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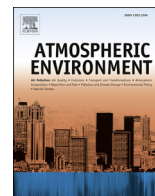
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Retrospective source attribution for source-oriented sampling



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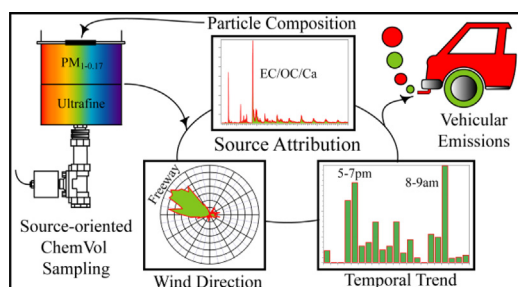
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HIGHLIGHTS

- Ambient size-segregated, source-oriented PM samples collected in real-time.
- Retrospective source attribution analyses performed to confirm sources sampled.
- Particle composition, site–source relation, wind data and temporal patterns correlated.
- Vehicles, cooking, residential heating and regional background successfully sampled.
- Results further substantiate validity of source-oriented sampling technique.

GRAPHICAL ABSTRACT



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ABSTRACT

Previous work successfully implemented a novel system that uses a single particle mass spectrometer to conditionally sample size-segregated, source-oriented particles from the ambient atmosphere in real-time. The underlying hypothesis is that the composition of individual particles is a metric of particle source and thus sampling particles based on composition should be synonymous with sampling based on source. System operation relies on real-time pattern recognition to control the actuation of different ChemVol samplers, where each ChemVol is associated with a unique composition signature. In the current work, a synthesis of data collected during these studies is used in retrospect to reconcile the actual source combinations contributing to the particles collected by each ChemVol. Source attribution is based on correlations between ChemVol sampling periods and coincident wind direction and temporal emissions patterns, coupled to knowledge of single particle composition and surrounding sources. Residential and commercial cooking, vehicular emissions, residential heating and highly processed regional background PM were identified as the major sources. Results show that real-time patterns in single particle mixing state correctly identified specific sources and that these sources were successfully separated into different ChemVols for both summer and winter seasons.

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1. Introduction

Epidemiological and toxicological studies have consistently associated exposure to air pollution with numerous adverse pulmonary and cardiovascular health impacts. Results from these studies have motivated local, state and federal agencies to adopt policies, such as the US EPA's National Ambient Air Quality Standards, to either regulate or mitigate these effects. The application of these policies changes the emissions landscape. Air quality accountability research is concerned with studying this new state of emissions to evaluate the impact of these regulations or efficacy of the mitigation strategies. This is the current state of air quality science and the research being presented here falls at the nexus of continuing to study the primary effects of air pollution while also evaluating the suitability of current regulatory paradigms and practices. More specifically, this work addresses the health effects of air pollution with the aim of identifying whether different sources elicit differential toxicity. The ultimate goal is to evaluate the viability of source oriented, or risk-based, emissions regulations.

In previous work (Bein et al., 2009), a novel system that uses single particle mass spectrometry to conditionally sample source-oriented particulate matter (PM) from the ambient atmosphere in real-time was designed and successfully deployed in two separate field studies conducted in Fresno, CA, during summer 2008 (S08) and winter 2009 (W09). Briefly, a single particle mass spectrometer (RSMS) (Bein et al., 2005) is used in a pre-study to characterize the temporal dynamics in the mixing state of the atmosphere and determine the types of particles observed, their observational frequency, the types of particle combinations observed, the temporal patterns in these observations and whether these patterns are stable enough in time for source-oriented samples to be collected. Based on these data, the prevailing particle types or combinations of particle types are assigned to each of 10 ChemVol (CV) samplers (Demokritou et al., 2002), which are high flow rate, impaction-based samplers. The size fractions collected during these experiments were ultrafine (UF; $D_p < 170$ nm) and submicron fine (SMF; $170 < D_p < 1000$ nm).

During the CV sampling phase of the experiments, RSMS particle composition observations are used in combination with various pattern recognition and sampling algorithms (Bein et al., 2009), as well as data collected during the pre-study, to control in real-time which CV samples so that each CV represents a unique particle composition, or combination of particle compositions. The system is operated for several weeks until enough PM has been collected in each of the CVs for subsequent toxicological studies and chemical characterization. The hypothesis here is that particle composition is generally an indicator of particle source and different sources typically emit particles with different compositions so that collecting particles based on composition should be synonymous with collecting particles based on their source. However, as a matter of integrity and to further substantiate the technique, retrospective source attribution analyses are necessary to (a) demonstrate that the particle compositions used to control the sampling algorithms were actually successful in separating different sources and source combinations into different CVs and (b) elucidate the specific sources contributing to the PM collected by each CV.

These objectives are achieved using a synthesis of data collected during these experiments to retrospectively reconcile the source inputs to each CV. Source attribution is based on correlations between CV sampling times and predominant wind directions coupled to knowledge of single particle composition and the geospatial distribution and activity patterns of surrounding sources. These methods are presented in the next section and individual CV

characteristics are discussed in the section after.

2. Methodology

In the source attribution efforts that follow, a synthesis of (a) single particle composition, (b) knowledge of the geospatial distribution of local and regional sources relative to the sampling site, (c) correlations between CV sampling periods and wind direction, (d) temporal trends in the activation and sampling times of individual CVs, (e) temporal patterns in certain emissions, and (f) compositional changes due to atmospheric processing are used to reconcile and characterize the sources and source combinations sampled by each of the CVs. These data are presented and briefly discussed in what follows. Conventional methods, such as non-negative matrix factorization and chemical mass balance, are not applicable here since (a) the source-oriented PM was already collected on separate filters, (b) each CV only represents a single time point so temporal variability in bulk phase particle composition cannot be assessed and (c) the CV filter samples were not chemically characterized given the small amount of PM mass collected for many of the sources relative to the amount required for the toxicological studies.

2.1. Single particle composition

Table 1 lists and briefly describes the various single particle composition classes observed during the S08 and W09 source-oriented sampling experiments that were used in the sampling algorithms to direct the operation of CVs. The table includes particle class name, abbreviation, season(s) observed, mass spectral composition and possible sources. Detailed discussions of these classes can be found in the Supporting information. Sources typically emit more than one particle class, and some particle classes are emitted by multiple sources, so it is the combination of particle classes that uniquely indicates a source, as discussed later and by Bein et al., (2009).

2.2. Site–source relation

The first step of source attribution is identifying the dominant sources emitting into the air shed and establishing the geospatial distribution of these sources relative to the sampling site; i.e. the site–source relation. Fig. 1 includes several Google Earth images of the sampling site and surrounding area at different spatial scales to show (a) sources within the immediate vicinity of the sampling site, which is located in the rear parking lot of the University of California Center on Shaw Avenue with Yosemite Freeway (CA SR 41) to the east, a large shopping center directly south across the street and a large residential area immediately to the north and northeast, (b) the surrounding residential sprawl and commercial sectors, largely composed of shopping centers, (c) a full view of the greater Fresno area, including the beginning of the agricultural sector and (d) the full width of the San Joaquin Valley.

