

1 Quantifying PM_{2.5} Source Contributions for the San
2 Joaquin Valley with Multivariate Receptor Models

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1 **Abstract**

2 UNMIX and Positive Matrix Factorization (PMF) solutions to the Chemical Mass Balance
3 (CMB) equations were applied to chemically speciated PM_{2.5} measurements from 23 sites in
4 California’s San Joaquin Valley to estimate source contributions. Six and seven factors were
5 determined by UNMIX for the low_PM_{2.5} period (February to October) and high_PM_{2.5} period
6 (November to January), respectively. PMF resolved eight factors for each period that
7 corresponded with the UNMIX factors in chemical profiles and time series. These factors are
8 attributed to marine sea salt, fugitive dust, agriculture-dairy, cooking, secondary aerosol, motor
9 vehicle, and residential wood combustion (RWC) emissions, with secondary aerosol and RWC
10 accounting for over 70% of PM_{2.5} mass during the high_PM_{2.5} period. A zinc factor was only
11 resolved by PMF. The contribution from motor vehicles was between 10 – 25% with higher
12 percentages occurring in summer. The PMF model was further evaluated by examining 1) site-
13 specific residuals between the measured and calculated concentrations, 2) comparability of motor
14 vehicle and RWC factors against source profiles obtained from recent emission tests, 3) edges in
15 bi-plots of key indicator species, and 4) spatiotemporal variations of the factors’ strengths. These
16 evaluations support the compliance with model assumptions and give a higher confidence level
17 to source apportionment results for the high_PM_{2.5} period.

18
19 **Keywords:** receptor model, PM_{2.5} source apportionment, San Joaquin Valley, PMF, UNMIX

1 **Introduction**

2 Persistent high particulate matter (PM) concentrations in California's San Joaquin Valley
3 (SJV) (1,2) stimulated initiation of the California Regional PM₁₀/PM_{2.5} Air Quality Study
4 (CRPAQS, 3). CRPAQS, and the associated Fresno Supersite (4), to identify the causes of
5 elevated PM levels and to evaluate means for remediation. An important CRPAQS objective is
6 to quantify source contributions to annual and high PM concentrations.

7 Presented here are results from the Positive Matrix Factorization (PMF) and UNMIX
8 solutions to the Chemical Mass Balance (CMB) equations (5) for PM_{2.5} (PM with aerodynamic
9 diameter <2.5 μm) source apportionment. These results can be compared with the single sample
10 effective variance solution (6) to the CMB equations and/or source contribution estimates from
11 source-oriented models so that a "weight of evidence" approach can be used to develop cost-
12 effective control strategies (7). Owing to the special topography and meteorology of the SJV and
13 the predominance of area and mobile emissions, urban and rural sites are influenced by similar
14 sources, but by differing amounts. This allows the application of receptor models to multiple-site
15 measurements over seasonal monitoring periods during which the emission rates and source
16 profiles are reasonably constant. This analysis: 1) demonstrates the applicability of PMF and
17 UNMIX to spatially as well as temporally distributed measurements, and 2) evaluates the
18 consistency and reliability of PMF and UNMIX solutions in preparation for comparison with
19 other receptor- and source-oriented models.

20 **Ambient Observations**

21 The CRPAQS ambient network covered a region ~600 km long by 200 km wide between
22 Bodega Bay on the northwest California Coast and Edwards Air Force Base in the Mojave
23 Desert (Figure 1). Site characteristics and measured parameters are described in the supporting
24 information (Table S-1) and Chow et al. (3). Twenty-four hour sampling based on the U.S. EPA
25 sixth-day compliance schedule was carried out from 12/2/1999 to 2/3/2001. During the winter of
26 2000–2001, intensive observation periods (IOPs) obtained speciated PM_{2.5} measurements five
27 times a day in the urban areas of Fresno (FSF) and Bakersfield (BAC) and at non-urban Angiola
28 (ANGI), Bethel Island (BTI), and Sierra Nevada Foothills (SNFH) sites on 15 days selected by
29 forecast (3). Most sites reported >90% data recovery between 1/1/2000 and 1/31/2001.

1 Chow et al. (3) and Rinehart et al. (8) describe the PM_{2.5} spatiotemporal characteristics.
 2 PM_{2.5} concentrations varied with elevation. While the valley floor experienced annual PM_{2.5} up
 3 to 30 µg/m³, concentrations generally decreased to <5 µg/m³ at the surrounding coastal,
 4 mountain, and desert monitors. For non-urban sites in the SJV, elevated PM_{2.5} in late fall and
 5 winter was mostly driven by ammonium nitrate (NH₄NO₃), while carbonaceous material
 6 exacerbated PM_{2.5} pollution in urban areas such as Modesto (M14), Visalia (VCS), Fresno (FSF),
 7 and Bakersfield (BAC). Regional transport occurs aloft at night through a valley-wide layer that
 8 is decoupled from a shallow (20-30 m) nighttime surface layer during winter (2) and through a
 9 well-defined daytime northwest-to-southeast flow during non-winter periods (9).

10 Based on these analyses, CRPAQS samples have been divided into low_PM_{2.5} (February to
 11 October) and high_PM_{2.5} (November to January) periods (3) that approximately correspond to
 12 the winter and non-winter emissions and climatological regimes. The high_PM_{2.5} period
 13 contributed 50–75% of annual PM_{2.5} at within-valley sites (lower elevation) with the highest
 14 contributions found in the urban areas. For three desert sites outside the SJV—China Lake
 15 (CHL), Mojave (MOP), and Olancho (OLW)—the high_PM_{2.5} period contribution was <25% of
 16 the annual average, consistent with a limited transport from the SJV to the Mojave Desert during
 17 winter.

18 **Multivariate Receptor Models**

19 UNMIX (10,11) and PMF (12,13) solve the CMB equations and are therefore subject to the
 20 same derivation of CMB from physical principles with its underlying assumptions. C_{it} , the
 21 concentration of the i^{th} chemical species measured at time or location t , is the linear sum of
 22 contributions from a number of independent sources or factors:

$$23 \quad C_{it} = \sum_j F_{ij} S_{jt} + E_{it} \quad (1)$$

24 F_{ij} is the fractional abundance of the i^{th} species in the j^{th} source type, S_{jt} is the normalized
 25 contribution of the j^{th} source at time and/or location t , and E_{it} represents the error between the
 26 measured and calculated ambient concentrations.

27 Receptor models such as PMF and UNMIX estimate F_{ij} and S_{jt} by minimizing:

$$28 \quad Q \text{ or } \chi^2 = \sum_i \sum_t [E_{it} / \sigma_{it}]^2 = \sum_i \sum_t [(C_{it} - \sum_j F_{ij} S_{jt}) / \sigma_{it}]^2 \quad (2)$$

1 where the weighting factor, σ_{it} , intends to represent the magnitude of E_{it} . Although ambient
2 measurement precisions are often used for σ_{it} (as in this study), this is an underestimation as most
3 of the uncertainty originates from variability in the emissions (6). UNMIX and PMF limit
4 solutions of Eq. (2) to nonnegative F_{ij} and S_{jt} . The resolved UNMIX and PMF factors should be
5 associated with emission sources by comparing the F_{ij} with measured source profiles.

