present at very low concentrations. Composites 1-3 and 7 are very similar with very low levels of the primary tracers. Composites 4-6 have higher n-alkanoic acids, and July 15th has a higher levoglucosan and n-alkane concentrations than the other composites. A complete table of the compounds quantified in the summer intensive samples is included in Appendix B.

The acid concentrations for these composites tell a more interesting story (Figure 7). As with the primary emission tracers, the composites can be grouped by their organic acid profile. Composites 1-3 , which are the periods of higher sulfate, all have a similar pattern of acid concentration, with significant aromatic acids, aliphatic diacids and pinonic acid. Composite 1 has the highest aromatic acid and sulfate concentrations of the three. Composite 2 has similar concentrations as composite 1 in Fig 7b and similar levels as composite 3 for the aromatic acids, while composite 3 has the highest pinonic acid within this set. These differences, however, are minimal when comparing this set to composites 4-6. The second set has higher concentrations and a different pattern for the aromatic acids, as compared to

composites 1-3. Composites 4-6, which are from a period of low sulfate, have higher concentrations for 1,4 and 1,3 benzenedicarboxylic acid and 1,2,4-benzenetricarboxylic acid. The most obvious difference, however, is the lack of detectable aliphatic diacids and pinonic acid in composites 4-6. This indicates a difference in emission sources or processing for these 2 sets of sampling events.

Composite 7 has no aromatic acids above the MDL, but has the second highest concentration for pinonic acid. The July 15th sample also has low aromatic acid concentration, and high concentrations for the aliphatic diacids and pinonic acid. Thus, composite 7 and the July 15th sample have a similar pattern for the organic acid species (Figure 7b), but not the primary emission species (Figure 6b).

To see if the differences in the organic acid concentration patterns could be linked to the aerosol source region, back trajectories were done for all the summer intensive sampling days using NOAA's HYSPLIT program [26]. The days have been grouped by composite number, and the 96-hour back trajectory beginning at noon is shown for each day. The trajectories start at 200m and are bounded in the north by the 55° line of latitude. Four trajectories (starting every 6th hour) for each individual day are included in Appendix C. The trajectories, grouped by composite, are shown in Figure 8. In Composites 1-3, although the source regions are not identical, most of the samples could be characterized as having residence time in the industrial/urban centers of the southeastern Midwest (US) and eastern Canada. These samples had higher ionic species including sulfate, and significant contribution from all three types of organic acids in Figure 7 (aromatic, aliphatic diacids, and pinonic acid), but little detectable primary emission tracers (Fig 6). This suggests that the source of the SOA precursors is urban plumes rich in SO_2.

The next set, composites 4-6, can be characterized as having source regions in the northwestern Midwest and central Canada. Although the noon trajectories for sampling days 8/14 and 8/17 appear to be closer to composite 1 than composite 5, in traveling through the urban Chicago area, the other 3 trajectories for the day show significant dilution of these air parcels with upper Midwestern air (Appendix C). These 3 composites (4-6) experienced much less impact from large urban centers, and were more diluted with air originating from north-central Canada. These composites were higher in

alkanoic acids and aromatic acids, but aliphatic diacids and pinonic acid were not detected. The sulfate and ammonium concentrations were also lower for these composites than composites 1-3. Ammonium concentration tracking with sulfate and nitrate is consistent with the idea that increased sulfate and nitrate in the aerosol as secondary products from combustion emissions would react with ammonia in the atmosphere and increase the particle phase ammonium.

Composite 7 had lower sulfate, nitrate, and ammonium concentrations and the back trajectories in Figure 7 confirm remote, north-central Canadian source regions for the air parcels. The uniqueness of the high organic mass concentrations in Figure 5 for July 15th is echoed in the very short back trajectory for this day; the July 15th air mass was very stagnant (Figure 7). Limited primary emission tracers can be measured for this day, with the possible exception of the wood smoke marker, levoglucosan. With pinonic acid and aliphatic diacid concentrations both relatively high and sulfate and aromatic acids quite low for July 15th and Composite 7, the notion is supported that both pinonic acid and aliphatic acids are from the oxidation of biogenic volatile organic carbon.

Overall, the combination of the monthly composites, the event-based composites, and the back trajectories serve to illustrate that the aerosol composition in remote regions is greatly impacted by long-term transport and atmospheric processing, especially in the summer months. Several important factors emerge in determining the characteristics of SOA in a given sample including, air mass source region, transport time, meteorological conditions, sulfate and bulk ion concentration in the aerosol, and SOA-precursor source. By sampling at a site with minimal impact from local primary emissions, these variables can be tracked in a natural environment and compared to the SOA acid species present in the fine particulate matter samples. The monthly composites illustrated the minimal impact of local primary sources on the increased organic carbon concentrations in the summer months and provided background information on seasonal trends in organic fine particulate matter. The summer intensive composites allowed an investigation into how factors such as air mass source region and bulk chemistry impact or relate to secondary organic acid composition. The PM2.5 high-volume summer intensive composites which sampled air masses having residence time in the urban/industrial southeastern