In general, the sampling site is surrounded by large residential areas such that residential activities – e.g. heating, cooking and driving – will comprise the largest contribution to air pollution within the immediate vicinity of the site. On a regional scale, Fresno is surrounded by agricultural lands such that agricultural related emissions, along with vehicular emissions, will represent one of the largest regional source inputs and thus will be a key component of the observed background PM. Furthermore, the San Joaquin Valley is frequently subjected to stagnation-inducing upper-level inversions that tend to trap and re-circulate pollutants for extended periods, resulting in high pollutant concentrations and significantly enhanced atmospheric processing. As a result, secondary

Table 1
Brief descriptions of the various single particle composition classes observed during the summer 2008 and winter 2009 source-oriented sampling experiments, including particle class name, abbreviation, season observed, composition and sources.

Particle class	Abb.	Season(s) observed	Mass spectral composition	Possible sources
Potassium	K	S08 & W09	K^+ with minor to trace organics $C_x^+/C_xH_y^+$	Local, primary, non-vehicular combustion emissions; likely biomass
Carbonaceous ammonium nitrate	CAN	S08 & W09	Ammonium nitrate NH_4^+/NO^+ , organics $C_x^+/C_xH_y^+/C_xH_yO_z^+/C_xH_yN^+/C_xH_yNO_z^+$ and possibly soot (C_x^+) and PAHs	Regional background PM originating from atmospheric processing of vehicular and agricultural emissions
Elemental carbon	EC	S08 & W09	Soot (C_x^+) and possibly PAHs (high C:H)	Local, primary vehicular emissions
Potassium/elemental carbon/organic carbon	K/EC/OC	S08 & W09	K^+ with organics $C_x^+/C_xH_y^+/C_xH_yO_z^+$ and possibly soot (C_x^+) and PAHs	Local biomass combustion; e.g. space heating, cooking and debris burning
Sodium/potassium	Na/K	S08 & W09	K^+ and Na^+ with trace organics $C_x^+/C_xH_y^+$	Local, primary, non-vehicular combustion emissions; likely biomass
Elemental carbon/organic carbon	EC/OC	S08 & W09	Organics $C_x^+/C_xH_y^+/C_xH_yO_z^+/C_xH_yN^+/C_xH_yNO_z^+$ and possibly soot (C_x^+) and PAHs	Local, primary vehicular emissions; possibly some biomass combustion
Calcium/elemental carbon/organic carbon	Ca/EC/OC	S08 & W09	Ca^+ with soot (C_x^+), variable organics $C_x^+/C_xH_y^+/C_xH_yO_z^+$ and possibly PAHs	Local, primary diesel emissions
Zinc/Pb	Zn/Pb	S08 only	Zn^+ and Pb^+ with variable trace metals Na/K/Cr/Fe...	Local, primary combustion particles; source unknown
Potassium carbonaceous ammonium nitrate	KCAN	W09 only	K^+ , ammonium nitrate NH_4^+/NO^+ , organics $C_x^+/C_xH_y^+/C_xH_yO_z^+/C_xH_yN^+/C_xH_yNO_z^+$ and possibly soot (C_x^+) and PAHs	Regional background PM originating from atmospheric processing of biomass combustion emissions



Fig. 1. Google Earth images of the sampling site (marked with a red dot) relative to the surrounding sources at several different spatial scales; see text for discussion. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

components such as ammonium nitrate and secondary organic aerosol (SOA) will also be a major component of the regional background PM. In total, the largest source contributions to the Fresno air shed are (Ham and Kleeman, 2011; Kleeman et al., 2009; Rinehart et al., 2006; Chu et al., 2004; Battye et al., 2003; Poore,

2002; Watson and Chow, 2002; Schauer and Cass, 2000; Watson et al., 2000):

- **vehicular emissions** – including cold starts, idling and low to high speed operation of internal combustion and diesel engines

on highways, commercial roads, country roads, residential streets and parking lots

- **residential and commercial emissions** – including cooking (barbequing, charbroiling, pan frying, flame broiling, deep frying, wood ovens...), space heating (fireplaces, wood stoves, pellet stoves, furnaces, propane and natural gas heaters...), construction (diesel trucks, generators, back hoe loaders, bull dozers, hydraulic breakers, pavers, trenchers, front wheel loaders...) and landscaping activities (two-stroke motors; lawn mowers, leaf blowers, hedgers, trimmers...)
- **agricultural emissions** – including cattle ranching (CH₄, NH₃...), agricultural machinery (tractors, trucks, off-road vehicles, harvesters, hullers, windrowers, balers, tillers, rakes...), biogenic emissions (crops, orchards, vineyards, silage, ...), waste and debris burning and the product transportation infrastructure (mainly diesel trucks and tractor trailers)
- **long range transport** – most notably wildfires but potentially trans-Pacific transport as well
- **atmospheric processing** – resulting in a myriad of gas and particulate phase organic (e.g. SOA) and inorganic (e.g. NH₄NO₃) secondary species.

As a result, and on a mass basis, particle composition will be largely dominated by organic carbon (including a suite of aliphatic and aromatic hydrocarbons such as PAHs, oxygenated species, nitrogen containing compounds such as amines, and organosulfates), elemental carbon (i.e. soot, black carbon and/or brown carbon) and inorganic salts (e.g., nitrates and sulfates); see references cited above. However, on a number basis and according to the single particle data, metals will constitute a large fraction of the particle population since most particles contain metals indicative of their source, most notably potassium from biomass combustion.

2.3. Directional relationship

Meteorology is the main driver transporting pollutants to the site, most importantly wind speed and direction and atmospheric stability. Since the source-oriented sampling experiments were conducted almost entirely during the nighttime hours beneath a nocturnal inversion, as explained elsewhere (Bein et al., 2009), wind speed and direction are the sole metrics used here to associate the detection of specific particle compositions, and thus operation of specific CVs, with the direction of the most likely source(s).

Correlating CV sampling periods with predominant wind directions is possible due to the high temporal resolution of the single particle data. The timestamp of each single particle mass spectrum can be used to associate it with concomitant wind speed and direction measurements. A wind speed and direction is assigned to each single particle mass spectrum and the spectra are sorted and organized according to CV sampling times. For a given CV, the wind data associated with the spectra are counted across all sampling intervals and binned in wind direction degree intervals showing the frequency with which the wind was blowing from each direction while that particular CV was sampling. These data are then normalized by the frequency distribution of all wind observations to elicit those directions preferentially sampled by each CV relative to the typical wind direction profile. If a CV is associated with a predominant wind direction, then this is a strong indicator that it is associated with a specific source, source-related activity or source category. Results are shown in Figs. 2 and 3 for each of the source-oriented CVs from the S08 and W09 experiments, respectively. The general conclusions from these figures are (a) specific CVs are highly correlated with specific wind directions, i.e. show high sampling directionality, and (b) different CVs are generally

associated with different wind directions.