6 When C_{it} are available from several times and locations, it is possible to expand Eq. (1) to a
7 three-way factor analysis (14,15). Such analyses contain a large number of factors and often
8 require additional constraints to stabilize the solutions. Source emissions are also assumed to be
9 reasonably similar for the range of sample times and locations.

10 UNMIX v2.3 software applied in this study limits itself to seven factors, while a newer
11 version (UNMIX v5, currently in beta testing) sets no limit. These UNMIX v2.3 results are
12 equivalent to those obtained from the beta version. EPA PMF v1.1 (16) software was applied
13 because it selects random initial points for multiple runs and allows bootstrap testing to evaluate
14 the uncertainty of rotational freedom (17). When running in a robust mode, PMF adapts the
15 Huber influence function, a technique for iterative reweighting of the input data values to lessen
16 the influence of extreme values (18).

17 UNMIX and PMF have been previously applied to many $PM_{2.5}$ source apportionment
18 studies (19-24), but their results do not always agree (23,24). Differences are attributed to: 1)
19 different strategies for treating uncertainties and seeking the best fit; 2) different constraints on
20 factor rotational freedom; and 3) different practitioner preferences. Applying both models to the
21 same measurements and reconciling their source contribution estimates with each other and
22 source-oriented models (e.g., 25) provides the basis for the weight of evidence approach.

23 **Source and Receptor Characteristics**

24 Potential sources of $PM_{2.5}$ in the SJV are summarized in the supporting information along
25 with expected chemical markers. For California, area sources, including road/fugitive dust,
26 residential and agriculture burning, construction, and cooking, account for about 76% of primary
27 statewide $PM_{2.5}$ emissions (Table S-2). Approximately half of the remaining directly emitted
28 $PM_{2.5}$ (12%) originates from on-road and off-road engine exhaust. Source activities are spatially
29 inhomogeneous but, as noted earlier, mixing within the SJV takes place within a day during
30 summer and over a few days during winter (2,3,9).

1 Each site had from 60 to 77 days of speciated PM_{2.5} measurements (Table S-3). Though
2 PMF and UNMIX do not specify a minimum number of samples, the stability of their solutions
3 increases with the number of samples. The sample sets must have a large variation in source
4 contributions among different samples. The chemical profiles of the contributing sources should
5 remain relatively constant within a source type but differ substantially between source types. The
6 CRPAQS PM_{2.5} dataset meets these requirements because area and mobile source profiles are
7 reasonably consistent, in the aggregate, throughout the SJV (i.e., not site-specific); and there is a
8 large expected variability between source contributions by sampling time and location (26).

9 Mineral processing, gas-fired electricity production, oil and gas extraction, and agricultural
10 processing are important stationary sources in central California, but their primary PM_{2.5}
11 emission rates are small compared to those of area and mobile sources (Table S-2). Some
12 CRPAQS sites were located within or next to dairies (FEDL), oilfields (FEL), and agricultural
13 operations (HELM). PMF and UNMIX are expected to identify profiles of these specific sources
14 and estimate much higher contributions from them at the nearby locations than at more distant
15 receptors. This situation is analogous to these and other factor models identifying a fireworks
16 factor that only contributes on the Fourth of July (*e.g.*, 27).

17 Emission factors and chemical profiles of the area and mobile sources are expected to differ
18 between seasons. Motor vehicle cold starts are more prevalent during the winter season. Wood
19 stoves and fireplaces are only used during winter, while agricultural burning and wildfires are
20 more prevalent during warm non-winter periods. The large change of temperature and relative
21 humidity from summer to winter alters the thermodynamic equilibrium between particle-phase
22 and gas-phase pollutants and possibly modifies the factors representing secondary aerosol
23 composed of NH₄NO₃, ammonium sulfate [(NH₄)₂SO₄] and organic matter. To ensure uniformity
24 of source profiles, the UNMIX and PMF analyses were limited to 23 “within-valley” sites
25 identified in Figure 1. The low_PM_{2.5} and high_PM_{2.5} periods that contain a total of 929 and 670
26 samples, respectively were analyzed separately.

27 **Results and Discussion**

28 Magliano et al. (28) used a nine-source single-sample effective variance solution to explain
29 81–91% of winter 1995 PM_{2.5}. Source types included two geological (i.e., road dust and
30 construction), three secondary aerosol (i.e., NH₄NO₃, (NH₄)₂SO₄, OC), vegetative burning,

1 vehicle exhaust, industry (oilfield), and marine emitters. Industry and construction contributed
2 minor fractions (<0.1%) at urban and rural sites. Schauer and Cass (29) estimated similar source
3 contributions for multi-day composites during winter 1995, but they resolved the motor vehicle
4 portions into gasoline and diesel contributions and the vegetative burning portions into
5 hardwood, softwood, and cooking contributions.

6 **UNMIX and PMF Analysis.**

7 $PM_{2.5}$ mass was not used as input to either model to obtain factors, but it was used to
8 apportion $PM_{2.5}$ to the factors. Initial UNMIX trials used nitrate (NO_3^-), sulfate (SO_4^{2-}),
9 ammonium (NH_4^+), ammonia (NH_3), soluble sodium (Na^+), soluble potassium (K^+), organic
10 carbon (OC), elemental carbon (EC), total carbon (TC), thermal carbon fractions (OC1–OC4, OP,
11 and EC1–EC3 quantified by the IMPROVE_TOR protocol (30)), and silicon (Si) measurements.
12 Na^+ , K^+ , and Si are the indicators for marine air intrusion, vegetative burning, and fugitive dust,
13 respectively. High temperature EC (EC2, EC fraction evolved at 700 °C in an oxidative
14 environment) dominates the PM emission from diesel engines but is a minor component of
15 gasoline emission and wood smoke (31,32). Although >80% of the variability in both
16 high_ $PM_{2.5}$ and low_ $PM_{2.5}$ samples would be explained by seven principle components, no
17 feasible solutions were found by UNMIX. By applying the UNMIX “OVERNIGHT” option to
18 evaluate all possible combinations, 6-factor and a 7-factor solutions were found for the
19 low_ $PM_{2.5}$ and high_ $PM_{2.5}$ periods, respectively, using common species NO_3^- , NH_4^+ , total
20 ammonium ($T-NH_3 = NH_3 + NH_4^+$), Na^+ , K^+ , OC, EC2, EC, TC, and Si, and an additional
21 species OC1 for the high_ $PM_{2.5}$ period only. Signal/noise ratios and strengths in both solutions
22 were ~2 or higher.