Midwest (USA) and eastern Cananda (composites 1-3) had higher concentrations of ionic species including sulfate and significant concentrations of aliphatic diacids, pinonic acid, and aromatic di-, tri-, and tetra-acids. This combination of sulfate and aromatic acids from urban plumes, with pinonic acid from biogenic VOC indicates a mixed SOA precursor profile. In contrast, summer intensive composites originating locally or from central Canada (composite 7 & July 15th) did not contain measurable aromatic acids, but had significant aliphatic diacids and pinonic acid, which suggests SOA from primarily biogenic precursors. Thus effective tracking of the impact of SOA on organic carbon concentration in fine particulate matter must include multiple organic species in order to truly account for the anthropogenic and biogenic components of SOA.

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Table 1. Monthly average fine particle elemental carbon (EC) and organic carbon (OC) concentrations at the Seney National Wildlife Refuge.

	EC ($\mu g\ m^{-3}$)	EC Uncertainty ($\mu g\ m^{-3}$)	OC ($\mu g\ m^{-3}$)	OC Uncertainty ($\mu g\ m^{-3}$)
November 2001	0.15	0.03	0.75	0.10
December 2001	0.07	0.02	0.38	0.09
January 2002	0.11	0.02	0.53	0.09
February 2002	0.17	0.02	0.32	0.09
March 2002	0.13	0.02	0.10	0.09
April 2002	0.07	0.02	0.58	0.09
May 2002	0.15	0.02	0.63	0.08
June 2002	0.27	0.02	2.44	0.09
July 2002	0.10	0.02	3.20	0.09
August 2002	0.00	0.02	1.70	0.08
September 2002	0.07	0.02	2.68	0.09
October 2002	0.10	0.02	0.91	0.08
November 2002	0.03	0.02	0.59	0.09
December 2002	0.10	0.02	0.67	0.09

Table 2. Source contributions to monthly average fine particulate organic carbon concentrations at Seney National Wildlife Refuge.

	Wood smoke[a]	Gasoline-powered motor vehicle	Diesel vehicle	Meat charbroiling[b]	Road dust	Total OC sources	Measured OC in µg/m^3
November 2001	0.011 ± 0.006	0.60 ± 0.22	0.085 ± 0.024	1.48 ± 0.38	0.034 ± 0.007	2.21 ± 0.45	0.75 ± 0.10
December 2001	0.007 ± 0.002	0.00 ± 0.12	0.046 ± 0.017	0.00 ± 0.22	0.008 ± 0.002	0.06 ± 0.25	0.38 ± 0.09
January 2002	0.008 ± 0.002	0.16 ± 0.13	0.071 ± 0.021	0.37 ± 0.24	0.010 ± 0.003	0.62 ± 0.27	0.53 ± 0.09
Febuary 2002	0.000 ± 0.001	0.00 ± 0.12	0.110 ± 0.027	0.00 ± 0.22	0.012 ± 0.003	0.12 ± 0.26	0.32 ± 0.09
March 2002	0.000 ± 0.001	0.00 ± 0.12	0.081 ± 0.022	0.00 ± 0.22	0.015 ± 0.004	0.10 ± 0.25	0.10 ± 0.09
April 2002	0.000 ± 0.001	0.00 ± 0.12	0.042 ± 0.017	0.00 ± 0.22	0.044 ± 0.009	0.09 ± 0.25	0.58 ± 0.09
May 2002	0.000 ± 0.001	0.00 ± 0.12	0.096 ± 0.024	0.00 ± 0.22	0.046 ± 0.009	0.14 ± 0.26	0.63 ± 0.08
June 2002	0.002 ± 0.001	0.00 ± 0.12	0.169 ± 0.037	0.00 ± 0.23	0.041 ± 0.008	0.21 ± 0.26	2.44 ± 0.09
July 2002	0.006 ± 0.002	0.00 ± 0.12	0.059 ± 0.019	0.00 ± 0.22	0.079 ± 0.016	0.14 ± 0.26	3.20 ± 0.09
August 2002	0.002 ± 0.001	0.11 ± 0.13	0.000 ± 0.014	0.54 ± 0.25	0.006 ± 0.003	0.67 ± 0.28	1.70 ± 0.08
September 2002	0.003 ± 0.002	0.00 ± 0.13	0.046 ± 0.018	0.47 ± 0.24	0.013 ± 0.004	0.53 ± 0.28	2.68 ± 0.09
October 2002	0.000 ± 0.000	0.00 ± 0.12	0.066 ± 0.020	0.00 ± 0.19	0.011 ± 0.003	0.08 ± 0.23	0.91 ± 0.08
November 2002	0.011 ± 0.006	0.00 ± 0.12	0.021 ± 0.015	0.00 ± 0.19	0.007 ± 0.002	0.04 ± 0.22	0.59 ± 0.09
December 2002	0.011 ± 0.006	0.00 ± 0.12	0.066 ± 0.020	0.00 ± 0.21	0.008 ± 0.003	0.09 ± 0.24	0.67 ± 0.09

[a] Uncertainty is the standard error reported by the chemical mass balance model (CMB vs. 8).
[b] The contributions from meat charbroiling likely include organic carbon from wetland emissions that also contain the source tracers for meat smoke; this is potentially causing a significant positive bias.