2.4. Temporal relationship

Temporal trends in the activation and sampling periods of each CV also indicate source. These data are shown in Figs. 4 and 5 for each of the source-oriented CVs from the S08 and W09 experiments, respectively, and are plotted as the fraction of total sampling time for a given CV as a function of hour of the day; note the differences in x-axes scaling. The fundamental idea here is that different sources are known to emit at different times of day and thus emissions from those sources should be more prevalent at certain times compared to others. For example, vehicular emissions should be largest during the morning and evening commutes while residential cooking emissions should be most prevalent during nighttime dinner hours. Therefore, similar to wind direction, if specific sources are highly correlated with specific times of day and different CVs are also associated with these temporal patterns, then this is another validation of the CV-source relationship. Again, these trends are clearly evident in the figures and help substantiate the source assignments as well as the technique.

3. CV source combination reconciliation

In this section, the source attribution data presented above are used to attribute specific CVs to specific sources, source categories or source combinations. The results for all CVs are summarized in Table 2 as the dominant particle types and associated sources by CV for both the S08 and W09 experiments. Specific CVs are discussed in detail in what follows.

Switching sampling between CVs as different air masses arrive at the site occurs in real time by algorithms described elsewhere (Bein et al., 2009). Since the algorithms must sample a number of particles before they can determine whether to sample from a different CV, each CV inevitably samples primarily from its assigned source or source combination but also from other ones. In addition, some sources emit multiple particle types mixed in the same air mass so cannot be separated by the method employed here. The fidelity of the sampling is quantified in more detail by Bein et al., (2009). Furthermore, since the sources and temporal patterns in mixing state that dominate the Fresno air shed are strongly dependent on season, the S08 and W09 sampling strategies and associated sampling algorithms and protocols were different, as detailed in the work referenced above.

3.1. Timed CVs

During the source-oriented sampling experiments, RSMS was operated daily from the evening until the following morning – 15:00–11:00 for S08 and 17:00–06:00 for W09 – and was off for the remainder of the time. This was due to the effects of daytime turbulent mixing on the concentration and mixing state of the air shed and thus on the ability of RSMS to (a) obtain sufficient particle hit rates and (b) isolate distinct sources from the atmospheric mixture for sufficient periods of time to conduct these experiments. As a result, the single particle instrument was off during these periods and a single CV (CV9 for both S08 and W09) was operated instead to capture the contents of the daytime mixed layer for comparative purposes. As a result, the source-oriented CVs (CVs 1–7 for S08 and 1–6 for W09) mostly represent local, nighttime sources emitting during the hours of ~17:00–09:00 and largely under a nocturnal inversion with minimal turbulent mixing. The average particle number distributions for this period, as determined from collocated SMPS data by averaging over the entire study period, are depicted as contour images in Fig. 6 for the S08

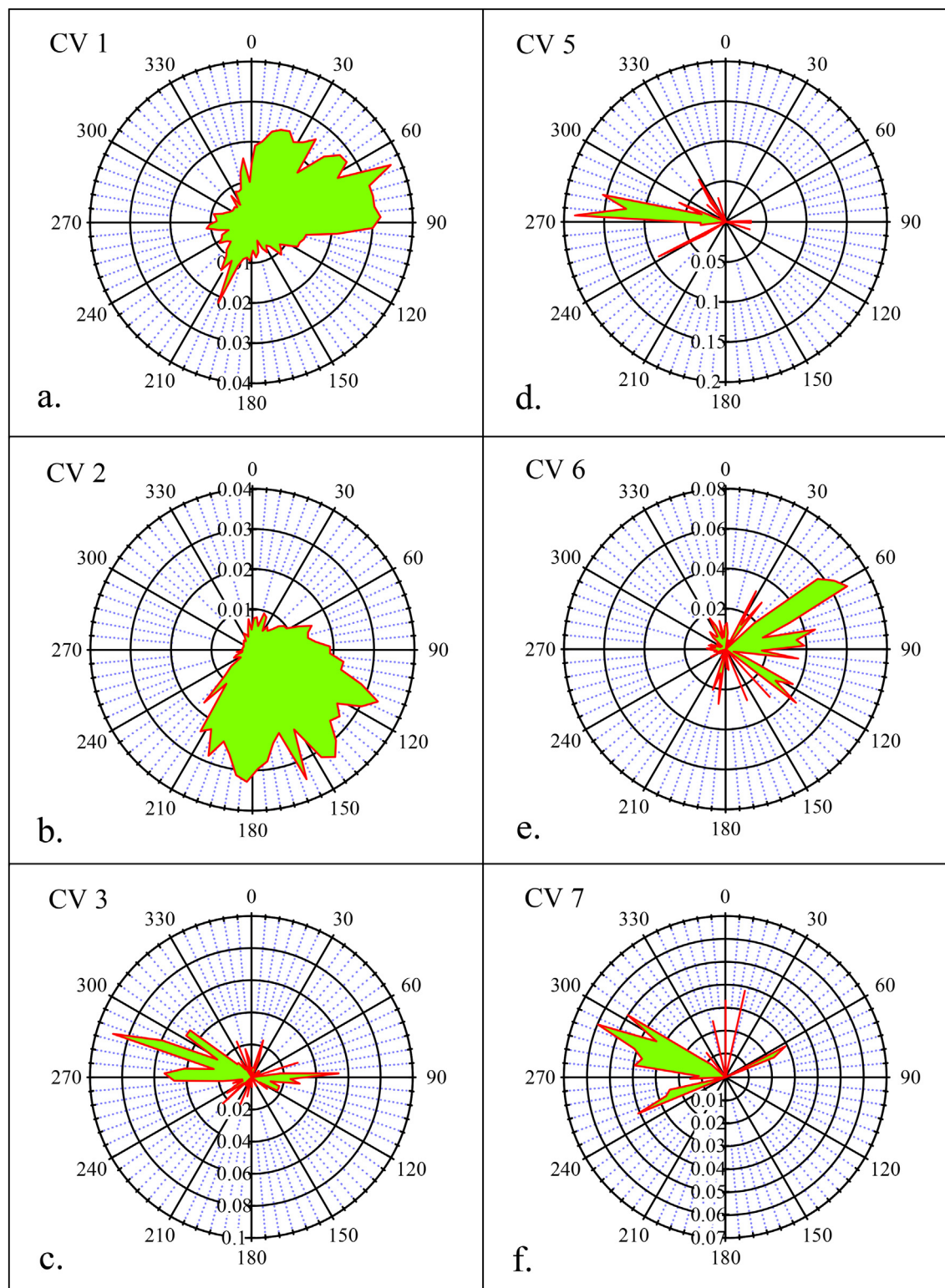


Fig. 2. Wind direction frequency distributions for the source-oriented ChemVols during the summer 2008 experiment; see text for a discussion of these plots.

and W09 experiments. The significant differences between the daytime structure in the dynamics of particle size distribution between S08 and W09 suggests significantly different daytime processes are occurring and offers an interesting basis for a comparative toxicological study. It is also interesting to note the apparent nucleation burst occurring almost daily from

~13:00–15:00 during the S08 experiment. This will be explored in more detail in a subsequent paper.