23 PMF included 27 species that were above lower quantifiable limits (LQL) for at least 50%
24 of the samples plus the eight thermal carbon fractions (Table S-3). Eight-factor solutions were
25 determined by PMF with the robust mode for both the high_ and low_ $PM_{2.5}$ periods. FPEAK and
26 FKEY are often adjusted to rotate PMF factors toward known source profiles or contributions
27 (e.g., 33,34). EPA PMF v1.1 software does not contain FPEAK or FKEY options, but the
28 uncertainty in PMF solutions can be estimated using a bootstrapping technique coupled with a
29 method to account for rotational freedom (16). Figure 2 presents the PMF factors with upper and
30 lower bounds determined from the 5th and 95th percentiles of 100 bootstrap values. The median Q

1 values were 20858 (low_PM_{2.5} period) and 18964 (high_PM_{2.5} period), compared to ideal values
2 of 31586 (low_PM_{2.5} period) and 22780 (high_PM_{2.5} period). The ideal Q is the number of C_{it} ,
3 assuming that the model contains only measurement uncertainty that has been accurately
4 determined (i.e., $E_{it}/\sigma_{it} = 1$). The Q analysis implied seven or eight factors for both periods.
5 Eight-factor models were selected for a better comparison of their profiles with UNMIX factors
6 and measured source profiles from recent emission tests.

7 The contribution of each factor to PM_{2.5} was estimated by an unweighted multiple linear
8 regression with zero intercept against the factor scores (S_{jt}) (e.g., 35,36). The regression
9 correlations were high; $r = 0.92(\text{UNMIX})/0.96(\text{PMF})$ and $0.79(\text{UNMIX})/0.87(\text{PMF})$ for the
10 high_ and low_PM_{2.5} period, respectively. The UNMIX factors were paired with the PMF factors
11 by ranking correlations of each of the UNMIX factors with each of the PMF factors in time
12 series. Each UNMIX factor correlated well (e.g., $r > 0.8$ for most cases) with one and only one
13 PMF factor (Table S-4), so there was no ambiguity in matching the pairs. Figure 2 compares the
14 UNMIX and PMF factors. Their common species agree within the PMF bootstrap uncertainties.

15 Based on source markers, seven common factors resolved by UNMIX and PMF for the high
16 PM_{2.5} period are: 1) marine (Na⁺); 2) fugitive dust (Si); 3) agriculture-dairy (T-NH₃, OC); 4)
17 cooking (K⁺, OC, EC); 5) secondary aerosol (NO₃⁻, NH₄⁺, OC); 6) motor vehicle (OC, EC2, EC);
18 and 7) residential wood combustion (K⁺, Cl⁻, OC1, OC, EC). The extra factor from PMF contains
19 a high zinc (Zn) content and could be related to brake and tire wear (37). For the low_PM_{2.5}
20 period, the six common factors are 1) marine; 2) fugitive dust; 3) agriculture-dairy; 4) cooking; 5)
21 secondary aerosol; and 6) motor vehicle exhaust. The additional two factors from PMF are Zn
22 and another secondary aerosol factor featuring (NH₄)₂SO₄.

23 Larger discrepancies between the UNMIX and PMF profiles occur for the marine factor
24 during the high_PM_{2.5} period (Figure 2), but neither model apportions PM_{2.5} mass to this factor.
25 PMF consistently allocates carbon and silicon to the agriculture-dairy factor for the low_PM_{2.5}
26 period, while UNMIX does not. Contribution estimates for these minor factors may contain
27 higher uncertainties. The residential wood combustion (RWC) factor appears only during the
28 wintertime high_PM_{2.5} period, and the sulfate factor appears only during the non-winter
29 low_PM_{2.5} period. This is consistent with the expected seasonal variations of these sources; i.e.,
30 residential heating demand increases during the winter while sulfate is more efficiently formed

1 during summer. The OC/EC ratio in the motor vehicle (MV) factor is lower (1.2 by PMF and 1.7
2 by UNMIX) for the high_PM_{2.5} period than for the low_PM_{2.5} period (2.8 by both PMF and
3 UNMIX. Cadle et al. (38) report a similar seasonal trend of OC/EC ratio for Denver, CO.

4 Annual average PM_{2.5} concentrations are well explained within ±1% by both UNMIX and
5 PMF factors (Table 1). Secondary aerosol, RWC, and vehicle contributions account for ~90% of
6 the PM_{2.5} mass during the high_PM_{2.5} period if the Zn factor is classified as a mobile source
7 contribution. UNMIX and PMF achieve similar source contribution estimates and are consistent
8 with Magliano et al. (28) and Schauer and Cass (29) for winter 1995. The portion of PM_{2.5} from
9 secondary aerosol and RWC are much lower for the non-winter (low_PM_{2.5}) period while the
10 portions due to fugitive dust and marine aerosol are larger compared to the winter period.

11 **Evaluation of Source Contribution Estimates**

12 Figure 3 compares the PMF MV and RWC factors with measured source profiles. RWC
13 samples were collected at a residential fireplace chimney burning Sierra Nevada hardwood (oak)
14 or softwood (juniper), commonly-available fuels throughout the SJV (39). The MV samples were
15 acquired in Las Vegas, NV during December 2003 (40) in source-dominated environments with
16 gasoline-powered vehicles or diesel engines. Las Vegas receives California-grade fuels by
17 pipeline from California refineries, and vehicle mixes are similar to those in California. The
18 source samples were analyzed for the same species using the same methods as applied to the
19 receptor samples. Contamination from road dust were removed from the MV samples by CMB
20 using known geological source profiles (41). Figure 3 includes profiles based on two to four
21 replicate measurements. Since both RWC and MV source profiles represent winter conditions,
22 they are only compared with the PMF factors for the high_PM_{2.5} period.

23 The OC/EC ratio in PMF MV is 1.2, compared to 1.9 in the gasoline and 1.2 in the diesel
24 profiles. The EC₂/EC ratio of PMF MV (0.80) is also closer to diesel (0.85) than to gasoline
25 exhaust (0.32). The gasoline source profile contains a substantial abundance of gaseous NH₃ (2.8
26 times the PM_{2.5} mass), Na⁺, and K⁺, which are not as abundant in the diesel and PMF MV
27 profiles. The PMF-derived MV profile appears to represent a combination of diesel and gasoline
28 emissions with a dominating influence from diesel. A clear edge in the OC versus EC scatter plot
29 (Figure 4) corresponds to the PMF MV factor, and this supports a consistent MV source profile
30 within the SJV. Strict emissions regulation and periodic compliance testing in Nevada and

1 California could account for the low influence of gasoline engine exhaust on ambient $PM_{2.5}$.
2 Increasing the number of factors does not distinguish the gasoline from diesel exhaust
3 contributions. Zn is found in both diesel and gasoline profiles, possibly owing to deterioration of
4 the galvanized exhaust systems. PMF attributed most of the Zn to a separate factor. Reducing the
5 number of factors in PMF does not merge this factor with the MV factor.

6 OC/EC ratios for softwood and hardwood burning are 8.1 and 12.4, respectively, compared
7 to 3.3 in the PMF RWC profile (Figure 4). The OC/EC ratio is known to vary with fuel and
8 burning conditions (32). The PMF RWC factor contains more abundant NO_3^- and NH_4^+ than the
9 measured wood burning profiles, but the NH_3 abundances are close. The K^+ abundance in the
10 PMF RWC factor is comparable to that of the measured hardwood burning profile. Among
11 carbon fractions, OC1 and POC show larger deviations between the measured profiles and PMF
12 factors.

