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UNIVERSITY OF CALIFORNIA, SAN DIEGO

Characterization of Ambient Aerosol Composition and Formation Mechanisms and Development of Quantification Methodologies Utilizing ATOFMS

A dissertation submitted in partial satisfaction of the requirements for the degree

Doctor of Philosophy

in

Chemistry

by

Xueying Qin

Committee in charge:

Professor Kimberly A. Prather, Chair Professor Charles Elkan Professor Elizabeth A. Komives Professor Andrew C. Kummel Professor Mark H. Thiemens

2007

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This dissertation of Xueying Qin is approved, and it is acceptable in quality and form for publication on microfilm:

Chair

University of California, San Diego

2007

To my parents,

Yi Qin and Ke Shi,

who made all of this possible, for their unconditional love and endless support.

And also to my husband,

Jianhan Chen,

who makes everyday wonderful,

for his love, inspiration and encouragement.

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<u>X. Qin</u>, J. R. Whiteaker, K. R. Coffee, G. Khairallah, D. T. Suess and K. A. Prather. Comparison of ATOFMS Single Particle Measurements at Fresno and Angiola in the San Joaquin Valley during the California Regional Particulate Air Quality Study (*in preparation*).

<u>X. Qin</u>, L. G. Shields, S. M. Toner and K. A. Prather. The Effect of APS Scaling Functions on the Quantification of Aerosol Time-of-Flight Mass Spectrometry Measurements (*in preparation*).

X. Qin, L. G. Shields, S. M. Toner and K. A. Prather. Single Particle Characterization in Riverside during the SOAR 2005 Campaign (*in preparation*).

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<u>X. Qin</u>, P. V. Bhave and K. A. Prather. Comparison of Two Methods for Obtaining Quantitative Mass Concentrations from Aerosol Time-of-Flight Mass Spectrometry Measurements. *Analytical Chemistry* 78, 6169-6178 (2006).

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W. Zhao, P. K. Hopke, <u>X. Qin</u> and K. A. Prather. Predicting Bulk Ambient Aerosol Compositions from ATOFMS Data with ART-2a and Multivariate Analysis. *Analytical Chimica Acta* 549, 179-187 (2005).

Fields of Study

Major Field: Chemistry

Studies in Atmospheric Chemistry: Professor Kimberly A. Prather

Studies in Analytical Chemistry and Mass Spectrometry: Professor Kimberly A. Prather

ABSTRACT OF THE DISSERTATION

Characterization of Ambient Aerosol Composition and Formation Mechanisms and Development of Quantification Methodologies Utilizing ATOFMS

by

Xueying Qin

Doctor of Philosophy in Chemistry

University of California, San Diego, 2007

Professor Kimberly A. Prather, Chair

Aerosols are solid or liquid particles suspended in the air. They are generated from a range of natural and anthropogenic sources. Aerosols also experience various reactions such as photo-oxidation and aqueous-phase processing, which constantly change their physical and chemical properties. Therefore, in order to determine the emission inventory, it is important to study aerosol reactions and transformation mechanisms in ambient atmosphere. The research described in this dissertation aimed to characterize temporal, spatial, and seasonal variations on ambient aerosol chemical compositions and formation mechanisms. The results contribute to the understanding of air pollution, climate change, and human health problems, and to devising necessary strategies and policies to resolve these problems.

The main experimental technique utilized in the current work is Aerosol time-offlight mass spectrometry (ATOFMS). It measures the size and chemical composition of individual particles in real-time, and can thus provide high time resolution information on aerosol mixing states, reaction mechanisms, and sources. Continuous ATOFMS measurements have been conducted to study the ambient aerosol properties in several highly polluted regions of California, including the Fresno and Angiola area and the Riverside area. The results provide important insights on the characteristics, distinct diurnal temporal trends, and seasonal variations of aerosols in both urban and rural locations. The second focus of this dissertation is on the quantification capability of ATOFMS, which had been limited by several factors including the size-dependant particle transmission loss and shot-to-shot variability of the desorption/ionization laser. It is demonstrated that, by scaling the ATOFMS measurements using the results from an aerodynamic particle sizer (APS) or a micro-orifice uniform deposit impactor (MOUDI) measurements, it is possible to obtain high temporal resolution mass concentrations from ATOFMS that are in very good agreements with standard beta attenuation monitor mass concentrations. This development substantially improves the quantitative capability of ATOFMS, and will be useful in future application of ATOFMS to study aerosol source apportionment.

Chapter 1

1 Ambient Aerosol Sources, Reactions and Characterization

1.1 INTRODUCTION TO AEROSOLS

The three essential elements that sustain human life are air, water, and food. Air is one of the key elements that we depend on for every moment of our life. Each day we are exposed to a great amount of air, ten times more than water and food in term of mass. At the same time, we are also exposed to the pollutants in the air. Aerosols are solid or liquid particles suspended in the air. Their sizes range from a few nanometers (nm) to more than 100 micrometer (µm) in diameter [Finlayson-Pitts and Pitts Jr., 2000]. Particles larger than 100 µm have short life times due to fast precipitation rates and typically fall out of the atmosphere within minutes after being generated. In general, smaller particles are emitted from combustion sources and larger ones formed through mechanical processes. Figure 1.1 shows the typical number concentration, surface area, and mass concentration distributions of hypothetical urban aerosols relative to their sizes. Particle number concentrations peak near the lowest size range between 0.01 µm and $0.02 \,\mu\text{m}$ and a minor peak is also visible at ~0.1 μm . The highest particle surface area is observed between 0.1 μ m and 0.2 μ m, with a smaller peak at ~0.02 μ m as well as a slight hump between 2 μ m and 7 μ m. Mass concentrations strongly correlate with particle volume and display a bimodal distribution peaking around 0.3 μ m and between 6 μ m and



Figure 1.1 Size distributions of urban ambient aerosols based on a) number, b) surface area, and c) mass (volume with an assumed density) concentration. (Adapted from J.H. Seinfeld and S.N. Pandis, *Atmospheric Chemistry and Physics*, p. 431, Copyright 1998 by John Wiley & Sons, Inc).

 $7 \mu m$. These distributions can be substantially affected by many factors such as local emission inventories and meteorological conditions like wind and precipitation.

Aerosols are often classified based on their sizes. One of the most important classes is particulate matter (PM) with an aerodynamic diameter of 2.5 μ m or less (PM_{2.5}). Particles within this size range have unique formation mechanisms and significant health effects that substantially differ from particles larger than 2.5 μ m as discussed in the following sections, and will be the focus of this work [*Schwartz et al.*, 1996; *Finlayson-Pitts and Pitts Jr.*, 2000].

1.2 IMPACT OF AEROSOLS ON VISIBILITY REDUCTION, CLIMATE, AND HUMAN HEALTH

Aerosols have tremendous impacts on our daily life and the entire planet in terms of air quality, human health, and climate [*Horvath*, 1993; *Robock*, 2000; *Dubovik et al.*, 2002; *Pope and Dockery*, 2006]. By scattering or absorbing incoming solar radiation, ambient aerosols can significantly reduce the visibility [*Charlson*, 1969]. Particles within the size range of $0.1 - 1.0 \mu$ m have diameters comparable to the wavelength of visible light and are most efficient in scattering light. They account for most of the light scattering effects [*Sinclair*, 1950; *Waggoner and Charlson*, 1976]. Aerosols can also absorb light. The absorption property is largely determined by the chemical composition, with elemental carbon being the strongest light absorber [*Horvath*, 1993].

Aerosols also play a major role in climate forcing. They can have direct effects by scattering incoming solar radiation back to space which results in cooling of the atmosphere, and/or by absorbing solar energy and converting it to heat, which causes



Figure 1.2 The global mean radiative forcing of the climate system for the year 2000 relative to 1750 (Adapted from R.T. Watson and the Core Writing Team, *Climate Change 2001: Synthesis Report. A contribution of Working Groups I, II, III to the third assessment report of the Intergovernmental Panel on Climate Change*, p. 8, Copyright 2001 by Cambridge University Press).

warming effects on climate. In addition, aerosols can also influence climate through indirect effects. Aerosols can form clouds and increase their lifetime by generating more cloud droplets with smaller diameters that tend to take longer to precipitate out [Haywood and Boucher, 2000; Takemura et al., 2007]. Indirect effects of aerosols can cause cooling since clouds reflect the incoming solar radiation back to space. Figure 1.2 shows the global mean radiative forcing of the climate system published in 2001 Intergovernmental Panel on Climate Change [IPCC] report [IPCC, 2001]. Unlike the well-studies atmospheric gas species, the IPCC lists aerosol climate forcing as one of the major uncertainties, with the greatest challenge existing in determining aerosol indirect effects. A semi-direct effect of aerosols has also been discovered in recent years concerning evaporation of cloud coverage as a consequence of aerosol heating effect after absorbing solar radiation. Thus such semi-direct effect also causes warming impact by reducing could coverage and letting in more solar energy [Johnson, 2003]. The complexity of aerosols allows for the broad range of climate effects leading to the large uncertainties on aerosol radiative forcing.

Health effects of aerosols are directly related to the quality of human life and are thus one of the most studied components in air as far as impacts on health [*Archer*, 1990; *Bates*, 1992; *Dockery and Pope*, 1994; *Bates*, 1995; *Brunekreef et al.*, 1995; *Brunekreef and Holgate*, 2002; *Gauderman et al.*, 2002; *Schwartz*, 2004; *Davidson et al.*, 2005; *Gauderman et al.*, 2005; *Pope and Dockery*, 2006]. Clearly, aerosols can have detrimental effects on human health, and the severity is determined by a combination of factors including size, chemical composition, and mass and number concentrations. For example, PM_{2.5} had been shown to strongly correlate with daily mortality counts during a eight-year study in six US eastern cities [Schwartz et al., 1996]. In another study conducted in Utah, it was demonstrated that respiratory hospital admissions strongly correlated with local steel mill operation [Pope, 1991]. Recent studies have also shown that PM_{2.5} can cause significant deficits in lung development and function in children, increase asthma and other respiratory disease in children, and even cause cardiovascular disease and cancer [Lewtas et al., 1997; Peters et al., 1999; Peters et al., 2001; Sorensen et al., 2003; Garshick et al., 2004; Millstein et al., 2004]. The most severe health effects are posed by ultrafine particles (diameter $< 0.1 \,\mu\text{m}$) [Gwinn and Vallyathan, 2006]. As shown in Table 1.1, ultrafine particles have larger surface area and several magnitudes higher number concentration compared to other $PM_{2.5}$ particles for a given mass concentration. Therefore, they can carry large amounts of adsorbed or condensed toxic air pollutants [Nel et al., 2006]. The small diameter also allows ultrafine particles to penetrate through the respiratory system and deposit efficiently in the lung [Hatch, 1961; Stuart, 1973; Anderson, 2000]. Studies show that ultrafine particles can even enter the vascular system and reach other organs including the brain, escalating the negative impacts [Campbell et al., 2005; Geiser et al., 2005; Oberdorster et al., 2005].

1.3 SOURCES OF AMBIENT AEROSOLS

Aerosols are emitted from both natural sources and anthropogenic sources. Major natural sources include the ocean, soil, volcanoes, and natural forest fire [*Satheesh and Moorthy*, 2005]. Among all the natural aerosols, sea salt particles have the highest natural production rate [*Winter and Chylek*, 1997]. They are generated by sea bubble

Particle Diameter (µm)	Particles/ml of air	Particle surface area (µm ² /ml of air)
2	2	30
0.5	153	120
0.02	2,390,000	3000

Table 1.1 Particle number and surface area for $10 \ \mu g/m^3$ airborne particles. (Reprinted from A. Nel, T. Xia, L. Madler and N. Li, *Science*, 311 (5761), 2006).

bursting and subsequently picked up by wind [Stuhlman Jr., 1932; Kohler, 1936; Kohler, 1941]. The ocean is also the major source for natural sulfate particles, which are first released into the atmosphere as dimethyl sulfide (DMS) vapor, followed by DMS oxidation into SO₂ and H₂SO₄, which are subsequently converted into particle phase sulfate by gas-to-particle conversion [Fitzgerald, 1991; Russell et al., 1994]. Dust particles are produced by the re-suspension of soils and usually contain abundant minerals [Prospero et al., 1983; Dalmeida, 1986]. Dust particles play a significant role in the heterogeneous reactions of SO₂ and NO_x, even in O₃ formation [Dentener et al., 1996]. Particles larger than 5 µm are mainly present near the source region. In contrast, those less than 5 µm can undergo long-range transport and can be detected in another continent even across the ocean, affecting the climate globally [Arimoto, 2001; Prospero et al., 2002; Gong et al., 2003; Darmenova et al., 2005]. Dust particles also have important implications in ecological systems. For example, iron rich dust particles can act as a nutrient for phytoplankton, affecting the biological production of the ocean [Falkowski et al., 1998; Fung et al., 2000; Huebert et al., 2003]. Volcanic emissions represent another important natural source of aerosols. By their high particle concentration released to the atmosphere during eruption, volcanogenic sulfur species can have comparable effects on global radiative forcing as anthropogenic sulfur, which is estimated to be about 7-10 Tg S/yr in the form of SO₂ [Graf et al., 1997; Andres and Kasgnoc, 1998; Graf et al., 1998; Halmer et al., 2002]. Agriculture is also affected significantly by volcano eruption due to the strong cooling effects caused by the dramatic increase of high sulfur-containing particles, which are very effective at scattering solar radiation [Kelly et al., 1996; Lucht et al., 2002; Engvild, 2003]. Natural forest fire is the

major natural source for biomass aerosols. Although these fires only account for roughly 10% of annual total fire occurrences in the United States, they are responsible for about 48% of the total area burnt and thus have substantial effect on the climate [*Price and Rind*, 1994; *Goldammer and Price*, 1998]. Forest fires are also one of the major natural sources of carbonaceous aerosols [*Cachier et al.*, 1985].

Aerosols emitted from numerous anthropogenic sources are believed to result in the largest perturbation on climate. Major anthropogenic organic aerosol sources include, but are not limited to, motor vehicles, marine vessels, power plants, oil refineries and biomass burning. Biomass burning includes the usage of fireplaces, stoves, furnaces and incinerators; it also includes the emissions from prescribed fires, meat cooking, and industrial processes. Major products of anthropogenic sources include elemental carbon, organic carbon including carboxylic acids, methoxyphenol, alkanes, alkanoic acids, benzoic acids, and toxic cyclic and polycyclic aromatic hydrocarbons (PAHs) [Jacobson et al., 2000]. Biomass and fossil fuel burning are the two most important global organic particle sources [Liousse et al., 1996; Jacobson et al., 2000]. Many studies have been conducted to identify the organic compounds released from these sources [Ligocki and Pankow, 1989; Schauer et al., 2001]. The percentage of anthropogenic biomass burning particles vary significantly depending on the season and was estimated to be 30% of PM_{2.5} mass in Fresno, California in the winter of 2000-2001 [Chow et al., 2007]. Vehicle emission is a major aerosol source in urban areas. Particle chemical composition, size distribution, and emission rate vary significantly depending on engine type, size, and age as well as the type of fuel and lubricant used. It is estimated that vehicle emissions account for about 13% of total PM_{2.5} mass in the same study in Fresno, with 7% coming from gasoline vehicle and 6% from diesel vehicle [*Chow et al.*, 2007]. Meat cooking is also a major source of aerosols in urban areas. The amount of emission depends on the type of meat, how the meat is prepared, and the method of cooking. Meat cooking is estimated to account for 12% of the PM_{2.5} aerosol production in the Fresno area [*Chow et al.*, 2007]. Anthropogenic sources of fugitive dust include construction, paved roads, unpaved roads, and agriculture and ranching activities. One study conducted in Mira Loma, CA estimated that 13% of the particles in that area were from road dust, break dust, and tire debris [*Sawant et al.*, 2004].

1.4 FORMATION MECHANISMS AND REACTIONS OF ATMOSPHERIC AEROSOLS

Based on the method of creation, aerosols can be classified into primary and secondary aerosols. Primary aerosols refer to solid or liquid particles that are emitted directly into the air, and secondary species generally refer to chemical species formed in the atmosphere by chemical reactions of gases followed by gas-to-particle conversion. Throughout this dissertation, we will also classify particles that are primary in origin as secondary aerosols if they have clearly undergone chemical and/or physical transformations.

1.4.1 Nucleation, Coagulation, and Condensation

Nucleation is the main mechanism of particle formation in the atmosphere. Homogeneous nucleation, the formation of new particles through the condensation of a single low-vapor-pressure species, is generally difficult due to the fact that the vapor pressure increases with decreasing particle size [*Adamson*, 1973]. As such, the system generally needs to be supersaturated for the homogeneous nucleation to occur, and this is not a dominant formation mechanism [*Friedlander*, 1983]. The most important mechanisms through which the majority of new particles are formed are binary and ternary nucleation [*Finlayson-Pitts and Pitts Jr.*, 2000; *Curtius*, 2006; *Holmes*, 2007]. Binary nucleation refers to the formation of particles from two different gas molecules, such as sulfuric acid and water. The presence of water helps to reduce the vapor pressure of sulfuric acid, making it easier for condensation to occur [*Marti et al.*, 1997]. Ternary nucleation involves one additional species, usually ammonia. The presence of ammonia can enhance the binary nucleation of sulfuric acid and water by several orders of magnitude [*Korhonen et al.*, 1999].

Particles can continue to grow through coagulation and condensation after being formed [*Holmes*, 2007]. Coagulation refers to the process of two particles colliding and sticking together to form a single, larger particle. This process can significantly reduce particle number concentration and increase their size distribution. At a fixed particle number concentration, the coagulation rate increases as a function of the ratio of the two particle radii [*Seinfeld and Pandis*, 1998]. Heterogeneous condensation refers to the process of low-vapor-pressure gas phase molecules partitioning into the preexisting particles. This process produces secondary aerosols and results in an increase of particle diameter. An example of heterogeneous condensation is the condensation of semivolatile species on particle surface. Heterogeneous condensation is a reversible process and can be affected by many factors including the diffusion of gas molecules onto particles and the probability of the gas molecule uptake [*Finlayson-Pitts and Pitts Jr.*, 2000]. Particle size can also change through hygroscopic growth, during which particles absorb water


Figure 1.3 Schematic of an atmospheric aerosol size distribution for the four modes. The solid line represents the original hypothesis of Whitby and co-workers and the dashed line shows the ultrafine mode and the two peaks in the accumulation mode. (Reprinted from B.J. Finlayson-Pitts and J.N. Pitts Jr., *Chemistry of the Upper and Lower Atmosphere: Theory, Experiments, and Applications*, p. 355, Copyright 2000 by Academic Press).

and grow in size as relative humidity increases [*Cruz and Pandis*, 2000]. Particle hygroscopic properties are very important in determining the ability of particles to act as cloud condensation nuclei. Representative aerosol formation mechanisms and size distributions are summarized in Figure 1.3.

1.4.2 Photochemical Reactions

Photochemical reactions began to draw great attention in the 1940's when the Los Angeles smog severely affected human health and killed plants [*Middleton et al.*, 1950]. The specific reaction involved the photo-oxidation of volatile organic compounds (VOC) by primary pollutants, NO_x, in the presence of sunlight, generating irritating gas as well as particle phase products including peroxyacetyl nitrate (PAN):

$$VOC + NO_{x} \xrightarrow{hv} O_{3} + PAN + HNO_{3} \cdots + Particles$$
 (1.1)

Photochemical reactions represent an important formation pathway of secondary aerosols, including nitrate, sulfate, and secondary organic aerosols. When the reaction products have lower vapor pressure, particles can be formed through the oxidation of gases followed by partitioning into the particle phase. Three gas species are found to be the main oxidants: the hydroxyl radical (OH), ozone (O₃), and the nitrate radical (NO₃) [*Jacobson et al.*, 2000]. Nitric oxide (NO) emitted from vehicles is the main source of the formation of the aforementioned oxidants in the troposphere, through the following reactions [*Finlayson-Pitts and Pitts Jr.*, 2000; *Jacobson et al.*, 2000; *Jenkin and Clemitshaw*, 2000]:

$$2NO + O_2 \to 2NO_2 \tag{1.2}$$

$$NO_2 + hv(\lambda < 430nm) \rightarrow NO + O$$
 (1.3)

$$O + O_2 \xrightarrow{M} O_3 \tag{1.4}$$

$$O_3 + hv(\lambda < 340 \, nm) \rightarrow O(^1D) + O_2 \tag{1.5}$$

$$O(^{1}D) + H_{2}O \to 2OH \tag{1.6}$$

$$NO_2 + O_3 \to NO_3 + O_2 \tag{1.7}$$

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{1.8}$$

Since OH is formed through O₃ photolysis followed by reaction with water, it is the major oxidant during the daytime. NO₃ is the major oxidant at nighttime due to the fact that it dissociates quickly during the daytime. In polluted areas, OH can also be formed from HONO and HOOH. Major reaction pathways of alkenes with OH are included in Figure 1.4 to illustrate the complexity of the reactions. The reaction mechanisms of common gas-phase organic compounds are discussed in detail by Atkinson and co-workers [*Atkinson*, 1990; *Carter and Atkinson*, 1996; *Atkinson*, 1997; *Atkinson and Arey*, 2003].

1.4.3 Heterogeneous Reaction

Heterogeneous reaction refers to reactions that occur on or in condensed phase involving reactants in two or more phases. This type of reaction has drawn some attention but has not been as extensively studied as the homogeneous gas phase reactions [*Vandoren et al.*, 1990; *Kolb et al.*, 1994; *Nathanson et al.*, 1996]. An example of heterogeneous reactions is the reaction between sea salt particles with gas phase species HNO₃:

$$NaCl_{(s \ or \ aq)} + HNO_{3(g)} \rightarrow HCl_{(g)} + NaNO_{3(s \ or \ aq)}$$
(1.9)



Figure 1.4 Some major pathways in the reaction of OH with isoprene. (Reprinted from B.J. Finlayson-Pitts and J.N. Pitts Jr., *Chemistry of the Upper and Lower Atmosphere: Theory, Experiments, and Applications*, p. 195, Copyright 2000 by Academic Press).

This reaction has not only been observed in bulk analysis and lab experiments [*Junge*, 1956; *Cadle and Robbins*, 1960], but also been directly observed with single particle mass spectrometry [*Gard et al.*, 1998].

1.4.4 Aqueous Phase Processing

Another important reaction pathway for secondary aerosol formation is aqueous phase processing [*Blando and Turpin*, 2000]. Particles first take up water such as fog or cloud droplets, which form an aqueous layer on the surface. Gas molecules like SO₂ can subsequently be absorbed into the aqueous layer, allowing aqueous phase chemical reactions between adsorbed molecules and other dissolved species or water. For example, SO₂ can be oxidized into sulfate, generating low volatility products. Finally, fog or cloud droplets evaporate and the aqueous phase reaction products remain in the particle phase, creating secondary aerosols [*Blando and Turpin*, 2000; *Finlayson-Pitts and Pitts Jr.*, 2000]. This above reaction pathway can explain up to 71% of the particle phase sulfate in certain regions [*Mchenry and Dennis*, 1994; *Herrmann et al.*, 2000; *Kreidenweis et al.*, 2003; *Verma et al.*, 2007].

1.5 EXPERIMENTAL CHARACTERIZATION OF AEROSOLS

A range of instruments can be used to measure physical and chemical properties of aerosols. In particular, recently developed real-time single particle mass spectrometry (RTSPMS) can simultaneously provide information on size and chemical composition of individual particles and has proven to be very useful for studying aerosol mixing state and source apportionment [*Carson et al.*, 1995; *Suess and Prather*, 1999; *Johnston*, 2000; *Noble and Prather*, 2000; *Thomson et al.*, 2000]. Comprehensive reviews on current

techniques for atmospheric aerosol measurements can be found elsewhere in the literature [*McMurry*, 2000; *Sullivan and Prather*, 2005]. In the following, we will provide an overview of the instruments that are directly used for the studies presented in this thesis.

1.5.1 ATOFMS

The main technique used to obtain the data throughout this dissertation is aerosol time-of-flight mass spectrometry (ATOFMS). This technique was developed by our group and has been improved tremendously over the years. Currently there are four versions of ATOFMS available, each focusing on different aerosol size ranges and having different physical dimensions and mobility features. The specific version used in this work is based on a design by Gard and co-workers [Gard et al., 1997]. It can efficiently detect particles between 0.2 μ m and 3.0 μ m in diameter. The lower detection limit is due to limited light scattering capability of particles smaller than 0.2 μ m. Scattered light is critical for determining particle size and triggering the ionization process as discussed below. Particles larger than 3.0 µm have low transmission efficiency and therefore it is difficult to obtain sufficient particle count to generate statistically significant results. Note that in order to directly compare with $PM_{2.5}$ measurements from other instruments, only particles between 0.2 μ m and 2.5 μ m will be taken into account during the data analysis. $PM_{2.5}$ can be further divided into submicron particles, those with diameters between 0.2 μ m and 1.0 μ m, and supermicron particles, those with diameters between 1.0 μ m and 2.5 μ m. These definitions will be used throughout this dissertation.

The operating principles, design and performance of ATOFMS have been described in detail by Gard and co-workers [*Gard et al.*, 1997]. Here we briefly review

the basic operating principles using the schematic diagram shown in Figure 1.5. Particles are first drawn into the vacuum system through a converging nozzle. Due to the difference between ambient pressure and the pressure after the nozzle, particles are accelerated to size-dependant terminal velocities, with smaller particles traveling faster than larger particles. Particles then enter the sizing region where they intercept with two continuous wave laser beams (532 nm diode pumped Nd:YAG) located 6 cm apart, generating two scattering signals. Each signal is collected by the corresponding photomultiplier tube (PMT) detector. Particle velocity can be calculated from the distance between the scattering lasers and the time delay between the scattering signals. This velocity can be used to determine particle aerodynamic diameter through an external calibration function, and it is also used to trigger the ionization laser (266 nm Nd:YAG) to fire at the exact time when the particle arrives at the center of the mass spectrometer ionization region. Both positive and negative ions are generated and detected using dual polarity time-of-flight mass spectrometers. As such, ATOFMS can simultaneously acquire aerodynamic diameter and chemical composition information on individual particles.