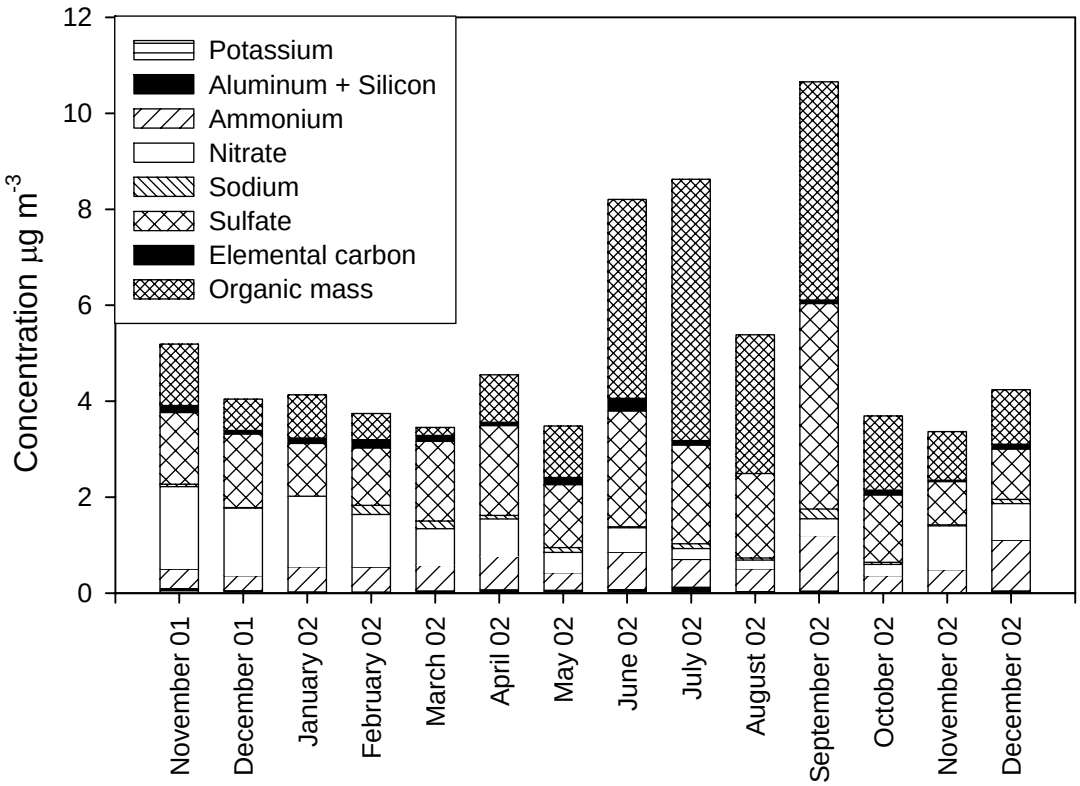

Figure 1 Major species contribution to the monthly average fine particle concentrations at Seney National Wildlife Refuge.

