Source Apportionment of Fine Particulate Matter by Clustering Single-Particle Data: Tests of Receptor Model Accuracy

PRAKASH V. BHAVE†
Environmental Engineering Science Department, MC 138-78, California Institute of Technology, Pasadena, California 91125-7800

DAVID P. FERGENSON AND KIMBERLY A. PRATHER
Department of Chemistry, University of California, Riverside, California 92521

GLEN R. CASS*
School of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, Georgia 30332-0340

The source apportionment accuracy of a neural network algorithm (ART-2a) is tested on the basis of its application to synthetic single-particle data generated by a source-oriented aerosol processes trajectory model that simulates particle emission, transport, and chemical reactions in the atmosphere. ART-2a successfully groups particles from the majority of sources actually present, when given complete data on ambient particle composition at monitoring sites located near the emission sources. As particles age in the atmosphere, accumulation of gas-to-particle conversion products can act to disguise the source of the primary core of the particles. When ART-2a is applied to synthetic single-particle data that are modified to simulate the biases in aerosol time-of-flight mass spectrometry (ATOFMS) measurements, best results are obtained using the ATOFMS dual ion operating mode that simultaneously yields both positive and negative ion mass spectra. The results of this study suggest that the use of continuous single-particle measurements coupled with neural network algorithms can significantly improve the time resolution of particulate matter source apportionment.

Introduction

To deliberately control atmospheric fine particle concentrations, the relative influences of the various contributing sources must be known (1, 2). Two approaches for identifying source contributions to atmospheric particle concentrations exist: source-oriented models and receptor-oriented models. Whereas source-oriented models begin with emission rates and atmospheric transport calculations to estimate the ambient pollutant concentration increments due to each source, receptor-oriented models begin with ambient pollutant concentration data and seek to subdivide the particulate mass among its different sources. Receptor-oriented models developed to date can be grouped into two basic categories: chemical methods and microscopic methods. The fundamental principles of various chemical methods for receptor modeling, including chemical mass balance (CMB) and multivariate methods, have been reviewed in detail (3–8). The first receptor modeling technique applied to ambient aerosol samples reported in the literature is a multivariate method using factor analysis (9), in which correlations between the concentration fluctuations of observed chemical species are used to determine groups of chemical elements that are transported together in nearly fixed proportions (indicating a common source). Factor analysis offers the advantage of not requiring prior knowledge of the chemical composition and size distribution of emissions from specific sources (source profiles) but has the drawback of being mathematically indeterminate, allowing a wide range of possible solutions even when it is applied to relatively simple simulated data sets (10). It is uncommon to resolve contributions from more than six sources by factor analysis (7), and resolution of four primary sources is a more typical result. CMB models infer source contributions by determining the best-fit linear combination of measured source profiles needed to reconstruct the measured chemical composition of an atmospheric sample (11). The number of resolvable sources using CMB models is strictly bound by the number of measurable chemical species in the ambient and emission source samples, although the number of sources actually resolved by these methods usually falls far short of that limit. Trace-element-based CMB analyses seldom resolve more than 6 or 7 sources (7), whereas organic compound-based CMB analyses have been shown to resolve up to 9 or 10 primary particle source types (12, 13).

Microscopic methods use the properties of individual particles and therefore have the potential to obtain a more thorough separation of the dozens of sources actually present in an urban atmosphere (7). Initially, development of these methods was limited by the highly skilled labor required to examine each sample (7), and methods were difficult to standardize because source identification relied on the ability of the microscopist to recognize the source of each particle by comparison to libraries of standard particles from many sources (4). Development of automated single-particle analysis methods such as computer-controlled scanning electron microscopy (CCSEM) with X-ray detection has alleviated the need for highly skilled microscopists in some cases (14), and the application of neural network analyses to spectroscopy data has provided a standardized and automated method by which individual particles can be classified into groups of like particles (15). Microscopic methods are still viewed as difficult and costly because many thousands of separate particles typically need to be processed following the actual field experiment, in order to characterize a single source or atmospheric sample.