1.5.2 APS

The aerodynamic particle sizer (APS) provides information on both single particle number concentration and high resolution size distribution utilizing the time-of-flight technique [*Wilson and Liu*, 1980; *Hinds*, 1999]. Figure 1.6 shows a schematic diagram of the APS. It sizes particles in a way similar to ATOFMS. Accelerated by the pressure difference when passing through the nozzle, each particle crosses through two partially overlapping laser beams, generating a two-crested scattering signal. Peak-to-peak time-



Figure 1.5 Schematic diagram of ATOFMS. (Reprinted from E. Gard, J.E. Mayer, B.D. Morrical, T. Dienes, D.P. Fergenson, and K.A. Prather, *Analytical Chemistry*, 69 (20), 1997.



Figure 1.6 Instrument schematic of the aerodynamic particle sizer. (Adapted from W.C. Hinds, *Aerosol Technology: Properties, Behavior, and Measurement of Airborne Particles*, p. 137, Copyright 1999 BY John Wiley & Sons, Inc).

of-flight is measured and used to calculate the terminal velocity. The frequency of light scattering is counted for particle number concentration. With an external calibration curve, particle aerodynamic diameter can be calculated from velocity. The APS can detect particles between 0.5 and 20 μ m with a maximum concentration of 1000 particles/cm³ [*TSI Incorporated*, 1997-2000; *Armendariz and Leith*, 2002]. Throughout this dissertation, only particles with aerodynamic diameter less than 2.5 μ m from the APS measurements will be used to compare with ATOFMS measurements within the same size range.

1.5.3 BAM

The beta attenuation mass monitor (BAM) is an automated method for measuring aerosol mass concentrations [*Hinds*, 1999; *McMurry*, 2000]. As shown in a schematic diagram in Figure 1.7, BAM detects the attenuation of beta ray through a particle-laden filter. First, beta ray transmission is measured through a clean filter. Particles are then drawn into the system and deposited on the filter. At the end of sampling, beta ray transmission is measured again for the particle-laden filter. The difference in the beta ray transmissions before and after the sampling, which is proportional to the amount of particles deposited on the filter, can be used to calculate aerosol mass concentrations with high accuracy. The Met One BAM 1020 has been designated by the U.S. Environmental Protection Agency (EPA) as an Equivalent Method for particulate matter smaller than 10 μ m (PM₁₀). It can measure mass concentrations up to 10 mg/m³ with a concentration resolution of 2 μ g/m³. The highest time resolution is 1 hour. Longer sampling times are needed during low mass concentration conditions, in order to obtain enough mass to



Figure 1.7 Instrument schematic of the beta attenuation mass monitor. (Reprinted from W.C. Hinds, *Aerosol Technology: Properties, Behavior, and Measurement of Airborne Particles*, p. 225, Copyright 1999 by John Wiley & Sons, Inc).

differentiate between the beta ray attenuation before and after sampling. Similarly, $PM_{2.5}$ mass concentration are measured with BAM and utilized throughout this work.

1.5.4 MOUDI

Micro-orifice uniform deposit impactors (MOUDI) based on particle impaction can provide size-resolved mass concentrations and aerosol chemical compositions. It is a bulk technique that obtains mass concentration by manually weighing the filters before and after sampling. Nonetheless, it has been used extensively for mass concentration measurements [*Marple et al.*, 1986; *Hinds*, 1999].

The basic operating principle of an impactor is shown in Figure 1.8a. The particle stream enters the system through a nozzle and is deflected against an impaction plate. The impaction plate causes a sharp bend in the streamlines resulting in a 90° change in the traveling direction. Particles larger than a certain size have higher inertia and can not change direction as readily. Therefore, they tend to collide with the impaction plate. On the contrary, particles smaller than this size are able to follow the streamlines without impacting the plate. As such, the impactor collects only particles larger than a certain size. As shown in Figure 1.8b, MOUDI utilizes a cascade of impactors, operating in series with decreasing nozzle diameter. Particles collected on each stage decrease in size with the largest particles collected on the top stage and smaller particles collected near the bottom. Detailed size ranges of each MOUDI stage are included in Table 1.2. By weighing each filter, particle mass concentration for each stage can be obtained. The size-resolved mass concentrations of each chemical composition can then be obtained by filter extraction and subsequent chemical speciation on each extract, utilizing techniques such as gas chromatography mass spectrometry, ion chromatography, inductively



Figure 1.8 Schematic diagram of (a) impactor and (b) micro-orifice uniform deposit impactor. (Reprinted from W.C. Hinds, *Aerosol Technology: Properties, Behavior, and Measurement of Airborne Particles*, p. 122 &129, Copyright 1999 by John Wiley & Sons, Inc).

Stage	Size Range (µm)
Stage 1	> 10
Stage 2	5.6 – 10
Stage 3	3.2 - 5.6
Stage 4	1.8 - 3.2
Stage 5	1.0 - 1.8
Stage 6	0.56 - 1.0
Stage 7	0.32 - 0.56
Stage 8	0.18 - 0.32
Stage 9	0.1 - 0.18
Stage 10	0.056 - 0.1
After-filter	< 0.056

Table 1.2 Example of the size cut for each stage in MOUDI.

coupled plasma mass spectrometry, high-pressure liquid chromatography, and thermal/optical analysis [*Hildemann et al.*, 1991; *Grosjean et al.*, 1999; *Chow et al.*, 2001; *Saitoh et al.*, 2003; *Ulrich and Wichser*, 2003].

Despite the ability to provide size segregated mass concentrations of individual chemical species, it is difficult for impactor based analysis to provide information on aerosol mixing state and obtain mass concentrations with low uncertainties [Chow, 1995; *McMurry*, 2000]. Firstly, long sampling duration is required for this type of technique in order to acquire enough mass on each impactor to acquire the mass concentration of individual chemical species. The time resolution in a polluted environment is normally a few hours, and much longer sampling times are necessary for cleaner environments. Therefore, MOUDI mass concentrations typically represent average values for extended periods and chemical variations that occur over shorter time intervals are lost. Secondly, by assuming the same chemical composition for particles on the same stage, information on the chemical associations within particles (i.e. mixing state) is completely lost. Such information is often critical for understanding the impacts of aerosols on climate, visibility, and human health [Heintzenberg, 1989]. Thirdly, being an off-line technique, particle-laden impactors are typically preserved for weeks or months before subsequent chemical analysis. Therefore, particles may react with each other or even with the filter media during the preservation, changing the particle chemical compositions and affecting the accuracy of the measurements [Zhang and McMurry, 1987]. Finally, during sampling and preservation, gas-particle equilibrium is disturbed and lead to repartitioning of the semivolatile species between different phases, also affecting the accuracy of the measurements [Smith et al., 1978; Witz et al., 1990; Ulrich and Wichser, 2003].

1.6 CHALLENGES IN RTSPMS QUANTIFICATION

As discussed above, real-time single particle mass spectrometry can provide continuous high temporal resolution measurements on single particle size and chemical composition. These measurements can provide important insight on the mixing state of individual particles and make it more tangible to establish links between emission sources and atmospheric processing. Nonetheless, various limitations remain. In particular, it is challenging to extract quantitative information on aerosol mass concentrations from RTSPMS. The main obstacles are discussed in this section.

The first obstacle is related to transmission of particles into the system. Most RTSPMS techniques introduce ambient aerosols into the system through a differentially pumped inlet. Particles are not equally transmitted through the inlet and the transmission efficiency is size-dependant [Dahneke and Cheng, 1979]. Recent studies have shown that the size-dependent transmission efficiency can be corrected by scaling with reference measurements [Allen et al., 2000; Bhave et al., 2002; Lake et al., 2003; Wenzel et al., 2003; Moffet et al., 2004; Sodeman et al., 2005; Allen et al., 2006; Qin et al., 2006]. With this scaling correction, the mass concentrations become more quantitative and are shown to agree well with the standard BAM measurements. Further details will be discussed in Chapter 6. Another obstacle is the variations in ion signal intensities produced by laser desorption/ionization utilized in most RTSPMS methods. Such variations are mainly caused by two factors. Under the same laser power setting, the actual lasing power often varies from shot to shot. Furthermore, when particles were ionized by the same power, the inhomogeneity in laser beam profile can also lead to the exposure of individual particles to various actual laser powers depending on where they

intercept with the laser beam. Both of these factors cause variance in ion signal intensity for identical particles under the same ionization laser power [Wenzel and Prather, 2004]. A recent study by Wenzel and Prather has shown very promising improvement where they used fiber optic to greatly reduce inhomogeneity of the laser beam profile [Wenzel and Prather, 2004]. Besides size-dependent transmission efficiency and variations in desorption/ionization laser energy, difficulty in obtaining quantitative results also arises from significant variations in instrument sensitivity to different aerosol chemical species. Sensitivity to the same chemical species can also change substantially depending on the matrix composition and particle size [Mansoori et al., 1994; Ge et al., 1998; Gross et al., 2000], making it difficult to fully characterize instrument sensitivity to each chemical species in every possible sampling matrix. A very promising result was obtained by Bhave and co-workers, where they proposed a field based approach to determine ATOFMS instrument sensitivities to ammonium and nitrate by scaling with co-located impactor measurements [Bhave et al., 2002]. For a given matrix, it is feasible to obtain quantitative information from ATOFMS measurements; laboratory studies are being conducted to demonstrate this capability. Finally, the data acquisition computer can also cause undesired variations in measured particle concentrations. For example, the ability of detecting incoming particles can be affected by so-called instrument busy time (mainly due to delays required for saving data to disk), especially during conditions with high ambient aerosol concentrations. This problem has been addressed by Allen et al., Bhave et al., and Qin et al. in studies by ATOFMS [Allen et al., 2000; Bhave et al., 2002; Allen et al., 2006; Qin et al., 2006]. Busy time constraint is no longer a problem after a recent upgrade on the computer and data acquisition system. The average ATOFMS scattering rate in a polluted urban environment has now tripled from less than 3.5 Hz to 9 Hz.

1.7 RESEARCH OBJECTIVES AND SYNOPSIS

Real-time information on single particle size and chemical composition obtained by ATOFMS has proven to be extremely useful in providing critical insights for understanding the formation, transformation, transport, and source apportionment of aerosols. One of the main research foci is to study ambient aerosol daily temporal variations, spatial distributions, and seasonal variations in polluted areas, to gain insights on region specific aerosol mixing state, formation mechanisms, and sources. Another emphasis of the current work is focused on methodological developments, with particular emphasis on enhancing quantification ability of ATOFMS on mass concentration measurements.

The rest of this dissertation is organized as follows. Chapter 2 focuses on biomass particles and high mass organic compounds (HMOC) observed in Fresno, CA during the California Regional Particulate Air Quality Study (CRPAQS). These particles displayed distinct diurnal variations, and their origin and formation mechanisms are also discussed in detail. Chapter 3 represents an overview of ATOFMS measurements during CRPAQS in Fresno and Angiola. Measurements in these two cities provide an interesting comparison between urban and rural areas. Differences in aerosol chemical compositions, diurnal variations, formation mechanisms, and degrees of transformation are discussed for these two locations. Chapter 4 discusses ambient aerosol seasonal variations during the Study of Organic Aerosols in Riverside (SOAR) during summer and fall of 2005 in Riverside, CA. Distinct diurnal variations were also observed during both seasons with substantial difference in chemical compositions. Ambient aerosols observed in both the CRPAQS and the SOAR studies are considerably aged; however, the major factors lead to particle transformation is different. Chapter 5 discusses two methods for obtaining quantification information from ATOFMS by correcting for particle transmission efficiency with either MOUDI or APS measurements. The results demonstrate that instrument transmission loss can be successfully corrected and these methods can be used to obtain high temporal resolution ATOFMS mass concentrations that are in very good agreements with BAM mass concentrations or other co-located measurements. Finally, Chapter 6 applies the APS scaling method to several studies. When there are no co-located APS measurements available for ATOFMS scaling, it is also possible to use the scaling function from a different study. Although the absolute mass concentrations of specific particle types may differ by one or two orders of magnitude, relative mass concentration of scaled ATOFMS individual particle types proves to be quite reliable, which enable us to compare measurements among different studies.

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Chapter 2

2 Impact of Biomass Emissions on Particle Chemistry during the California Regional Particulate Air Quality Study

2.1 SYNOPSIS

This paper describes aerosol time-of-flight mass spectrometry (ATOFMS) measurements of the size and chemical composition of individual particles during the California Regional Particulate Air Quality Study (CRPAQS) (December 2000 – February 2001). In Fresno, biomass particles display distinct diurnal variations, peaking at night and reaching a minimum during the day. These biomass particles are small (Da $\leq 1.0 \ \mu$ m) and comprise 25% of the total analyzed particles with fractions ranging from 5% during the day to more than 60% at night. In addition, a unique collection of high mass organic carbon particles (HMOC) was identified with similar diurnal variations. The HMOC particles contain characteristic peaks between mass-to-charge (m/z) 100 and 200 in both the positive and negative ion mass spectra. HMOC particles only appear at night and have larger aerodynamic diameters (Da $\leq 1.0 \ \mu$ m). Furthermore, the HMOC particles show fragment ions of organic carbon, aromatic compounds, as well as nonmineral potassium, levoglucosan, and marker ions indicative of fog processing. We hypothesize the observed diurnal variations are due to an increase in direct biomass

emissions followed by gas/particle partitioning of semivolatile species which undergo aqueous phase processing at night.

2.2 INTRODUCTION

The San Joaquin Valley (SJV) is located in central California with mountains on three sides. Pollutants are trapped in the valley due to the secluded geographic features [Whiteaker et al., 2002] which leads to a deterioration of the air quality. During the winter, PM_{2.5} and PM₁₀ concentrations reach their highest in urban areas when multiple sources simultaneously contribute to the aerosol concentrations [Watson and Chow, 2002a]. Furthermore, secondary ammonium nitrate and carbonaceous species represented the two largest constituents of the PM in the SJV during the winter [Watson and Chow, 2002a; Watson and Chow, 2002b]. In atmospheric studies, carbonaceous particulate matter is typically categorized into organic carbon (OC) and elemental carbon (EC). Elemental carbon is the product of incomplete combustion [Lighty et al., 2000], and diesel exhaust is one of the largest EC sources in the SJV [Watson et al., 1994]. Fine particulate organic carbon concentrations are dominated by biomass burning emissions in winter time in Fresno based on source apportionment using chemical mass balance receptor models [Schauer and Cass, 2000]. Therefore biomass burning is one of the most important sources of ambient aerosols in the SJV during the winter months.

The wintertime meteorological conditions in SJV are very different from other seasons. Mixing depth and ventilation are low and accompanied by the highest relative humidity (RH) of all seasons [*Chow et al.*, 1992]. The low mixing depth favors the accumulation of primary emissions. High relative humidities lead to aqueous phase

processing of the primary aerosol particles, changing the aerosol composition [*Blando and Turpin*, 2000; *Fahey et al.*, 2005]. Therefore, the composition of SJV ambient aerosols is fairly complex during the winter and strongly affected by the liquid water content of the aerosol.

While ammonium nitrate in the SJV has been intensively studied during the last decade [*Blanchard et al.*, 2000; *Chow et al.*, 1994; *Chow et al.*, 1992; *Chow et al.*, 1993; *Richards et al.*, 1999], less is known about the components making up the carbonaceous fraction of the aerosols, in particular the semivolatile organic compounds. The formation mechanisms, chemical reactions, and concentrations of organic compounds in the atmosphere are far less understood than other inorganic species, such as sulfate and nitrate [*Turpin et al.*, 2000]; thus, understanding the emission sources, particle transport, and mechanisms of chemical reactions of organics in particulate matter will further our understanding of a variety of atmospheric phenomena [*Pandis et al.*, 1995], which will ideally allow for the development of policies to help alleviate air pollution problems.

Organic compounds are most frequently measured using filter and/or impactor based bulk analysis techniques. While providing valuable information, these techniques require off-line analysis and have several limitations. First, bulk analysis techniques usually require extended collection periods (hours to days) in order to collect enough particle mass for chemical analysis. Therefore, it is nearly impossible to obtain real-time or high temporal correlations between chemical species and atmospheric conditions. Furthermore, information on the chemical associations (particle mixing state) cannot be measured with bulk analysis techniques, and one must assume that all particles in the same size range have the same bulk chemical composition [*Heintzenberg*, 1989]. In addition, chemical reactions may occur on or with the filter media during transport and preservation before chemical analysis, thus changing the initially collected aerosol chemical composition [*Zhang and McMurry*, 1987]. Finally, the gas-particle equilibrium is disturbed by most sampling methods, causing aerosol re-partitioning between different phases; this often causes a bias in the measurement of semivolatile species [*Volckens and Leith*, 2002; *Volckens and Leith*, 2003]. For example, most filter and impactor techniques operate at pressures below atmospheric pressure. Semivolatile organic compounds particle-to-gas phase transfer may occur under such low pressure conditions.

Real-time single particle mass spectrometry (SPMS) measurements of carbonaceous particles are able to provide unique information on many species by correlating the instantaneous carbonaceous particle composition with rapidly changing atmospheric conditions [Guazzotti et al., 2001; Noble and Prather, 1997]. Many of these techniques are able to obtain both size and chemical composition information on individual particles with high temporal resolution [Hinz et al., 1994; McKeown et al., 1991; Murphy and Thomson, 1995; Prather et al., 1994]. Single particle mass spectral analysis can analyze several particles/second under polluted ambient conditions, allowing for a higher temporal resolution than that which can be achieved using filter-based methods. In addition, the residence time of the single particles in the mass spectrometry instrument is less than 1 ms, minimizing changes in particle morphology and the repartitioning of chemical species that can occur at reduced pressures. Therefore, SPMS measurements can provide valuable information for studying organic aerosols, as well as semivolatile species. The challenge for SPMS measurements has involved providing quantitative information. One major obstacle is that fluence inhomogeneities in the LDI

laser beam utilized by most SPMS measurements result in variations of the ion signal intensities in the mass spectra of identical particles; moreover, instrumental sensitivities to different aerosol components vary with matrix composition [*Mansoori et al.*, 1994]. Recently, researchers in multiple labs have begun to explore quantification using SPMS measurements [*Allen et al.*, 2006; *Bhave et al.*, 2002; *Lake et al.*, 2003; *Moffet et al.*, 2004; *Qin et al.*, 2006a; *Sodeman et al.*, 2005].

Potassium is a common component of biomass burning particles as observed with filter measurements and electron microscopy with energy-dispersive X-ray spectrometry [Hudson et al., 2004; Li et al., 2003; Liu et al., 2000b; Posfai et al., 2003]. In recent studies, direct online measurements of biomass aerosols were carried out with another SPMS to investigate the composition and chemical associations of individual biomass particles. Both the Particle Analysis by Laser Mass Spectrometry (PALMS) and the Time-of-flight Mass Spectrometry (ATOFMS) measurements observe Aerosol potassium, organic carbon, and nitrogen-containing species from single particle biomass mass spectra [Hudson et al., 2004; Silva et al., 1999]. In this work, the time series of biomass burning emission particles and other unique organic particle types in Fresno and Angiola were investigated using an ATOFMS. The unique organic particles, unlike most other particle types detected, display fairly intense peaks between mass-to-charge (m/z)100 and 200 in the mass spectra and are referred to throughout the paper as high mass organic compounds (HMOC). The possible sources of HMOC particles are described and the temporal variations are presented and discussed. Results from this work will provide useful information on the sources and processes contributing to the organic

compounds present in the SJV region as well as other urban areas impacted by high biomass emissions and regional fogs.

2.3 EXPERIMENTAL

This field campaign was conducted from November 30, 2000 to February 4, 2001 as part of the California Regional Particulate Air Quality Study (CRPAQS). The size and chemical composition of individual particles in the 0.2 μ m – 3.0 μ m size range were measured. The urban Fresno site was located in the center of San Joaquin Valley in a residential neighborhood, and the rural Angiola tower site was located about 80 km southeast of Fresno in the middle of an agricultural area [*Watson et al.*, 2000]. The results of the measurements taken from January 9, 2001 to February 4, 2001 in Fresno and Angiola are presented in this paper, representing 711,289 particles in Fresno and 614,915 particles in Angiola.

2.3.1 Data Acquisition

The operating principles, design, and performance of the ATOFMS are discussed in section 1.5.1 and the details are included in the work by Gard and co-workers [*Gard et al.*, 1997]. Briefly, particle size is correlated to its speed, which can be calculated by particle time-of-flight between two known distance scattering lasers, and the chemical composition is acquired by a dual-polarity time-of-flight mass spectrometer. Thus, information on both single particle size and chemical composition can be determined. ATOFMS is particularly efficient at detecting aromatic compounds. Due to the relatively large molar extinction coefficients at 266 nm ($\varepsilon = 10^3 - 10^5$ Lmole⁻¹cm⁻¹) [*Berlman*, 1971; *Finlayson-Pitts and Pitts*, 2000], mono- and polycyclic aromatic hydrocarbons
(PAHs) and their derivatives are easily ionized and detected by ATOFMS with high sensitivity. During this study, the ATOFMS ionization laser was operated at reduced power (<1.0 mJ instead of the normal 1.5 mJ) during certain times to study the effect of laser power on ion fragmentation. Due to the fact that particle counts collected within the same amount of time are affected by laser power, reduced power sampling periods are excluded from the discussion and figures.

In this paper, measurements conducted with several other instruments co-located at the Fresno site are also presented for comparison purposes. $PM_{2.5}$ particle mass concentrations were obtained by the Beta Attenuation Monitor (Met One BAM 1020) and total particle-bound PAH concentrations were acquired by Photoelectric Aerosol Sensor (Ecochem Analytics PAS 2000).

2.3.2 Data Analysis

Single particle mass spectra and aerodynamic size information were saved during the field study. A custom software program was used to calibrate the mass spectra and extract a list of ion peaks in the spectra. These peak lists were then imported into YAADA, a single particle mass spectrometry data analysis tool, for further analysis [*Allen*, 2002].

To obtain a general picture of the aerosol composition over the course of the study, particle information obtained by the ATOFMS is classified using an adaptive resonance theory-based clustering method (ART-2a). ART-2a classifies particles according to the existence and intensity of ion peaks in individual single particle mass spectra and groups particles into the same cluster if they have similar mass spectral fingerprints [*Song et al.*, 1999].

2.4 RESULTS AND DISCUSSION

2.4.1 ATOFMS Raw Counts and Mass Concentration Measurements

The unscaled particle counts obtained directly by the ATOFMS do not represent the ambient particle number concentrations. They can be scaled with other measurements such as a micro-orifice uniform deposit impactor or an aerodynamic particle sizer to obtain quantitative number concentrations [Allen et al., 2000; Bhave et al., 2002; Qin et al., 2006a; Suess and Prather, 1999]. However, for the purposes of this paper, it is important to note that the raw ATOFMS counts show similar variations to those observed with other measurements. Similar agreement between ATOFMS nitrate counts and nitrate mass concentrations from an automated particle nitrate monitor have been shown in previous studies [Liu et al., 2000a]. In this study, hourly temporal variations of ATOFMS total hit particle counts obtained in Fresno and PM_{2.5} mass concentration acquired by the beta attenuation monitor (BAM) are compared in Figure 2.1. Data points were excluded if the ATOFMS was offline for more than 30% of a particular hour or low laser power was utilized during that hour. Figure 2.1 illustrates the excellent agreement between the time series of the ATOFMS counts and mass concentration measurements: ATOFMS total particle raw counts reach maxima and minima at nearly the same times as the measurements made using the BAM. The fact that ATOFMS raw counts and mass concentrations track one another in this study supports the use of unscaled data to provide an indication of the relative particle concentration changes discussed throughout this paper.



Figure 2.1 Time series of ATOFMS total particle counts and $PM_{2.5}$ mass concentration acquired with a beta attenuation monitor (BAM) in Fresno.

2.4.2 Mass Spectral Characteristics of Biomass and HMOC in Fresno

After running ART-2a on ATOFMS measurements in Fresno, two unique particle types stood out from all of the other types. The single particle mass spectra of the first type contain a very intense potassium signal (m/z 39) with relatively low intensity positive ion carbonaceous peaks. We refer to the first type as biomass burning particles because nonmineral potassium is a commonly used tracer for wood smoke [*Malm and Gebhart*, 1997; *Schauer et al.*, 2001; *Sexton et al.*, 1985; *Sheffield et al.*, 1994]. This biomass particle type accounts for more than 25% of the total analyzed particles, ranging from less than 5% during the day to up to 65% at night. Particles of the second type generally show unique peaks between m/z 100 and 200 in both positive and negative ion spectra in addition to carbonaceous peaks at lower m/z ratios that are similar to biomass type. Specifically, peaks at m/z 115, 128, 139, 153, 165, 178, 189, 202 and peaks at -109, -123, -137, -151, -163, -177, and -191 are the characteristic peaks in these particles.

The digital color histograms of the biomass and HMOC particle types are shown in Figure 2.2. The y-axis of the digital color histograms represents the fraction of particles for a given particle type that contain an ion with a peak area within a particular range, as shown in the legend, at each given m/z value. Digital color histograms provide valuable information on mass spectral characteristics and the chemical associations for the two particle types. As shown in Figure 2.2a, nearly 100% of the biomass particles contain potassium (m/z 39) in their positive ion spectra, and 40% of them have extremely intense K⁺ signals (area > 10,000). A small fraction of the biomass particles (< 20%) also contain characteristic HMOC peaks (m/z 115, 128, 139, 153, 165, 178, 189, 202, -109,



Figure 2.2 Digital color stacks of (a) biomass and (b) HMOC particles.