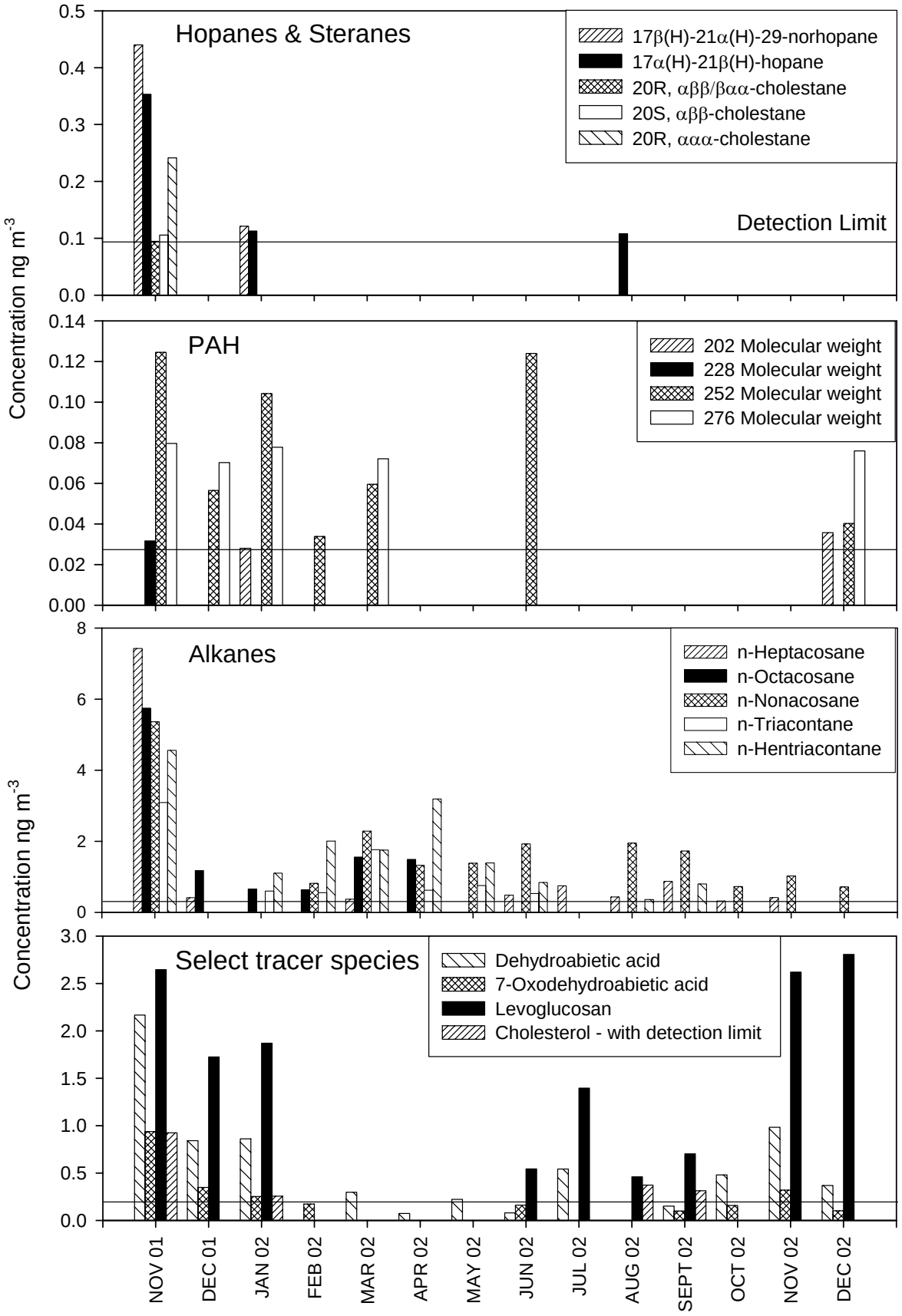

Figure 2 Monthly average fine particle concentrations of select organic primary emission molecular markers.