Aerosol time-of-flight mass spectrometry (ATOFMS), a relatively new technique capable of simultaneously measuring the size and chemical composition of individual aerosol particles in real time as they are sampled from the atmosphere (16, 17), provides a breakthrough in the level of particle description and speed of analysis, which may make it possible to distinguish particles from different sources at the same time that they are measured in the atmosphere. Initially, ATOFMS presented the problem that data were acquired at a rate far exceeding the rate of data analysis by conventional methods (18). More recently, the application of an adaptive resonance theory-based neural network algorithm (ART-2a)
Simulation of ATOFMS Data. One goal of the present study is to estimate the ability of the ART-2a neural network algorithm to group particles according to their source, using ATOFMS measurements of single-particle mass spectra.
Because manual classification of the ATOFMS data is slow, labor intensive, and subject to operator bias (18), automated computer software is used to generate a peak list that contains the areas, heights, and mass-to-charge ratios of all peaks in a particle spectrum. A variety of data analysis programs such as the ART-2a algorithm use these peak lists and the corresponding aerodynamic diameter measurements to group the particles into meaningful classes. With the ART-2a neural network algorithm capable of chemically grouping particles at a rate that approaches the rate of ATOFMS data acquisition (19), applying the algorithm as a receptor modeling tool potentially allows source attribution of particles in real time as the particles are sampled from the atmosphere.

To estimate the ability of the ART-2a neural network algorithm to perform receptor modeling-based calculations on ATOFMS measurements, we first simulate how the three sets of synthetic data representing the Long Beach, Fullerton, and Riverside aerosols would be described (both quantitatively and qualitatively) if they had been sampled by an ATOFMS instrument. ATOFMS instruments possess the

FIGURE 1. Chemical composition of fine particle emissions from major sources in Southern California.
TABLE 1. Relative Sensitivity Factor Estimates for Species Detected by ATOFMS Instruments

<table>
<thead>
<tr>
<th>Species</th>
<th>Positive Ion Mode</th>
<th>Negative Ion Mode</th>
<th>Dual Ion Mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>aluminum</td>
<td>0.5e</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>ammonium</td>
<td>0.014c</td>
<td>0.014</td>
<td></td>
</tr>
<tr>
<td>bariium</td>
<td>4.0e</td>
<td>4.0</td>
<td></td>
</tr>
<tr>
<td>calcium</td>
<td>3.0e</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>carbon</td>
<td>0.005e</td>
<td>0.02e</td>
<td>0.05</td>
</tr>
<tr>
<td>cesium</td>
<td>7.9f</td>
<td>7.9</td>
<td></td>
</tr>
<tr>
<td>chloride</td>
<td>0.1e</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>copper</td>
<td>0.3e</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>iron</td>
<td>3.5e</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>lead</td>
<td>0.5e</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>magnesium</td>
<td>0.8e</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>manganese</td>
<td>0.5e</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>molybdenum</td>
<td>0.5e</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>nitrate</td>
<td>0.018d</td>
<td>1.0e</td>
<td>1.0</td>
</tr>
<tr>
<td>phosphorus</td>
<td>5.1c</td>
<td>5.1</td>
<td></td>
</tr>
<tr>
<td>potassium</td>
<td>6.0e</td>
<td>6.0</td>
<td></td>
</tr>
<tr>
<td>silicon</td>
<td>0.09h</td>
<td>0.09</td>
<td></td>
</tr>
<tr>
<td>silver</td>
<td>1.0e</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>sodium</td>
<td>20.0e</td>
<td>20.0</td>
<td></td>
</tr>
<tr>
<td>strontium</td>
<td>0.35e</td>
<td></td>
<td></td>
</tr>
<tr>
<td>sulfate</td>
<td>0.5e</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>tin</td>
<td>0.35e</td>
<td>0.35</td>
<td></td>
</tr>
<tr>
<td>titanium</td>
<td>0.13e</td>
<td>0.13</td>
<td></td>
</tr>
<tr>
<td>vanadium</td>
<td>0.05e</td>
<td>0.05</td>
<td></td>
</tr>
</tbody>
</table>

* a Nonzero entry indicates chemical species is commonly detected in the given single ion mode. b Greater of the single ion mode sensitivity factors is applied to dual ion mode test cases. c Determined from laboratory experiments (34). d Determined from field experiments based on comparison with impactor measurements (35). e Estimates based on ionization potential and laboratory experience (36).

The sensitivity of ATOFMS instruments for detecting individual chemical components present in the mixed ambient aerosol varies dramatically from one chemical component to another. For example, recent laboratory work has demonstrated that ATOFMS instruments detect Na+ in individual particles with 70 times greater sensitivity than NH4+ (34). To simulate the effect of this variation in instrument sensitivity to different substances, one must rescale the mass concentrations of chemical components within each particle in the test cases to reflect the fact that some substances stand out clearly even when present at small concentrations within a single particle. Sensitivity factors for NH4+ and the group I cations (Li+, K+, Rb+, and Cs+) have been determined relative to Na+ in the laboratory (34). Sensitivity factors of NO3− (an indicator ion for NO3− during positive ion mode ATOFMS instrument operation) and NH4+ relative to Na+ were estimated on the basis of the comparison of side-by-side ATOFMS and cascade impactor measurements made during the 1996 field study described earlier (35). Sensitivity factors for the remaining species listed in Table 1 relative to Na+ are estimated on the basis of the ionization potential and lattice energies of the species, along with practical laboratory experience (36). For chemical species that are detectable in both positive and negative ion operating modes (e.g., nitrate, carbon), the greater of the two sensitivity factors is applied to the dual ion mode test cases. Converting the mass concentrations produced by the aerosol processes trajectory model to molar concentrations per particle and then applying sensitivity factors to a test case result in a list of particles with increased apparent concentrations of chemical species having sensitivity factors greater than unity and decreased apparent concentrations of species having sensitivity factors less than unity.