-123, -137, -151, -163, -177, and -191) with very low intensities. The biomass particles show signs of atmospheric aging as indicated by the ammonium marker peak at m/z 18 (NH₄⁺), nitrate marker ions at -46, -62, and -125 (NO₂⁻, NO₃⁻, and HNO₃NO₃⁻), and sulfate ions at -80 and -97 (SO₃⁻ and HSO₄⁻). Some biomass particles (< 30%) are associated with mono-aromatic species based on the peaks at m/z 77 (C₆H₅⁺) and m/z 91 (C₇H₇⁺) [*Silva and Prather*, 2000], and polyaromatic compounds indicated by an ion peak at m/z 63 [*McLafferty and Turecek*, 1993].

Almost 80% of the HMOC particles also contain a potassium peak as shown in Figure 2.2b. The peak at m/z 43 is a marker for aged organics and most commonly corresponds to $C_2H_3O^+$ in the ATOFMS; it is the most common peak detected in 90% of the HMOC particles, indicating a higher degree of transformation of the HMOC particles compared to biomass particles. In recent studies in Riverside, the peak at m/z 43 is shown to be correlated with highly aged particles and tracks ozone concentrations [Qin et al., 2006b]. There is also the possibility that some fraction of this peak might be due to $C_{3}H_{7}^{+}$ and $C_{2}H_{5}N^{+}$. Additionally, as illustrated in Figure 2.2b, approximately 80% of the HMOC particles are associated with levoglucosan, an indicator of biomass burning, which has characteristic peaks at m/z -45, -59 and -71 according to the study by Silva et al. [Silva et al., 1999]. Characteristic HMOC peaks (m/z 115, 128, 139, 153, 165, 178, 189, 202, -109, -123, -137, -151, -163, -177, and -191) exist in over 50% of the HMOC particles as shown in Figure 2.2b; moreover, the peaks adjacent to the characteristic peaks show high abundances and exist in nearly 40% of the HMOC particles. Interestingly, the peaks appear as a pattern of clusters separated by m/z 12 and 14 m/zunits (i.e. -109, -123, -137, -151, -165, -179); this type of repetitive pattern is often

attributed to oligomers or HULIS species. The HMOC particles are associated with ammonium, nitrate, sulfate, and mono- and polycyclic aromatic compounds. A substantial fraction of the HMOC particles (~ 50%) are also associated with fog processing marker peaks at -81 and -111 (HSO₃⁻ and HOCH₂SO₃⁻) [*Whiteaker and Prather*, 2003], suggesting they have undergone some amount of aqueous phase fog processing. A further discussion of this is provided below.

The biomass and HMOC share many common peaks; the major differences are ion peak intensities and the fraction of particles that contain the characteristic markers. As detailed below, the most likely source of the HMOC particles are biomass burning emissions that have partitioned to the particle phase in the cooler evenings and undergone fog processing [*Graham et al.*, 2002; *Mayol-Bracero et al.*, 2002].

2.4.3 Possible Assignments of Ion Peaks Above m/z 100

Definitive assignments for the high m/z peaks (m/z above 100) are difficult to make a priori since more than one isobar exists for each m/z value. In order to make these assignments, information is taken from a combination of previous source characterization studies using filters and ATOFMS, ATOFMS mass spectral fragmentation patterns, ATOFMS lab studies of organic standards, and detailed local emission profiles for the Fresno area. Table 2.1 lists the most likely assignments. Furthermore, dual ion information and an understanding of the ion peaks produced by a particular organic compound class yields further insight into the peak identification. For example, both protonated and deprotonated methyl guaiacol peaks are observed by ATOFMS at m/z 139 (MH⁺) and m/z -137 (M-H⁻) (molecular weight 138). It is possible that instead of being individual compounds, the above peaks are fragment ions of high

m/z	MW	Most Possible Assignments
-109	110	dihydroxybenzene
-123	124	guaiacol
128	128	naphthalene
-137, 139	138	methyl guaiacol
-151, 153	152	ethy guaiacol / vanillin / acenaphthylene
-163, 165	164	eugenol
-177, 178, 179	178	methyl eugenol / phenanthrene / anthracene
202	202	pyrene / fluoranthene

Table 2.1 Possible peak assignments of m/z above 100.

molecular weight species. In Fresno, more than 50% of the fine organic carbonaceous particles are emitted from residential biomass burning in the winter [*Poore*, 2002; *Schauer and Cass*, 2000]. Schauer and coworkers reported that guaiacols, phenols, and their substituted derivatives accounted for approximately 20% of the total mass of semivolatile gas-phase organic compounds emitted from wood combustion [*Schauer et al.*, 2001]; other studies revealed that biomass burning also emits substantial amounts of methoxyphenols and PAHs [*Kjallstrand et al.*, 2000; *Lemieux et al.*, 2004; *Mandalakis et al.*, 2005; *Xu et al.*, 2006; *Yang et al.*, 2006]. It is important to note that the ATOFMS is particularly sensitive to these aromatic compounds due to the use of the 266 nm laser. Thus many of the above peak assignments of for peaks above m/z 100 are based on the known fragmentation patterns and sensitivity of the ATOFMS technique to specific classes of organic compounds.

2.4.4 Temporal Variations of Biomass and HMOC Compounds in Fresno

Figure 2.3 shows the temporal variations of biomass and HMOC unscaled counts and the percentages of these types measured each hour. Distinct diurnal variations are evident in both biomass and HMOC particles. As shown in Figure 2.3a, biomass particle counts/concentrations remain relatively low during the daytime, increase significantly during late afternoon, and reach maxima between 8:00 PM – 3:00 AM on most days. The biomass count percentage shows similar diurnal temporal variations. Similar diurnal temporal variations of the HMOC particle counts and count percentages are shown in Figure 2.3b. The temporal variations of HMOC and biomass counts track each other very well with a high correlation coefficient of 0.84. The sum of biomass and HMOC



Figure 2.3 (a) Time series of ATOFMS biomass particle counts and percentages; (b) time series of ATOFMS HMOC particle counts and percentages.

particles account for approximately 50% of the total particles detected at night, sometimes even rising above 65%, making them an important fraction of nighttime Fresno aerosol.

2.4.5 Diurnal Trends of Biomass Particles in Fresno

The distinctive diurnal variations observed for the biomass particles can be explained by a number of factors, including an increase in residential biomass burning activities at night [Chow et al., 1999; Watson and Chow, 2002b], accumulation of primary PM emissions, gas/particle phase partitioning of biomass emissions, and a nighttime decrease in the height of the inversion layer. Direct biomass emissions late in the day directly contribute to the observed increase in the ambient biomass aerosols during the evening. Another important factor is gas/particle phase partitioning. Based on partitioning theory, the particle phase concentrations of a particular species will be proportional to its gas phase concentration and the amount of total suspended particulate matter in the atmosphere [Jang et al., 1997; Mader and Pankow, 2002; Pankow et al., 1994]. During the nighttime, both the amount of total suspended particulate matter and biomass emissions increase. Gas phase emissions can partition onto the increased available surface area of the particle phase, increasing the total number of particles that contain biomass emission markers. In addition, lower nighttime temperatures induce semivolatile components to partition to the particle phase. Moreover, other nighttime meteorological conditions further assist in the formation of diurnal variations of biomass particles in Fresno. The nighttime wind speed was low during the study as is typical for winter conditions in the SJV; these stagnant conditions aid in the accumulation of primary emissions. In addition, the lower nighttime inversion layer leads to an increase

in the ground level primary particle concentrations. All of these factors contribute to the observed increase in nighttime biomass particle phase concentrations in Fresno, as measured with the ATOFMS.

During the day, direct biomass burning emissions nearly cease. In addition, ambient biomass aerosols and ion markers are transformed and lost during the day through various reaction (i.e. photochemistry) and deposition processes; furthermore, when the inversion layer rises during the day, particles are released to higher altitudes, causing their concentrations to decrease at ground level. All of these factors contribute to the decrease in biomass particle counts during the daytime.

2.4.6 Sizes and Diurnal Variation of HMOC Particles in Fresno

The size distributions of the different particle types can provide insight into their sources and formation mechanisms. Hydroxymethanesulfonate (HOCH₂SO₃⁻, m/z -111) is a known product of fog processing and therefore can be used as an indicator of aqueous phase processing of individual particles [*Whiteaker and Prather*, 2003]. A comparison of the sizes of biomass, HMOC, and fog processed particles (reduced by 3 in order to be shown on the same scale) are presented in Figure 2.4. Although biomass and HMOC particle types have very similar temporal variations and many common peaks in their mass spectra, the particle size distributions of these two types differ from one another. The majority of the biomass particles are submicron (Da $\leq 1.0 \ \mu$ m) with aerodynamic diameters peaking in the lowest detectable sizes (0.5 µm). Conversely, the HMOC and fog processed particles are primarily supermicron sized particles (Da > 1.0 µm) and have similar size distributions. The respective sizes suggest the biomass particles are directly emitted, whereas the HMOC particles are fog processed and have grown to larger sizes.



Figure 2.4 Size distributions of Fresno biomass, HMOC, and fog processed particles.

The similar time series and mass spectra of the HMOC and biomass particles suggest that biomass emissions produce the precursors of the HMOC species that partition to the particles during the night when cooler temperatures and higher RH conditions exist and undergo aqueous phase processing, increasing the size of the processed particles, [*Feng and Moller*, 2004; *Hoffer et al.*, 2004].

Comparing the temporal correlation between HMOC and other species can help identify the sources and factors contributing to their formation. Figure 2.5a shows a comparison between the time series of ATOFMS HMOC particle counts and measurements made with a co-located photoelectric aerosol sensor (PAS) at the Fresno site. The signal obtained by the PAS is proportional to the concentration of particlebound PAHs [Burtscher, 1992; Dunbar et al., 2001], species which are often emitted in biomass emissions [Mandalakis et al., 2005; Xu et al., 2006; Yang et al., 2006]. ATOFMS HMOC raw particle counts display diurnal variations similar to those observed in PAS measurements. The difference between the two measurements from January 19 to January 23 suggests the presence of other (non-biomass) major PAH sources. The strong correlations ($R^2 = 0.60$) suggest that HMOC compounds and PAHs are both emitted in biomass emissions. Another useful marker, levoglucosan, has been shown to be a unique marker for wood-smoke aerosols, representing up to 30% of the fine particle organic compound emissions [Schauer et al., 2001; Simoneit et al., 1999]. In this analysis, particles containing levoglucosan are selected as those with a relative area of the ion mass signal at each marker peak (m/z - 45, -59 and -71) with a relative area of greater than 1%. The temporal variations of HMOC particles and levoglucosan are strongly correlated ($R^2 = 0.84$) as shown in Figure 2.5b, this correlation supports the conclusion



Figure 2.5 Time series of (a) HMOC and PAS; (b) HMOC and levoglucosan; (c) HMOC and fog processed particles.

that the HMOC species in particles in Fresno originate from biomass burning emissions. The correlation between HMOC and fog processed particles are shown in Figure 2.5c. The temporal variations of these two particle types reach maxima and minima at about the same time. It is important to note that a substantial fraction of HMOC particles (nearly 50%) contain the fog processing indicator peak at m/z -111, strengthening the conclusion the HMOC species were formed via fog processing. So far the only other ATOFMS field studies where particle types with similar signatures to this HMOC type were observed were two coastal studies where it was hypothesized that these species were formed by aqueous phase processes in cloud droplets during long range transport across the ocean [Holecek et al., 2006]. All the above evidence suggests that the HMOC particles mainly resulted from a combination of biomass emissions, gas/particle partitioning of semivolatile biomass precursors, followed by aqueous phase processing. Previous studies have shown that humic-like substances (HULIS) are generally high mass aromatic compounds with hydroxyl, carboxyl, and carbonyl groups formed in fog/cloud water by oligomerization reactions which were proposed to originate from biomass emissions based on the high concentrations of levoglucosan detected [Facchini et al., 1999; Feng and Moller, 2004; Gelencser et al., 2003; Graber and Rudich, 2006; Hoffer et al., 2004; Krivacsy et al., 2001; Krivacsy et al., 2000; Samburova et al., 2005]. As described, the HMOC are HULIS most likely formed by aqueous phase reactions from lower molecular weight semivolatile biomass species (for example, methoxyphenols). At this stage, we can not exclude the possibility that a small fraction of HMOC are HULIS directly emitted from biomass emissions, since HULIS has also been reported to be released from primary biomass emissions [Graber and Rudich, 2006]. In other studies,

ambient photo-oxidation reactions have also been shown to generate HULIS and oligomeric species which correlated with O₃ concentration [*Gross et al.*, 2006; *Kalberer et al.*, 2004; *Samburova et al.*, 2005]. In contrast, in the current study, the concentrations of the HMOC particles peaked at night thus indicating that photo-oxidation was not the dominant formation mechanism.

The diurnal variations of the HMOC particles appear to be most affected by ambient RH and biomass burning emissions in Fresno. During the nighttime, direct biomass emission increases, making more water soluble organic compounds (WSOC) available as the precursor of HULIS [*Facchini et al.*, 1999; *Hoffer et al.*, 2004; *Krivacsy et al.*, 2001]; nighttime low temperature also favors the particle phase partitioning of volatile and semivolatile biomass emissions; high nighttime RH condition (~ 90%) substantially increases the liquid water content (LWC) on the particle surface, which can dissolve WSOC and lead to the formation of HULIS through aqueous phase reaction. Thus the diurnal patterns of RH and biomass burning emission lead to a higher HULIS concentration at night, which is observed on ATOFMS as the diurnal temporal variation of HMOC particles. During the daytime, as ambient RH decreases (~ 50%), so do biomass burning emissions. Thus much lower HMOC (HULIS) particle counts were detected by the ATOFMS in Fresno during the day.

2.4.7 Comparison of Temporal Variations of Biomass and HMOC Particles in a Rural Area

It is interesting to the compare single particle results obtained close to the source (Fresno) with those obtained in a distant rural site 80 km away (Angiola). Temporal variations of Angiola biomass particles are presented in Figure 2.6. Overall, a much



Figure 2.6 Time series of biomass particle counts and percentages in Angiola. The particle counts presented here do not include low laser power sampling periods or the periods when the instrument was offline for more than 30% of the hour.

lower average percentage of particles with strong biomass signatures (7%) was measured in Angiola. In general, Angiola biomass particle fractions were below 10% for most of the sampling period but occasionally grew over time to nearly 40%. Figure 2.6 illustrates how no obvious diurnal pattern was detected for the Angiola biomass particles. Angiola is located in a remote rural area with very few local emission sources. Thus, the differences in the temporal behavior between Fresno and Angiola are most likely explained by transformations and deposition losses occurring as the biomass particles are transported to Angiola.

It is highly likely that by the time the particles reached Angiola their signatures had evolved to another particle type with a different pattern. This is supported by the observation that rather than having one distinct HMOC type as measured in Fresno, most Angiola particles (> 90%) were associated with high mass ions, most likely HULIS species, between m/z 100 and 200 in the positive mass spectra. The presence of these high mass (HULIS) species can be explained by processing occurring during transport. Characteristic high mass ion peaks vary from particle to particle with only a few peaks at the same m/z as those detected in the Fresno HMOC particle types. Major high mass-to-charge peaks that stand out in the spectra among most Angiola types are m/z 140, 152, and 160. Negative ion spectra contain a greater amount of nitrate, indicating a higher degree of aging. As particles are transported from different source regions to Angiola, different sources and precursors encountered along the way produce different characteristic high mass peaks.

2.5 CONCLUSIONS

ATOFMS measurements made during the CRPAQS study provide information on particle size, composition, chemical associations, and the temporal variations of biomass burning and HMOC particle types in Fresno and Angiola. Based on a comparison of their size distributions, the larger HMOC particles are most likely HULIS species formed by fog processing. Both time series of the biomass and HMOC particles display a strong diurnal pattern in Fresno, with relatively low daytime particle counts which rapidly increase from late afternoon and peak at night. We hypothesize the diurnal variations are due to an increase in direct biomass emissions followed by gas/particle partitioning of semivolatile species which undergo aqueous phase processing at night. The SJV winter time low inversion layer also contributes to increased levels of these particles at night. In contrast, biomass particles in the rural Angiola area were more heavily transformed, chemically diverse, and show more of a gradual build-up over time. These observations suggest the particle chemistry in Angiola was controlled by long range transport into the area as opposed to by local sources.

The results in this paper demonstrate how single particle measurements can be used to better understand how specific sources and meteorological conditions affect ambient particle mass concentrations. Real-time information on the sizes and temporal variations of biomass and HMOC particles can be used as inputs for models [*Held et al.*, 2004] to determine the factors playing the most significant roles in controlling concentrations of organic compounds in the San Joaquin Valley.

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Chapter 3

3 Comparison of ATOFMS Single Particle Measurements at Fresno and Angiola in the San Joaquin Valley during the California Regional Particulate Air Quality Study

3.1 SYNOPSIS

Aerosol time-of-flight mass spectrometry (ATOFMS) measurements were conducted in Fresno and Angiola during the California Regional Particulate Air Quality Study (CRPAQS) from December 2000 to February 2001. The goal of this study is to compare particle chemical compositions, diurnal variations, formation mechanisms and the emission sources in urban and rural locations in the San Joaquin Valley. Distinct temporal variations were present at each location. Most Fresno particle types generally peaked at night due to the decreased inversion layers and increased biomass burning activities from residential heating. In contrast, at the rural Angiola site, particle types primarily peaked during the day since the majority of the pollutants were transported from urban locations from aloft, and mixed vertically with ground level particles during the day when inversion layer dissipated. The chemical composition of the particles was strongly influenced by meteorological conditions. In Fresno, the dominant chemical classes were aged sea salt, biomass burning, and dust in clean periods, biomass burning and aged sea salt in buildup periods and biomass burning, organic carbon (OC), and elemental carbon (EC) particles in the stagnant polluted periods. Periodic changes on chemical composition were present at Angiola with aged sea salt and dust being the major chemical components during the clean events and biomass-OC and ammonium nitrate-rich particles (NH_4NO_3) during the stagnant periods. The stagnant conditions in Angiola led to the exposure of particles to high levels of locally emitted ammonia; thus Angiola particles contained higher amounts of secondary ammonium and nitrate than those in Fresno, indicating a higher degree of aerosol processing. The major particle types during high mass concentration periods were biomass burning, OC, and NH₄NO₃-OC particles in Fresno and aged biomass particles with ammonium nitrate in Angiola.

3.2 INTRODUCTION

The San Joaquin Valley (SJV) is located in central California with the Coastal Mountain range to the west, the Sierra Nevadas to the east, and the Tehachapi Mountains to the south [*Chow et al.*, 2006a]. It is the nation's top agriculture producing region covering over 40,000 km². Wintertime meteorological conditions feature slow ventilation and low mixing depths, leading to prolonged air stagnation [*Watson et al.*, 2006a], with the lowest inversion layers (often < 100 m) observed during late night and early morning hours [*Brown et al.*, 2006]. The major air pollution ventilation mechanisms are gusty winds and frontal passes [*Chow et al.*, 1992]. The winter also features high relative humidities (RH) and low ambient temperatures, which coupled with the stagnant conditions, can increase the amount of secondary aerosols formed through fog processing [*Qin and Prather*, 2006]. The secluded geographical characteristics and stagnant wintertime meteorology make the valley basin ideal for pollutant accumulation, resulting in high concentrations of particulate matter (PM)

smaller than 2.5 μ m (PM_{2.5}) and 10 μ m (PM₁₀). PM_{2.5} has been shown to positively correlate with mortality rates and have adverse health effects [*Dockery et al.*, 1993; *Pope et al.*, 2002; *Smith et al.*, 2003]. Both wintertime PM_{2.5} and PM₁₀ levels in the SJV constantly exceed the National Ambient Air Quality Standards (NAAQS), endangering the health of nearly 3.5 million residents [*Gorin et al.*, 2006; *Turkiewicz et al.*, 2006].

In order to address air pollution problems in this region of California, numerous studies have been carried out in the SJV over the past two decades. Major studies include the Valley Air Quality Study from 1988 to 1989 [Chan et al., 1990; Chow et al., 1992], the San Joaquin Valley Air Quality Study/Atmospheric Utility Signatures, Predictions, and Experiments in 1990 [Lagarias and Sylte, 1991; Chow et al., 1996; Chow et al., 1998], the Integrated Monitoring Study of 1995 [Chow et al., 1999; Magliano et al., 1999; Solomon and Magliano, 1999], and the California Regional PM₁₀/PM_{2.5} Air Quality Study (CRPAQS) [Watson et al., 1998]. The goal of CRPAQS was to understand the cause of elevated particle concentration and determine the emission sources in an effort to alleviate air pollution problems [Watson et al., 1998]. This campaign had the longest sampling duration of any previous major study, covering 14 months from November 1999 to February 2001 with data acquired from 38 monitoring sites in the SJV with many state-of-art instruments [Chow et al., 2006a]. Aerosol timeof-flight mass spectrometry (ATOFMS) measurements were also conducted during the CRPAQS, which, for the first time, characterized SJV ambient aerosols at the single particle level.

Out of the 38 SJV sampling sites operated during CRPAQS between December 2000 and February 2001, the highest ambient $PM_{2.5}$ levels were observed in Fresno, the

largest metropolitan city in the SJV located in the central valley with a population of more than 950,000 [*Brown et al.*, 2006]. Ambient measurements were made at the 3425 First Street Site since 1990 by the California Air Resources Board [*Watson et al.*, 2000]. Located in a residential neighborhood and affected by moderate vehicular emissions, this site is representative of urban pollution in the SJV. To allow a direct comparison between an urban center in Fresno and a rural location, ambient measurements were also conducted at a rural site in Angiola during CRPAQS. Surrounded by agriculture, Angiola is situated in a flat field ~90 km southeast of Fresno and halfway between Fresno and Bakersfield, the two largest SJV urban centers. This rural site is influenced by minimal primary PM emissions and represents the pollution gradient between central and southern valley urban areas [*Chow et al.*, 2006a; *Chow et al.*, 2006b]. In the winter, PM_{2.5} concentrations in Angiola approach similar levels as those in Fresno and Bakersfield.

Important findings characterizing wintertime ambient aerosols in the SJV were obtained from previous studies. The highest $PM_{2.5}$ concentrations are observed in winter accounting for ~80% of PM_{10} mass concentrations with the highest levels observed in the central and southern SJV and decrease rapidly as altitude increases [*Chow et al.*, 1992; *Chow et al.*, 1993; *Chow et al.*, 2006a]. Secondary ammonium nitrate is the largest $PM_{2.5}$ component accounting for more than 50% of the particle mass, followed by organic carbon (OC), and elemental carbon (EC) which when combined constitute 20-40% in urban areas [*Chow et al.*, 1992; *Chow et al.*, 1993; *Watson et al.*, 2000; *Watson and Chow*, 2002a; *Watson and Chow*, 2002b; *Brown et al.*, 2006]. However, the Fresno urban area is an exception, because the carbonaceous particles overtake ammonium

nitrate as the dominant components [*Turkiewicz et al.*, 2006]. PM_{2.5} in non-urban areas contains higher fractions of ammonium nitrate and lower fractions of carbonaceous particles (OC and EC) compared to urban areas [*Watson and Chow*, 2002a]. The highest PM_{2.5} levels are [*Chow et al.*, 2006a].

Besides of the relative fractions of the major aerosol chemical components, urban and rural areas in the SJV also differ in the emission sources and temporal variations of the aerosol. Influenced by emission profiles and pervasive meteorological conditions, $PM_{2.5}$ generally peaks at night and early morning in urban regions, whereas rural areas experience peak PM_{2.5} concentrations during the day [Chow et al., 1999; Watson and *Chow*, 2002a]. Higher ammonium nitrate concentrations are observed during the day with similar concentrations across the valley, which end up playing a major role in the valleywide exceedances of the PM standard [Watson and Chow, 2002a; Turkiewicz et al., 2006]. Based on the conceptual model developed by Watson and Chow [Watson and Chow, 2002a; Brown et al., 2006; Chow et al., 2006a], the combination of urban nitrogen oxides emission [Turkiewicz et al., 2006], nighttime aloft nitric acid formation and horizontal transport [Atkinson et al., 1986; Stockwell et al., 2000; Pun and Seigneur, 2001], and daytime vertical mixing provide the main reasons for the aforementioned ammonium nitrate diurnal pattern. The major sources of wintertime SJV carbonaceous particles are residential wood combustion (RWC) and vehicle emissions [Magliano et al., 1999; Schauer and Cass, 2000; Gorin et al., 2006]. Peak carbonaceous concentrations occur during the nighttime in urban areas due to a low inversion layer and elevated RWC [Watson et al., 2000; Qin and Prather, 2006; Chow et al., 2006b]. Weaker diurnal

variations and lower carbonaceous concentrations are observed in rural areas because of the minimal primary emission sources [*Chow et al.*, 1999].