CV10, also termed the auxiliary CV, was operated during the nocturnal hours during periods when the source mixture could not be definitively discerned or did not match one of the predetermined source combinations assigned to the source-oriented

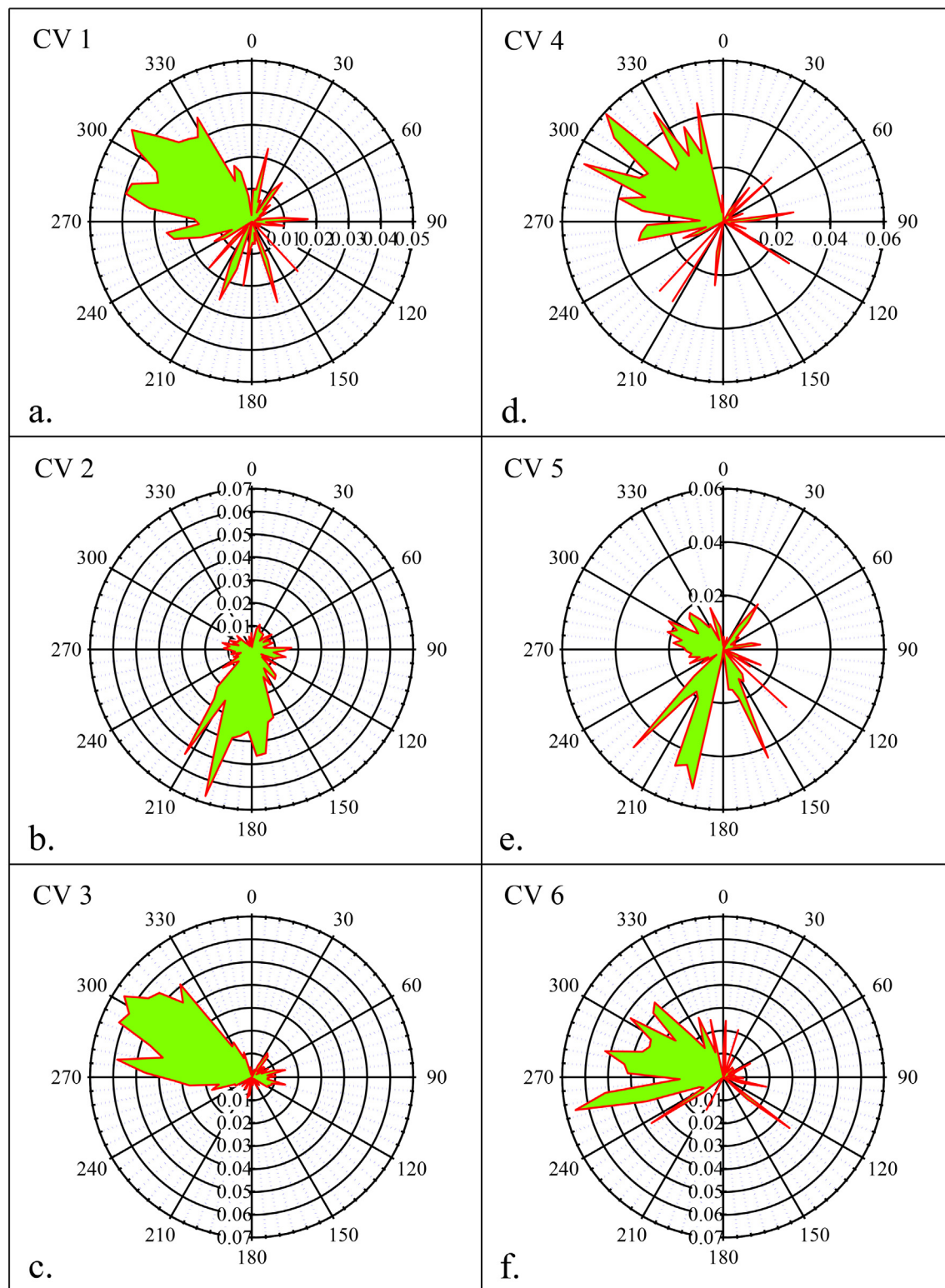


Fig. 3. Wind direction frequency distributions for the source-oriented ChemVols during the winter 2009 experiment; see text for a discussion of these plots.

CVs. As a result, CV10 was by far the most frequently operated CV due to the nature of these experiments and thus should be fairly representative of the background nighttime mixture.

During the W09 experiment, CV8, similar to CV9, was timed, rather than source-oriented. It was operated daily from

06:00–09:00 to isolate vehicular emissions originating from the morning rush hour commute. These emissions can be seen in Fig. 6b as the large increase in ultrafine particle number concentrations occurring in the period 06:00–09:00.