After the estimated and experimentally determined sensitivity factors have been applied in the above manner, the synthetic particle data sets are further degraded to simulate the inability to detect species present at very low levels in particles due to interference from spectral noise. Instrument noise is simulated by discarding data for chemical species having sensitivity-adjusted apparent molar concentrations < 2.0% of the sum of the apparent molar concentrations of all detectable species in the individual particle (37). Discarded data that fall below the 2.0% noise level are replaced with zeros in the test cases.

By postprocessing the air quality model output into synthetic single-particle data sets according to the procedure described above, we obtain an approximation of how the synthetic atmospheric particles would be quantitatively described if they had been measured by an ATOFMS instrument in a format analogous to the peak lists described above. The application of relative sensitivity factors in the method described above does not account for so-called matrix effects. The detectability of certain chemical components is known to be dependent on the chemical composition of the given particle (38). These matrix effects are not well quantified at this time, so for the present study, sensitivity factors are applied uniformly to all particles regardless of the presence or absence of other chemical components that may affect the sensitivity of the ATOFMS instruments to the component of interest.

Simulation of Qualitative ATOFMS Particle Descriptions. In the absence of a current capability to quantify the exact amount of each substance in a particle, ATOFMS data often are reduced to the point where only the presence or absence of each chemical component in the particles is disclosed (31, 37, 39). To simulate the ability of the ART-2a algorithm to cluster particles from sources when the particle contents are known only to the extent that an element is present or absent, selected test cases are produced by further degrading the quantitative approximations of ATOFMS data described above. In these selected test cases, chemical components with nonzero apparent molar concentrations are replaced...
with a value of “1” and the remaining components are given a value of “0”. Therefore, for each of the three synthetic single-particle data sets (representing the Long Beach, Fullerton, and Riverside aerosols), a total of six test cases simulating ATOFMS measurements are created (three operating modes: dual ion, positive ion, and negative ion, each presented in two data formats, quantitative and qualitative).

Adaptive Resonance Theory-Based Neural Network (ART-2a). Adaptive resonance theory-based (ART) neural network algorithms were introduced as theoretical models, describing selected aspects of the brain’s classification behavior (40, 41). They attempt to unite two contradictory behavioral features of the human brain: robust against outliers, but adaptive to slight changes and new knowledge. ART-based neural network algorithms are capable of solving complicated pattern recognition tasks by finding classes of similar data within large data sets with many variables. Most importantly, they have the ability to generate a new class in the event that a data point falls outside a preset proximity to all existing classes. ART-based neural networks have been used in a variety of practical applications (42) ranging from Chinese character classification (43) to chemical pattern recognition (44). The most recent incarnation of the ART-based neural network is a particularly efficient algorithm called ART-2a (45). The ART-2a neural network algorithm was previously used to identify particle classes on the basis of off-line CCSEM single-particle shape and elemental composition measurements (15, 46) as well as ATOFMS measurements of ambient aerosol sampled in real time (19).

Recently, the ART-2a algorithm was used as a source apportionment tool for distinguishing particles from two to three different sources (47, 48). The question posed by the present study remains: “How accurate is the ART-2a algorithm in achieving source separation when supplied with ATOFMS measurements of ambient aerosols?”