Most chemical speciation information in previous SJV studies was obtained by the traditional off-line filter-based analysis [Chow et al., 1992; Chow et al., 1998; Chow Although these methods are able to provide mass concentration of et al., 1999]. individual chemical composition, they have limitations due to low time resolution, labor intensive analysis, sampling artifacts, and limited to no information on aerosol mixing state [Smith et al., 1978; Zhang and McMurry, 1987; Witz et al., 1990; Eatough et al., 1993; Chow, 1995]. A different approach for studying aerosol chemical composition is real-time mass spectrometry analysis [Suess and Prather, 1999; Johnston, 2000; Noble and Prather, 2000]. ATOFMS is a real-time single particle mass spectrometry (RTSPMS) method which collects continuous on-line information regarding the size and chemical composition of every single particle. This method can not only provide more insight on aerosol mixing state by obtaining the chemical species association within individual particles, but also capture instantaneous ambient events with the benefit of high time resolution, which are more likely to be averaged out in filter-based measurements. The disadvantage of most RTSPMS methods had been the lack of quantitative information due to the size-dependant transmission efficiencies, inhomogeneities of the ionization laser beam, instrument sensitivities coupled with matrix effect, and the data acquisition system speed limit [Dahneke and Cheng, 1979; Gross et al., 2000; Bhave et al., 2002; Wenzel and Prather, 2004; Allen et al., 2006]. Recent efforts have been dedicated to quantifying RTSPMS measurements to obtain high time resolution concentrations [Allen et al., 2000; Bhave et al., 2002; Lake et al., 2003;

Qin et al., 2006]. ATOFMS measurements have been scaled with reference methods and generated high time resolution mass concentrations that are in very good agreements with micro-orifice uniform deposit impactor (MOUDI) and beta attenuation monitor (BAM) mass concentrations [*Allen et al.*, 2006; *Qin et al.*, 2006].

Herein, we present an RTSPMS characterization of the wintertime ambient aerosols in the SJV utilizing ATOFMS. Continuous measurements were conducted during the CRPAQS at an urban site in Fresno and a rural site in Angiola during the winter of 2000-2001. Major particle types, as well as their chemical associations and diurnal temporal variations are described and compared. ATOFMS measurements provide insights into the differences in ambient aerosol transformation and mixing state between the two locations from a single particle perspective.

3.3 EXPERIMENTAL METHODS

Two ATOFMS instruments were operated simultaneously from November 30, 2000 to February 4, 2001 at Fresno and Angiola for real-time ambient single particle size and chemical composition measurements as part of the CRPAQS. Dual-polarity mass spectra of nearly 2 million particles were collected at each location. The Fresno site was located on the 2nd floor of a 2-story office building in a mixed commercial and residential area; the sampling inlet passed through the roof extending to 10 meters above the ground. The ATOFMS at the Angiola site was situated in a trailer with the sampling inlet extending through the roof to approximately 7 meters above the ground. Detailed information on the sampling sites is described elsewhere [*Watson et al.*, 2000; *Watson and Chow*, 2002a].

ATOFMS detects particle size by measuring the time-of-flight through two continuous-wave lasers separated by a known distance, and the chemical composition obtained in corresponding positive and negative ion mass spectra. The detailed operating principles, design and performance of ATOFMS are described in Section 1.5.1 and in the work by Gard and coworkers [*Gard et al.*, 1997]. This chapter focuses on 0.2-2.5 µm particles collected from January 9, 2001 to February 4, 2001, representing 711,289 particles in Fresno and 614,915 particles in Angiola. During most of the study periods, both ATOFMS instruments ran continuously with a 1.5 mJ desorption/ionization laser power with less than 1 hour daily downtime for maintenance. Reduced laser power (<1.0 mJ instead of the normal 1.5 mJ) was also utilized sporadically throughout the sampling period to study the effect of laser power on ion fragmentation. Since particle collection rate is affected by laser power, reduced laser power sampling periods are excluded from the discussion and figures.

ATOFMS mass spectra were calibrated with custom software, and information regarding individual ion peaks for each particle was extracted into a list. The peak lists were then imported into a single particle mass spectrometry data analysis tool YAADA [*Allen*, 2002], where particles can be selected and classified based on many criteria, such as particle size, collection time, and ion peak intensities. An adaptive resonance theory-based clustering method (ART-2a) was used to classify particles according to the existence and intensity of the ion peak patterns in individual single particle mass spectra fingerprints [*Song et al.*, 1999]. The weight matrix refers to the "quintessential" mass spectra that represent the overall characteristics of particles in a particular cluster. Submicron ($0.2 \leq$
$D_a < 1.0 \ \mu m$) and supermicron ($1.0 \le D_a \le 2.5 \ \mu m$) particles for each location were classified separately using ART-2a. Major particle types for each size range in each study were obtained by manually combining clusters with similar compositions. The top 50 clusters with the highest particle counts account for ~90% of the total ART-2a classified particles in both Fresno and Angiola and are used for the discussion of aerosol chemical composition in the upcoming sections.

Measurements conducted using several other co-located instruments are presented in addition to ATOFMS. PM_{2.5} mass concentrations at each site were obtained by BAM (Met One 1020). Continuous nitrate concentrations were measured with a Particulate Nitrate Monitor (RP8400N). Fresno ground level wind speeds were measured with a Wind Anemometer (Met One 010-SC). In Angiola, wind speeds at 324 feet were obtained from January 9, 2001 to January 31, 2001 by Wind Profiling Radar (NOAA-ETL 915 MHz), and were used for comparison due to the lack of ground level measurements. Angiola atmospheric liquid water content (LWC) was acquired with Particulate Volume Monitor (PVM-100), which was not available at the Fresno site.

3.4 RESULTS AND DISCUSSION

3.4.1 BAM, Wind Speed, LWC and Characteristic Meteorological Periods

The $PM_{2.5}$ mass concentrations, wind speeds and rain occurrences at each location for the period of our interest are included in Figure 3.1, as well as the Angiola LWC measurements, which were not available at the Fresno site. Strong diurnal variations of BAM measurements were observed in Fresno. $PM_{2.5}$ mass concentrations mostly peak at night between 21:00 and 1:00 due to the increased particulate emission and substantially



Figure 3.1 Wind speed, BAM $PM_{2.5}$ mass concentrations, liquid water content (LWC), and rain events at the CRPAQS sampling locations for (a) Fresno and (b) Angiola.

decreased inversion layer, and reach minimum values in the afternoon between 14:00 and 16:00 because of the daytime vertical mixing and lower particle emissions [*Watson and Chow*, 2002a]. In contrast, Angiola $PM_{2.5}$ mass concentrations showed weaker diurnal trends and mostly peaked during the day around noon. This daytime concentration increase was due to the downward flux of high altitude aerosols in the rural area when the inversion layer breaks and the photochemical conversion of urban pollutants are transported to this area. An extra nighttime $PM_{2.5}$ peak can also be observed in Angiola which corresponded to the increase due to the decrease in the height of the inversion layer. The above urban and rural diurnal variations are consistent with findings from previous studies [*Chow et al.*, 1999; *Watson and Chow*, 2002a; *Chow et al.*, 2006b].

Fresno ground level and Angiola wind speeds taken at 324-feet are plotted in light gray bars in Figure 3.1. Using higher altitude wind speed is part of the reason that Angiola wind speeds are much higher than those in Fresno, and these data are used as relative approximations for ground level Angiola wind speed variations. Nonetheless, in both Fresno and Angiola, high wind speeds corresponded to low $PM_{2.5}$ mass concentrations, illustrating that wind effectively facilitated the ventilation during the wintertime. Figure 3.1 also shows the days with precipitation occurrences marked with dashed vertical lines. Rain events were accompanied by low $PM_{2.5}$ mass concentrations showing that precipitation scavenging was very effective. Angiola LWC measurements are presented in dark gray line with solid dots. An anti-correlation trend was observed between Angiola $PM_{2.5}$ mass concentrations and LWC, suggesting high LWC can also serves as a removal mechanism for $PM_{2.5}$ particles. These results agree with the findings

by Chow and co-workers showing that the major wintertime cleaning and ventilation mechanisms in the SJV involve gusty winds and frontal passages [*Chow et al.*, 1992].

Due to the periodic changes in meteorological conditions and PM_{2.5} mass concentrations, the sampling durations described in this chapter were separated into 7 distinct periods. Period 1 (P1), from January 9 0:00 - January 10 12:00, featured moderate mass concentrations and relatively low wind speed; no precipitation was observed during this period. Periodic rain accompanied by high wind speeds was observed during Period 2 (P2), from January 10 12:00 – January 12 2:00; accordingly, extremely low PM_{2.5} mass concentrations were measured during this time. During Period 3 (P3), January 12 2:00 – January 18 0:00, wind speeds were lower than those in P2. PM_{2.5} mass concentrations showed a gradual buildup in Angiola; however, those at Fresno site increased quickly due to the stagnant meteorological conditions. Period 4 (P4), from January 18 0:00 - January 23 23:00, featured stagnant conditions with continually high levels of PM_{2.5} and low wind speeds. Periods 5-7 (P5, P6, and P7 respectively) featured similar conditions as those in period 2-4, experiencing precipitation, buildup and stagnation, correspondingly. One difference in Fresno is that unlike P3 when PM_{2.5} concentrations built up rapidly, those during P6 increased slowly due to increased wind speeds. The specific time cuts for the last 3 periods are: January 23 23:00 – January 26 6:00 (P5), January 26 6:00 – January 30 0:00 (P6), and January 30 0:00 - February 4 10:00 (P7). Substantial differences in chemical composition were measured during each period, which will be shown in detail in the upcoming sections.

3.4.2 Chemical Composition of Major Particle Types in Fresno

The weight matrices of the major particle types sampled in Fresno and Angiola are presented in Figures 3.2 and 3.3, respectively. Each weight matrix corresponds to the dual polarity cluster of a particular particle type. Similar major particles types were found in both Fresno and Angiola; however, somewhat different mass spectral characteristics, particular with regards to secondary species, were different at each location. Common marker ion peaks representing secondary species are m/z 18 (NH₄⁺), 30 (NO⁺), -46 (NO₂⁻), -62 (NO₃⁻), -79 (PO₃⁻), -80 (SO₃⁻), -97 (HSO₄⁻/H₂PO₄⁻), -125 (HNO₃NO₃⁻), and -188 ((HNO₃)₂NO₃⁻). The association of particles with secondary species provides important information on the degree of aging.

Fresno particles are classified into 10 major particle types as shown in Figure 3.2. OC represent typical organic carbon particles with the most intense positive peak at m/z 37 (C_3H^+), accompanied by 12 (C^+), 27 ($C_2H_3^+/CHN^+$), 36 (C_3^+), 39 (K^+), 43 ($CH_3CO^+/CHNO^+$), 50 ($C_3N^+/C_4H_2^+$), 51 ($C_3HN^+/C_4H_3^+$), and 63 ($C_4HN^+/C_5H_3^+$). These particles also contain ammonium (m/z 18), as well as nitrate (m/z 46, -62, -125) and sulfate (-97). Another organic carbon type OC2 has very similar positive spectra to OC, with the exception that m/z 27 is the most intense peak. Ammonium, nitrate, phosphate and sulfate are also observed in this type of particles. Unlike OC type, OC2 particles do not contain the peak at m/z -125, which represents nitrate clusters formed when high amounts of nitrate partition to the particles. Biomass particles contain a very intense potassium peak at m/z 39 accompanied by low intensity organic carbon peaks; this assignment is consistent with the results from many studies which have shown that potassium is a marker for biomass emissions [*Sexton et al.*, 1985; *Schauer et al.*, 2001].



Figure 3.2 ART-2a weight matrices of major particle types in Fresno.



Figure 3.3 ART-2a weight matrices of major particle types in Angiola.

These biomass particles also contain ammonium, nitrate, and sulfate. HMOC are particles that contain high mass organic compounds with distinct marker peaks between m/z 100 and 200 in both the positive and the negative spectra; in another paper describing further details from CRPAQS by Qin and Prather, these particles are shown to originate from biomass emissions and have undergone aqueous phase processing [*Qin and Prather*, 2006]. For the ECOC particle type, m/z 36 (C_3^+) is the most intense positive ion peak, accompanied by lower intensity carbon ion peaks at m/z 12 (C^+), 24 (C_2^+), 48 (C_4^+), and 60 (C_5^+); in addition, these particles contain organic carbon, ammonium, and nitrate markers. EC is dominated by elemental carbon with continuous, intense C_n^+/C_n^- peaks (where n is an integer) extending to m/z 200 in both the positive and negative mass spectra.

Four particle types are dominated by inorganic species. The sea salt particle type features an extremely intense sodium peak at m/z 23, and lower intensity peaks 39 (K⁺) and 81 (Na₂Cl⁺) in the positive ion mass spectra; the negative ion mass spectra contain m/z -16 (O⁻), -17 (OH⁻), -26 (CN⁻), -35/-37 (Cl⁻), -93/-95 (NaCl₂⁻), and less intense nitrate markers (m/z 46 and -62). Aged sea salt particles are more transformed as illustrated by the substantial decrease in the primary Cl⁻ peaks intensities (m/z -35 and -37) and significant increase in the secondary nitrate peaks intensities (m/z -46 and -62). In addition to the peaks observed in sea salt particles, aged sea salt particles also contain m/z 108 (Na₂NO₃⁺) and -147 (Na(NO₃)₂⁻), plus ammonium, nitrate, sulfate and organic carbon. Dust particles contain one or more metal species including sodium, aluminum, potassium, calcium, vanadium, manganese, and iron. In Figure 3.2, Fresno dust particles are represented by calcium-containing particles with m/z 40 (Ca⁺), m/z 57 (CaOH⁺), and

96 (Ca₂O⁺). NH₄NO₃-OC is a unique particle type featured by dominant secondary ammonium nitrate ion markers at m/z 18, 30, 35 ((NH₃)₂H⁺), -62, and -125. These particles also contain organic carbon and the nitrate cluster peak at m/z -188 ((HNO₃)₂NO₃⁻), which is not commonly observed in the negative spectra of Fresno particles.

3.4.3 Chemical Composition of Major Particle Types in Angiola

The major particle types in Angiola were similar to those in Fresno, but with some differences shown in Figure 3.3. Possibly due to instrumental issues, a substantial fraction of Angiola particles only have positive mass spectra, including the majority of biomass particles; thus this particles type is represented with the weight matrix containing only positive ions [Moffet et al., 2004]. Specific differences between the Fresno and Angiola particle types are described here. The Angiola ECOC particles have similar elemental carbon patterns to the Fresno ECOC particles; however, the spectra contain more and higher intensity organic carbon peaks in Angiola, possibly due to further transformation of ECOC particles as they undergo transport from urban to rural areas. In addition to m/z 23, 39 and 81, the Angiola sea salt particles also contain m/z 46 (Na₂⁺), 62 (Na₂O⁺), 63 (Na₂OH⁺), and 139/141 (Na₃Cl₂⁺) in the positive spectra; the negative spectra show significant chloride peaks, as well as m/z -58 (NaCl⁻), -120 (NaClNO₃⁻), -147 (Na(NO₃)₂), and -151/-153 (Na₂Cl₃). Some of the extra peaks are due to the associations with water and nitrate. Similarly, Angiola aged sea salt contain m/z 165 $(Na_3SO_4^+)$ and -120 $(NaClNO_3^-)$ also due to particle aging, which were not present in Fresno aged sea salt particles. Higher intensity organic carbon ion peaks are observed on Angiola NH₄NO₃-OC particles comparing to the corresponding type in Fresno.

Moreover, high levels of particle phase ammonium in Angiola leads to distinct ATOFMS ammonium clusters on NH₄NO₃-OC as observed by the positive peaks at m/z 52 $((NH_3)_3H^+)$, 98 $((NH_3)_3NO_2H^+)$, and 115 $((NH_3)_4NO_2H^+)$. No equivalent OC2 particle type is observed in Angiola. There is a unique Pos59 type in Angiola with the most intense peak at m/z 59 $(NC_3H_9^+)$ accompanied by organic carbon peaks in the positive spectra and nitrate peaks in the negative spectra; these are amine particles and have been observed in other studies [*Angelino et al.*, 2001; *Moffet et al.*, 2004].

Two particle types were observed in Angiola, but not in Fresno. The K-ECOC type is very similar to the Angiola ECOC type, except that the most intense positive ion peak is m/z 39. This type looks like a combination of ECOC and biomass particles possibly due to agglomeration. The NH₄NO₃ type is similar to NH₄NO₃-OC; however, NH₄NO₃ is dominated by ammonium cluster peaks in the positive spectra with m/z 35 being the most intense peak, followed by 18 (NH₄⁺), 30 (NO⁺), 52 ((NH₃)₃H⁺), 98 ((NH₃)₃NO₂H⁺) and 115 ((NH₃)₄NO₂H⁺). Very low intensity organic carbon peaks are present in the positive spectra. Negative spectra show intense nitrate markers at m/z -62, -125, and -188. This is the first time that dual polarity ammonium and nitrate rich particles were observed during ambient measurements. Although similar particle type was observed once in a previous study in Riverside, only single polarity mass spectra were acquired and the positive peaks above m/z 46 was assumed to be organic compounds, rather than ammonium and nitrate clusters that are presented in this study [Liu et al., 2000].

3.4.4 Fresno and Angiola Particle Phase Ammonium and Nitrate

Compared to Fresno, the Angiola particles were more aged and contained more nitrate based on the mass spectral ion intensities. The more nitrate is available in the desorption/ionization plume, the easier it is to form nitrate clusters. Therefore, the progression of ATOFMS peaks from m/z -46 (NO₂), -62 (NO₃), -125 (HNO₃NO₃) to -188 ((HNO₃)₂NO₃⁻) represent increasing amounts of particle-phase nitrate. The association of particle types with nitrate and ammonium at Fresno and Angiola are compared in the ternary plots in Figure 3.4 with corresponding particle types at each location placed next to each other. The ternary plots show the relative amount of different nitrate marker peak areas on representative particles of each type (around 200 particles from each type evenly distributed over the study period). In each plot, a particle mostly containing intense peak representing relatively low amount of nitrate (m/z - 46)would appear at the lower left vertex; a particle containing a medium amount of nitrate (m/z - 62) would appear at the lower right vertex; a particle mostly containing an intense peak representing higher amount of nitrate (m/z - 125) would appear at the top vertex. If a particle contains equally intense peaks at m/z -46, -62, and -125, it would appear at the center of the plot. The color of each dot represents the peak area of ammonium $(m/z \ 18)$ for the corresponding particle with purple showing the lowest peak area and red and black showing the highest. Since the area of ATOFMS marker peaks is related to the amount of specific species on each particle, and instrument sensitivities are comparable for similar particle types which essentially provide similar ionization matrix, peak areas can be used to represent the amount of a specific species on each particle [Bhave et al., 2002]. Biomass is not included since these figures are made based on the negative



Figure 3.4 Ternary plots of corresponding particle types in Fresno and Angiola showed particle associations with secondary ammonium and nitrate. In each plot, a particle contains low amount of nitrate would appear at the lower left vertex, contains medium amount of nitrate would appear at the lower right vertex, and contains high amount of nitrate would appear at the top vertex. The color of each dot represents the area of ammonium peak of the corresponding particle with purple showing the lowest peak area and red and black showing the highest.

spectra which were missing for many biomass particles in Angiola. Fresno OC2 and Angiola Pos59 are also not included because these two types do not have corresponding particle types at both locations.

Using the HMOC particles as an example, Fresno HMOC particles are mostly distributed along the low-nitrate and mid-nitrate line and rarely contain more than 20% of the high-nitrate marker on the particles. In addition, these particles have low ammonium peak areas (mostly below 250). The Angiola HMOC particles also spread along the lownitrate and mid-nitrate line; however, more of these particles are significantly closer to the high-nitrate vertex, meaning that there is more nitrate on these particles. Another major difference is that ammonium peak areas (vary from 250 to 15000) for Angiola HMOC particles are much higher than Fresno HMOC particles (ammonium peak areas mostly below 250). Therefore, the Angiola HMOC particles contained higher amounts of ammonium and nitrate compared to the Fresno HMOC particles. This finding is consistent with mass concentrations of ammonium and nitrate during the study. Trends similar to the HMOC particles are consistent with most other particle types shown in Figure 3.4, especially for the carbonaceous related particle types. The nitrate cluster peak at m/z -188 ((HNO₃)₂NO₃) is present in many of the Angiola particle mass spectra but only appeared on NH₄NO₃-OC in Fresno as shown in Figures 2 and 3, adding another piece of evidence illustrating that particle phase nitrate was more abundant in Angiola. The association with secondary ammonium and nitrate for various particle types in the same study illustrates the degree of aerosol transformation, with EC and sea salt being the relatively fresh particles and the rest are more aged.

The above observations are consistent with previously reported particle formation and transformation mechanisms in the SJV. The Fresno urban site is greatly influenced by primary emission sources with no significant sources of ammonia. Freshly emitted particles experience aging at night and are dissipated during the day due to vertical mixing. Therefore, particles observed in Fresno are less aged and contain lower amounts of ammonium and nitrate. Angiola is located in a remote agriculture area, where the major activities are farming and ranching; therefore, this site experiences higher ammonia levels than urban areas due to fertilizer and animal husbandry emissions [Chow et al., 2006b], resulting in a higher amount of ammonium in the particle phase as detected by ATOFMS. Also being in a remote location, there are minimal primary emission sources in Angiola, and most of the carbonaceous particles at this location are emitted and transported from urban areas, which pick up nitrate during the transport. Therefore, Angiola particles, especially carbonaceous particles, contain higher amounts of nitrate compared to the relatively fresh Fresno particles. In summary, Angiola particles contain more ammonium and nitrate than those in Fresno, most likely due to aerosol aging and the higher amount of ammonia available in Angiola due to agriculture and ranching activities.

3.4.5 Diurnal Temporal Variations and Size Distributions of Fresno Particle Types

Figure 3.5 and Figure 3.6 correspond to the hourly temporal variations and the size distributions of the number fractions of the major particle types for the top 50 clusters for a) Fresno submicron, b) Fresno supermicron, c) Angiola submicron and d) Angiola supermicron particles. In Figure 3.5, BAM PM_{2.5} measurements at each location are superimposed on each plot in black traces, and the 7 periods are marked at the top of







Figure 3.6 Size resolved major particle types number fractions for the top 50 clusters with a size resolution of 0.05 μ m for submicron range and 0.10 μ m for supermicron range for (a) Fresno submicron particles, (b) Fresno supermicron particles, (c) Angiola submicron particles, and (d) Angiola supermicron particles.

the plots. The size resolution is $0.05 \ \mu m$ for submicron and $0.1 \ \mu m$ for supermicron particles with the size cut indicated on the bottom axis in Figure 3.6. The following discussions of temporal variations refer exclusively to the ATOFMS particle type number fractions unless otherwise specified.

Most particle types in Fresno displayed distinct diurnal temporal variations as shown in Figure 3.5a and 3.5b. In particular, the biomass particles mainly peaked at night between 21:00 and 3:00 in both the submicron and supermicron modes; similarly, HMOC peaked at the same time though mostly in the supermicron range. Previously, the biomass particles were found to have been directly emitted from wood burning, and HMOC were composed of biomass and aqueous phase processed semivolatile biomass species. Therefore, these two types had similar temporal trends with HMOC particles exhibiting a larger size distribution due to the growth during processing [Qin and Prather, 2006] (Figure 3.6a-b). One reason for the diurnal variations is due to increased nighttime fireplace usage due to residential heating. Moreover, the inversion layers reach the lowest altitude from late night to early morning, which further aids in concentrating these particles [Brown et al., 2006]. Therefore, it is the combination of increased nighttime emissions and the decrease in inversion layers that caused the biomass and HMOC types to peak between 21:00 and 3:00.

Following the biomass and HMOC peaks, the OC particles peaked between 3:00 and 8:00. The weight matrices in Figure 3.2 showed that OC particles contained more ammonium and nitrate than biomass (more intense peaks at m/z 18 and -125 in the OC type). Based on this observation, the OC particles are very likely aged biomass particles. The time delay between the biomass and OC peaks could be indicative of the time

required for the biomass particles to transform to the OC particles and pick up secondary markers. This time lag varied depending on ambient conditions. A small fraction of OC particles could also come from morning traffic emissions which occurred around 6:00 - 7:00 [Magliano et al., 1999; Schauer and Cass, 2000]. The elemental carbon particles ECOC and EC mainly peaked during midday between 11:00 and 15:00 with occasional spikes in the morning rush hours. These particles are likely the aged particles originally emitted from morning vehicular sources but grow into size ranges detectable by ATOFMS after processing in early afternoon [Park et al., 2006]. EC are mostly in the submicron range, but ECOC have a broader size distribution falling in both the submicron and supermicron size ranges as shown in Figure 3.5 and Figure 3.6 a-b. The ternary plots for these two types in Figure 3.4 show that ECOC contained more nitrate than the EC particles. Both the size distributions and the chemical associations suggest that ECOC are more aged than EC particles and grow in size during transformation.

Sea salt particles were primarily observed on rainy days. These particles were mainly supermicron in size and were fairly fresh since precipitation cleaned out most pollutants which otherwise would have reacted with sea salt. Aged sea salt particle fractions rapidly increased following the sea salt peak then gradually decreased over time. Since aged sea salt particles were transported into the SJV by westerly winds from the ocean, more daytime aged sea salt peaks were observed than nighttime due to the high wind speeds during the day. OC2 often seemed to occur around the same time as aged sea salt particles, although it was a carbonaceous type and had the smallest size distributions as shown in Figure 3.6a. These were probably the freshly emitted particles, which transformed more slowly during clean conditions, thus becoming a substantial particle fraction. Dust particles were mainly in the supermicron range and were a background component. Although these particles did not have distinct diurnal variations, they tended to spike when wind speeds were high due to re-suspension processes.

The NH_4NO_3 -OC particle type peaked during the daytime mostly between 13:00 and 16:00. Ammonium nitrate concentrations increased during the daytime due to the downward flux of ammonium nitrate from aloft, resulting in the observed peaks [Watson and Chow, 2002a; Brown et al., 2006]. Sometimes, ammonium nitrate can be in the gas phase around midday due to the high temperatures, and does not condense onto particles until later in the afternoon when temperatures dropped, resulting in the 16:00 spike of ATOFMS NH₄NO₃-OC particle fractions. This observation is consistent with the study by Chow and co-workers, during which Fresno particle phase ammonium nitrate peaked in early afternoon [Chow et al., 2006a]. When comparing the temporal variations of ATOFMS NH₄NO₃-OC particle raw counts with continuous particulate nitrate concentrations, the high NH₄NO₃-OC counts correlated with the periods of the highest nitrate concentrations, confirming that NH₄NO₃-OC represent highly aged particles loaded with fairly high amounts of ammonium nitrate. However, it is important to note that all other particle types during these time periods also contained ammonium nitrate, although the ammonium and nitrate marker peaks were not as intense as those in NH₄NO₃-OC particles as shown in Figure 3.2. PM_{2.5} mass concentrations peaked simultaneously with the supermicron OC and biomass fractions, showing that biomass and OC were the major components by mass in Fresno.