13 The PMF MV and RWC factors combined explain $10.4 \mu g/m^3$ TC or ~82% of the measured
14 value, including 28% from MV and 54% from RWC. When the Zn factor is included, motor
15 vehicles contribute up to 31% of TC, in better agreement with the UNMIX estimate (36% of TC).

16 The difference between measured and calculated species concentration divided by the
17 measurement uncertainty, i.e., scaled residual, is a useful performance measure. Data with scaled
18 residual > 4 or < -4 are downweighted in the PMF analysis with robust mode and therefore have
19 low impacts on the source apportionment results. For the high_ $PM_{2.5}$ period, PMF determines
20 $PM_{2.5}$ scaled residuals within ± 4 for ~80% of the data (Figure 5a). The sign and magnitude of the
21 scaled residual vary by site, but no outlier sites or spatial trends are identified from Figure 5a.
22 The low_ $PM_{2.5}$ period, however, contains three outliers, ANGI, FSF, and BAC (Figure 5b),
23 where PMF underestimates the $PM_{2.5}$ mass for $>60\%$ of the data. This substantial unapportioned
24 mass implies unknown sources and/or different source profiles at these sites.

25 The PMF factors explain TC and NO_3^- concentrations well for the high_ $PM_{2.5}$ period (see
26 Figure S-2 in the supporting information); for every site, the scaled residuals are mostly within
27 ± 4 . Broader distributions of scaled residuals for TC and NO_3^- are found during the low_ $PM_{2.5}$
28 period. PMF underestimates TC at ANGI, FSF, and BAC, which is consistent with the situation
29 for $PM_{2.5}$ mass. PMF also underestimates NO_3^- at FSF and BAC for the low_ $PM_{2.5}$ period. PMF

1 explains source markers such as Si, K⁺, and EC concentrations reasonably well across all sites
2 for both periods (Figure S-2).

3 Adsorption of organic vapors on quartz-fiber filters that is under-corrected by blank
4 subtraction inflates OC and TC concentrations, the ratio of OC to other species, and PM_{2.5} mass
5 closure by differing degrees (42). Better PM_{2.5} mass closures (closer to 100%) are found at ANGI,
6 FSF, and BAC during the low_PM_{2.5} period (3). This partially explains why the three sites are
7 forced into outliers in the receptor modeling that combines all sites together. Moreover, the
8 fraction of volatilized NO₃⁻ was the highest at FSF and BAC during the low_PM_{2.5} period (3).
9 Variability of the organic and nitrate sampling artifacts are not part of the analytical uncertainty
10 considered in Eq. (2). Source apportionment for the high_PM_{2.5} period is likely more reliable,
11 since the sampling artifacts are relatively minor compared to high ambient TC and NO₃⁻
12 concentrations.

13 **Spatial and Temporal Variations**

14 Figure 6 compares the PMF contributions among different sites during the high_PM_{2.5}
15 period. Similar comparisons for the low_PM_{2.5} period are in the supporting information (Figure
16 S-3). There is no clear spatial trend for the marine contribution during the high_PM_{2.5} period,
17 though during the low_PM_{2.5} period the distribution of marine contributions is consistent with
18 lower elevation and frequent land-sea exchange in the northern SJV.

19 During the high_PM_{2.5} period, higher contributions from fugitive dust occurred south of
20 FSF with the highest contribution observed at ANGI. This may be explained by the nearby
21 unpaved road and extensive tilling and harvesting of cotton fields in the area.

22 Contributions from agriculture-dairy are high in some rural areas and relatively minor at
23 urban sites such as FSF, S13, and BAC. The largest contribution in the agriculture-dairy
24 distribution (Figure 6) represents the dairy site (FEDL), where the NH₃ concentration was at
25 least an order of magnitude higher than at any other site. This factor would probably not appear
26 in PMF or UNMIX if this source-oriented site was unavailable.

27 The RWC factor dominates at urban sites, including Fresno, Bakersfield, Modesto, Merced,
28 Visalia, and Sacramento, and is a low contributor at non-urban sites such as ANGI. The cooking
29 factor shows a similar spatial distribution. The urban influence of the MV factor is less than that
30 of RWC and cooking. Even rural sites could be impacted by major highways such as I-5 and CA-

1 99 that are major north/south arterials. Farm equipment and other non-road engines are also used
2 throughout the SJV. Contributions of the MV factor at FSF, FREM, and FRES that are in
3 commercial (rooftop), roadside, and residential microenvironments, respectively in Fresno are
4 2.7, 4.7, and 4.8 $\mu\text{g}/\text{m}^3$ $\text{PM}_{2.5}$ for the high_ $\text{PM}_{2.5}$ period, compared with a more uniform RWC
5 contribution of 24 – 27 $\mu\text{g}/\text{m}^3$.

6 Secondary aerosol contributions are highest in the southeastern SJV with little urban-rural
7 contrast (Figure 6). This factor also contains substantial OC that is possibly of secondary origin
8 in winter (*e.g.*, 43). The source of factor Zn is thought to be mobile-related, though its spatial
9 distribution is somewhat between the RWC and MV factors.

10 Figure 7 shows the monthly PMF factor contributions averaged over the network. The
11 reconstructed mass agrees with the measured $\text{PM}_{2.5}$ within $\pm 10\%$ even for the low_ $\text{PM}_{2.5}$ period.
12 A rapid increase in $\text{PM}_{2.5}$ concentration from October to November results from increasing
13 influences from RWC and secondary aerosol. These two factors also dominate the monthly highs
14 in January 2001 (over 85 $\mu\text{g}/\text{m}^3$ at FSF and BAC). Secondary aerosol is the most important
15 factor everywhere except at FSF, where RWC was a large contributor at times during the winter.
16 The secondary nitrate contribution decreases rapidly after January and reaches its lowest level
17 between June and September.

18 Although dust contributes to no more than 20% and 5% of $\text{PM}_{2.5}$ mass for the low_ and
19 high_ $\text{PM}_{2.5}$ period, respectively, it was the dominant factor in the SJV between August and
20 September 2000 (monthly contribution: 2.7 and 2.0 $\mu\text{g}/\text{m}^3$ $\text{PM}_{2.5}$, respectively). The cooking
21 factor does not show a clear seasonal trend, but was high in January 2000. Since this factor
22 shares three major indicators, K^+ , OC, and EC, with RWC, some overlaps of its contribution with
23 RWC are expected during the high_ $\text{PM}_{2.5}$ period. The cooking factor may be influenced by other
24 types of burning during the low_ $\text{PM}_{2.5}$ period, such as agricultural burning and forest fires.
25 Besides K^+ , EC2 is the most influential marker for distinguishing MV from the RWC
26 contributions. Inclusion of organic markers specific to RWC, MV, and cooking in the receptor
27 models should improve the resolution (29,44). This would require measurement of organic
28 compounds on hundreds of individual samples, which is not yet practical using extractive
29 methods, but it may be possible using thermal methods with more specific detectors (45).