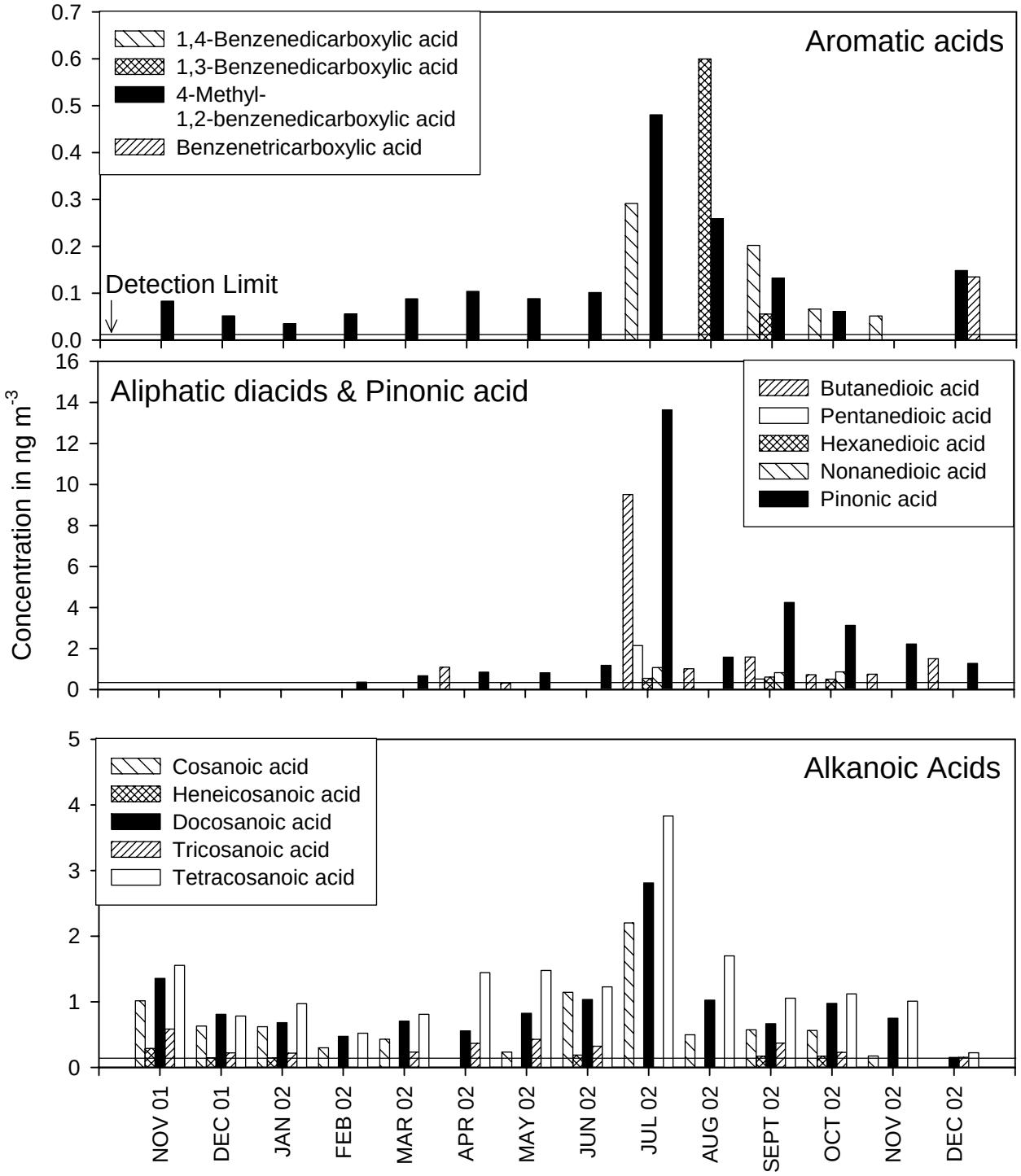

Figure 3. Monthly average fine particle concentrations of organic acids.

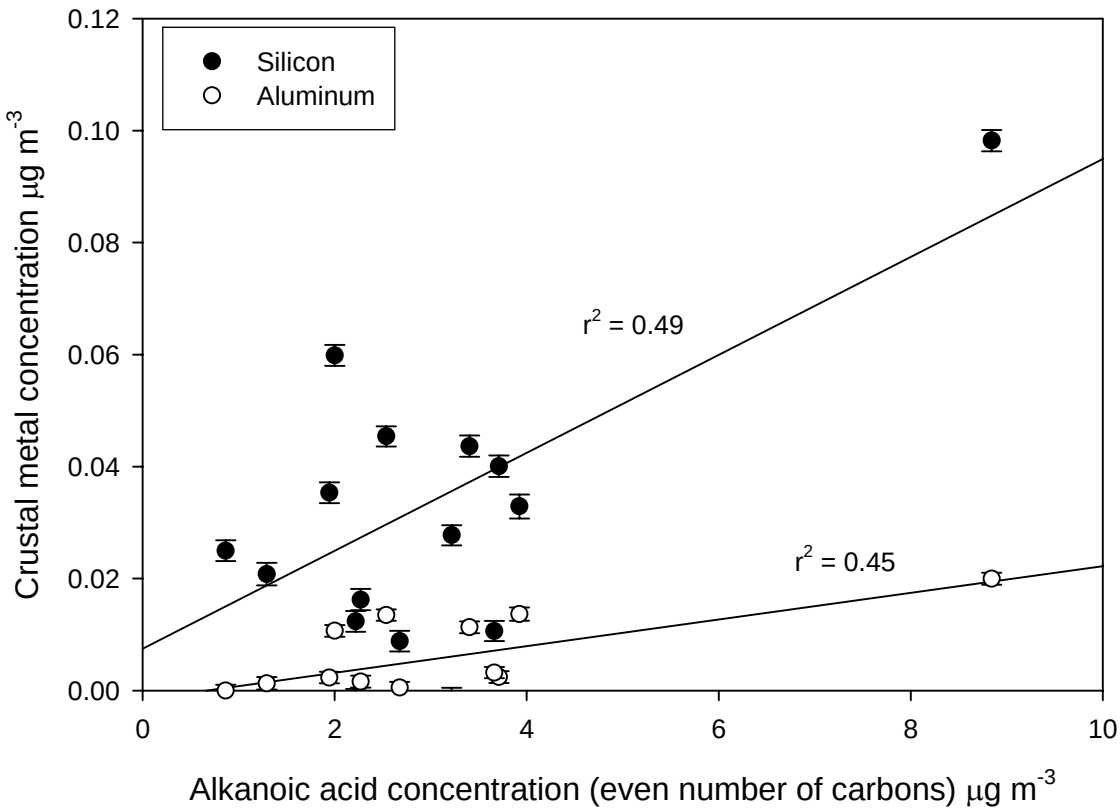

Figure 4. Correlation of n-alkanoic acids with Aluminum and Silicon in fine particles.