3.4.6 Periodic Changes in Fresno Particle Chemical Compositions

It is also interesting to observe the changes in the Fresno particle chemical composition throughout the study period from P1 to P7 (defined in section 3.1). Figure 3.7 shows 50-meter representative air mass HYSPLIT back trajectories ending at Fresno and Angiola throughout the study periods [Draxler and Rolph, 2003]. Fresno trajectories were plotted in black and Angiola trajectories in grey. The air masses arriving at Fresno and Angiola were traced back 48 hours with a 6-hour time resolution, shown by each open circle; the only exception is Figure 3.7b in which only 24-hour back trajectory data were available. The HYSPLIT trajectories provided the origin of the air mass at different time periods of the study, and the distance correlated with the speed of air mass movement. As shown below, the chemical compositions observed during each period could be readily correlated with the origin of the air mass.

The Fresno submicron size range was dominated by biomass and OC particles throughout the study period. As discussed before, biomass particles emitted from wood combustion, peaked each night in both submicron and supermicron sizes throughout the study. A substantial fraction of biomass particles were subsequently converted into OC, which peaked a few hours later. The major significant changes occurred during the rainy periods P2 and P5, when aged sea salt and OC2 fractions increased considerably, and OC decreased due to scavenging. Substantial changes in particle chemical composition are more obvious in the supermicron range; therefore, the following discussions will focus on supermicron particles.

The Fresno supermicron size range was dominated by aged sea salt, biomass, or OC particles depending on the period. Other major components were dust, HMOC, and



Figure 3.7 HYSPLIT 48-hour air mass back trajectories representative of each period in Fresno (black traces) and Angiola (grey traces). The trajectory height is 50 meters and the time resolution is 6 hours as represented by each open circle.

ECOC particles. Major Fresno supermicron chemical components during P1 were OC, biomass, and ECOC, which also accounted for the majority of the mass concentrations in this period. PM_{2.5} mass concentrations were not as high as P3, P4, and P7. OC particles were mainly in submicron range, but under very polluted conditions, they were able to grow in size and eventually spread into supermicron range as observed during this period. Notably, it is likely these particles contained a substantial fraction of water. The high fractions of supermicron ECOC particles also indicated that aerosols in P1 were fairly aged and picked up secondary species and water. Figure 3.7a shows the origin of the corresponding air mass arriving in Fresno (black trace) at 6:00 on January 10. This air mass started over the ocean 48 hours before and had spent a substantial amount of time (the last 42 hours) over land before reaching Fresno, therefore leading to significant amounts of aging.

Wind and precipitation cleaned out most pollutants in P2 as shown by the very low BAM measurements. Supermicron particles in this period were quite fresh and mainly composed of biomass, dust, and sea salt. It is worth pointing out that the increase in biomass and dust particle fractions were mainly due to the decrease in other particle types; the absolute amount of these two types actually decreased. Aged aerosols like OC and ECOC were hardly visible during P2. Consistently, HYSPLIT back trajectory in Figure 3.7b showed that air mass originated from the ocean 24 hours ago, but spent only around 12 hours over land, which did not provide enough time to transform under such clean environment.

P3 was a buildup period. Daytime supermicron particles were dominated by aged sea salt with fairly low PM_{2.5} mass concentrations; whereas nighttime was dominated by

biomass and HMOC with extremely high $PM_{2.5}$ concentrations of 192 µg/m³ observed on January 14. The OC fraction was still very low during P3, showing that particles during this period were less aged than those in P1. Relatively fresh biomass particles accounted for the majority of aerosol mass during this period. Figure 3.7c shows that the air mass arriving at Fresno at 0:00 on January 15 had been circulating inside the valley for the previous 2 days, consistent with biomass dominating chemical composition at night.

P4 featured stagnant meteorological conditions and continuously high PM_{2.5} mass concentrations. The major supermicron particle types during this period were biomass and OC. Throughout this period, OC fractions kept increasing and biomass fractions continually decreased. Due to the stagnation, freshly emitted biomass particles accumulated in Fresno and aged, leading to an increase in OC particles; accordingly, the gradual decrease in the relative fractions of the newly emitted biomass particles are due to the increase of total amount of particles due to stagnation. Substantial fractions of ECOC particles were also observed in P4 due to particle aging. Significant fractions of NH₄NO₃-OC particles were observed and expected in this period, as they represented severely transformed particles containing high amount of ammonium and nitrate. Comparing P1 and P4, these two periods had similar meteorological conditions and aerosol chemical compositions, except that considerable fractions of NH₄NO₃-OC particles and higher PM_{2.5} mass concentrations were observed in P4 but not in P1. The high ammonium nitrate levels is likely the key factor accounting for the differences and leading to the extremely high PM_{2.5} mass concentrations in P4. Turkiewicz and coworkers also proposed that ammonium nitrate is the major component causing PM_{25} exceedance in the SJV [Turkiewicz et al., 2006], which is consistent with our findings.

Although the highest mass concentrations during P4 (~190 μ g/m³) were comparable to those in P3 (~192 μ g/m³), relatively fresh biomass particles were mainly responsible for the PM_{2.5} high mass concentrations in P3, whereas those in P4 consisted of a substantially increased amount of aged particles including OC, ECOC, and NH₄NO₃-OC besides the relatively fresh biomass. Figure 3.7d showed that air mass arriving at Fresno at 0:00 on January 23 hardly moved during the past 48 hours, supporting the conclusion that primarily emitted particles were accumulated and reacted at the same location, causing severe particle aging.

Major particle types in P5, P6 and P7 are similar to those in P2, P3 and P4, respectively. The precipitation event during P5 ended the stagnant condition and cleaned out the air, resulting in a decrease in particle mass concentrations with biomass, aged sea salt and dust being the major chemical components. P6 was a gradual buildup period dominated by relatively fresh biomass and aged sea salt; however the nighttime mass concentrations did not increase as high as those in P3, possibly due to the relatively high wind speeds which disfavored the buildup. Finally, the stagnant conditions during P7 repeated those in P4; OC, ECOC and NH₄NO₃-OC fractions increased with a decrease in the biomass fraction. Air mass back trajectories during the above periods showed consistent results as shown in Figure 3.7 e-h. PM_{2.5} mass concentrations during P5 and P6 were mostly accounted due to relatively fresh biomass particles, whereas those in P7 included more aged particles like OC.

3.4.7 Diurnal Temporal Variations and Size Distributions of Angiola Particle Types

Angiola particles were more aged compared to the Fresno particles with lower PM_{2.5} mass concentrations due to the limited primary emissions; the majority of carbonaceous particles in Angiola were transported from urban locations, however, there were relatively low amounts of biomass particles directly emitted from small towns nearby. Comparing the major particle types at the two locations shown in Figure 3.5 and 3.6, Angiola submicron contained considerably higher fractions of ECOC and OC particles due to aging, accompanied by a substantial decrease in the relatively fresh biomass particles. K-ECOC was also a dominant submicron component and was only observed in Angiola. These particles were also aged, and they had different diurnal variations from other particles as discussed in the following sections. Supermicron particles were dominated by either aged sea salt particles, or ECOC, K-ECOC, NH₄NO₃-OC, and NH_4NO_3 particles. NH_4NO_3 is another particle type unique to Angiola and this type represented particles with extremely high amount of ammonium nitrate. NH_4NO_3 -OC and NH₄NO₃ were essentially the same type of particles, only NH₄NO₃ contained higher amount of ammonium than NH_4NO_3 -OC particles. The spikes of these particles also coincided with the high nitrate concentrations measured by Particulate Nitrate Monitor. No substantial OC particles were present in the Angiola supermicron size range. In fact, more common in Angiola were NH₄NO₃-OC particles due to the excessively available ammonia relative to organic carbon species in the rural locations.

Similar to the PM_{2.5} mass concentrations, the major particle types in Angiola, including ECOC, EC, biomass, OC, NH₄NO₃-OC, and NH₄NO₃, generally peaked during

the day. An extra peak shortly before midnight was also observed for these particle types. The daytime peak was due to the downward flux of the high altitude aerosols when the inversion layers broke around 11:00, and nighttime peak was likely caused by the decrease in the height of inversion layer. K-ECOC, HMOC and Pos59 had very different temporal trends peaking between 2:00 and 8:00, which were determined by the formation mechanism of these particles. Since HMOC are aqueous phase processed biomass species, the fraction of these particles peaked at night when RH was high and decreased during the day due to vertical mixing and further particle aging [Qin and Prather, 2006]. These particles were likely formed from biomass particles emitted near Angiola, not transported from Fresno, because the HMOC particles were easily converted into more aged particle types through various ambient reactions especially photooxidation, and thus were less likely to survive during the transport. Pos59 are amine particles formed by photo-oxidation of gas-phase low molecular weight amines. Therefore Pos59 were generally small in size and semivolatile, therefore being detected in the particle phase at night when low temperature and high RH occurred [Angelino et al., 2001]. Similar diurnal variations of amine particles were also observed in ATOFMS studies in Riverside and Atlanta [Angelino et al., 2001; Qin et al., 2007]. K-ECOC often replaced ECOC and became the most dominant particle type at night. It is not clear what determines the nighttime spike of these particles, it might be related to the high RH.

There were no distinct diurnal trends for dust, sea salt and aged sea salt particles. dust particles were present all the time mostly in the supermicron range; high fractions were observed during windy days due to particle re-suspension. Sea salt appeared during rainy days, and aged sea salt spiked right after sea salt, and then gradually decreased. Angiola $PM_{2.5}$ mass concentrations tracked closely to particles containing high intensity ammonium nitrate makers, namely NH_4NO_3 -OC and NH_4NO_3 . This correlation was especially evident during the polluted days, showing that ammonium nitrate dominated the Angiola $PM_{2.5}$ particles by mass. This finding is consistent with the study by Chow et al., during which ammonium nitrate was shown to cause elevated $PM_{2.5}$ levels at non-urban sites in the SJV [Chow et al., 2006a].

3.4.8 Periodic Changes in Angiola Particle Chemical Compositions

Similar to the results in Fresno, no substantial periodic changes were observed for the Angiola submicron particle types. It was only during the rainy days during P2 and P5 when a change was observed for the increased fraction of aged sea salt particles.

Supermicron particle types showed significant changes during each period as shown in this section, which were consistent with the air masses origins shown in Figure 3.7. The air mass in P1 started over the ocean and then spent 42 hours over land. K-ECOC and aged sea salt were the major particle types observed. The PM_{2.5} mass concentrations during this period were fairly low, indicating that K-ECOC and aged sea salt were not the main contributors to high aerosol mass concentrations. P2 was dominated by dust, sea salt and some biomass. The precipitation during this period removed K-ECOC leaving only freshly emitted aerosols. P3 was a buildup period that experienced a gradual increase of PM_{2.5} mass concentrations. Compared to the rapid increase of Fresno PM_{2.5} mass concentrations during this period, the gradual increase in Angiola was possibly due to high wind speeds which disfavor particle buildup. aged sea salt, dust and a mixture of carbonaceous particles were dominant during P3. P4 is the stagnation period with very high particle mass concentrations.

NH₄NO₃-OC, NH₄NO₃, K-ECOC, and ECOC. The stagnant condition aided in particle accumulation at Angiola, exposing the particles to constant ammonia emissions, resulting in an extremely high amount of particle phase ammonium. With similar meteorological conditions, the mass concentration difference between Angiola P4 and P1 is mostly due to the increased fraction of ammonium nitrate rich particles; thus, ammonium nitrate is the main factor leading to high mass concentrations in Angiola. This finding is consistent with the study by Watson et al. and Turkiewicz et al. [*Watson and Chow*, 2002a; *Turkiewicz et al.*, 2006]. P5 – P7 repeated P2 – P4 showing periodic changes in PM_{2.5} mass concentrations and supermicron particle chemical compositions. Supermicron biomass and EC were present throughout the study periods accounting for a very low fraction (~6% of top 50 particles when combining the two types, ranging from 0% up to the occasional 20%) as shown in Figure 3.5d. The OC particle fractions were extremely low as shown in Figure 3.6d since they were transformed into NH₄NO₃-OC and NH₄NO₃ due to the elevated ambient ammonia levels.

Through comparison of the Fresno and Angiola supermicron particle chemical compositions, we see that particles containing high levels of ammonium nitrate occurred around the same times, meaning that high levels of ammonium nitrate were present at the same time in both locations. This observation is consistent with the findings by Chow and co-workers that the ammonium nitrate level is relatively homogeneous throughout the valley [Chow et al., 2006a].

3.4.9 Scaled ATOFMS Mass Concentrations

Utilizing the scaling method discussed in Chapter 5, the mass concentrations of major ATOFMS particle types are obtained. Figure 3.8 shows the temporal variations of



Fresno ATOFMS measurements are scaled with MOUDI measurements and Angiola ATOFMS measurements Figure 3.8 Temporal variations of the mass concentrations of major particle types in Fresno and Angiola. are scaled with APS measurements.

the mass concentrations of major particle types in Fresno and Angiola. The mass concentrations are obtained by scaling ATOFMS measurements with MOUDI measurements at Fresno, and by scaling with aerodynamic particle sizer (APS) measurements at Angiola. In Fresno, submicron particles dominated the $PM_{2.5}$ mass concentrations. Supermicron was dominated by aged sea salt and biomass particles during the clean periods, and the stagnant events were dominated by the relatively aged OC particles. Angiola submicron particle type mass concentrations also accounted for a large fraction of the $PM_{2.5}$ mass concentrations. Low mass concentrations were observed throughout the entire study except during the stagnant periods when the highest mass concentrations were observed. The scaled ATOFMS mass concentrations are consistent with the $PM_{2.5}$ mass concentrations obtained by BAM.

3.5 CONCLUSIONS

ATOFMS measurements during the CRPAQS in Fresno and Angiola provided important information on the differences between urban and rural particle size, composition, chemical associations, and the temporal variations of major particle types from a single particle perspective. These measurements are very helpful in studying aerosol formation mechanism and source apportionment.

Located in an urban center, Fresno particles were a mixture of fresh and aged aerosols. Major particle types in Fresno displayed distinct diurnal variations mostly peaking at night, except for the ECOC and EC types which peaked during the day due to local traffic emissions. The submicron size range was dominated by carbonaceous and biomass particles. Supermicron chemical composition was greatly influenced by meteorological conditions, with aged sea salt and biomass dominating during the clean periods and biomass, OC and NH_4NO_3 -OC dominating during the polluted periods. biomass, OC, and NH_4NO_3 -OC were the major $PM_{2.5}$ components by mass, the relatively fresh biomass particles can be as efficient as the aged OC and NH_4NO_3 -OC particles leading to extremely high $PM_{2.5}$ mass concentrations.

Angiola particles were more aged than those in Fresno and contained higher amounts of ammonium nitrate. Particles in urban areas transported to rural areas from aloft, thus Angiola particle types peaked during the day due to the down flux of particles when the daily inversion layers broke. The peaks of K-ECOC, HMOC and Pos59 at night were likely due to the influence of temperature and RH on their formation mechanisms. The Angiola submicron size range was dominated by ECOC, K-ECOC and OC particles, and the supermicron particles were alternately dominated by aged sea salt, or K-ECOC, ECOC, NH₄NO₃-OC, and NH₄NO₃ depending on the period. Unlike Fresno, ammonium nitrate was the factor leading to high PM_{2.5} mass concentrations in Angiola.

Besides the aforementioned advantages, ATOFMS measurements are able to provide information on aerosol aging, even during the same study and under similarly high levels of PM_{2.5} mass concentrations, which is difficult for other measurements to achieve. Even though similar high mass concentrations were observed in Fresno during P3 and P4, the major particle type by mass was the relatively fresh biomass during P3 and the combination of biomass, OC (aged), and NH₄NO₃-OC (aged) during P4. Angiola particles were also shown to be more aged compared to those in Fresno due to the increased amount of secondary ammonium and nitrate observed on a single particle level.

The results from this study demonstrated the ability of ATOFMS in obtaining information on ambient aerosol compositions, chemical associations, size distributions, diurnal variations, formation mechanisms, and aging. It can also determine the major chemical components that led to the high PM_{2.5} mass concentrations. The results of this study will also be very helpful in making policies to effectively control the pollutants in both urban and rural areas in the SJV.

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Chapter 4

4 Single Particle Characterization in Riverside, CA during the SOAR 2005 Campaign – Part 1: Seasonal Comparisons

4.1 SYNOPSIS

Aerosol time-of-flight mass spectrometry (ATOFMS) measurements were conducted during the Study of Organic Aerosols in Riverside, California (SOAR) field campaign in the summer and fall of 2005. Time and size-resolved number fractions of the major particle types are presented for the size range of $0.2-2.5 \mu m$. In general, carbonaceous particles which were mixed with nitrate, sulfate and ammonium dominated (>75%) the aerosols below 1.0 µm, and aged sea salt, dust and aged carbonaceous particles were the major particle types above 1.0 µm, except during the fall Santa Ana periods when dust and biomass particles were prevalent over the whole size range. Most of the major particle types during the summer displayed strong diurnal variations, with high carbonaceous number fractions appearing from night until the morning and aged sea salt, dust, biomass, and OC-vanadium particles peaking in the afternoon. In contrast, fall measurements showed distinct episodic events dominated by different particle types. The majority of the ambient particles contained secondary nitrate and sulfate with higher amounts of particle phase sulfate in the summer and nitrate in the fall. In both seasons, the beta attenuation monitor measurements displayed similar temporal trends when compared to the ATOFMS total carbonaceous fractions, indicating that carbonaceous

particles mixed with sulfate, nitrate, and ammonium were the major component of the PM_{2.5} mass concentrations.

4.2 INTRODUCTION

The city of Riverside, California covers ~200 km² of area in the eastern Los Angeles (LA) basin and encounters some of the worst air pollution problems in the United States. In 2000, Riverside-San Bernardino was one of the six US metropolitan areas out of 296 that exceeded National Ambient Air Quality Standard levels due to high concentrations of O_3 , SO_2 and particulate matter; furthermore, out of the nation's 94 largest metropolitan areas, Riverside-San Bernardino was one of three areas with unhealthy air quality levels for sensitive groups on more than 120 days each year between 1999 and 2002 [*EPA*., 2003]. Great attention and effective policies are needed to alleviate the air pollution problem.

In addition to affecting climate and reducing visibility [*Horvath*, 1993; *Robock*, 2000; *Dubovik et al.*, 2002], ambient particles with aerodynamic diameters (D_a) less than or equal to 2.5 µm (PM_{2.5}) can cause serious adverse health effects [*Brunekreef and Holgate*, 2002; *Pope and Dockery*, 2006]. For example, a strong association was found between PM_{2.5} concentration and mortality rate, particularly cardiopulmonary mortality [*Pope and Dockery*, 2006]; further, exposure to PM_{2.5} and elemental carbon (EC) can lead to significant deficits in children's lung function growth and increase incidents of asthma [*Gauderman et al.*, 2002]. The distribution and deposition of inhaled particles strongly depend on particle size with smaller particles penetrating further into the respiratory system and even entering the blood stream [*Hatch*, 1961; *Stuart*, 1973; *Geiser*]

et al., 2005]. Therefore, in addition to aiding in source apportionment of aerosols in the LA basin and areas with similar emissions inventories and geographical and meteorological conditions, size-resolved ambient aerosol composition and chemical association will also provide valuable information for health effects studies.

Riverside is located along a typical air parcel pathway crossing the LA basin and is the receptor area of LA air pollutants, which transport east and transform along the way. In previous studies, the major components of PM_{2.5} in Riverside were found to be nitrate, ammonium, EC and organic carbon (OC) by mass [*Chow et al.*, 1994]. Vehicle exhaust is the primary source of carbonaceous particles (EC and OC) [*Chow et al.*, 1992], and the high ammonium concentrations are mostly influenced by emissions from nearby upwind Chino dairy farms, which is the largest single source of ammonia in the greater LA area [*Hughes et al.*, 2002]. In summer, PM_{2.5} concentrations reach maxima during the day due to elevated photochemical reactions as well as increased aerosol transport from the LA area in the west; whereas wintertime PM_{2.5} concentrations peak at night due to the decrease in the altitude of inversion layers [*Kim et al.*, 2002; *Fine et al.*, 2004; *Sardar et al.*, 2005]. Thus, the aerosol chemical composition and formation mechanisms vary considerably by season.

Numerous studies have been conducted in Riverside and other cities in the LA basin during the last three decades to study urban photochemical smog formation, aerosol transport and evolution across the basin, and size-resolved chemical composition of ambient particles [*Lawson*, 1990; *Chow et al.*, 1992; *Chow et al.*, 1994; *Hughes et al.*, 1999; *Kim et al.*, 2002; *Pastor et al.*, 2003; *Fine et al.*, 2004; *Sardar et al.*, 2005; *Singh et al.*, 2006]. Recent developments in on-line techniques for aerosol analysis have enabled

high temporal resolution for particle number and size measurements. Studies investigating seasonal variability of particle number concentrations, size distributions, and chemical composition were also conducted in Riverside recently [*Sardar et al.*, 2005; *Singh et al.*, 2006]; however no detailed seasonal comparison is available on temporal variations of individual chemical classes and aerosol mixing state.

Aerosol time-of-flight mass spectrometry (ATOFMS) is an on-line mass spectrometry technique which allows the measurement of size and chemical composition of individual particles in real-time [*Noble and Prather*, 1996]. ATOFMS can examine complicated aerosol mixtures on a single particle level and provide quantitative high temporal resolution chemical composition, size distribution, and chemical association information [*Qin et al.*, 2006], which is useful for source apportionment. Previous continuous ambient ATOFMS measurements in Riverside were conducted in 1996 and 1997 [*Hughes et al.*, 1999; *Hughes et al.*, 2000; *Pastor et al.*, 2003]; however, single polarity spectra without wide dynamic range (WDR) were collected, and seasonal differences were not the focus [*Qin et al.*, 2006]. Recent ATOFMS developments have allowed for simultaneous dual polarity collection with WDR, improving our ability to classify particles and identify aerosol associations especially with secondary signatures of nitrate and sulfate.

This paper presents summer and fall seasonal differences in aerosol size distribution, composition, and chemical association in Riverside from continuous ATOFMS single particle measurements. Particles with sizes between 0.2 and 2.5 μ m are discussed, along with the meteorological conditions which play an important role in aerosol composition and formation mechanisms. Significant differences are observed

between summer and fall temporal variations and percentages of individual chemical species. This work is the first attempt to study the seasonal variability of ambient aerosols using ATOFMS single particle measurements, illustrating the changes in the relative concentrations of the major particle types both by time and by size.

4.3 EXPERIMENTAL METHODS

4.3.1 SOAR Campaign

The Study of Organic Aerosols in Riverside (SOAR) field campaign was conducted in the summer and fall of 2005 on the campus of the University of California, Riverside (UCR) for ambient aerosol characterization and source apportionment [*Docherty and Jimenez*, 2005]. The sampling site was located in the southeast of the UCR campus (33°58′18″N, 117°19′22″W), and a map is included in Figure 4.1. Immediately to the east and west of the sampling site are the satellite chiller plant and greenhouses, respectively, and a parking lot with a capacity of 129 parking spaces lies directly to the south. A major freeway (I-60/215) with heavy traffic neighbors the campus to the west and southwest and is ~600 meters away from the sampling site. Due to freeway construction, heavy traffic was observed as early as 3:00 and as late as 22:00. All data are presented in Pacific Standard Time (PST).

4.3.2 Ambient Sampling

A standard ATOFMS was housed inside a mobile laboratory from July 30 to August 15 (SOAR-I) and from October 31 to November 21 (SOAR-II) with ~1 hour of downtime daily for maintenance mostly between 20:00 and 21:00. A co-located aerodynamic particle sizer (APS, TSI 3321) and UV photometric O₃ analyzer (TEI 49C)



Figure 4.1 Map of SOAR sampling site on UCR campus.

measurements were also available. Both the ATOFMS and APS sampled off the same cylindrical stainless steel manifold which connected to the ambient atmosphere on one side with a single port and to several instruments on the other side through multiple ports. To prevent alteration of ambient aerosol composition, the sampling lines outside the mobile laboratory were covered with reflective insulation wrap to minimize the loss of semivolatile species during the daytime; the sampling lines inside the mobile laboratory were covered with insulated foam, placed inside of a large diameter plastic tubing and surrounded by constant flow of ambient air to prevent condensation of semivolatile species and water due to the temperature difference between ambient and mobile laboratory air.

The California Air Resources Board ambient air quality monitoring site at Rubidoux, CA is located ~10 km northwest of SOAR sampling site [*Chow et al.*, 1992]. Due to the absence of beta attenuation monitor (BAM) data at SOAR sampling site, ambient $PM_{2.5}$ mass concentrations are represented by Rubidoux BAM measurements, which are good estimates of the sampling site $PM_{2.5}$ levels during most of the study periods. Wind data, ambient temperature and relative humidity (RH), taken at the SOAR sampling site, were provided by the Goldstein group at University of California, Berkeley.