General descriptions of the ART-2a algorithm appear elsewhere (15, 45–48), so only a description focusing on its application to the synthetic single-particle data sets will be presented here. For the purposes of the present study, the ART-2a algorithm is used to identify various classes of particles based on their chemical composition. Ideally, each class of particles should represent particles from a different source or meaningfully related group of sources. To visualize a class, it is convenient to generate a “quintessential” particle that represents the class. The set of quintessential particles is called the weight matrix, and members of that set are referred to as weight vectors. Particle vectors are generated by normalizing the compositional description of each particle to unit length, using the Euclidian norm. Particles are selected in a random order and compared to each weight vector (by evaluating the dot product of the particle vector and the weight vector) until the weight vector with minimum Euclidian distance to the particle vector is found. If the dot product of the particle vector and the “winning” weight vector is greater than or equal to a predefined vigilance parameter, the particle is said to be in resonance with the weight vector and is assigned to the class that the winning weight vector represents. The winning weight vector is then shifted in the direction of the particle vector by a fixed amount called the learning rate. In this manner, the weight matrix is allowed to adapt in response to small changes in particle composition. If the dot product of the particle vector with the winning weight vector is less than the vigilance parameter, the neural network has discovered a novelty and that particle is considered to be representative of a previously unidentified class. When a novelty is encountered, the new particle vector is appended to the weight matrix, one at a time, until all are classified. The weight matrix is maintained between iterations, and this process is repeated, allowing the weight vectors to nucleate classes of increasingly similar particles from one iteration to the next. After a given number of iterations or training cycles, the particle classification is complete.

The ART-2a algorithm can be adjusted to yield many or few particle classes, depending on the predetermined value of the vigilance parameter. A vigilance parameter of 1.0 will yield a separate class for each individual particle, whereas a vigilance parameter of 0.0 will place all particles into a single class. In a previous study, a vigilance parameter of 0.70 was found to be appropriate in classifying particles of marine origin (19) and hence is used as the baseline for this study. A perturbation analysis of the value of the vigilance parameter is conducted, as will be discussed shortly. Forty training cycles are used in this study with a learning rate of 0.05. The ART-2a program is written in MATLAB and executed on an IBM-compatible microcomputer.

Receptor Modeling Procedure. To determine the utility of the ART-2a algorithm as a receptor modeling tool, the analyst applied the neural network classification algorithm to each of the test cases described. During the tests that follow, the operator of the ART-2a computer program (D. P. Ferguson) was not given any information on how the test cases were generated. He was completely blind to the knowledge of which time and geographic location were represented by a particular test case so that he could not use this knowledge to judge the quality of his answers. Furthermore, the chemical species in the particles were concealed and presented in an unknown order that varied from data set to data set. The source of each particle core and the age of each particle since the time of emission or entry into the study region were not disclosed to the analyst. Particle size information also was omitted from the test cases provided to the analyst, because it was unclear how much weight the particle size data should be given relative to the chemical composition information in the neural network algorithm.

Finally, the test cases themselves were shuffled and renamed so that the analyst could distinguish neither which monitoring site (Long Beach, Fullerton, or Riverside) a particular set of particles represented nor whether the test case contained direct unaltered trajectory model descriptions of atmospheric particles or a simulation of ATOFMS data nor, in the latter case, which ATOFMS operating mode (positive, negative, or dual ion) was being simulated. The only test case feature apparent to the analyst was whether the chemical composition information contained therein was qualitative or quantitative. At the end of the ART-2a classification process, the ART-2a class assigned to each particle was reported to the operator of the air quality trajectory model, who then compared the ART-2a classification of each particle to the known source of the particles as documented by the trajectory model.

Preliminary testing of the ART-2a algorithm revealed that species which are present at trace quantities in the particles have minimal influence on the classification results. This feature of the algorithm hinders its ability to classify particles on the basis of their source because many of the conservative trace elements, when present in particles, make up a very small fraction of the particle mass (see Figure 1). To give all chemical species roughly equal weight in the classification algorithm, each chemical component concentration in a given test case was transformed to have zero mean and unit variance (z transformation) and range scaled such that all values of the given chemical component lay between 0 and 1. This pretreatment method is applied to all test cases containing qualitative particle descriptions before they are presented to the analyst and has been used in previous applications of the ART-2a algorithm for the classification of single particles (47). Test cases containing qualitative particle descriptions are unaffected by this transformation. Application of this pretreatment method to real ATOFMS data
presents the potential risk of magnifying spectral noise in the case of an occasional noise peak extending above the noise rejection threshold and therefore should be exercised with caution.

Results and Discussion

Model Results. The upper row of Figure 2 summarizes the bulk properties of the aerosol trajectory model results from which the synthetic atmospheric particle data sets were generated. The subplots of Figure 2 are positioned in columns, from left to right, in the order of increasing time that the air parcel spent traveling over the urban area before reaching the given monitoring site. On the basis of trajectory calculations using interpolated wind fields (49, 50), the air parcel studied here spent 20 h above the urban area before reaching the Long Beach monitoring site from the west, 23 h before reaching the Fullerton site, and 45 h before reaching Riverside. Particle mass concentrations increase during transport across the air basin, with the highest particle concentrations present at Riverside, the furthest inland monitoring site. Changes in particle origin and mass concentration are modest between Long Beach and Fullerton and much larger between Fullerton and Riverside. The sharp increase in mass concentration between the latter pair of monitoring sites reflects the accumulation of both primary and secondary particulate matter in the Lagrangian air parcel during its 23 h travel time from Fullerton to Riverside. PM$_{2.5}$ concentrations predicted by the model are 42.2 $\mu$g/m$^3$ in Long Beach, 52.2 $\mu$g/m$^3$ in Fullerton, and 131.4 $\mu$g/m$^3$ in Riverside. These values are slightly larger than the model results tabulated in ref 32 because these are predictions of concentrations at a single time in the afternoon rather than 24-h average concentrations. Note that the vertical axis scale in the Riverside subplots is significantly larger than that used in the Long Beach and Fullerton subplots, for the purpose of readability.