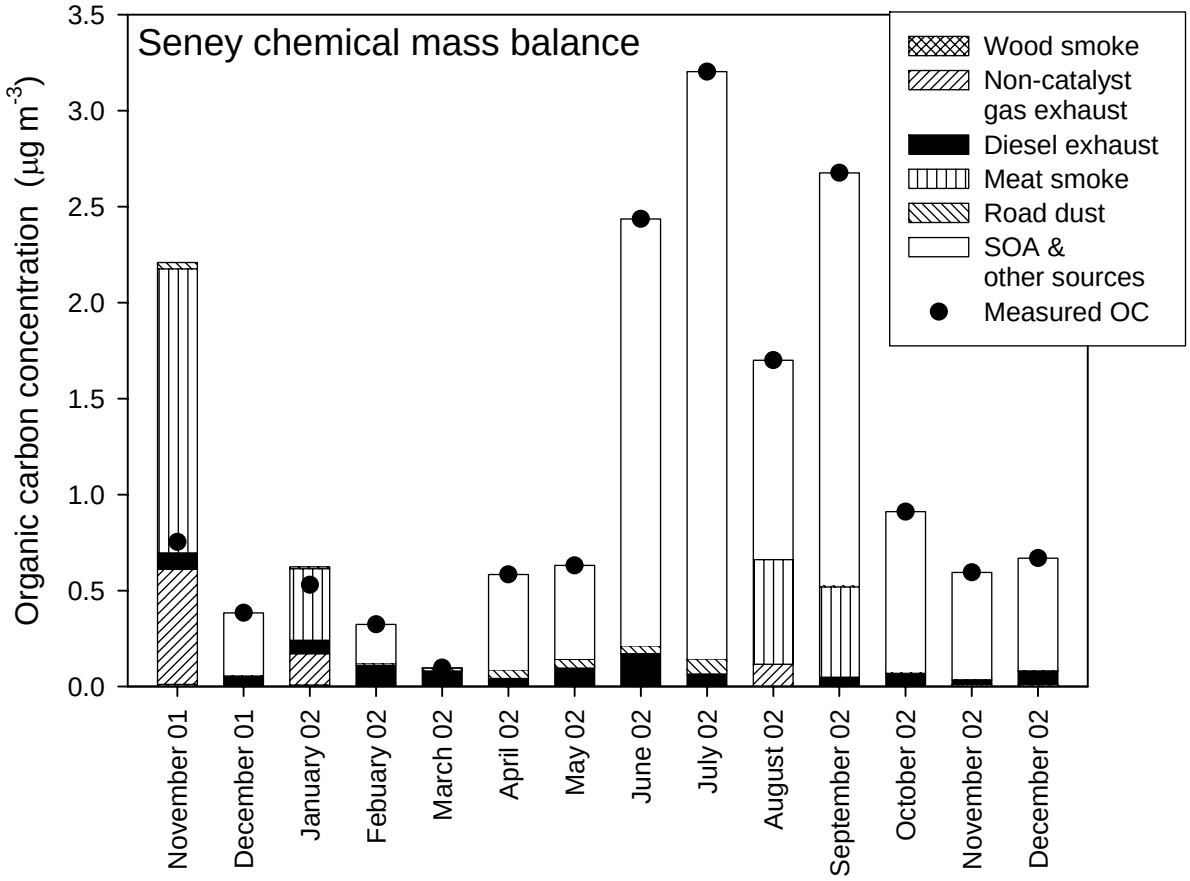

Figure 5. Source contribution to monthly average fine particulate organic carbon concentrations as determined by a molecular marker CMB model. The contributions from meat charbroiling likely include organic carbon from wetland emissions that also contain the source tracers for meat smoke; this is potentially causing a significant positive bias.