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5 **Supporting Information Available**

6 Supporting information is available free of charge via the Internet at <http://pubs.acs.org>.

1 **Figure Captions**

2 **Figure 1.** Ambient PM_{2.5} sampling network for CRPAQS. Sites in bold are included in this study.

3 (ACP: Angels Camp; ALT1: Altamont Pass; ANGI: Angiola; BAC: Bakersfield; BODG:
4 Bodega Marine Lab; BRES: Bakersfield Residential; BTI: Bethel Island; CARP: Carrizo Plain;
5 CHL: China Lake; CLO: Clovis; COP: Corcoran; EDI: Edison; EDW: Edwards Air Force Base;
6 FEDL: Dairy; FEL: Fellows; FELF: Foothills above Fellows; FREM: Fresno Roadside; FRES:
7 Fresno Residential; FSF: Fresno; HELM: Helm-Central Fresno County; KCW: Kettleman City;
8 LVR1: Livermore; M14: Modesto; MOP: Mojave-Poole; MRM: Merced; OLD: Oildale-Manor;
9 OLW: Olancho; PAC: Pacheco Pass; PIXL: Pixley Wildlife Refuge; PLE: Pleasant Grove; S13:
10 Sacramento; SELM: Selma; SFA: San Francisco; SNFH: Sierra Nevada Foothills; SOH:
11 Stockton-Hazelton; SWC: Southwest Chowchilla; TEH2: Tehachapi Pass; VCS: Visalia Church
12 St.)

13
14 **Figure 2.** UNMIX (vertical lines) and PMF (bars) factor profiles for (a) high_PM_{2.5} and (b)
15 low_PM_{2.5} periods, in terms of average contributions to PM_{2.5} mass and fitting species. The
16 upper and lower triangle represents the upper and lower bounds of the PMF factor contribution,
17 respectively, determined from the 95th and 5th percentile bootstrapping values. RWC = residential
18 wood combustion.

19
20 **Figure 3.** Comparisons of PMF motor vehicle (MV) and residential wood combustion (RWC)
21 factors with measured source profiles (normalized to average source contributions during
22 CRPAQS). The uncertainties of PMF factors are those in Figure 2 while the uncertainties in
23 measured profiles are determined from the standard deviation of averages from different emitters
24 within the source type.

25
26 **Figure 4.** OC versus EC for all samples and by site collected during the high_PM_{2.5} period. Solid
27 lines indicate the OC/EC ratios in the MV, RWC, and cooking PMF factors.

28
29 **Figure 5.** Cumulative PMF scaled residuals (difference between calculated and measured PM_{2.5}),
30 by site, for the high_PM_{2.5} and low_PM_{2.5} periods. The vertical lines indicate scaled residuals of

1 ± 4 ; i.e., the difference between calculated concentration from the measured value is four times
2 the measurement uncertainty.

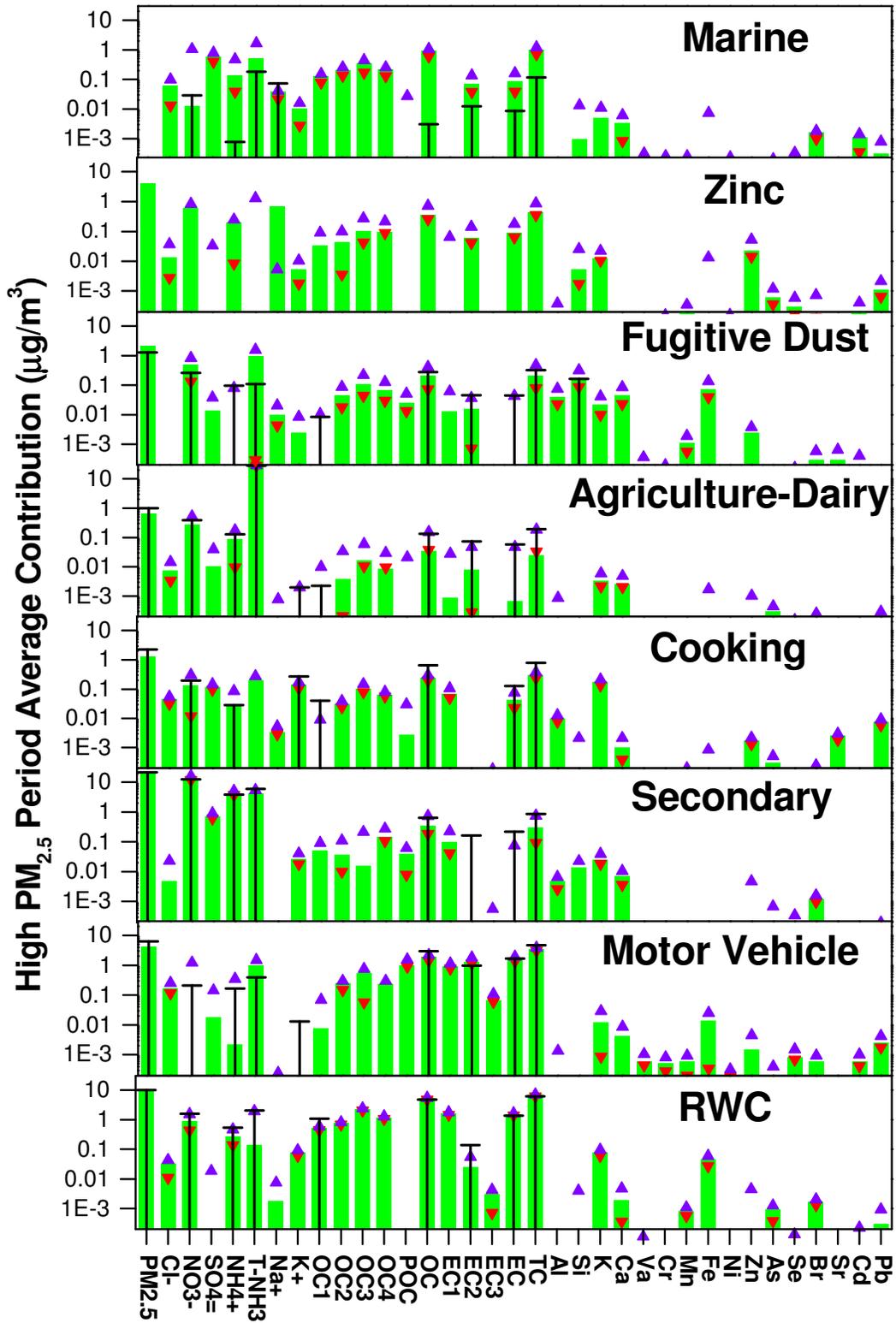
3

4 **Figure 6.** Spatial distributions of temporally averaged PMF factor contribution estimates for the
5 high_PM_{2.5} period (Nov. – Jan.). The distribution of marine factor during the low_PM_{2.5} period
6 is also presented (last panel).