Each bar in the upper panels of Figure 2 represents the ambient fine particulate matter concentration increment contributed by particles whose initial core originated from...
a given emission source category, as predicted by the aerosol processes trajectory model. Non-sea-salt background particles, largely sulfate particles, are injected into the air basin from over the Pacific Ocean and transformed by gas-to-particle conversion processes occurring in the urban atmosphere, are predicted to make the largest contribution to PM$_{2.5}$ concentrations at all three sampling sites during the indicated times of interest. Much of the increase in mass associated with background sulfate particles is due to ammonium nitrate accumulation over time on these hygroscopic particle cores. Sea salt particles, which are injected into each trajectory air mass as it crosses the surf zone at the coastline, once transformed by atmospheric reactions constitute the second largest source contribution to PM$_{2.5}$ concentrations at each site during the times of interest. The relative importance of particles having primary cores from other source categories to the PM$_{2.5}$ mass concentrations depends on the location of the sampling site within the air basin. Particles emitted from diesel engines and from the combustion of sulfur-bearing fuel are prominent in Long Beach and Fullerton at the indicated times. The contribution from crustal material (other than paved road dust) is shown to increase substantially between Fullerton and Riverside, becoming the single largest nonbackground source of fine particle mass in Riverside, whereas crustal material is shown as one of the smaller contributors to PM$_{2.5}$ concentrations in the Long Beach subplot. This reflects the drier and dustier soil conditions as well as the lower proportion of paved road surface in the agricultural Riverside area compared to the conditions of the near-coastal plain. Particles having cores emitted from food cooking and catalyst-equipped gasoline-powered motor vehicles, on the other hand, make relatively small contributions to the total PM$_{2.5}$ concentration at all three monitoring sites during the times of interest.

Source Apportionment Accuracy Given Maximum Compositional Detail. The first test of the ART-2a algorithm attempts to simulate how well this source apportionment procedure could work if given essentially complete information on each atmospheric particle. The air quality trajectory model is exercised with particle emissions from 10 separate source types. The fully quantified chemical description of every particle tracked by the air quality trajectory model then is supplied to the ART-2a analyst with no rescaling or other attempt to simulate how ATOFMS instruments would measure each particle. The lower panels of Figure 2 display the classification results of the ART-2a algorithm based on this most complete and realistic description of the ensemble of fine particles that can be predicted by air quality models given recent source test data. Each bar within the lower panels of Figure 2 represents a particle class ("class") isolated by the ART-2a algorithm. The masses of individual particles in each particle class are added together such that the height of each bar corresponds to the fine particle mass concentration in the ART-2a class. The number of bars in each subplot (11 in Long Beach, 13 in Fullerton, and 9 in Riverside) reflects the number of ART-2a classes containing at least 0.5% of the total fine particle mass concentration at the given site. To facilitate the present discussion, the bars of each subplot will be referred to as class 1, class 2, class 3, etc., in the order of decreasing PM$_{2.5}$ mass concentration. The source of the primary particle cores of those particles falling into each class is represented by different shading patterns in Figure 2, to illustrate how the neural network algorithm classifies particles originating from each of the 10 real source categories present. A bar shaded with more than one pattern indicates that the ART-2a algorithm is unable to distinguish particles originating from multiple emission source categories. Appearance of the same shading pattern in more than one bar indicates that particles from a single source are being mistakenly placed into multiple classes. If the neural network algorithm were able to correctly differentiate all ambient particles according to the emission source of their primary cores, the lower panels of subplots would appear identical to the upper row of subplots in Figure 2.