4.3.3 ATOFMS Data Analysis

The chemical composition and D_a of 1,076,812 and 1,061,506 ambient particles were collected using ATOFMS during SOAR-I and SOAR-II, respectively. The detailed design and operating principles of ATOFMS are discussed in detail by Gard and coworkers [*Gard et al.*, 1997]. The desorption/ionization laser power used in the SOAR

studies was 1.5 mJ, which has been shown to be able to fully ionize particles smaller than 1.0 µm [Bhave et al., 2002]. A custom software package was used to calibrate the mass spectra, and ion peaks were extracted into a peak list which were imported into Matlab using a single particle mass spectrometry data analysis tool, YAADA, for further analysis [Allen, 2002]. The area and relative area of marker peaks in ATOFMS mass spectra can be related to the amount of specific species on each particle [Gross et al., 2000; Bhave et al., 2002]. To obtain major particle types over the study, an adaptive resonance theorybased clustering method (ART-2a) was used to classify ATOFMS measurements [Song et al., 1999]. By comparing the existence and intensity of ion peaks in single particle mass spectra, ART-2a classifies particles into separate clusters based on their mass spectral fingerprints. The "quintessential" mass spectra which represent the overall mass spectral characteristics of each cluster are referred to as its weight matrix. Submicron (0.2 μ m \leq $D_a < 1.0 \ \mu m$) and supermicron (1.0 $\mu m \le D_a \le 2.5 \ \mu m$) particles during SOAR-I and SOAR-II were classified with ART-2a separately. A vigilance factor of 0.80 was used in this work, and particles in the most populated 50 (top 50) clusters account for ~90% of total ART-2a classified particles in both size ranges for SOAR-I and SOAR-II. Therefore, the top 50 clusters are representative of the overall aerosol composition and are the focus of this paper. The purpose of this paper is to present general pictures of major aerosol compositions over the course of the study during each season; thus information on unique species (such as metals) and distinct events will be the focus of future papers.

4.4 RESULTS AND DISCUSSION

General meteorological conditions exhibited diurnal variations for both seasons and are summarized in Figure 4.2. In summer, westerly winds dominated during the daytime between 6:00 and 18:00 reaching their maximum speeds at approximately 14:00. At night, the wind direction came from the east, associated with a decrease in wind speed. Temperature and O₃ concentrations showed similar diurnal trends as wind speed, while RH showed the opposite trend. Maximum temperature and O₃ concentrations and minimum RH were observed at approximately 14:00; minimum temperature and O₃ concentration and maximum RH occurred around 5:00. Overall, ambient meteorological conditions exhibited strong diurnal pattern without substantial day-to-day variation during SOAR-I.

Similar diurnal trends of wind speed, temperature, RH, and O₃ concentrations were still present during SOAR-II but the trend was weaker. Distinct differences were observed during certain periods including daytime wind directions. Easterly wind was observed at night throughout most sampling duration, which switched to westerly winds between 9:00 and 16:00 from November 2 to November 14. October 31 to November 1 and November 15 to November 21 were Santa Ana periods, during which warm, dry, and gusty offshore winds blows from the east-northeast to Southern California. Maximum wind speeds in SOAR-II (~1.6 m/s) were generally lower than those in SOAR-I (~2.5 m/s) except during the Santa Ana periods when wind speed can reach above 2.5 m/s. Moreover, wind speed spiked frequently in early mornings during SOAR-II besides the daytime peak. Compared to SOAR-I, SOAR-II O₃ concentration displayed a similar diurnal variation with more irregularity during Santa Ana periods. However, the highest



Figure 4.2 Temporal variations of ambient wind speed, wind direction, temperature, relative humidity, and ozone concentration during SOAR-I (a) and SOAR-II (b).

 O_3 concentration throughout SOAR-II was only 70 ppb, whereas in SOAR-I, the daily O_3 concentration maximum frequently exceeded 100 ppb. SOAR-II will be segregated into more detailed episodes in the forthcoming sections.

4.4.1 PM_{2.5} Concentrations

BAM mass concentrations and APS size-resolved number concentrations for ambient $PM_{2.5}$ are compared in Figure 4.3 for both SOAR-I and SOAR-II. The contour plots represent hourly temporal and size-resolved APS number concentrations in log scale with red being the highest concentrations and purple being the lowest. Hourly BAM measurements (brown line) are superimposed on APS measurements for more clear comparison. In SOAR-I, $PM_{2.5}$ mass concentrations displayed diurnal variations peaking mostly around noon with 79 µg/m³ being the highest concentration observed. This daytime peak was likely due to a combination of transport of LA morning traffic pollution and secondary aerosol formation from photochemical reactions, which was dissipated by the increase in wind speed in early afternoon hours (from ~1.5 m/s to 2.5 m/s). No consistent diurnal trend was observed in SOAR-II ambient $PM_{2.5}$ concentrations, but there were episodes of extremely low mass concentrations during Santa Ana periods, as well as a gradual buildup between November 2 and November 7 with the highest concentration of 106 µg/m³ in the Fall.

APS number concentration measurements showed results consistent with BAM measurements. The highest number concentrations during SOAR-I typically occurred around noon in the size range of $0.5 - 1.0 \mu m$, during which the BAM also displayed daily peaks. The particles between $0.5 - 1.0 \mu m$ account for majority of particle mass and have a larger size distribution due to aging compared to freshly emitted particles.



Figure 4.3 Hourly temporal variations of BAM $PM_{2.5}$ mass concentration and sizeresolved hourly APS $PM_{2.5}$ particle number concentration during SOAR-I (top) and SOAR-II (bottom). Contour plots represent APS number concentration in log scale, and the red lines correspond to BAM data.

Late afternoons were generally characterized by the lowest particle number concentrations, which also agreed well with the trends shown by the BAM. SOAR-II episodes were also easily discerned with APS measurements. Similar to the agreement in SOAR-I, APS and BAM measurements displayed similar patterns in SOAR-II. Santa Ana periods featured extremely low number concentrations even in the smallest size ranges; a gradual buildup period between November 2 and November 7 was characterized by increased APS concentrations, with a maximum of >500 particles/cm³ observed in the early morning of November 7. ATOFMS raw particle counts typically tracked well in both seasons with APS measurements having an R^2 of 0.59 in SOAR-I and 0.84 in SOAR-II.

4.4.2 Chemical Composition of ART-2a Clusters

The ART-2a weight matrices of major Riverside particle types have been presented previously by Pastor et al. [Pastor et al., 2003]. Most particle types in Pastor's work were observed in the current studies although a few clusters were categorized differently based on more experience with ATOFMS measurements. Similar particle classes dominated both SOAR-I and SOAR-II; however, their relative fractions were different. The association of clusters with secondary species provides important information on aerosol aging. As observed previously in Riverside, the most common secondary marker peaks in this study are m/z 18 (NH₄⁺), 30 (NO⁺), 86 (C₅H₁₂N⁺), -46 (NO₂⁻), -62 (NO₃⁻), -80 (SO₃⁻), -97 (HSO₄⁻/H₂PO₄⁻), and -125 (HNO₃NO₃⁻). The peak at m/z 43 (CH₃CO⁺/CHNO⁺) is also a secondary marker photo-oxidation reaction. Figure 4.4 showed SOAR-I temporal variation of O₃ concentrations and the hourly average peak area of m/z 43. They track each other very closely indicating that m/z 43



Figure 4.4 Hourly temporal variations of O_3 concentration and hourly average peak area of m/z 43.

 $(CH_3CO^+/CHNO^+)$ is a secondary marker indicative of photo-oxidation reaction. No similar correlation was observed during SOAR-II, possibly due to the decrease in O₃ concentrations. Overall, secondary organic aerosol concentrations are lower in the Fall [*Na et al.*, 2004; *Spencer et al.*, 2007].

Representative ART-2a weight matrices of the SOAR major particle types are included in Figure 4.5. Aged OC1 represent typical OC particles showing the most intense fragment peaks at m/z 27 ($C_2H_3^+/CHN^+$), 37 (C_3H^+), and 43; their mass spectra also contain low intensity peaks representing secondary species including 18, 30, 86, and 118 ($(C_2H_5)_3NOH^+$). No negative ions were detected for this particle type. Aged OC-SO₄ have similar positive mass spectral features as aged OC1; additionally, they have intense negative spectra showing associations with nitrate (m/z - 46, -62 and -125) and sulfate (m/z - 80 and -97). The positive spectra of ECOC contain both EC and OC signatures. These particles contain similar OC mass spectral patterns as aged OC1 and have no negative spectra, but the most intense positive peaks are from characteristic EC fragments at m/z 12 (C⁺) and 36 (C₃⁺) along with other low intensity EC peaks. ECOC- SO_4 particles have similar positive spectra compared to ECOC and similar negative spectra to aged OC-SO₄; these particles contain a mixture of OC, EC, nitrate, and sulfate. Vanadium-rich particles contain mostly OC in the positive spectra, with the dominant peaks being m/z 51 (V⁺) and 67 (VO⁺). Aged sea salt and biomass are both associated with nitrate and sulfate as shown in their negative spectra. The most intense positive peak of aged sea salt particles is the peak at m/z 23 (Na⁺), followed by lower intensity $m/z 81 (Na_2Cl^+)$, 108 $(Na_2NO_3^+)$, 39 (K^+) and carbonaceous peaks. Hughes and co-



Figure 4.5 ART-2a weight matrices of representative particle types during SOAR-I and SOAR-II.

workers showed that sea salt is the only significant sodium source in Riverside [Hughes et al., 2000]. The most intense positive peak in biomass particles is m/z 39 (K⁺) accompanied by low intensity OC peaks; many studies have shown that potassium is the marker for biomass emissions [Sexton et al., 1985; Schauer et al., 2001; Qin and Prather, 2006]. Dust particles are mostly distributed in supermicron range and contain one or more inorganic species including sodium, magnesium, aluminum, silicon, potassium, calcium, iron, and manganese; the weight matrix of iron-rich particles is presented here as an example. The positive weight matrices of all the above particle types are consistent with the major ones presented previously in Pastor et al. [Pastor et al., 2003]. Having only single positive spectra limited the ability of Pastor et al. in differentiating between aged and fresh particle types (i.e. aged OC1 and aged OC-SO₄ and ECOC and ECOC-SO₄). These types are shown to have very different temporal variations in the following sections.

Four additional Riverside particle types were identified in the SOAR studies that were not shown in Pastor et al. EC is an elemental carbon dominant type showing very distinct continuous C_n^+/C_n^- patterns (where n is an integer) in both polarities extending beyond m/z 150. Amine particles are organic carbon particles with m/z 86 and 118 being the most intense positive peaks [Angelino et al., 2001]. NH₄NO₃–rich OC-containing particles are characterized by intense ammonium and nitrate cluster peaks in the positive spectra at m/z 18, 30, 35 ((NH₃)₂H⁺), 52 ((NH₃)₃H⁺), 98 ((NH₃)₃NO₂H⁺), and 115 ((NH₃)₄NO₂H⁺); their negative spectra are dominated by nitrate peaks. This type is quite different from the ammonium nitrate particles in Pastor et al., which mainly contain m/z 18 and 30 [Pastor et al., 2003]. Aged OC2 is a low abundance OC cluster (<2% on average). The positive spectra of this type show distinct envelope patterns peaking around m/z 27 and 29; 39, 41 and 43; 55 and 57; 69 and 71; 81 and 83; 95 and 97. Compared to particle types in Pastor et al., the most likely reasons for observing the above four particle types in the SOAR studies are classifying submicron and supermicron particles separately and using a higher vigilance factor, although we cannot exclude a change in the ambient air quality between 1997 and 2006. All particles during the SOAR studies show some degree of aging based on the associations between the major particle types and secondary ammonium, amines, nitrate, and sulfate.

4.4.3 SOAR-I Diurnal Variation

In SOAR-I, the fractions of the major particle types showed distinct diurnal trends throughout the sampling period. Submicron aerosols were dominated by carbonaceous particles; while supermicron aerosols were alternately governed by either carbonaceous particles or dust and aged sea salt particles depending upon the time of day. Figure 4.6 a-d presents the hourly temporal variations of the number fractions of major particle types for the top 50 clusters, with BAM measurements superimposed on each plot in red trace. The following discussions of temporal variations refer exclusively to the ATOFMS particle type number fractions unless otherwise specified. Also included in Figure 4.6 are the size distributions of total PM_{2.5} in each season. Figure 4.7 shows the size-resolved number fractions of each of SOAR-I top 50 ART-2a clusters at various time of day: 3:00, 9:00, 15:00 and 21:00. Clusters with similar chemical compositions are placed next to each other with the same theme color but various patterns and the data for each hour were obtained by taking the average of the same hour data over all sampling days. The size







Figure 4.7 Hourly size-resolved number fractions of SOAR-I top 50 clusters from ART-2a results averaged for 3:00, 9:00, 15:00 and 21:00 over all sampling days. Size resolution is $0.05 \ \mu m$ for the submicron range and $0.10 \ \mu m$ for the supermicron range.

resolution is 0.05 μ m for submicron and 0.1 μ m for supermicron particles with the starting size indicated on the bottom axis.

SOAR-I aged OC1 and ECOC peaked in early morning around 5:00 as shown in Figure 4.6 a-b. These two types of particles only had positive spectra. They were likely the fairly aged aerosols experienced daytime photochemical reaction and nighttime aqueous phase processing, but high RH values in the early morning suppressed the negative ions on these particles, causing them to peak at 5:00. EC showed a similar temporal trend and also peaked around 5:00. Based on the low intensity of secondary marker peaks, these particles were freshly emitted and were most likely from local vehicle sources. Figure 4.7 presents complimentary information showing the highest aged OC1 and ECOC fractions appearing close to 3:00 in both submicron and supermicron ranges and lowest fractions were observed near 9:00 and 15:00, mainly distributed in the submicron range. EC, however mostly fell in the supermicron range, which is a little un-expected since freshly emitted particles are usually small in diameter $(< 0.2 \mu m)$. There might be contributions from other local source that generate larger EC particles. The low wind speeds at night coupled with low inversion layers assisted the buildup of particles and led to the observed high carbonaceous fractions. Aged $OC-SO_4$ and $ECOC-SO_4$ mostly peaked subsequently later in the morning around 9:00 and showed a second peak around 14:00. The morning peaks likely correspond to transformed organic aerosols from early morning vehicle emissions and the time of the peaks was affected by local aerosol transformation rates. The afternoon peaks are due to the combination of local secondary aerosols formed through photochemical reactions and the transport of LA pollutants, which were originally emitted from LA early morning rush hour vehicles and were transported to Riverside by summer daytime westerly winds after about 8-10 hours as shown by the air mass trajectories. This afternoon peak was also observed in other studies, and the transport time have been estimated to range from a few hours to more than one day [Pandis et al., 1992; Sardar et al., 2005]. Thus the variation in the afternoon peak hours was partly due to aerosol transport time. Aged OC-SO₄ were mostly submicron particles as shown in Figure 4.7. A substantial fraction of ECOC-SO₄ particles were in supermicron ranges, which possibly transformed from supermicron EC particles. Overall, carbonaceous particles mixed with nitrate, sulfate and ammonium dominated the submicron range throughout the day (75% - 90%), and were the major supermicron components in the morning periods.

Biomass, vanadium-rich, dust and aged sea salt particle types all peaked in the afternoon and were transported from the LA area by the daytime prevailing westerly wind. Biomass and vanadium-rich were mostly submicron particles; whereas dust and aged sea salt particles mostly fell in the supermicron range and when combined often comprised 90% of supermicron particle counts at their maxima. Dust particles also displayed a minor peak in the morning, which is likely from local sources. Figure 4.7 also shows that aged sea salt and dust governed the supermicron range especially around 15:00 in the largest size bins. Vanadium has been observed in particle phase in many studies and are one of the major metal components of ship emissions [Vouk and Piver, 1983; Isakson et al., 2001; Xie et al., 2006]. Although a minor fraction can be emitted from vehicle exhaust [Sodeman et al., 2005], the vanadium-rich particles during the SOAR studies were most likely emitted from ships in LA and Long Beach Harbors and were transported inland to Riverside. Vanadium measurements by Singh and co-workers

in Riverside [Singh et al., 2002] show consistent results where vanadium concentrations peak from late afternoon to early evening; however, the major source of vanadium was proposed to be vehicle emissions instead of ship engine exhaust in their paper [Singh et al., 2002]. As shown in Figure 4.7, SOAR-I vanadium-rich particles peaked around 15:00. The highest fractions of vanadium particles occurred in the low submicron size range, indicating that these particles were generated from combustion sources instead of crustal material, and grew to fine range during transport.

Amine particles were associated with both nitrate and sulfate. They were only observed in the submicron range and peaked between 17:00 and midnight as shown in Figure 4.6 and 4.7. Similar diurnal variations of ambient amine particles have been observed in previous studies in Riverside and Atlanta [Angelino et al., 2001]. Amine particles are small in diameter and are semivolatile because they are formed through photo-oxidation of gas-phase low molecular weight amine. [Angelino et al., 2001]. Therefore, most amine particles were detected at night when they participated into particle phase at low ambient temperature and high RH [Angelino et al., 2001]. The highest amine fractions occurred in the smallest size bins.

NH₄NO₃-rich particles represented highly aged aerosols containing a great amount of ammonium and nitrate as demonstrated by their weight matrix. These particles mostly fall into the supermicron range due to particle growth during aging as shown in Figure 4.6 a-b. High NH₄NO₃-rich particle fractions occurred around noon on August 5, as well as less distinguishable spikes from August 2 to August 9 around the same time in SOAR-I. High concentrations of nitrate particle precursors were generated from LA area morning vehicle emissions and formed nitrate as the particles were transported inland. Large amounts of NH₄NO₃ were produced when the high concentration nitrate particles crossed Chino dairy farm area upwind and were continuously transported east causing sharp spikes (3-5 hrs) in Riverside NH₄NO₃ concentrations. Similar NH₄NO₃ production mechanisms in Riverside have been proposed previously by Kleeman and Cass and by Singh and co-workers [Kleeman and Cass, 1998; Singh et al., 2002]. Hughes and co-workers observed a higher mass fraction of NH₄NO₃ in particles in 1.0-1.8 µm compared to 0.56-1.0 µm during filter analysis, which is consistent with the higher NH₄NO₃-rich particle fractions in the supermicron range by ATOFMS [Hughes et al., 1999; Hughes et al., 2002]. Single particle analysis by Pastor et al. showed a temporal anti-correlation between sea salt and NH₄NO₃ particles [Pastor et al., 2003]. This anti-correlation is not observed in the SOAR studies; in fact the relative fractions of aged sea salt and NH₄NO₃-rich particles sometimes peak around the same time.

Overall, the SOAR-I particles are fairly aged, and most particle types displayed distinct diurnal variations. Total carbonaceous fractions were high from late night to late morning, whereas amine, vanadium-rich, biomass, and aged sea salt fractions peaked in late afternoons. The daytime was greatly influenced by LA pollutants due to the prevailing westerly wind; nighttime was affected by low speed easterly wind, thus local emissions dominate aerosol composition. In most cases, BAM measurements showed maxima when carbonaceous particle fractions were the highest, indicating that carbonaceous particles which associated with nitrate, sulfate and ammonium were the major PM_{2.5} components by mass.

4.4.4 SOAR-II Episodic Variations

While SOAR-I and SOAR-II had similar major particle types, episodic temporal variations were observed in SOAR-II particles fractions as shown in Figure 4.6 c-d. Although no consistent diurnal trends exist with the exception of the NH₄NO₃-rich, SOAR-II sampling period can be characterized into unique episodes based on ambient PM_{2.5} mass concentration levels. Specifically, the episodes are: SantaAna1, October 31 0:00 – November 1 19:00; Buildup1, November 1 19:00 – November 6 15:00; HighMass, November 6 15:00 – November 7 18:00; Buildup2, November 7 18:00 – November 8 22:00; Scavenging, November 8 22:00 – November 11, 13:00; Buildup3, November 11 13:00 – November 15 5:00; and SantaAna2, November 15 5:00 – November 21 10:00.

Figure 4.8 presents the hourly-averaged size distributions of the top 50 clusters number fractions during each episode. Similar to Figure 4.7, clusters with the same composition are positioned next to each other and represented with the same color but different patterns. Submicron and supermicron size distributions are shown with size resolutions of 0.05 µm and 0.10 µm, respectively. The PM_{2.5} mass concentrations within each respective episode are highlighted in green in Figure 4.8. Also included are seven representative HYSPLIT 48-hour back trajectories ending at Riverside with 4-hour time resolution [Draxler and Rolph, 2003]. The HYSPLIT trajectories provided the origin of the air mass during each episode; the total traveling distance correlates with the speed of air mass movement. The end times of each trajectory correspond to one day in each episode at 6:00. All of the HYSPLIT plots in Figure 4.8 have the same latitude-longitude scale except for SantaAna2, during which the air mass traveled very far during the past 48 hours; therefore, a much larger geographical region is needed to display the complete



Figure 4.8 Size-resolved number fractions of SOAR-II top 50 clusters from ART-2a results averaged over each episode along with corresponding PM2.5 levels and representative 48-hour HYSPLIT back trajectories.

trajectory. All of the back trajectories illustrated the common conditions for each episode; while particular hours within the episodes could have different trajectories, they are not representative of the general conditions.

In addition to the low ambient particle mass and number concentrations, low RH and high temperature are the distinct characteristics of both Santa Ana periods. HYSPLIT back trajectories in Figure 4.8 show that SantaAna1 air mass reaching Riverside at 6:00 on November 1 started from Nevada 48 hours before and consecutively traveled east through Utah, Arizona, then west to Nevada, California, and finally reached the sampling site. The air mass traveled a much greater distance compared to the non-Santa Ana periods and carried a large amount of dust particles to Riverside, while taking away many of the carbonaceous particles to the west. Even faster air mass transport was observed during the SantaAna2 period. The air mass ending at 6:00 on November 16 traveled east from the Gulf of Alaska through Canada, then south to the US during the past 48 hours. The stronger weather condition in SantaAna2 led to lower APS counts, lower PM_{2.5} mass concentrations, and lower carbonaceous fractions comparing to SantaAna1. Consistent with the trajectory plots, ATOFMS measurements observed great fractions of dust particles during Santa Ana periods due to the desert influence. Figures 4.6 and 4.8 show that carbonaceous (\sim 50% of total counts), biomass, amine, and dust types were the major components of submicron particles; whereas supermicron particles were composed of \sim 75% dust, \sim 15% biomass and \sim 5% aged sea salt with very low (<5%) carbonaceous fractions in these episodes. The particle type fractions in Figure 4.6c do not appear as smooth during SantaAna2 as in other days, due to the low particle counts detected in this period. Substantial fractions of amine and biomass particles were

observed; however, the increases in their relative fractions were most likely caused by much lower overall particle counts, and the actual counts for the two types were in fact lower than those during other episodes. These types are more likely emitted from local sources due to the absence of an LA influence. Vanadium-rich particle fractions were extremely low since they are mostly generated from ship emissions from the west, and the Santa Ana air masses originated from the eastern desert.

High RH and low temperature aided aerosol accumulation during Buildup1. The representative HYSPLIT trajectories show that the air mass was fairly stagnant during this episode resulting in a gradual increase of $PM_{2.5}$ mass concentrations with daily maxima occurring in the daytime. APS measurements showed consistent results with the BAM and also peaked during the day as shown in Figure 4.3. Carbonaceous particles not only dominated the submicron range, but also the supermicron range. Among the major particle types, aged OC1 spiked more at night due the effect of RH and ECOC-SO₄ peaked more during the day, which is consistent with SOAR-I patterns. The west-originating air mass and the accumulation aided in the formation and buildup of NH₄NO₃, therefore substantial fraction of NH₄NO₃-rich particles were observed in the supermicron range peaking around 1.5 μ m.

HighMass was a 27-hour episode spanning overnight from November 6 15:00 to November 7 18:00 when the highest concentrations of the Fall study were observed. The stagnant meteorological conditions featuring 10-hours of low wind speeds led to the highest $PM_{2.5}$ particle number and mass concentrations (>500 particles/cm³, 106 µg/m³) on November 7 0:00 – 6:00. Once again, carbonaceous particles which were associated with nitrate, sulfate and ammonium accounted for more than 85% below 1.0 µm, and also dominated the supermicron range. NH₄NO₃-rich particles were also observed in the HighMass period. Besides the large particles fraction in submicron range, NH₄NO₃-rich particles even spread into supermicron range due to the very stagnant condition. These particles only occurred during high ammonium nitrate episodes. Ambient mass concentrations started to decrease midday on November 7 as the wind speed rose.

The highest mass concentrations in Buildup2 occurred around noon on November 8. Air masses during this episode traveled north along the coast of Baja from Mexico to San Diego, eventually moved inland to Riverside. Thus, ATOFMS measurements show carbonaceous particles in the submicron mode, as well as an increased fraction of aged sea salt in the supermicron range due to a marine influence. No NH₄NO₃-rich particles were observed during this episode because the air mass did not pass over the Chino dairy The Scavenging episode featured very low particle number and mass area. concentrations due to precipitation events on November 9 and 10. Air mass back trajectories and major particle fractions are similar to those in Buildup2, however, aged sea salt dominate the supermicron range with low carbonaceous fractions. Finally, Buildup3 was a particle buildup period. Aerosol mass concentrations gradually increased on November 11 and 12 and displayed diurnal variations between November 13 and November 15 showing maxima at night. The air mass originated from the west and thus similar particle types were observed compared to Buildup1, with substantial NH_4NO_3 rich particles.