7

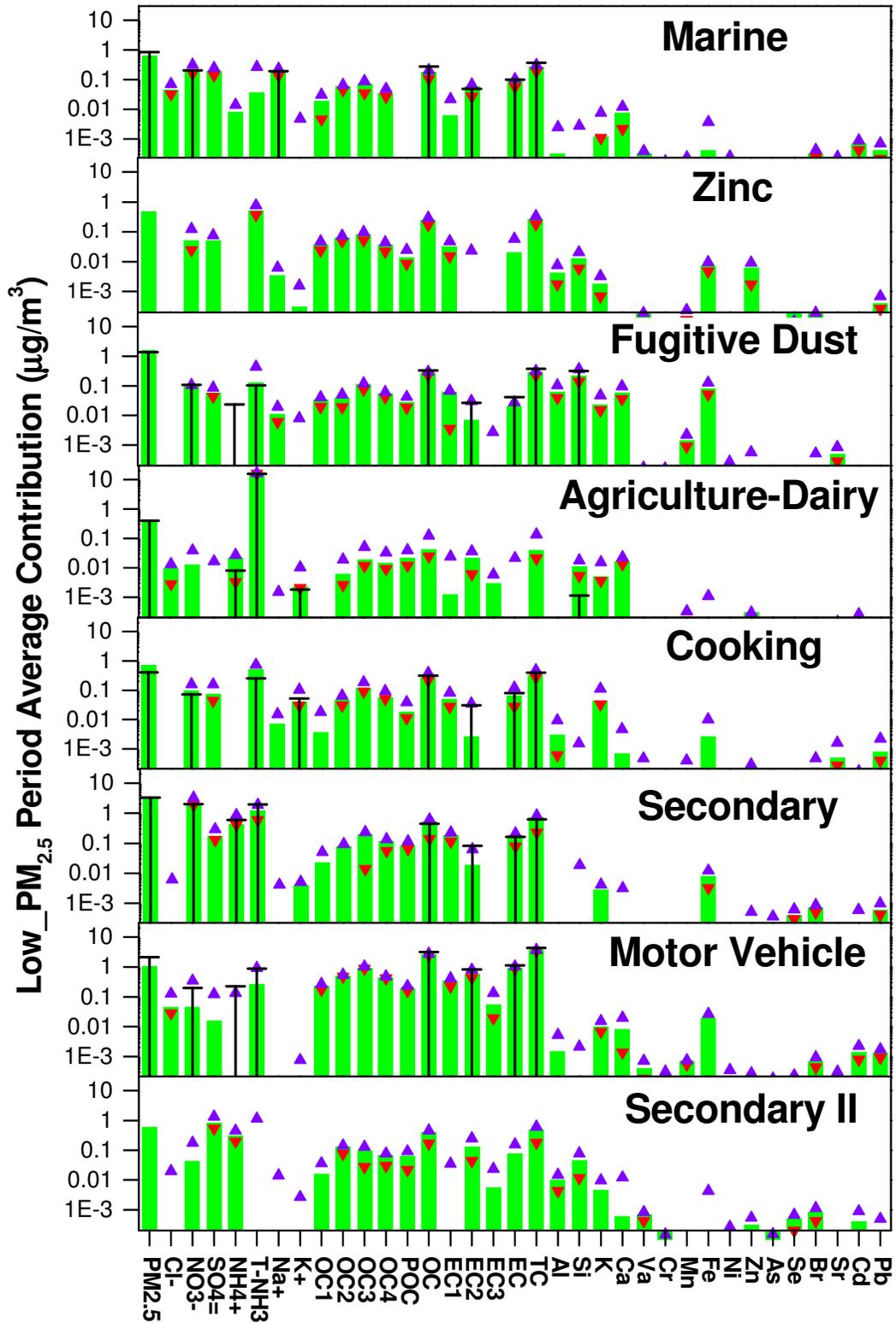
8 **Figure 7.** Monthly PMF factor contribution estimates averaged over the 23 CRPAQS sites.

1 Figure 2a.



2

1 Figure 2b



2

Figure 3.