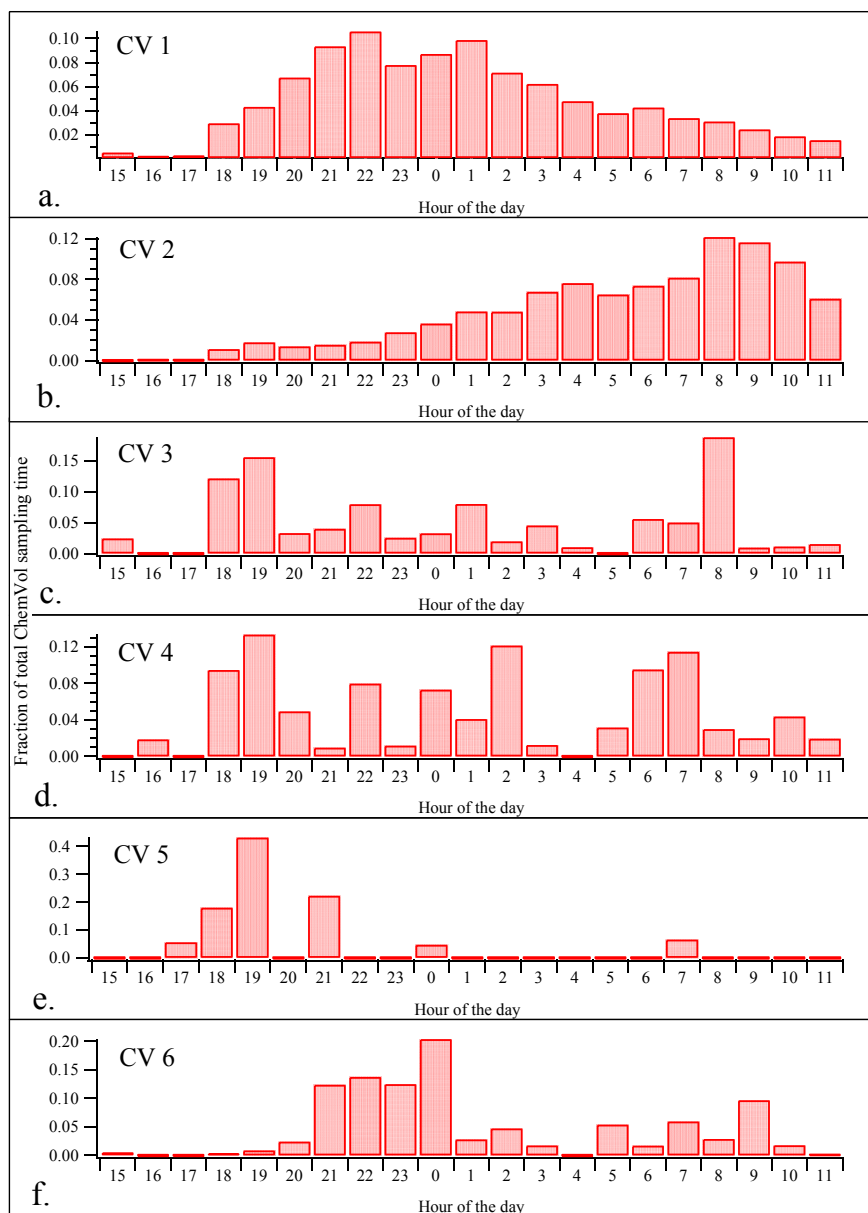


Fig. 4. The fraction of total ChemVol sampling time as function of hour of the day for the source-oriented ChemVols from the summer 2008 experiment; see text for discussion.

3.2. Source-oriented CVs – summer 2008

Summer and winter sampling protocols Each particle class represents a distinct particle type defined by its mass spectrum. Each particle source is identified by a combination of these particle classes, forming a spectrum of spectra (Bein et al., 2009). Here we discuss the combination of particle classes corresponding to each source.

3.2.1. CV1

On a particle class basis, the percent source composition of CV 1 is 50.2% K, 14.3% CAN, 12.6% EC, 9.3% K/EC/OC and 4.4% Na/K. Although it is not possible to completely isolate a specific particle type from the background mixture, the presence of other particle types does not necessarily indicate the influence of multiple sources. As stated previously, sources and source categories can emit multiple types of particles and it is likely that a large fraction of the EC, K/EC/OC and Na/K particles comprising this CV originated from

the same source category as the K particles.

As discussed in the Supporting information, these particles originated from local sources close to the site and most likely from some type of biomass combustion. In the general absence of residential heating during summer and minimal agricultural related burning in the growing season, the source of these particles is somewhat elusive within the traditional framework of well-known single particle source signatures. Although intensely flaming wildfires are known to produce these types of particles and wildfire activity in California was moderately high during the 2008 wildfire season, this cannot account for the frequency, consistency, persistence and number concentrations of the observed particles. Furthermore, these particles exhibit no signs of atmospheric processing associated with medium-to long-range transport and their number concentrations follow the expected trends for sources emitting under a nocturnal inversion. This can be directly inferred from the temporal trend depicted in Fig. 4a, which indicates that the source(s) of these particles begin emitting around 18:00 and

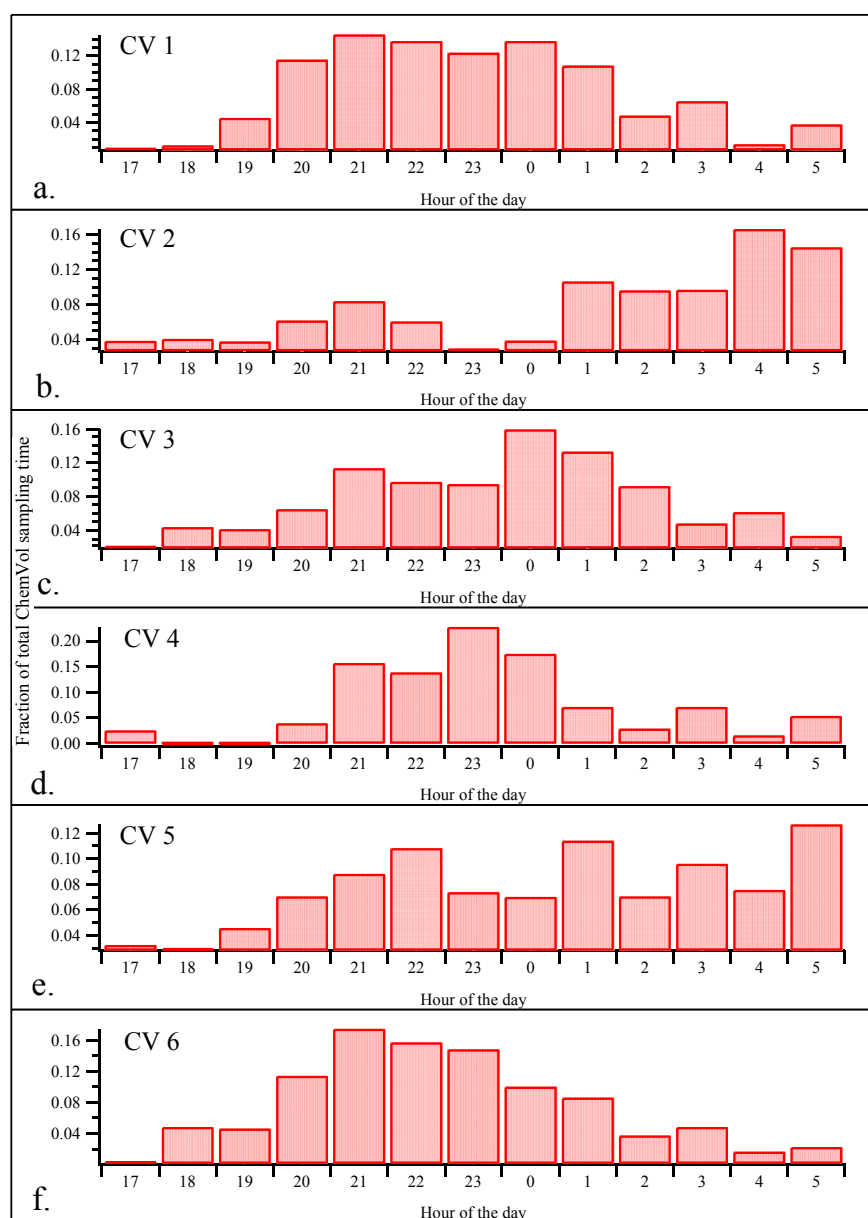


Fig. 5. The fraction of total ChemVol sampling time as function of hour of the day for the source-oriented ChemVols from the winter 2009 experiment; see text for discussion.

continue to emit as the nocturnal inversion develops – signified by the increase in sampling time from 19:00–22:00, which directly correlates to an increase in number concentration and particle detection – and then appear to stop emitting around 22:00, as evidenced by the plateau in CV sampling time. These particles begin to disappear around 02:00–03:00, corresponding to the observed decrease in CV sampling time, most likely due to a shift in wind direction and the emergence of a different dominant particle type.