ART-2a classification results in Figure 2 illustrate that identification of the source of the primary core of individual particles becomes increasingly difficult as one moves downwind of an urban area, even when given essentially complete information on each atmospheric particle. Near the coastline, the ART-2a algorithm is able to isolate particles from the majority of the different source categories actually present. Of course, an analyst will know only the chemical composition of the particle clusters created but not the names of the source categories represented by each cluster and therefore must be careful to interpret the source identities correctly by reference to source profile data available in the scientific literature and appropriate ion marker combinations obtained from source characterization studies by ATOFMS. At the far inland Riverside site, particles from different sources become virtually indistinguishable from one another because they have reacted with a common gas phase over a period of 30–40 h, thereby becoming coated with gas-to-particle conversion products that disguise the initial differences between the particles at their source. Figure 3 provides a detailed description of the chemical features of the particles that are grouped into each ART-2a class, along with information on the sources that contributed the primary cores of the particles in each group. The vertical axis of each subplot in Figure 3 is linearly scaled, ranging from zero to one, indicating the relative mass concentrations of selected chemical components present in each ART-2a particle class. The mass concentrations of trace species are summed together and represented by the bar labeled "tc".

When applied to the Long Beach data set, the ART-2a algorithm performs as a fairly accurate receptor-oriented model (see Figure 2). The algorithm successfully isolates particles originating from sea salt (class 2), paved road dust (class 6), crustal material (class 8), and food cooking emissions (class 11) into distinct particle classes. Particles emitted from the combustion of sulfur-bearing fuel and other industrial sources are also correctly isolated from all other source categories, but the ART-2a algorithm separates these particles into two classes (classes 3 and 7). The left-hand column of Figure 3 reveals the reason for this separation. Class 7 particles at Long Beach primarily consist of sulfate, organic compounds, calcium, and other trace species. In addition to these chemical components, class 3 particles at Long Beach contain significant mass contributions from ammonium and nitrate, indicating that the class 3 particles have undergone further transformation by gas-to-particle conversion processes relative to the class 7 particles. The ART-2a algorithm also separates particles emitted from diesel engines at Long Beach into two classes (classes 1 and 5). The source-oriented air quality trajectory model results reveal that diesel particles in class 5 at Long Beach have an average atmospheric age of 7.4 h since emission to the atmosphere, whereas class 1 diesel particles at that site on average have been transported through the urban atmosphere for 12.2 h. Figure 3 illustrates that class 5 diesel particles are primarily composed of organic compounds and elemental carbon. The aged diesel particles in class 1, on the other hand, contain substantial quantities of secondary reaction products including ammonium, sulfate, and nitrate. Because particles emitted from catalyst-equipped gasoline engines and non-catalyst-equipped gasoline engines have similar chemical source profiles (see Figure 1), the particles emitted from all gasoline-powered motor vehicles at Long Beach are lumped together by the ART-2a algorithm. Gasoline-powered motor vehicle emissions at Long Beach are found primarily in class 4 and contribute a small fraction of the class 1 particle mass as well. Particles from other sources
FIGURE 3. Chemical composition of ART-2a particle classes generated from source-oriented model predictions with maximum speciation.
that are not separately tracked by the air quality model are found primarily in classes 4, 9, and 10 at Long Beach. The ART-2a algorithm groups all of the non-sea-salt background particles at Long Beach into class 1. This class also contains reacted diesel particles as well as minor contributions from aged particles that were originally emitted from gasolene-powered vehicles, paved road dust, and the combustion of sulfur-bearing fuel.

When operating on the particle descriptions generated by the source-oriented air quality trajectory model predictions at Fullerton, the ART-2a algorithm once again successfully separates particles originating from sea salt (class 2), paved road dust (class 3), crustal material (class 5), and food cooking (class 12). Class 1 at Fullerton contains those particles that have accumulated the largest quantities of secondary aerosol reaction products. This class includes all of the non-sea-salt background particles as well as heavily transformed particles from various other sources. Particles emitted from diesel engines are found in classes 1, 7, and 8 and have average ages since emission to the atmosphere of 12.9, 6.9, and 4.9 h, respectively. Particles emitted from the combustion of sulfur-bearing fuel and other industrial sources also are assigned to three distinctly different particle classes (classes 4, 9, and 13) at Fullerton. Particles emitted from gasolene-powered motor vehicle engines are primarily assigned to two classes in the Fullerton data set (classes 6 and 8). The separation of diesel exhaust particles and sulfur-bearing fuel combustion emissions into three separate classes in the Fullerton data set (as opposed to two classes in Long Beach) and the separation of gasolene-powered motor vehicle emissions into two particle classes in the Fullerton data set (as opposed to a single class in Long Beach) illustrate an important effect of atmospheric aging on particle composition. Particles that were originally emitted from a single source category at different points along the air parcel trajectory evolve to have chemical compositions that are sufficiently different from one another such that multiple particle classes are created by the ART-2a algorithm. The effects of aging on particle size and chemical composition are described in detail by Kleeman and Cass (22).