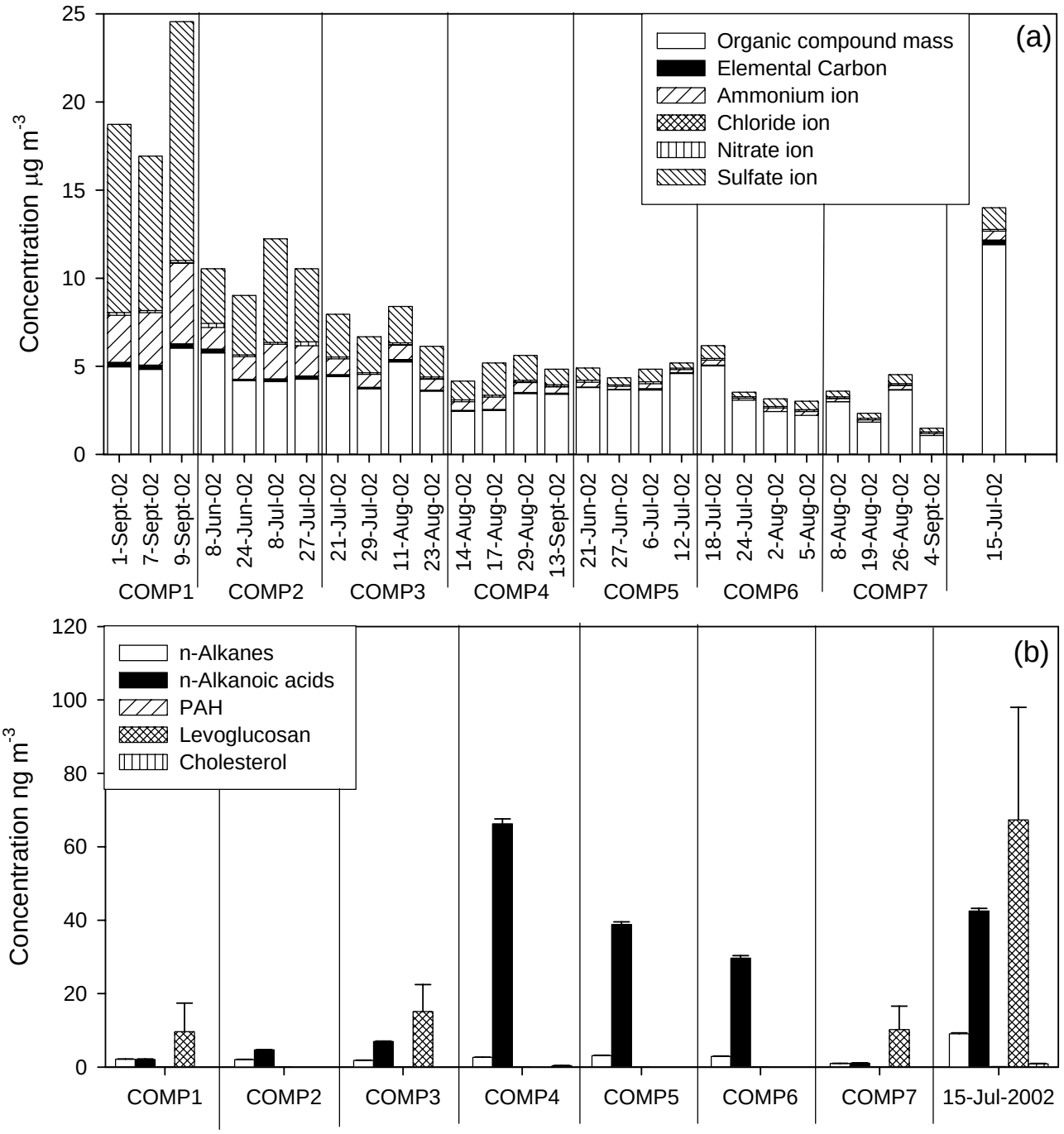

Figure 6. Concentrations of fine particulate matter collected in the Summer, 2002 at Seney National Wildlife Refuge: a) major particulate matter components, (b) tracers for primary emission sources.