According to the wind direction frequency distribution shown in Fig. 2a, CV1 samples most frequently when the wind originates from the NE quadrant and, from the Google Earth images in Fig. 1b, it is clear that this quadrant is almost entirely residential in nature. As a result, and from the confluence of these data, we posit here that this CV represents a combination of residential and commercial dinnertime cooking emissions. Furthermore, from onsite real-time observations, we further posit that a large fraction of these emissions result from residential backyard barbecuing. Various

types of cooking, such as pan frying, barbecuing and char and flame broiling, can certainly be classified as biomass combustion and potassium is an active component in almost all living tissues so this connection is not unreasonable. However, a full mechanistic description of possible particle inception and formation dynamics within the context of biomass composition and the relevant physicochemical processes associated with various cooking activities will not be attempted here. Note that fuels combusted to produce heat during cooking, such as charcoal and wood chips, can also be sources of these emissions.

3.2.2. CV2

The particle class percent composition of CV2 is 60.9% CAN, 17.0% K, and 11.1% EC. Given the complexity of source-oriented sampling in the Fresno air shed, an excellent separation of the CAN particle class was obtained by this CV and dominates the source profile. From previous discussions, including those in the Supporting information, these are highly processed background

Table 2
Summary of the dominant particle type(s) and source(s) associated with each ChemVol for the S08 and W09 experiments.

Experiment: Summer 2008			Winter 2009	
ChemVol	Dominant particle type(s)	Dominant source(s)	Dominant particle type(s)	Dominant source(s)
1	K	Local dinnertime cooking emissions	K/EC/OC	Local residential heating
2	CAN	Highly processed regional background PM	CAN	Highly processed regional background PM
3	EC	Local vehicular emissions; Diesel enhancement	EC; EC/OC	Local vehicular emissions; gasoline and diesel
4	CAN; K; EC/OC	Source mixture	K/CAN	Highly processed biomass combustion PM
5	EC; EC/OC	Local vehicular emissions; Gasoline and diesel	CAN; K/CAN	Regional source mixture; vehicular, biomass combustion, agriculture
6	Metals	Unknown	K/EC/OC	Local dinnertime cooking emissions
7	K; Na/K	Local dinnertime cooking emissions	Timed ChemVol ~ 17:00–20:00	Evening commute and dinnertime cooking
8	N/A	ChemVol not used	Timed ChemVol ~ 06:00–09:00	Morning commute
9	Timed ChemVol ~ 11:00–15:00	Daytime mixed layer	Timed ChemVol ~ 09:00–17:00	Daytime mixed layer
10	Uncertainty ChemVol	Nighttime nocturnal inversion	Uncertainty ChemVol	Nighttime nocturnal inversion

particles originating from regional sources and containing significant amounts of secondary components, including both organic and inorganic species. As seen in Fig. 4b, the majority of CV2 sampling begins as CV1 sampling declines (around 02:00–03:00) and continues to increase through the early morning hours. Perhaps the most revealing trend here is the fact that CV2 sampling time continues to increase to a maximum as the nocturnal inversion dissipates and the mixed layer begins developing, peaking around 08:00–10:00, and then begins declining as the mixed layer continues growing and turbulent mixing increases in the early afternoon (~11:00–12:00). The implication is that highly processed regional background PM trapped aloft in the residual layer from the previous day is entrained and mixed down by the developing mixed layer, rapidly increasing surface level concentrations of these particles, and then dilution takes over as the mixed layer matures and turbulent mixing intensifies, rapidly decreasing number concentrations and thus detection of these particles and CV2 sampling time.

The transition in sampling prevalence from CV1 to CV2 observed in the temporal trends is accompanied by a significant shift in wind direction from the NE quadrant to predominantly southerly to south-southwesterly, as depicted in Fig. 2b. This direction correlates to a large shopping center complex within the immediate vicinity of the site and the greater Fresno area at larger scales, as seen in Fig. 1. However, in this case, the significance of the shift in wind direction is not in identifying new sources but rather in explaining why the prevalence of K particles associated with CV1 starts declining and the emergence of the CAN particles, and thus CV2 sampling, begins.

In total, the contrast between CV1 and CV2 in all metrics – including particle composition, source, atmospheric processing, temporal variation and wind direction – is so prominent and convincing that the comparative toxicological analysis between these two CVs offers an excellent opportunity to test one of the most fundamental hypotheses of this work; i.e. the differential toxicity of local, unprocessed particles originating from a specific source compared to regional, highly processed particles originating from different sources and subjected to a greater degree of atmospheric transformation.

3.2.3. CV3

Comprised of 32.1% EC, 24.4% K, 17.6% CAN and 5.7% Ca/EC/OC particles, CV3 offers the cleanest separation of EC particles that could be obtained in this experiment and a good opportunity to

examine the toxicity of fresh vehicular emissions. As discussed in the Supporting information, EC particles are a common single particle signature of vehicular emissions and the elevated levels of Ca/EC/OC particles also sampled by this CV corroborate this (Ca is common dispersant in lubricants used in vehicle engines), and further suggest an enhancement in diesel tractor-trailer emissions. It should be noted that the presence of K particles in the summertime Fresno air shed was so prevalent that it was impossible to fully eliminate their presence in any of the source-oriented CVs.

The temporal trend in CV3 sampling time depicted in Fig. 4c further substantiates the association of this CV with fresh vehicular emissions by showing dramatic increases in sampling time for both the evening (~18:00–20:00) and morning (~08:00–09:00) rush hour commutes. Also, CV3 sampling is highly correlated with wind direction, as shown in Fig. 2c, and samples most frequently when the wind originates from the west to northwest. It is clear from Fig. 1 that this is the direction of the north-south running Yosemite Freeway (CA SR 41), a major expressway in the area with an entrance/exit ramp intersection at Shaw Avenue where high accelerations and corresponding high emissions regularly occur.

3.2.4. CV4

CV4 appears to be largely a source mixture, containing 30.4% CAN, 29.3% K, 18.3% EC, 5.8% EC/OC and 5.2% K/EC/OC particles. It was originally included to isolate the EC/OC particle class but shifted more towards the CAN class during sampling, which can be attributed to the clustering thresholds of the sampling algorithms. Fig. 4d suggests a strong vehicular influence with CV4 sampling frequency showing similar trends to CV3 and peaking close to conventional evening and morning rush hour traffic periods. However, CV4 sampling is significantly less correlated with wind direction, pointing to sources in both the east and west; not included in Fig. 2.