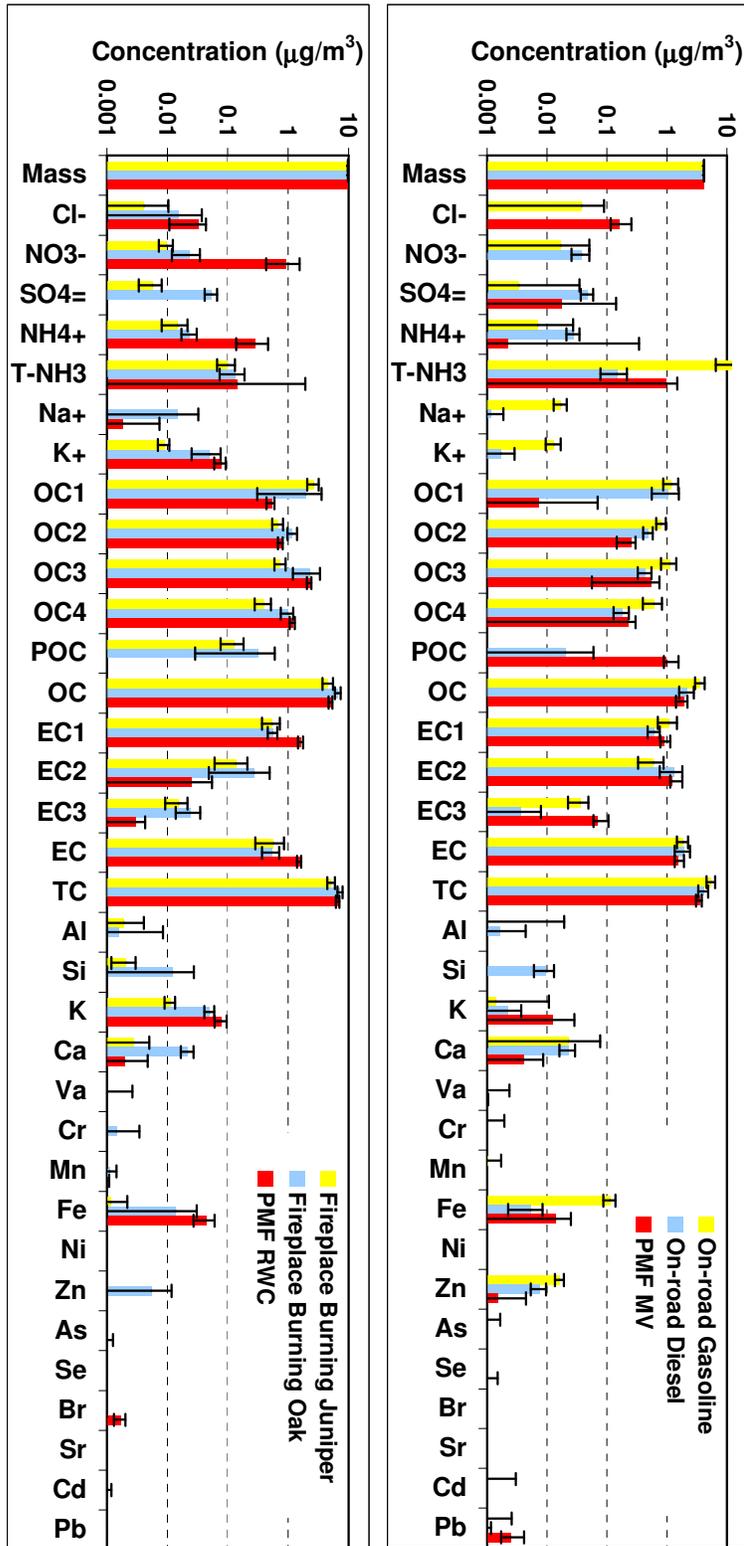
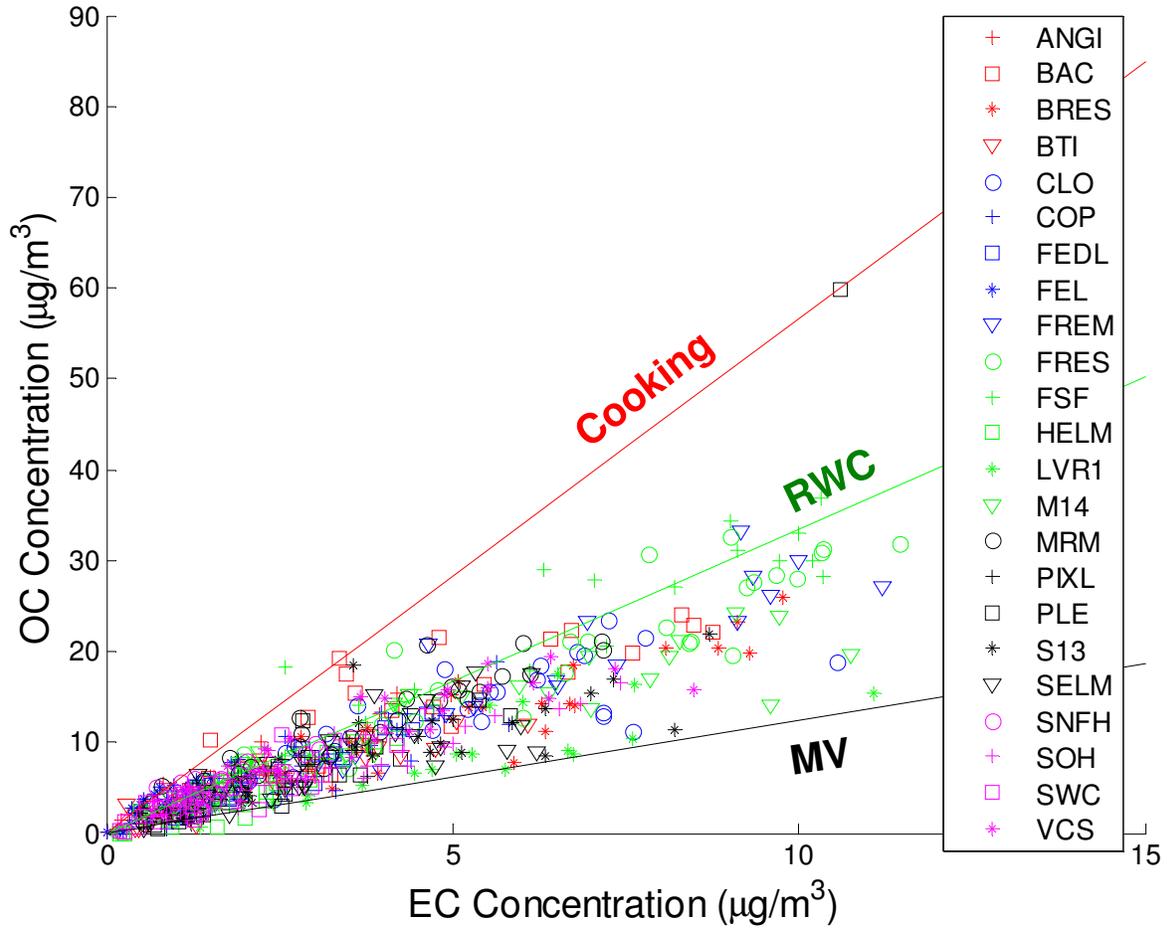


Figure 4.



20

Figure 5.

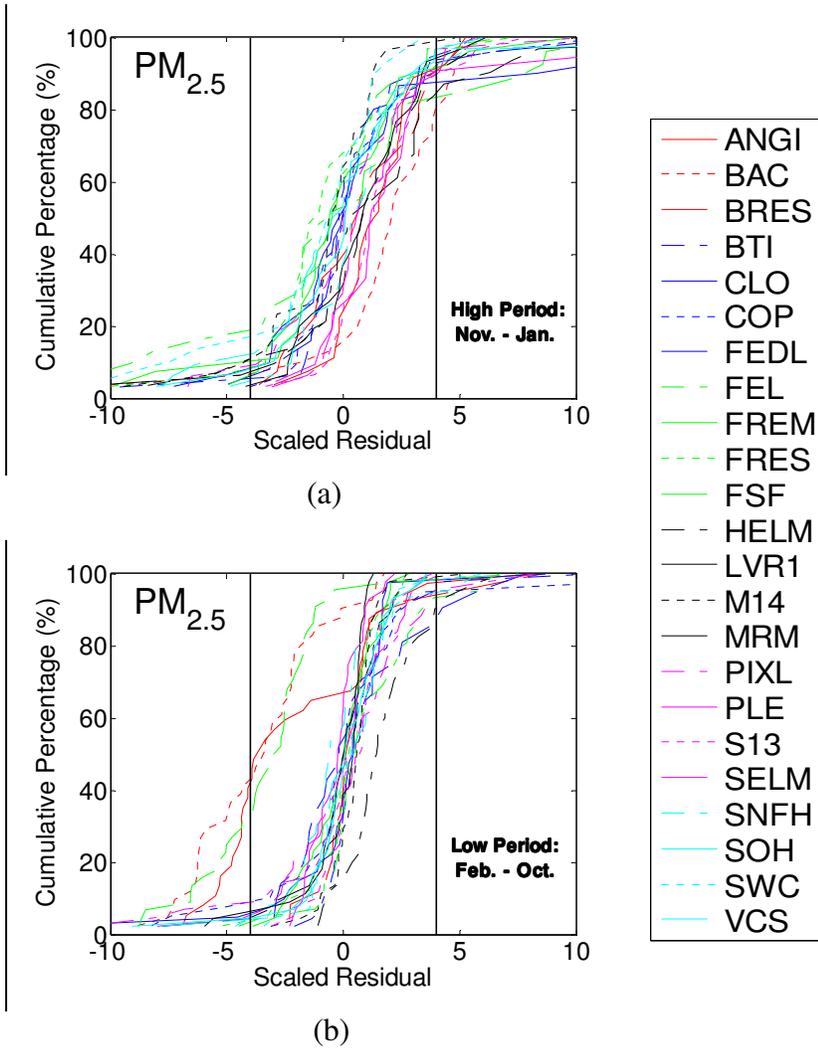


Figure 6.