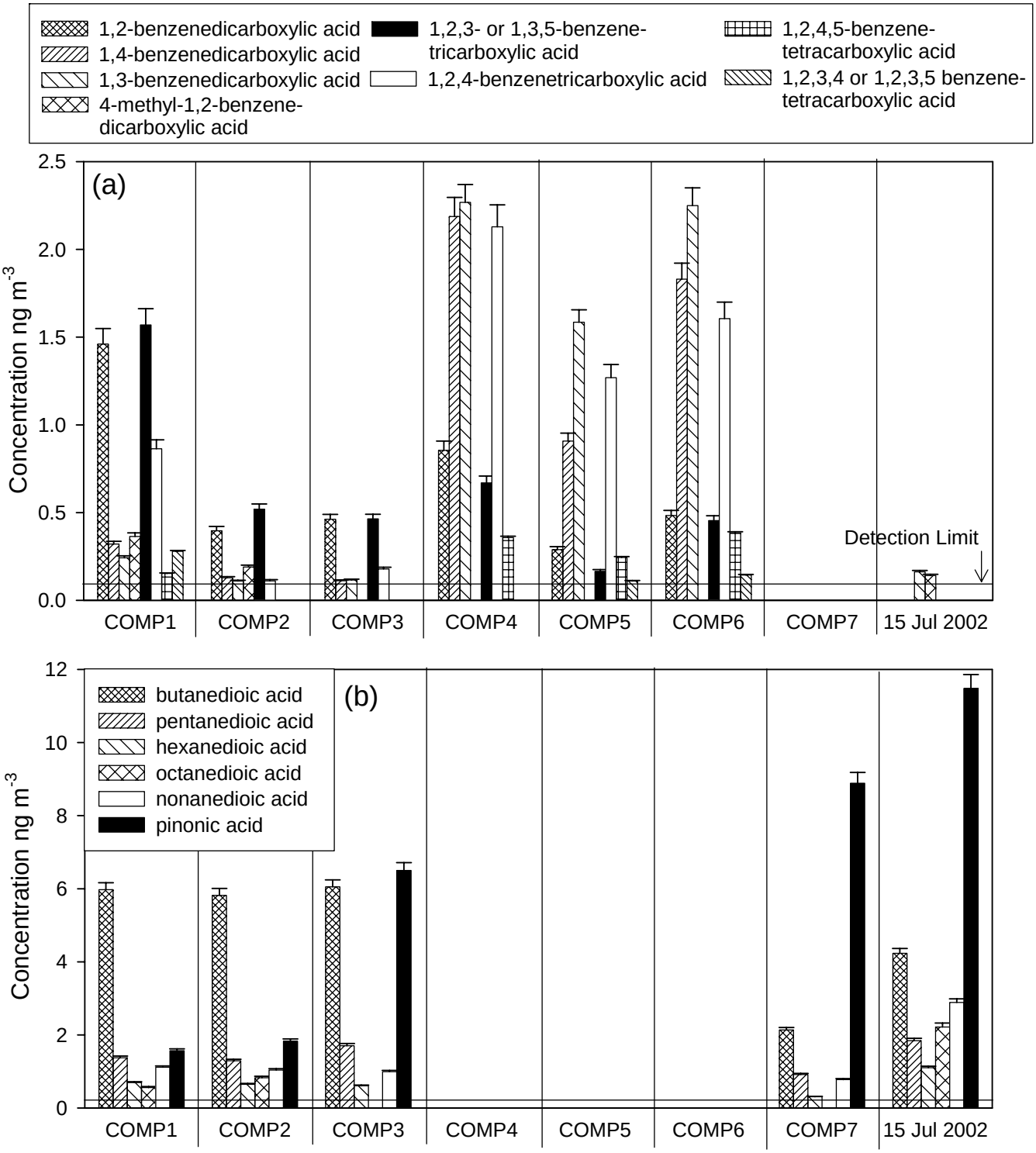

Figure 7. Fine particle concentrations of organic acids in sample composites collected at Seney National Wildlife Refuge. See Figure 6 for sampling dates of each composite.

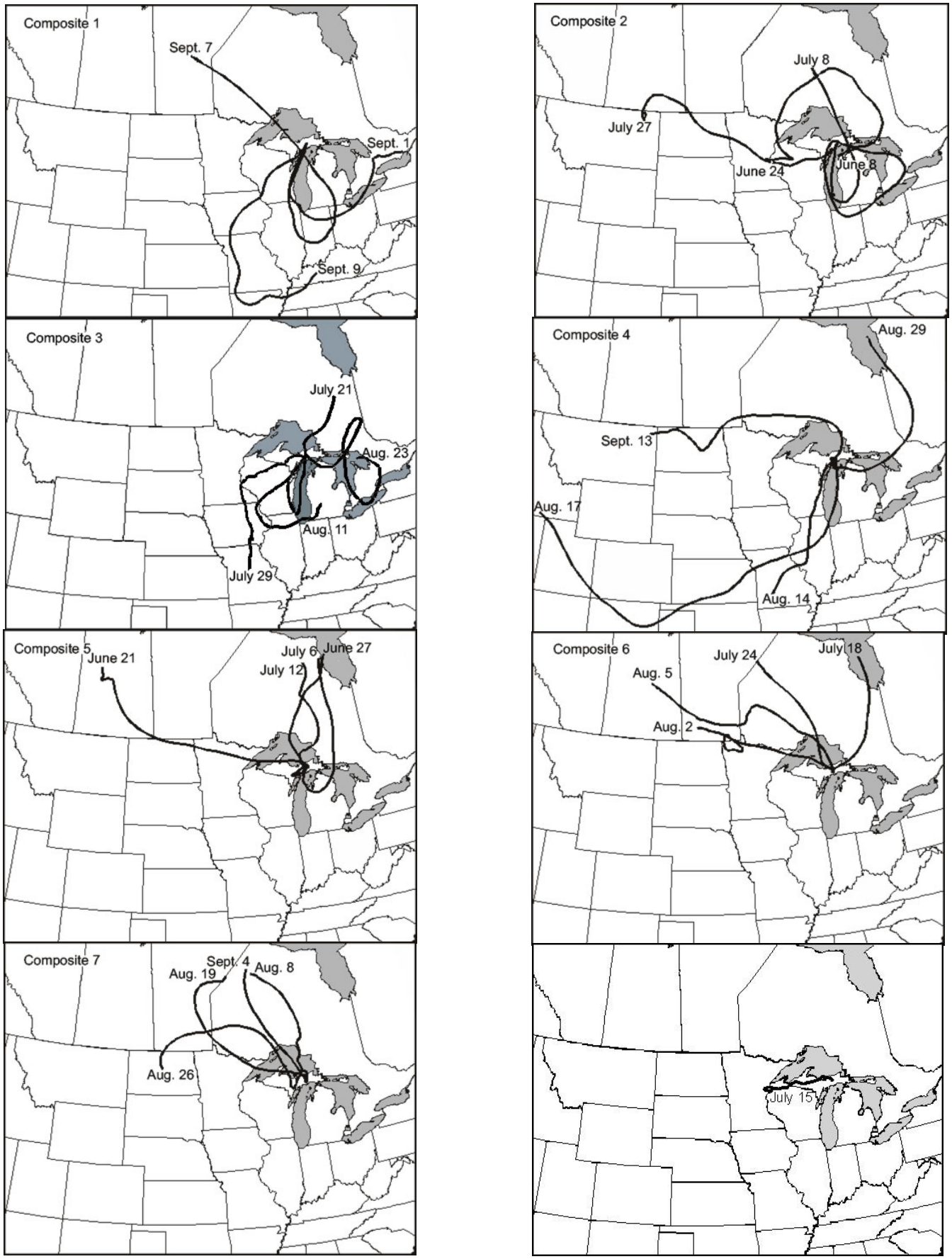

Figure 8. Back trajectories of sampling days used for composites collected during the Summer, 2002 at Seney National Wildlife Refuge.