3.2.5. CV5

Similar to CV3, CV5 symbolizes a relatively clean separation of fresh vehicular emissions, with a particle class percent contribution of 23.8% EC, 21.4% EC/OC, 21.4% CAN, 16.7% K and 11.9% K/EC/OC. However, the increased detection of EC/OC particles and the absence of the Ca/EC/OC particle class suggest a significant enhancement of light duty vehicle emissions relative to CV3. Furthermore, CV5 sampling is highly spatiotemporally resolved, as shown in Figs. 2d and 4e, clearly capturing the evening rush hour but with limited sampling during the morning commute and

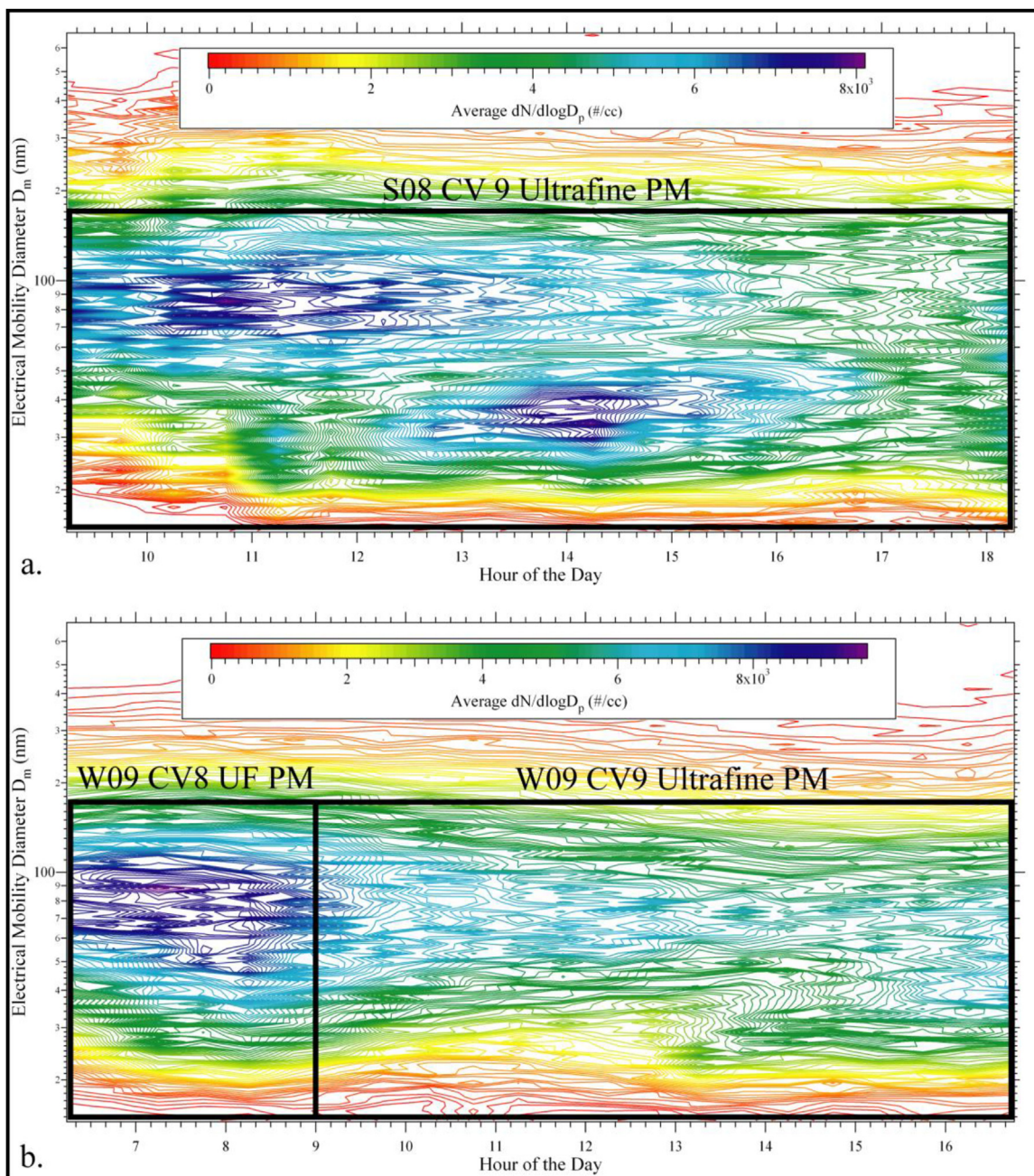


Fig. 6. Contour plots showing the study average daytime particle number distribution for the (a) summer 2008 and (b) winter 2009 experiments. The time periods corresponding to the various timed ChemVols are outlined and labeled in the figures; see text for details.

always sampling when the wind is blowing from the direction of the Shaw Avenue and Yosemite Freeway interchange.

3.2.6. CV6

CV6 is the best resolution that could be obtained for some of the more infrequently observed metallic particles, most notably Zn/Pb particles. Several particle classes were intentionally lumped together in the pre-study representation of this CV, subsequently used during sampling, to obtain a composite of these rare particle types. The particle class percent contribution is 34.5% K, 17% CAN, 12.5% EC, 12.4% Zn/Pb, 8.4% K/EC/OC, 4.6% Sn/Cr and 3.9% Na/K. From Figs. 2e and 4f, CV6 sampling was largely confined to the early night hours (~21:00–01:00) and almost exclusively when the wind

was blowing from the northeast. The exact source of these particles is not immediately clear, but they appear to originate from local combustion sources within the residential sector and are somehow correlated to the detection of K particles.

3.2.7. CV7

CV7 was included to isolate an enhancement of the Na/K particle class. The end result was relatively successful and CV7 consists of 39.4% K, 18.2% Na/K, 13.1% CAN, 11.1% EC, 5.1% Sn and 5.1% K/EC/OC particles. Although not as temporally resolved, due largely to relatively infrequent sampling, CV7 most closely mimics the temporal trends of CV1 but is highly associated with sources in the opposite direction to the west-southwest, as shown in Fig. 2f.

Besides the major expressway, Fig. 1 shows a major shopping center complex housing a suite of different restaurants in this area, followed by another large residential neighborhood. For reasons similar to those discussed previously, and due to their high correlation with K particles, we posit here that the Na/K particles also originate generally from biomass combustion associated with different cooking activities. Again, this is a reasonable assignment given the presence of both Na and K in food, the ubiquitous use of NaCl salt and the high temperature pyrolysis, char forming and flaming conditions associated with many types of cooking. In total, we posit that CV1 captured dinnertime cooking emissions, largely charcoal- and wood-fired outdoor barbecuing, from residential sources to the north of the site while CV7 predominantly captured commercial dinnertime cooking emissions from sources to the west of the site. As shown in companion work (Plummer et al., 2015), this turns out to be an important distinction since the toxicity of these two sources is quite different.

3.3. Source-oriented CVs – winter 2009

3.3.1. CV1

The percent composition of the wintertime version of CV1 on a particle class basis is 36.8% K/EC/OC, 25.2% K/CAN, 16.2% CAN, 9.4% EC/OC, 6.8% EC and 5.5% K, making this CV clearly attributable to local sources of biomass combustion. As mentioned in the Supporting information, the large organic content of these particles is indicative of sources sustaining mixed phase combustion, such as woodstoves and fireplaces, and thus CV1 can be attributed almost entirely to wintertime residential heating. This is corroborated by the temporal trend shown in Fig. 5a where sampling typically begins around 19:00, increases rapidly over the next couple of hours, plateaus throughout the night from 21:00–01:00 and then decreases in the early morning hours. Furthermore, CV1 is highly correlated to wind direction, as shown in Fig. 3a, and points to the collective effect of residential neighborhoods in the NW quadrant as the most likely source.