When supplied with the most complete particle descriptions produced by the source-oriented air quality trajectory model at Riverside, the source apportionment accuracy of the ART-2a algorithm is greatly reduced relative to the success encountered when operating on the Long Beach and Fullerton data sets (see Figure 2). When applied to the Riverside data set, the ART-2a algorithm places 65.5% of the PM$_{2.5}$ mass concentration into a single particle class. As shown in Figure 3, class 1 particles at Riverside primarily consist of ammonium and nitrate, with small amounts of sulfates and organics. The largest contributors to the class 1 particle mass at Riverside began as non-sea-salt background particles, which originally consisted of ammonium, sulfate, and organic compounds and which accumulated secondary organics and ammonium nitrate while being transported across the polluted air basin. In addition, class 1 at Riverside contains 42% of the fine particle mass originating from aged sea salt particles. The remainder of the aged sea salt particles are found in class 3, as the ART-2a algorithm easily identifies most sea salt particles on the basis of their large sodium content (see Figure 3). The ART-2a algorithm is unable to identify the source of class 1 sea salt particles because they have submicrometer diameters, such that their relatively low sodium content is overwhelmed by accumulation of secondary ammonium nitrate on their relatively large surfaces. Aged sea salt particles and non-sea-salt background particles advected into the study region from over the Pacific Ocean, class 1 at Riverside contains particles originating from vehicle emissions, crustal material, paved road dust, food cooking emissions, the combustion of sulfur-bearing fuel, and other sources that are not separately tracked by the model. Class 1 particles originating from these continental sources all have undergone significant chemical transformations as a result of gas-to-particle conversion processes. Among the continental particle sources, paved road dust and crustal material are the least readily transformed by gas-to-particle conversion processes because their initial particle cores are relatively large and hydrophobic (see Figure 1). As a result, the ART-2a algorithm correctly isolates most particles that were originally emitted from sources of crustal material (class 2) and paved road dust (class 4). Smaller particles such as diesel and gasolene engine exhaust particles, which dominate the aerosol surface area distribution and which in some cases (e.g., submicrometer sea salt and non-sea-salt marine background particles) have hygroscopic cores, are readily transformed by gas-to-particle conversion processes and can become virtually indistinguishable from one another by the time that they reach Riverside.

A perturbation analysis of the vigilance parameter (0.7 ± 0.2) provided some insight regarding the impact of vigilance parameter selection on ART-2a source apportionment accuracy. Reducing the vigilance parameter to 0.5 combined the crustal material and paved road dust particles into a single class at all three sites and resulted in poorer classification of the particles arriving at Riverside. Increasing the vigilance parameter to 0.9 split classes of particles that originated from a single source into multiple classes, without noticeably improving the source separation obtained during the baseline experiments.

Source Apportionment Accuracy Based on Simulated ATOFMS Data. Figure 4 shows the ART-2a algorithm classification results obtained when operating on test cases that simulate qualitative ATOFMS data in which the particles are described by the presence or absence of a particular chemical substance without any information on the relative amount of each substance. The top panel of Figure 4 displays the mass concentration associated with particles having a primary core emitted from the indicated sources (the “correct” source identification), and the lower three panels display the ART-2a classification results based on the positive, negative, and dual ion mode test cases. The source-oriented trajectory model results shown in the upper panel include all particles with physical diameter <2.5 μm. Certain high-density particles with physical diameters ~2.0–2.5 μm and larger are excluded from the ATOFMS data simulations if their aerodynamic diameters exceed the 3.5μm aerodynamic diameter detection limit of the ATOFMS instruments. For this reason, summations of the fine particle mass concentrations displayed in the lower panels of Figure 4 are slightly smaller than the total PM$_{2.5}$ mass concentrations displayed in the top row of subplots for the corresponding locations and times.

When supplied with qualitative particle descriptions from simulated ATOFMS dual ion mode measurements, the ART-2a algorithm is fairly successful at classifying particles into the correct number of source categories at Long Beach (see lower left panel of Figure 4). With dual ion mode capability, diesel emissions are classified separately from the sulfur-bearing fuel combustion particles in both Long Beach and Fullerton. This separation occurs because sulfates are detectable in the dual ion mode and the sulfate content of most diesel exhaust particles falls below the 2% noise threshold, whereas the sulfur-bearing fuel combustion particles contain a large quantity of sulfates. The dual ion mode capability also permits the ART-2a algorithm to separate aged sea salt dust and crustal material particles from other particle sources at all three monitoring sites. This separation is possible because silicon is detectable in the dual ion mode, and silicon is present above the noise threshold only in paved road dust and crustal material
particles. The source apportionment accuracy of the ART-2a algorithm grows progressively worse between Long Beach and Riverside for all three ATOFMS operating modes, due to the effects of aging on particle composition discussed above. Among the three ATOFMS operating modes, negative ion mode test cases yield the least amount of particle composition information (six chemical components) and hence result in the poorest source apportionment. Operating on the quali-
tative negative ion mode test cases, the ART-2a algorithm is unable to isolate particles from any source category into a single class. The qualitative positive ion mode test cases yield better results. In the Long Beach and Fullerton positive ion mode data simulations, the ART-2a algorithm successfully isolates non-sea-salt background particles, aged sea salt particles, particles from gasoline-powered vehicles, and food cooking particles into separate classes.