The only SOAR-II particle type that showed distinct diurnal variations was the NH₄NO₃-rich type. Four distinct NH₄NO₃-rich particle spikes appeared in both size ranges around November 6 12:00, November 7 15:00, November 13 18:00, and

November 14 18:00, along with minor spikes shown in Figure 4.6 c-d. Most peaks occurred slightly later between 15:00-17:00 comparing to SOAR-I NH₄NO₃-rich type. Although SOAR-I NH₄NO₃-rich type peaked around 11:00 (PST), the actual local time corresponded to 12:00. The time delay between summer and fall NH_4NO_3 -rich peaks is likely caused by the longer time required to form nitrate due to weaker solar radiation in the fall. The filter analysis by Hughes et al. showed that ammonium and nitrate fractions peak between 14:00 and 18:00 over October 31-November 1 in 1997, similar to the ATOFMS measurements in SOAR-II [Hughes et al., 2002]. Again, the NH₄NO₃ particles were formed as the nitrate particles crossed the upwind Chino area. Additionally, each NH₄NO₃-rich peak was followed by a high PM mass concentration spike; thus high ambient NH_4NO_3 levels could be one of the factors triggering high ambient mass concentrations. Similar behavior was observed by Turkiwicz et al. where NH₄NO₃ drove the PM_{2.5} exceedances in San Joaquin Valley [Turkiewicz et al., 2006]. Similar to SOAR-I, the temporal variations of the BAM measurements tracked carbonaceous particle number fractions, especially in the supermicron range, indicating that carbonaceous particles with nitrate, sulfate and ammonium are the major components in mass concentrations.

4.4.5 SOAR-I and SOAR-II Comparison

Although similar ATOFMS particle types were observed in both SOAR-I and SOAR-II, temporal variations and particle fractions of major types were different in summer and fall. In general, the submicron size range was dominated by carbonaceous particles and the major particle types in supermicron range were aged sea salt, dust and carbonaceous, except during the Santa Ana periods when dust dominated. The top OC and EC types are very similar in both summer and fall, and no new major particle type was observed in either season.

Figure 4.6e-f shows the raw particle size distributions measured by ATOFMS during SOAR-I and SOAR-II with a resolution of 0.10 μ m. Despite the size-dependant transmission efficiency [Dahneke and Cheng, 1979], the SOAR-I particle size distribution peaked around 1.6 μ m with more supermicron particles detected than submicron particles; whereas the size distribution in SOAR-II peaked around 0.5 μ m, dominated by submicron particles. The differences in size distributions are indicative of various degrees of aerosol aging. SOAR-I particles were highly transformed through photochemical reactions and other reaction pathways. Particles grew in size during aging, leading to high supermicron particle counts. SOAR-II particles were less aged thus their original sizes were not altered as much through processing. The decrease in solar radiation during the fall is one reason for the reduction in aerosol aging. It is also evident that higher fractions of aged OC (aged OC1+aged OC-SO4) were observed in SOAR-II han SOAR-II, further indicating that SOAR-I aerosols were more aged than SOAR-II aerosols.

The ternary plots of SOAR-I and SOAR-II representative submicron aged OC-SO₄ particles (~300 particles evenly distributed over the study period) are included in Figure 4.9. These plots showed the relative amount of nitrate, sulfate and ammonium on every single particle. A particle mostly containing nitrate (m/z -62) would appear at the lower left vertex; a particle mostly containing sulfate (m/z -97) would appear at the lower right vertex; a particle mostly containing ammonium (m/z 18) would appear at the top vertex. SOAR-I aged OC-SO₄ particles evenly distributed between nitrate and sulfate



Figure 4.9 Ternary plots of SOAR-I and SOAR-II submicron aged OC1 particles. In each plot, a particle mostly containing nitrate would appear at the lower left vertex, a particle mostly containing sulfate would appear at the lower right vertex, a particle mostly containing ammonium would appear at the top vertex.

vertex, showing that the amount of nitrate and sulfate were comparable on these particles. In contrast, SOAR-II aged OC-SO₄ particles mostly distributed near lower left corner, illustrating that SOAR-II particles contained more nitrate than sulfate. Suring SOAR-I, ammonium and nitrate were baked off particle phase due to the high ambient temperature, thus there comparable amount of sulfate and nitrate in the particle phase; whereas the lower temperature in SOAR-II favors the condensation of ammonium and nitrate onto the particle phase, thus more nitrate was observed than sulfate, and ATOFMS detected the NH₄NO₃-rich particles during the Buildup and HighMass periods. Secondary processing of ambient aerosols will be addressed in detail in future papers.

The mass concentrations of major particle types during SOAR-I and SOAR-II are shown in Figure 4.10. The mass concentrations were obtained by scaling ATOFMS measurements with APS measurements, and the detail of scaling is discussed in Chapter 5. The sum of the major particle type mass concentrations has similar trend as the PM_{2.5} mass concentrations for both SOAR-I and SOAR-II. While the major particle chemical compositions were similar in the summer and fall, these seasons were dominated by different aerosol formation mechanisms and showed different temporal trends in major particle type mass concentrations. The LA influence was observed in the current work, and carbonaceous particles associated with secondary species were found to be the major PM_{2.5} component by mass in Riverside. The detailed analysis of SOAR-I and SOAR-II ATOFMS measurements in this paper provide further understanding on ambient aerosol composition, chemical associations on a single particle level, and provide important information on ambient aerosol aging process in the LA basin and similar areas with strong vehicular emission influence and intense sunlight.





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Chapter 5

5 Comparison of Two Methods for Obtaining Quantitative Mass Concentrations from Aerosol Time-of-Flight Mass Spectrometry Measurements

5.1 SYNOPSIS

Aerosol time-of-flight mass spectrometry (ATOFMS) measurements provide continuous information on the aerodynamic size and chemical composition of individual particles. In this work, we compare two approaches for converting unscaled ATOFMS measurements into quantitative particle mass concentrations using (1) reference mass concentrations from a co-located micro-orifice uniform deposit impactor (MOUDI) with an accurate estimate of instrument busy time, and (2) reference number concentrations from a co-located aerodynamic particle sizer (APS). Aerodynamic-diameter-dependent scaling factors are used for both methods to account for particle transmission efficiencies through the ATOFMS inlet. Scaling with APS data retains the high-resolution characteristics of the ambient aerosol because the scaling functions are specific for each hourly time period and account for a maximum in the ATOFMS transmission efficiency curve for larger sized particles. Scaled mass concentrations obtained from both methods are compared with co-located $PM_{2.5}$ measurements for evaluation purposes. When compared against mass concentrations from a beta attenuation monitor (BAM), the MOUDI scaled ATOFMS mass concentrations show correlations of 0.79 at Fresno, and 0.91 for the APS scaled results at Angiola. Applying composition dependent density corrections leads to a slope of nearly one with zero intercept between the APS scaled absolute mass concentration values and BAM mass measurements. This paper provides details on the methodologies used to convert ATOFMS data into continuous, quantitative, and size resolved mass concentrations that will ultimately be used to provide a quantitative estimate of the number and mass concentrations of particles from different sources.

5.2 INTRODUCTION

Over the past two decades, the number of studies on airborne particulate matter has increased substantially due to increased awareness of the role of aerosols in reducing visibility, affecting climate change, and endangering human health [*Brunekreef and Holgate*, 2002; *Horvath*, 1993; *Jacobson et al.*, 2000; *McClellan*, 1987; *Oberdorster*, 2001; *Robock*, 2000; *Sydbom et al.*, 2001]. Health risks have been shown for particles with aerodynamic diameters less than 2.5 μ m (PM_{2.5}), based on mortality rates which show a positive correlation with particles in this size range [*Pope*, 2000]. Therefore, it is very important to perform regional-scale long term monitoring in order to better understand the major sources impacting the annual PM_{2.5} mass concentrations.

Although traditional off-line filter based measurements are able to provide robust information on aerosol mass concentration and chemical composition, they still have limitations such as low time resolution, sampling artifacts [*Zhang and McMurry*, 1987], and very limited information on aerosol mixing state which is essential for understanding

the impacts of aerosols on climate and visibility [*Heintzenberg*, 1989]. Real-time single particle mass spectrometry (SPMS) measurements provide continuous on-line information on single particle size and chemical composition [Johnston, 2000; Noble and Prather, 2000; Suess and Prather, 1999]. These measurements can be used to provide further insight into the associations between chemical species within individual particles, allowing one to link composition with specific sources and atmospheric processing. Particles are rapidly analyzed (<1 ms), minimizing the changes in particle morphology and the repartitioning of chemical species during the analysis. Despite these advantages, it has been a challenge for real-time SPMS instruments to provide quantitative information on aerosol mass concentrations. Several factors present obstacles in First, particle transmission efficiency is sizequantifying SPMS measurements. dependent and needs to be corrected using number concentrations from other co-located instruments [Dahneke and Cheng, 1979]. Second, in most real-time SPMS methods, the ion signals in the mass spectra for identical particles can vary considerably from shot-toshot due to inhomogeneities in the laser beam [Wenzel and Prather, 2004]. Third, instrument sensitivities to different aerosol chemical species vary [Gross et al., 2000; Mansoori et al., 1994], and can change as a function of matrix composition [Reilly et al., 2000] and particle size [Bhave et al., 2002]. Fourth, when instrument operation and data acquisition are controlled by the same computer, the ability to detect incoming particles decreases with increasing ambient particle concentration due to instrument busy time [Allen et al., 2006].

Due to the aforementioned issues, the quantitative potential of SPMS measurements has not been fully realized. A number of efforts have been dedicated to

acquiring high temporal resolution quantitative information from SPMS data by scaling with co-located reference measurements [Allen et al., 2006; Allen et al., 2000; Bhave et al., 2002; Lake et al., 2003; Moffet et al., 2004; Sodeman et al., 2005; Wenzel et al., 20031. Among the various SPMS instruments developed to date, most of the quantification efforts have been applied to aerosol time-of-flight mass spectrometry (ATOFMS), which acquires real-time information on single particle aerodynamic diameter (D_a) and chemical composition. Although ATOFMS measures D_a, only Allen et al. [Allen et al., 2006; Allen et al., 2000], Bhave et al. [Bhave et al., 2002], and Moffet et al. [Moffet et al., 2004] used D_a-based reference measurements to reconstruct quantitative results from ATOFMS data. Allen et al. [Allen et al., 2006; Allen et al., 2000] and Bhave et al. [Bhave et al., 2002] used a micro-orifice uniform deposit impactor (MOUDI) as the reference method for quantification. Typical MOUDI measurements have a time resolution of $5 \sim 8$ hours and a size resolution of 4 bins per decade. Moffet et al. [Moffet et al., 2004] compared ATOFMS measurements against aerodynamic particle sizer (APS) measurements, which provide higher time and size resolution than the MOUDI, to obtain quantitative number concentrations.

In this paper, we compare both MOUDI scaling and APS scaling methods to quantify ATOFMS single particle measurements taken during a field campaign conducted in central California. We adapt the busy-time estimation methodology of Allen et al. [*Allen et al.*, 2006] to account for recent changes in the ATOFMS data acquisition procedure. We advance the APS scaling methodology of Moffet et al. [*Moffet et al.*, 2004] by utilizing composition dependent density values to obtain quantitative mass concentrations. We present the first evaluation of scaled ATOFMS mass

concentrations against multiple, independent co-located $PM_{2.5}$ measurement devices. These scaling approaches will be used for future ambient studies to obtain quantitative ATOFMS mass concentrations and can be easily applied to other SPMS measurements.

5.3 EXPERIMENTAL SECTION

As part of the California Regional Particulate Air Quality Study (CRPAQS), two ATOFMS instruments were operated continuously, sampling ambient aerosols from November 30, 2000 to February 4, 2001. The two sampling sites were an urban site in Fresno and a rural site in Angiola, both of which are located in central California [*Watson et al.*, 2000]. Single particle size and chemical composition information on more than 2 million particles was acquired at each site. ATOFMS data are scaled with MOUDI (MSP Corp.) measurements at Fresno and with APS (TSI 3320) measurements at Angiola to obtain quantitative information. Other PM_{2.5} measurements are also used for comparison and evaluation, including a beta attenuation monitor (BAM, Met One BAM 1020), tapered element oscillating microbalance (TEOM, Rupprecht & Patashnick TEOM 1400A), dust aerosol monitor (TSI DustTrak 8520), nephelometer (Radiance Research M903), and aethalometer (Magee Scientific RTAA1000). Only the measurements taken from January 9, 2001 to February 4, 2001 are presented in this work, representing 711,289 particles in Fresno and 614,915 particles in Angiola.

5.3.1 ATOFMS Data Acquisition

ATOFMS acquires single particle diameter utilizing particle time-of-flight and obtains particle chemical composition based on the mass spectra. The design and operating principles of ATOFMS have been described in section 1.5.1 and are also discussed in detail elsewhere [*Gard et al.*, 1997]. Not all particles that are sized produce a corresponding mass spectrum, due to differences in the particle trajectories between the light scattering and ion source regions. Particles that produce both aerodynamic diameters and mass spectra are called hit particles, whereas particles that only yield aerodynamic diameters are called missed particles. A special ATOFMS operating condition is the fast scatter mode. When operating under this condition, ATOFMS only records missed particle size information without attempting to acquire mass spectra. Fast scatter measurements were often used for obtaining overall particle size distribution.

After the field study, an in-house software program was used to calibrate the mass spectra and make a list of the individual ion peaks for each particle. These peak lists were then imported into a single particle mass spectrometry data analysis tool YAADA, for further analysis [*Allen*, 2002].

5.3.2 MOUDI Measurements

The MOUDI is based on particle impaction and has been extensively used for obtaining size resolved particle mass and composition measurements [*Marple et al.*, 1986]. During the CRPAQS study, MOUDI data were collected at Fresno during six intensive operating periods (IOPs) within the time of interest for this study: 31 January 1000-1600; 1 February 0500-1000; 2 February 0000-0500; 2 February 1000-1600; 3 February 0500-1000; and 3 February 1600-2400. Angiola MOUDI measurements were not used in this study since we were unable to accurately estimate ATOFMS busy time at that site due to a change in the data acquisition hardware in the middle of the study period.

5.3.3 APS Measurements

The APS provides information on both single particle number concentrations and aerodynamic diameter via light scattering and time-of-flight measurements [*Wilson and Liu*, 1980]. It detects particles in the size range of 0.3 μ m to 20 μ m, with accurate size-resolved counting of particles with aerodynamic diameters between 0.5 and 20 μ m. APS measurements were not collected at Fresno during the CRPAQS. At Angiola, measurements were obtained with a commercial APS (TSI 3320, Minnesota) from December 1, 2000 to February 4, 2001 with a temporal resolution of 5 minutes. The APS data were averaged over 1-hour time periods. These hourly data are used in the scaling procedure described below

5.4 RESULTS AND DISCUSSION

5.4.1 Scaling with MOUDI

Previous investigations have shown that by comparing co-located ATOFMS and MOUDI data, quantitative information on particle mass concentrations can be acquired from ATOFMS measurements [*Allen et al.*, 2006; *Allen et al.*, 2000]. The advantage of scaling with MOUDI measurements is that they not only provide information on size segregated total particle mass concentrations, but also the size segregated concentrations of individual chemical species which allow the derivation of ATOFMS relative sensitivity factors to different chemical species [*Bhave et al.*, 2002]. The disadvantage is that MOUDI samples are analyzed offline and provide coarse temporal- and size-resolution data. In this work, we adapt and modify the busy time estimation method

developed by Allen et al. [*Allen et al.*, 2006] and use it to scale the Fresno ATOFMS dataset with MOUDI measurements.

5.4.1.1 ATOFMS Busy Time

Busy time (t_b) is defined as the amount of time that an ATOFMS instrument cannot detect incoming particles because it is busy processing data from a particle that just arrived. Previous studies revealed that three parameters are needed to compute ATOFMS instrument busy time: the time required to record a missed particle (A), the time required to record the first hit particle in a folder (B), and the incremental increase in time required to save each subsequent hit particle in a folder (C). Laboratory experiments have been conducted to estimate these parameters, but when lab-based parameters are applied to field data, the results are at times not physically meaningful (e.g., busy time occasionally exceeds total sampling time). Thus, empirical methods have been developed to estimate busy time directly from field data. During the 1999 Bakersfield Instrument Intercomparison Study (BIIS), the ATOFMS instrument was operated alternately in normal data collection mode and fast scatter mode. Allen et al. [Allen et al., 2006] used data collected in fast scatter mode to estimate particle arrival rates (λ). They demonstrated that Poisson with Busy Time (PBT) distributions in conjunction with λ values can be used to compute A, and that this information in combination with the particle data collected in normal operating mode can be used to compute *B* and *C*.

During CRPAQS and subsequent field campaigns, ATOFMS instruments were not routinely operated in fast scatter mode so the methodology of Allen et al. [*Allen et al.*, 2006] cannot be applied directly. In the present study, we adapt the previous methodology to estimate busy time parameters for the ATOFMS instrument that was stationed at Fresno. An analysis of the Fresno data set reveals five discrete time periods when the rate of missed particle detection (r_m) doubled while the hit particle detection rate (r_h) dropped substantially: 16 January 2150 – 17 January 0200; 28 January 0335 – 1115; 31 January 0430 – 0845; 1 February 0750 – 1040; and 2 February 0610 – 1000. As an example, Figure 5.1a illustrates the time series of r_m and r_h in 6-minute intervals throughout 28 January. Several possible reasons for these "high-miss periods" were explored, but a definitive conclusion was not obtained. Nevertheless, even without a full understanding, it was determined that the data from these high-miss periods may be exploited to calculate *A*. The strong anti-correlations between r_m and r_h suggest that the busy time associated with missed particles caused the hit rate to drop during each high-miss periods is determined by the time remaining to record hit particles after all missed particles are recorded,

$$\frac{N_{Hit}}{N_{EstHit}} = \frac{t - (A \cdot N_{Missed})}{t - (A \cdot N_{EstMissed})}$$
(5.1)

where *t* is the length of each sampling interval; N_{Hit} and N_{Missed} are the number of hit and missed particles recorded during a sampling interval; and N_{EstHit} and $N_{EstMissed}$ are the estimated number of hit and missed particles if the high-miss event had not occurred. As illustrated in Figure 5.1a, N_{EstHit} and $N_{EstMissed}$ are calculated in 6-minute intervals by linear interpolation of r_h and r_m , respectively, over each high-miss period. By solving



Figure 5.1 (a) Linear interpolation over the Fresno high-miss period to obtain estimated hit counts and estimated missed counts for the period of January 28th, 3:35 - 11:15; (b) estimated missed particle recording time vs. missed particle detection rate for all five high-miss periods with a time resolution of 6 minutes for Fresno dataset.

Equation (5.1) for A, we obtain:

$$A = \frac{t \cdot (N_{Hit} - N_{EstHit})}{(N_{Hit} \cdot N_{EstMissed}) - (N_{EstHit} \cdot N_{Missed})}$$
(5.2)

The values of *A* calculated during 6-minute time intervals within each high-miss period are plotted against r_m in Figure 5.1b. The five different colors in Figure 5.1b represent results from different high-miss periods. As can be seen, there is remarkable consistency in the values of *A* across all five high-miss periods when r_m exceeds 2.5 Hz. These time intervals occurred at the peak of each high-miss period, when the instrument was devoting the vast majority of the sampling time to detecting missed particles. Thus, the *A* values calculated during these times are most robust. Whether setting the minimum r_m thresholds at 2.0, 2.5, 3.0, or 3.5 Hz, the mean value of *A* remains fairly constant at 0.26 seconds with the standard deviation being less than 0.05 seconds. Based on the above inspection, we use 3.0 Hz as the minimum r_m threshold since at this frequency, *A* values are quite robust and some data from all five high-miss periods are included. We therefore conclude that $A = 0.264 \pm 0.013$ s. Note that the standard deviation is less than 5% of the mean *A* value.

PBT distributions using A = 0.264 are used to estimate λ throughout the study period by following the procedure of Allen et al. in reverse order [*Allen et al.*, 2006]. Excluding the "high-miss periods" when the application of PBT distributions is not justified, hourly λ values range between 0.11 Hz and 15.1 Hz, with an average of 3.5 Hz. The best-fit *B* and *C* values are also calculated according to Allen et al. [*Allen et al.*, 2006], but the C value is not statistically significant due to smaller folder limits used during CRPAQS (500 spectra per folder) relative to the BIIS (1000). We use our best-fit B value of 0.264 s, and a C value of 0.00024 s taken from laboratory experiments conducted under similar conditions (H. Furutani, Personal Communication). The difference between the A values from this study and previous studies is attributed to a change in the ATOFMS data acquisition mode. ATOFMS can be operated in either nonwide dynamic range (non-WDR) or wide dynamic range (WDR) data acquisition mode [Dienes, 2003]. When connecting two identical digitizers via a signal splitter to the signal source and attenuating one digitizer (30 db), WDR mass spectra (signal level ranging from 0 to 8000 instead of 0 to 255) can be obtained by combining the two signals [Beavis, 1996]. Although operating ATOFMS in WDR mode produces mass spectra with a much greater dynamic range, it requires significant computer time and significantly increases both the A and B values. During the current study, WDR spectra were acquired for positive ions, leading to a value of A that is higher than that in previous work when only non-WDR spectra were acquired [Allen et al., 2006]. The lab experiments also support our conclusion that A and B are comparable when operating in WDR mode, since the most time-consuming process in obtaining single particle data is the data transfer from the acquisition board to the computer; the actual data saving time represents only a minor fraction of the data transfer process.

5.4.1.2 Scaling ATOFMS Measurements with MOUDI Measurements

Scaled mass concentrations are calculated based on the effective sampling duration which excludes instrument busy time and offline periods. After obtaining ATOFMS busy time parameters, ATOFMS hit and missed particle information was processed for comparison with the MOUDI measurements. Hit particles were binned

into size and time bins matching the MOUDI data. The MOUDI size bins are: 0.18 -0.32, 0.32 - 0.56, 0.56 - 1.00, and $1.00 - 2.50 \mu m$. The time frame is limited to the six MOUDI IOPs listed above. A total of 24 time-size bins are considered in the comparison, but data from two bins are excluded from the scaling procedure for the following reasons: (a) the MOUDI mass concentration was less than twice the mass uncertainty in the 1.00-2.50 µm bin on 31 January 1000 – 1600, indicating high uncertainty in the MOUDI measurement; and (b) the total number of hit particles by ATOFMS in the 0.18-0.32 µm bin on 1 February 0500 – 1000 was less than 100, which is deemed too few for a statistically representative measurement. Ultimately, mass concentrations in 22 bins were compared for quantitative analysis. Single particle sizes and counts were collected for each bin within the specified size range and time range. Using the measured flow rate through the instrument, an ATOFMS total particle mass concentration was calculated for each bin assuming all the particles were spherical. Morawska and coworkers obtained an overall average ambient submicron particle density of 1.7 g·cm⁻³ [Morawska et al., 1999]. The average density of supermicron particles would be even higher due to the increased fraction of sea salt and dust particles which have densities of 1.9 g·cm⁻³ and 2.7 g·cm⁻³, as reported by Hänel and Thudlum [Hänel and Thudium, 1977]. Thus we use a density of 1.9 g·cm⁻³ for all PM_{2.5} particles in mass concentration calculation instead of the 1.3 g·cm⁻³ value used in previous work [Allen et al., 2006; Allen et al., 2000; Bhave et al., 2002; Pastor et al., 2003]. The scaling factor, ϕ_{MOUDI} , was constructed as the parameter to compensate for the difference between ATOFMS and MOUDI measurements. ϕ_{MOUDI} represents the inverse of the ATOFMS

particle detection efficiency and is defined with the following expression:

$$\phi_{MOUDI} = \frac{m_{MOUDI}}{m_{ATOFMS}} \tag{5.3}$$

where m_{MOUDI} is MOUDI mass concentration, and m_{ATOFMS} is ATOFMS mass concentration before scaling. ϕ_{MOUDI} is a function of particle size and can be expressed with a power law relationship with D_a :

$$\phi_{MOUDI} = \alpha \cdot D_a^{\ \beta} \tag{5.4}$$

where α and β are the best-fit parameters determined by non-linear regression of m_{MOUDI} on m_{ATOFMS} over all 22 bins. Physically, $1/\alpha$ is the particle detection efficiency for a 1.0 μ m particle and β represents the degree to which particles with sub-optimal sizes are deflected from the centerline in the ATOFMS inlet. Based on Equation (5.4), it is clear that varying the density value will not affect the scaled results; only the scaling parameters will change. The best-fit values of α and β are 1747.52 ± 363.96 and -4.41 ± 0.28 for this study, so ϕ_{MOUDI} varies from 3.4×10⁶ for a 0.18 μ m particle to 31 for a 2.5 μ m particle.

Upon obtaining α and β , the value of ϕ_{MOUDI} was calculated for every single particle using Equation (5.4) based on the measured particle diameters by ATOFMS. The following equation was used to calculate scaled ATOFMS mass concentrations:

$$m_{ATOFMS-MOUDI} = \sum_{i} \phi_{Da,i} \cdot m_i$$
(5.5)

where $m_{ATOFMS-MOUDI}$ is the ATOFMS mass concentration after scaling with MOUDI, ϕ and m_i are the scaling factors and mass concentrations for each single particle respectively. Comparison of the scaled ATOFMS and the MOUDI mass concentrations for all 22 bins results in an R² value of 0.85 as shown in Figure 5.2, indicating that two parameters (α and β) are sufficient to explain 85% of the variability in ATOFMS transmission efficiencies over the 0.18 – 2.5 µm D_a range during 6 different IOPs. It is important to note that the high R² value would not have been obtained if busy-time corrections had not been applied. Note the mass concentrations for the non-IOP periods can be calculated with the same scaling function at higher temporal resolution (1 hour) if one assumes that the ATOFMS scaling factors do not change over time. There is some uncertainty associated with this assumption, so scaling with real-time particle concentration measurements may be favorable for obtaining total mass concentrations as described in the next section.