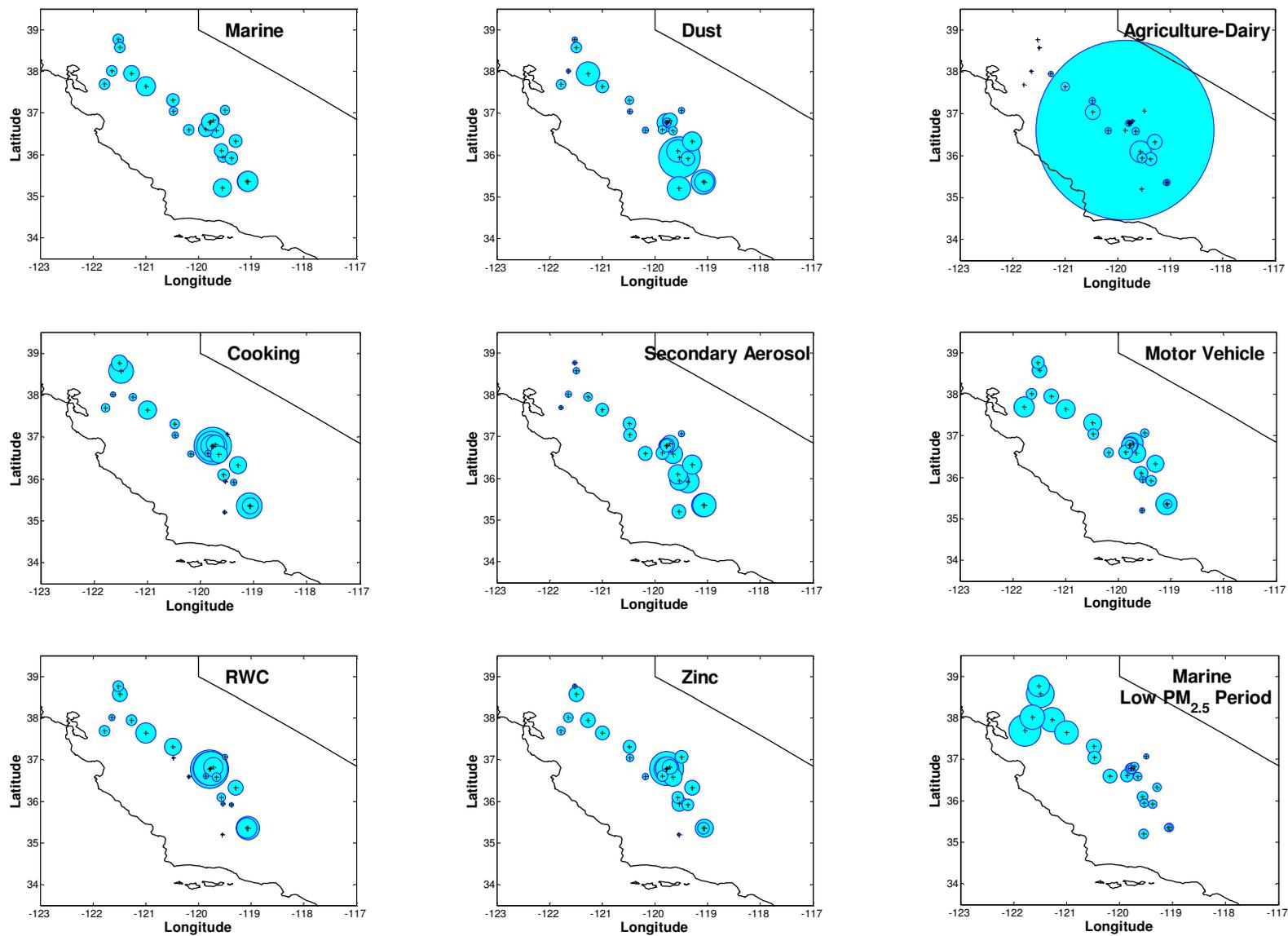


Figure 7.

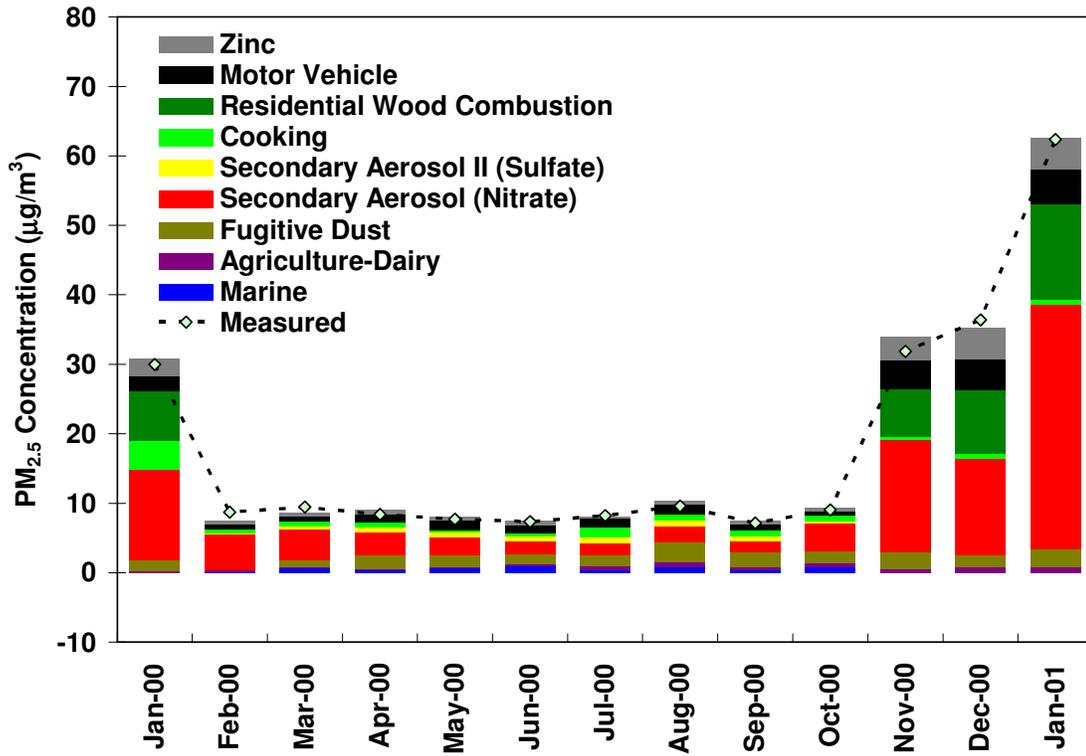


Table 1. Fractional contributions of UNMIX and PMF factors to PM_{2.5} during winter and non-winter periods.

Contribution to PM _{2.5}	High_PM _{2.5} (Nov. - Jan.)		Low_PM _{2.5} (Feb. - Oct.)	
	UNMIX	PMF	UNMIX	PMF
Marine	0%	0%	10%	7%
Fugitive Dust	3%	5%	16%	19%
Agriculture-dairy	2%	2%	5%	4%
Cooking	5%	3%	5%	9%
Secondary Aerosol	51%	48%	38%	36%
Motor Vehicle	15%	10%	25%	13%
Residential Wood Combustion	24%	23%		
Secondary Aerosol II	-		-	7%
Zinc	-	9%	-	6%

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