Figure 5 illustrates the level of source apportionment accuracy that might be attainable if the ART-2a algorithm were applied to ATOFMS data that quantitatively conveyed the varying heights and areas of the peaks in the mass spectra.
of each particle rather than reducing the particle compositions to a qualitative statement of the simple presence or absence of each detectable chemical substance. Overall, these results appear to be quite similar to the results shown in Figure 4 when purely qualitative particle descriptions were processed, although a few key differences exist. For all three ATOFMS operating mode test case results shown in Figure 5, the ART-2a algorithm is able to consistently differentiate the grouped combination of paved road dust and crustal material from particles emitted from all other sources when given quantitative information on peak areas. Operating on the qualitative particle descriptions, this separation is only possible given dual ion mode data (see Figure 4). In two cases shown in Figure 5 (Fullerton positive ion mode and Long Beach dual ion mode), the ART-2a algorithm is further able to distinguish paved road dust particles separately from other crustal material.

Applying the ART-2a algorithm to quantitative ATOFMS data also has drawbacks, however. When the ART-2a algorithm is applied to quantitative ATOFMS data, non-sea-salt background particles are no longer classified separately from sulfur-bearing fuel combustion particles (compare Figures 4 and 5). Similarly, classification of particles based on simulated ATOFMS data in which peak areas are quantified results in particles from gasoline-powered engines being lumped together with diesel engine particles, whereas the ART-2a algorithm is able to distinguish particles from these sources when provided with qualitative data. This effect results from the fact that creation of qualitative data in which only the presence or absence of each chemical substance is noted greatly increases the relative importance of trace elements while suppressing differences between particles that occur as particles of different ages accumulate differing amounts of gas-to-particle conversion products. In the future, it may be possible to combine the strengths of the use of both qualitative and quantitative descriptions of the ATOFMS data.

On the basis of the foregoing analysis, the ART-2a neural network algorithm is capable of separately grouping individual particles emitted from the majority of sources actually present when given complete data on particle size and chemical composition for particles measured at monitoring sites located near their original emission sources. When single-particle data are modified to simulate the biases in ATOFMS measurements, the source apportionment accuracy of the method is reduced. This result demonstrates the general necessity of understanding the impacts of measurement methods on data analysis. When simulated ATOFMS data are classified by the ART-2a algorithm, the best source apportionment results are obtained for dual ion mode data. As particles are transported across the polluted air basin and accumulate coatings of gas-to-particle conversion products, particles from multiple sources become indistinguishable from one another. In the future, it may be possible to devise an algorithm that places greater importance on the presence or absence of specific trace species which are unique to certain emission sources or an algorithm with a built-in bias against secondary aerosol components (e.g., sulfates and nitrates) that otherwise may disguise the primary source of the particles. If properly executed, such algorithms may overcome the difficulty of identifying the original sources of individual particles that have undergone significant accumulation of gas-to-particle conversion products.

Acknowledgments
This research was supported by the U.S. Environmental Protection Agency under Agreement R826371-01-0 and by funds granted to the Caltech Center for Air Quality Analysis. Thanks are due to Philip Hopke and Xin-Hua Song from Clarkson University, Michael Kleeman from the University of California at Davis, Philip Silva from the University of California at Riverside, and Annmarie Elderding of the Jet Propulsion Laboratory, for their assistance with this research.

Literature Cited
(20) Stevens, R. K.; Pace, T. G. Atmos. Environ. 1984, 18, 1499–1506.
(23) Taback, H. J.; Brienza, A. R.; Macko, J.; Brunet, N. FineParticle Emissions from Stationary and Miscellaneous Sources in the South Coast Air Basin; final report to California Air Resources Board; KVB, Inc.: Tustin, CA, Feb 1979.

Silva, P. J. University of California, Riverside, personal communication, 1999.


Received for review October 9, 2000. Revised manuscript received February 12, 2001. Accepted February 14, 2001.

ES0017413