3.3.2. CV2

Showing striking similarity to CV2 from the S08 experiment, the winter version of this source combination consists of 61.2% CAN, 13.3% K/CAN, 11.2% K/EC/OC, 7.3% EC, 3.7% EC/OC and 3.2% K particles. Again, a clear separation of the CAN class is observed, representing highly processed regional background particles, as well as a temporal sampling trend that is anti-correlated to that of CV1 (Fig. 5b) accompanied by a shift in prevalence from northwesterly driven CV1 sampling to southerly driven CV2 sampling (Fig. 3b). As a result, CV2 presents an excellent opportunity to make a comparison between the seasonally-dependent toxicological effects of a given particle type; i.e. differences in toxicological response to highly processed regional background PM observed during summer versus winter. Although CV2 is highly correlated to wind direction in both S08 and W09, which helps explain the shift in the type of particles observed compared to CV1, it is important to note that regional background air pollution can be transported into Fresno from just about any wind direction.

3.3.3. CV3

The large EC/OC content of CV3 – 27.7% EC and 24.7% EC/OC particles – is strongly indicative of a prevalence of fresh vehicular emissions. This is supported further by a high sampling directionality corresponding to the Yosemite Freeway, as shown in Fig. 3c. However, the temporal trend in Fig. 5c largely excludes the evening rush hour traffic – CV 8 was configured to capture the morning commute so source-oriented sampling was terminated prior to that period – and CV3 samples relatively uniformly throughout the

night. This certainly does not preclude it from representing fresh vehicular emissions but biomass combustion can also emit these types of particles, although typically at significantly lower number concentrations compared to K-containing particles; the percent contributions for CV 3 were 15.6% K/EC/OC, 13.5% K/CAN and 3.2% K. Furthermore, although it was possible to capture diesel and gasoline engine emissions separately during the S08 experiment, this was not the case during the W09 experiment and so all vehicle emissions were sampled into a single CV.

3.3.4. CV4

Included to isolate the K/CAN particle class, which represents moderately to highly processed biomass combustion particles, CV4 comprises 55.3% K/CAN, 15.4% K/EC/OC, 10.3% CAN, 7.0% EC/OC, 6.4% EC and 5.7% K particles. The temporal trend and wind direction correlation for CV4, shown in Figs. 3d and 5d, respectively, trace those of CV1 fairly well and thus are not particularly revealing in this case. Therefore, the distinguishing factors are based solely on differences in single particle composition.

3.3.5. CV5

CV5, with a particle class percent composition of 27.9% CAN, 25.1% K/CAN, 15.1% EC/OC, 13.2% K, 10.0% K/EC/OC and 8.8% EC, most closely resembles a mixture of CV2 and CV4. This is also evident in Figs. 3e and 5e where the directionality and temporal trend of CV5 appears as a superposition of those for CVs 2 and 4. As a result, CV5 is considered representative of highly processed particles originating from a mixture of regional emissions, including both vehicular and biomass combustion sources, as well as any wintertime agricultural emissions that may also be present.

3.3.6. CV6

CV6 does a fairly good job of isolating the K/EC/OC particle class, which represents 41% of the detected particles associated with this CV. The remaining 59% is spread relatively evenly over the remaining particle classes. Although CV1 demonstrated a similar prevalence of K/EC/OC particles, the wind direction correlation and temporal trend of CV6, shown in Figs. 3f and 5f are distinct in that sampling generally begins and ends earlier (~18:00 and 23:00, respectively), more abruptly and is more correlated with westerly rather than northwesterly winds. As a result, we posit that CV6 is more heavily influenced by biomass combustion emissions associated with cooking than residential heating. However, due to similarities in particle composition, once these emissions start mixing in the atmosphere it becomes increasingly difficult to distinguish these two sources using RSMS alone.

4. Conclusions

Typically, PM is collected on filter or impactor substrates and then chemically analyzed via traditional bulk phase analytical techniques. This compositional data is then analyzed using mathematical source apportionment models, such as non-negative matrix factorization or chemical mass balance, to identify source composition profiles that can be used to resolve different sources from the bulk phase mixture. For the source-oriented sampling experiments discussed here, however, an alternate approach was taken. A single particle mass spectrometer was used to identify sources so that the PM was collected separately for each source. As a result, the source apportionment models are not applicable here and the current work evaluates how well each collected sample represents the source it was intended to capture using a novel source attribution technique.

Source-oriented sampling experiments were conducted during two separate seasons in Fresno, CA, where a single particle mass

spectrometer was used to control in real-time a bank of 10 CV samplers so that different CVs sampled air masses dominated by specific single particle compositions, or combinations of compositions. The governing principle of this study is that particle composition is generally an indicator of particle source and different sources typically emit particles with different compositions so collecting particles based on composition should be synonymous with collecting particles based on source. In the current work this idea is substantiated by performing a retrospective source attribution analysis – including single particle composition and site–source directional and temporal relations – to show that different CVs are, in fact, associated with different sources.

Results show that source oriented sampling is frequently correlated with certain wind directions and times of day, trends strongly indicative of the source-oriented nature of the samples. Detailed analyses of individual CVs allowed for a full reconciliation of the specific sources and source combinations contributing to each one. The dominant sources successfully isolated during both seasons include vehicular emissions, cooking emissions, residential heating emissions and the highly processed regional background, which is largely influenced by agricultural emissions and photochemical processing. One of the more important conclusions of this work is further validation of the source-oriented sampling technique. In companion work (Plummer et al, 2015), the differential toxicity of each source was investigated using various pulmonary endpoints, showing that (a) different sources do, in fact, elicit significantly different toxicological responses, (b) similar sources are more or less toxic depending on season and size, (c) different sources are toxic in different ways and (d) some sources elicit no toxicity above control. In combination, these results corroborate the feasibility and rationale of a paradigm shift from current regulatory practices of treating all emissions equally to a source- or risk-based regulatory strategy. The source-oriented samples described in this work have been extracted from the collection substrates using a novel extraction technique and subjected to differential toxicity testing using a variety of pulmonary and cardiovascular endpoints. Results from those efforts are published elsewhere (Bein and Wexler, 2014; Carosino et al, 2015).

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necessarily reflect the views of the Agency and no official endorsement should be inferred. The statements and conclusions in this publication are those of the contractor and not necessarily those of the California Air Resources Board. The mention of commercial products, their source, or their use in connection with material reported herein is not to be construed as actual or implied endorsement of such products.

Appendix A. Supporting information

Supporting information related to this article can be found at <http://dx.doi.org/10.1016/j.atmosenv.2015.08.051>.

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