5.4.1.3 Comparison between MOUDI Scaled ATOFMS Measurements and BAM Measurements

Both hourly BAM and hourly TEOM PM_{2.5} mass measurements were made at the Fresno site. Because the TEOM inlet was heated to 50 °C during sampling in order to remove interferences from water, other semivolatile compounds were also removed [*Charron et al.*, 2004], yielding values that were systematically lower than the co-located BAM measurements by an average of 42%. Therefore, since ATOFMS does not remove water or semivolatile compounds to a significant extent due to short analysis times, hourly BAM mass concentration measurements (m_{BAM}) were chosen as the reference mass concentration to evaluate $m_{ATOFMS-MOUDI}$ for the entire study period as shown in



Figure 5.2 Comparison of scaled ATOFMS mass concentrations and MOUDI measurements in Fresno.

Figure 5.3. Both mass concentration measurements show distinct diurnal temporal variations, reaching maxima and minima at nearly the same time each day. Particulate matter concentrations remained relatively low during the day and increased substantially at night in Fresno during this study. The correlation between m_{BAM} and $m_{ATOFMS-MOUDI}$ is notably high with a \mathbb{R}^2 value of 0.79. However, Figure 5.3 also shows that $m_{ATOFMS-MOUDL}$ is systematically lower (about 30% less) than m_{BAM} . The ratio of mean values between these two measurements is 0.69 over the 26-day sampling period of interest. Several factors account for this difference. First, particles below 0.20 µm are not included in the $m_{ATOFMS-MOUDI}$ value as this represents the lowest size detectable by the ATOFMS instrument used in this study. An analysis of the MOUDI data during the six IOPs of interest indicates that particles larger than 0.18 µm make up 86% of the total PM_{2.5} mass summed over all impaction stages from 0 - 2.5 μ m (Σm_{MOUDI}). Second, the mean value of m_{MOUDI} during the six IOPs is only 88% of the mean value of m_{BAM} . These two factors alone make it so the value of $m_{ATOFMS-MOUDI}$ cannot exceed 76% of the m_{BAM} value (0.86 × 0.88 = 0.76). Furthermore, the scaling function derived from the six IOPs most likely varied during the 26-day period. Thus, these factors result in the absolute values of $m_{ATOFMS-MOUDI}$ being 30% lower than the m_{BAM} values.

5.4.2 Scaling with the APS

5.4.2.1 Scaling ATOFMS Measurements with APS Measurements

Another quantification approach involves comparison of the ATOFMS particle counts at Angiola with particle number concentrations acquired with a co-located APS. Although APS measurements are not able to provide mass concentrations of individual chemical species like the MOUDI, they can provide particle number concentrations with



Figure 5.3 Temporal variation of hourly BAM and scaled ATOFMS PM2.5 mass concentrations in Fresno. The scaling function for the ATOFMS was obtained by comparison with MOUDI measurements.

very high temporal and size resolutions. This high resolution reference data can potentially provide more accurately scaled ATOFMS mass concentrations.

To scale the ATOFMS data with APS measurements, we follow an approach similar to the MOUDI scaling method by deriving scaling functions to correct for To take advantage of the high time resolution ATOFMS particle undercounting. properties of both measurements, one scaling function was constructed for each hour of the entire study period. Within each hour, single particle number counts collected by both ATOFMS and APS were segregated into 12 size ranges: 0.300-0.523, 0.523-0.605 μm, 0.605-0.699, 0.699-0.807, 0.807-0.933, 0.933-1.077, 1.077-1.243, 1.243-1.435, 1.435-1.655, 1.655-1.911, 1.911-2.207, and 2.207-2.547 µm. These size bins were adapted directly from the APS size bins by combining pairs of adjacent bins between $0.523 \,\mu\text{m}$ and $2.547 \,\mu\text{m}$ so that higher ATOFMS hit particle counts could be obtained for each bin. The smallest APS bin (0.300 - 0.523 µm) is also included in this calculation. When the smallest APS bin is not used, the results do not change substantially from the 12 bin scaling discussed below. Since scaling is performed hourly, the factors that affect ATOFMS sampling, such as busy time and instrument offline time, are accounted for implicitly. The scaling factor, ϕ_{APS} , is defined as the following:

$$\phi_{APS} = \frac{Count_{APS}}{Count_{ATOFMS}} \tag{5.6}$$

One scaling factor was acquired for each size bin with Equation (5.6) for each hour. Like the scaling factors used in MOUDI scaling, ϕ_{APS} is also size dependant. By plotting the scaling factors against D_a , a scaling curve can be constructed for particles with aerodynamic diameters below 2.5 µm. Figure 5.4a shows the hourly scaling curves

for the ATOFMS instrument stationed at Angiola on February 3. The error bars are generally not significant except for those at 5:00 and 6:00 during which APS measurements showed variations. The instrument was offline between 13:00 and 14:00, and therefore no scaling curve for this time period is presented. In Figure 5.4a, we see that ϕ_{APS} varies substantially from hour to hour. In the largest size bin, this variation spans nearly one order of magnitude. Most of this variability results from differences in ambient particle concentrations leading to differences in instrument busy times [Sodeman et al., 2005]. This result further emphasizes the importance of high time resolution (hourly) scaling. The scaling factors obtained with MOUDI measurements will not be as accurate as ϕ_{APS} due to the time and size resolution limit and will not be able to reflect short term ambient particle concentration changes. In general, the APS scaling curve reaches a minimum at 1.655 μ m – 1.911 μ m size bin (bin midpoint is 1.783 μ m) due to the higher ATOFMS transmission efficiency of particles in this size range than others. Two scaling functions were obtained for each hour by fitting the scaling curve separately on each side of the minimum point. Examples of the fitting of the scaling curve are included in Figure 5.4b and Figure 5.4c for 22:00 on February 03, 2001. The scaling function for the size range of $1.783 \,\mu\text{m}$ and below was obtained by exponential regression and was extrapolated down to $0.2 \,\mu m$ to obtain the scaling factors for smaller particles in the mass concentration calculation. The scaling function for the size range above 1.783 µm was obtained by a 2nd order polynomial regression. Thus, each scaling function can be fully described with five parameters which are used to calculate ϕ_{APS} as shown in Equation (5.7):



Figure 5.4 APS scaling curve for Angiola measurements. (a) hourly scaling curve for February 03, except for 13:00; (b) exponential regression of left half of scaling curve at 22:00; (c) polynomial regression of right half of scaling curve at 22:00.

$$\phi_{APS} = \begin{cases} C_1 \cdot e^{C_2 \cdot D_a} & (when \ D_a < 1.783 \ um) \\ C_3 \cdot D_a^2 + C_4 \cdot D_a + C_5 & (when \ D_a \ge 1.783 \ um) \end{cases}$$
(5.7)

Five parameters were obtained for each hour of data collected at Angiola to correct ATOFMS measurements with APS measurements, generating number concentrations with 1 hour temporal resolution. The form of Equation (5.7) will allow a similar relationship to be applied other studies to obtain APS scaling factors.

With the scaling functions acquired, quantitative ATOFMS mass concentrations $(m_{ATOFMS-APS})$ were calculated. The ϕ_{APS} value for each particle can be obtained using the D_a measured and the time when the datum was acquired. $m_{ATOFMS-APS}$ is calculated with the following equation knowing the instrument nozzle flow rate and assuming particles are spherical:

$$m_{ATOFMS-APS} = \sum_{i} \frac{M(D_{a,i}) \cdot \phi_{APS}(D_{a,i})}{V_{ATOFMS}}$$
(5.8)

where $M(D_{a,i})$ is the mass of each particle and V_{ATOFMS} is the volume of flow within each time period. Equation (5.8) makes it possible to construct quantitative particle mass concentration information for individual particle classes with any size and temporal resolution from ATOFMS measurements assuming no preferential transmission of certain particle classes. Unlike MOUDI scaling, $m_{ATOFMS-APS}$ is sensitive to assumed particle density values. Rather than assuming all particles have the same density, we may assign different density values to particles with different sizes or chemical compositions for improved estimates of the total mass concentration.

5.4.2.2 Comparison between BAM Measurements and APS Scaled ATOFMS Mass Concentrations Obtained with Different Density Values

The most straightforward approach to obtaining mass concentrations from ATOFMS data is to assign a single density value to all particles. Figure 5.5a shows the correlation between m_{BAM} and $m_{ATOFMS-APS}$ when utilizing fixed density values of 1.8 g·cm⁻³, 1.9 g·cm⁻³, and 2.0 g·cm⁻³, respectively, for APS scaling. The slope of each regression represents the ratio of mean values between m_{BAM} and $m_{ATOFMS-APS}$. The value for $m_{ATOFMS-APS}$ shows the best agreement with m_{BAM} is obtained when utilizing a density of 1.9 $g \cdot cm^{-3}$ (shown in red in Figure 5.5a). The temporal variations of the above two mass concentrations are presented in Figure 5.6. They track each other extremely well with an R² value of 0.91. The Angiola aerosols were aged and dominated by carbonaceous aerosols with significant quantities of nitrate and ammonium associated with them. Based on ATOFMS chemical analysis, more than 80% of Angiola particles were aged carbonaceous particles. As particles age, they become more internally mixed aerosols composed of organic carbon, ammonium, nitrate, sulfate, and water, and in general, the particle-to-particle chemical variability decreases over time. Thus the good agreement between ATOFMS mass concentrations scaled with a single density and BAM measurements is most likely due to the chemical homogeneity of aged ambient aerosols. When applying the above method to scale ATOFMS measurements in a region where fresh emissions occur and many distinct particle types dominate, it is likely that applying one density value for all particles will not be sufficient.

Since ATOFMS measures the aerodynamic diameter of individual particle, it is possible to apply specific density values based on particle size. The unscaled ATOFMS



Figure 5.5 Correlations between BAM and APS scaled ATOFMS mass concentrations. (a) ATOFMS mass concentrations are obtained with single density (ρ) values for all particles ($\rho = 1.8 \text{ g} \cdot \text{cm}^{-3}$, $\rho = 1.9 \text{ g} \cdot \text{cm}^{-3}$, or $\rho = 2.0 \text{ g} \cdot \text{cm}^{-3}$); (b) ATOFMS mass concentrations are obtained with different density pairs for submicron and supermicron particles: 1.2 and 2.7 g \cdot \text{cm}^{-3}, 1.7 and 2.2 g \cdot \text{cm}^{-3}, 1.7 and 2.7 g \cdot \text{cm}^{-3}, 1.7 and 3.2 g \cdot \text{cm}^{-3}, and 2.2 and 2.7 g \cdot \text{cm}^{-3}.



Figure 5.6 Temporal variation of Angiola particulate mass concentrations obtained with BAM and APS scaled ATOFMS ($\rho = 1.9 \text{ g} \cdot \text{cm}^{-3}$).

ambient particle size distribution shows that particles smaller than 1.0 um in aerodynamic diameter account for a large portion of total particle numbers in Angiola. ATOFMS chemical composition measurements have shown that particles smaller than 1.0 µm are mainly carbonaceous particles with associated secondary inorganic components, while the relative fraction of inorganic particles increases substantially above 1.0 µm [Noble and Prather, 1996]. Thus we segregate particles into two size ranges: submicron $(0.2 < 10^{-3})$ $Da < 1.0 \mu m$) and supermicron (1.0 < $Da < 2.5 \mu m$). We use literature value of 1.7 g·cm⁻³ as the density for submicron particles [Morawska et al., 1999], and 2.7 g·cm⁻³ for supermicron particles, an intermediate value for the various chemical components reported in this size range [Hänel and Thudium, 1977]. The scatter plot between $m_{ATOFMS-APS}$ acquired with this pair of density values and m_{BAM} is included in Figure 5.5b (in red). Scaled ATOFMS and BAM mass concentrations track each other very well with a high correlation coefficient of 0.91. The absolute values are quite close to one another and nearly on top of the 1:1 line. We also varied the densities by $0.5 \text{ g} \cdot \text{cm}^{-3}$ in both directions for the sub- and super-micron particles separately. The correlations between each of these density pairs with the BAM measurements are also included in Figure 5.5b. The correlation values remain high ($R^2 \sim 0.91$) in all cases and only the ratios between $m_{ATOFMS-APS}$ and m_{BAM} are different. From the change in slope it is apparent that the total scaled ATOFMS mass concentrations are more sensitive to the submicron particle density than the supermicron particle density. This is due to the fact that the majority of the Angiola particle mass is in the submicron size mode.

We can go beyond just using size information and utilize chemically specific density values applied to each different particle type to obtain scaled ATOFMS mass

concentrations. To convert from number to mass concentrations, we used the density value of 1.9 g·cm⁻³ for carbonaceous particles, 2.7 g·cm⁻³ for dust particles, 1.9 g·cm⁻³ for Na rich salt particles, 2.0 g·cm⁻³ for biomass emission particles and EC rich particles, and 1.9 g·cm⁻³ for the rest of the particle types [*Hänel and Thudium*, 1977; *McMurry et al.*, 2002; *Pitz et al.*, 2003]. The multi-density scaled ATOFMS mass concentrations also show a strong and very similar correlation with BAM measurements with a high R² of 0.91. As discussed earlier in this section, the advantages of utilizing various density values for each chemical composition are not fully realized in this particular study due to the fact that Angiola ambient particles are aged and thus very chemically homogeneous. In regions or seasons with more fresh emissions, it will most likely become necessary to assign chemically specific density values for individual particle types. Additional lab and field investigations are underway to develop universal scaling factors that use specific density and shape factors for each particle type.

5.4.3 PM_{2.5} Measurement Intercomparison

A number of different continuous particle measurements were available in both Fresno and Angiola during the CRPAQS. Thus it is possible to compare the correlations among different measurements. Such comparisons are helpful for evaluating the different methods used for scaling the ATOFMS mass concentrations. At the Fresno site, the available continuous $PM_{2.5}$ measurements are BAM, TEOM, Dust Aerosol Monitor (DAM), Nephelometer, Aethelometer, and *m*_{ATOFMS-MOUDI}. Several hours of nephelometer data points were removed in the morning periods of January 30, January 31 and February 1 due to the extraordinarily high uncertainties in nephelometer measurements. The continuous $PM_{2.5}$ measurements for the Angiola site include BAM,

nephelometer, aethelometer, and $m_{ATOFMS-APS}$ with density values of 1.9 g·cm⁻³ for all particles. Although the measurements of all these instruments represent the total PM_{2.5} particle mass concentrations, each instrument is based on a different theory and has its own strengths and weaknesses. Therefore, it is quite reasonable to expect the correlation between any two measurements to be less than 1 [*Lee et al.*, 2005].

The correlation coefficients between every pair of measurements are tabulated in Table 5.1 for both Fresno and Angiola. For Fresno site comparisons, using an R^2 value of 0.7 and above to represent a good correlation, only the BAM measurement shows a fairly good correlation with all the other measurements with correlation coefficients ranging from 0.73 - 0.93. The TEOM measurement only correlates well with BAM and aethelometer measurements. This suggests that in this environment, the heated TEOM does not provide measurements of mass concentrations that are as accurate as those of the The *m*_{ATOFMS-MOUDI} correlates well with the BAM, DAM, and nephelometer BAM. measurements. The overall correlation for MOUDI scaled ATOFMS PM2.5 mass concentrations is as good as most other PM_{2.5} measurements in Fresno. Similarly, Angiola correlation comparisons are shown in Table 5.1b. The BAM, nephelometer, and $m_{ATOFMS-APS}$ measurements show high correlation coefficients of greater than 0.90. The aethelometer measurements differ substantially and show lower correlation coefficients with the other three measurements. The strong correlation of ATOFMS mass concentrations with other PM_{2.5} measurements provides support that the ATOFMS data can be scaled using peripheral instruments, such as the APS, to provide a measure of real ambient particle mass concentrations. The ultimate goal in developing this scaling procedure is not to just provide total PM_{2.5} mass concentrations since these can be

Table 5.1 Correlation coefficients of $PM_{2.5}$ measurements. (a) Fresno site. (b) Angiola site.

(a)	Fresno R ²	BAM	TEOM	DAM	NEPH	AETH	ATOF-M
	BAM	1.00	0.86	0.93	0.75	0.79	0.79
	TEOM	0.86	1.00	0.59	0.60	0.94	0.64
	DAM	0.93	0.59	1.00	0.70	0.53	0.78
	NEPH	0.75	0.60	0.70	1.00	0.58	0.81
	AETH	0.79	0.94	0.53	0.58	1.00	0.62
	ATOF-M	0.79	0.64	0.78	0.81	0.62	1.00

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Angiola R ²	BAM	NEPH	AETH	ATOF-N
BAM	1.00	0.92	0.60	0.91
NEPH	0.92	1.00	0.77	0.93
AETH	0.60	0.77	1.00	0.63
ATOF-N	0.91	0.93	0.63	1.00

BAM: beta attenuation monitor DAM: dust aerosol monitor NEPH: nephelometer AETH: aethelometer TEOM: tapered element oscillating microbalance ATOF-N: APS scaled ATOFMS mass concentrations ATOF-M: MOUDI scaled ATOFMS mass concentrations measured using a variety of other dedicated techniques, but instead to use ATOFMS to provide mass concentrations of particles from specific sources. Thus, this study represents a critical step in the development of the most appropriate scaling procedures that will allow us to use ATOFMS to obtain quantitative source apportionment results in future studies.

5.5 CONCLUSIONS

In this paper, we compare two methods for scaling ATOFMS measurements using reference measurements to obtain quantitative particle mass concentrations. By comparing ATOFMS single particle measurements with MOUDI mass measurements, we obtain scaled ATOFMS mass concentrations that correlate well ($R^2 = 0.79$) with a BAM, which serves as an independent mass concentration reference method. However, the absolute values of scaled ATOFMS mass concentration is only close to MOUDI measurements during the IOPs within the specified size range. Reduced ratios between the scaled ATOFMS and BAM mass concentrations are obtained when applying the scaling function to other periods during the study. Increasing the time resolution of the scaled ATOFMS mass concentrations to 1 hour (i.e. shorter than that of the MOUDI which is 5-8 hours) also introduces uncertainties. Both of these factors result in the absolute values of scaled ATOFMS mass concentration being only 70% of those measured by the BAM over the full study. Some of this difference can be explained by the underestimation of particles smaller than $0.18 \,\mu\text{m}$ by ATOFMS. The main advantage of scaling with the MOUDI measurements is to obtain size segregated mass concentrations of individual chemical species, making it possible to derive relative sensitivity factors [*Bhave et al.*, 2002].

APS measurements provide high temporal resolution particle number concentrations. By scaling ATOFMS particle counts with the APS and applying composition specific density values to the ATOFMS particle types, we are able to obtain ambient particle mass concentrations that correlate extremely well with BAM measurements ($R^2 = 0.91$). Future papers will address using chemically specific scaling factors which correct for density and shape factors.

In conclusion, continuous and quantitative ambient particle mass concentrations can be obtained from ATOFMS measurements by scaling with measurements from a colocated MOUDI or APS. The MOUDI method should be used if one is interested in deriving chemical sensitivity factors for different species. If one is more interested in real-time variations in particle mass concentrations (i.e. from different sources), the APS method is a more appropriate choice. The use of these methods for scaling extends ATOFMS to a more quantitative tool for studying ambient aerosol composition, transformations, and reaction mechanisms. When applying these scaling methods to individual particle types measured by the ATOFMS and correcting for chemical differences, quantitative mass concentrations of individual particle (or source) types with high time and size resolution can be obtained. The ultimate goal is use these scaling procedures to obtain quantitative mass fractions of particles from different sources in future ambient source apportionment studies.

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Chapter 6

6 The Effect of APS Scaling Functions on the Quantification of Aerosol Time-of-Flight Mass Spectrometry Measurements

6.1 SYNOPSIS

Aerosol time-of flight mass spectrometry (ATOFMS) single particle measurements provide real-time, size-resolved information on single particle mixing state. Quantitative mass concentrations of different particle types can be obtained by scaling the ATOFMS data with aerodynamic particle sizer (APS) number concentration measurements. A question arises as to the stability of this procedure in multiple field locations. In this study, the effect of correcting ATOFMS measurements of two studies in Fresno and Angiola with APS scaling functions from different reference field studies conducted in other locations was investigated. Notably, the particle type mass fractions obtained within the submicron $(0.2 \le D_a < 1.0 \ \mu m)$ size range were almost identical, regardless of the reference APS scaling function used. More differences (0.089% - 15%)were obtained in the supermicron $(1.0 \le D_a \le 2.5 \ \mu m)$ mass fractions, mainly due to the shift in the minima of scaling curves at higher sizes. Higher mass fractions (~5% more) of aged sea salt particles and lower fractions of carbonaceous particles were obtained when scaling supermicron particles of object studies with the APS scaling functions from APMEX and NC-CCS-II studies. No substantial differences were observed when scaling the specific studies with either the co-located or reference scaling functions. Therefore,

this study demonstrates that an estimate of the submicron particle type mass fractions within 10 % and of supermicron particle type mass fractions within 19% can be obtained by scaling ATOFMS measurements with APS scaling functions from other studies if no co-located APS measurements are available.

6.2 INTRODUCTION

Traditionally, particulate matter is characterized with off-line filter/impactor based techniques, which normally require long sampling durations and labor-intensive analysis. Newly developed real-time particulate mass measurements, like the beta attenuation monitor, the tapered element oscillating microbalance, the Dusttrak sampler, and the continuous aerosol mass monitor, are able to provide high temporal resolution of particulate matter mass concentrations by utilizing the absorbing or scattering properties of the particles; however, no information on individual chemical species can be obtained from these methods [*Jaklevic et al.*, 1981; *Patashnick and Rupprecht*, 1991; *Babich et al.*, 2000; *Chung et al.*, 2001].

Real-time single particle mass spectrometry (RTSPMS) measurements are able to overcome many disadvantages of the above techniques and provide continuous on-line particulate matter measurements [*Suess and Prather*, 1999; *Johnston*, 2000; *Noble and Prather*, 2000]. Despite the fact that extensive information on individual particle size and chemical composition can be acquired with RTSPMS measurements, it has been a challenge for these methods to provide quantitative aerosol mass concentrations. Most of the RTSPMS measurements introduce particles into a vacuum from atmospheric pressue via a supersonic expansion through an orifice. During transmission into the reduced pressures of a mass spectrometer, only a certain fraction of the particles are able to reach the center of the ionization region and become ionized [*Dahneke and Cheng*, 1979]. In order to compensate for these transmission losses, efforts are made to scale the data to obtain quantitative number or mass concentrations of ambient particles [*Allen et al.*, 2000; *Bhave et al.*, 2002; *Lake et al.*, 2003; *Wenzel et al.*, 2003; *Moffet et al.*, 2004; *Sodeman et al.*, 2005; *Allen et al.*, 2006].

In a recent study, Qin et. al demonstrated the ability to obtain high temporal and size resolved quantitative particulate matter mass concentrations from ATOFMS measurements by scaling with reference methods [Qin et al., 2006]. ATOFMS measurements provide the aerodynamic diameter and mass spectra of individual particles in real-time, enabling the study of particle transformation, mixing state, and source apportionment. One of the reference methods used for this study was an aerodynamic particle sizer (APS) which measures number concentrations for sizes between 0.2 and 2.5 μm. APS acquires real-time particulate aerodynamic size distribution by accelerating particles to different size-dependant terminal velocities which can be calculated with particle time-of-flight through the scattering lasers [Wilson and Liu, 1980]. By comparing ATOFMS and APS measurements for individual size ranges, a size dependent scaling function can be constructed, which is further used to acquire a scaling factor for each particle. The scaling factor represents the degree that ATOFMS undercounts particles for different sized particles. By multiplying ATOFMS measurements by scaling factors to correct for undercounting, a true representation of the ambient aerosols without biases due to transmission losses can be obtained. Qin and co-workers demonstrated that the APS scaled ATOFMS mass concentrations strongly correlate with independent beta

attenuation monitor mass measurements, effectively providing quantitative particulate matter mass concentrations [*Qin et al.*, 2006]. The above scaling method also enables one to obtain the mass concentrations of individual ATOFMS particle classes, assuming no preferential transmission of particles in each type and similar detection efficiencies.

The procedure used by Qin et al (2006) works well when APS data are available. A question arises as to how to scale ATOFMS data when no APS is available in a study. One also might ask whether this approach for scaling is universal and can be applied to all field studies with an ATOFMS. In this paper, the ATOFMS measurements from two field studies were scaled with APS scaling functions from five different field studies to study the effect of using different scaling functions on the scaling results. The ATOFMS data from the two test studies were acquired during the California Regional Particulate Air Quality Study (CRPAQS) in Fresno and Angiola [Qin et al., 2007]. The five reference studies that provided APS scaling functions from a broad range of ambient conditions and aerosol types are the: Texas Air Quality Study in 2000 (TexAQS) 2004], North Carolina Ambient Coarse Particle Concentrator [Sodeman, Characterization Study (NC-CCS) [Moffet et al., 2004], Cloud Indirect Effects Experiment (CIFEX) [Holecek et al., 2007], UCSD Freeway Study (Freeway) [Toner et al., 2007], and Atmospheric Brown Clouds Post-Monsoon Experiment (APMEX) [Spencer et al., 2007]. Co-located APS data were also available during the Angiola study, which will be used to compare the results between using scaling functions from both the same study and the reference studies.

6.3 EXPERIMENTAL SECTION

All studies including Angiola, TexAQS, NC-CCS, CIFEX, Freeway, and APMEX had side-by-side ATOFMS and APS measurements, except for the Fresno study where no APS measurements were made. A TSI APS Model 3320 was used during the TexAQS and Angiola studies, and Model 3321 was used for all other studies (TSI, Minnesota). The details of the transportable ATOFMS have been described by Gard and co-workers [*Gard et al.*, 1997].

6.3.1 CRPAQS ATOFMS Measurements and Data Analysis

California's San Joaquin Valley is one of the most polluted areas of the country, experiencing extremely high particulate matter mass concentrations throughout the winter season due to the stagnant meteorological conditions [Watson and Chow, 2002]. In order to better understand particulate matter pollution and identify major emission sources, a multi-year, multi-agency field campaign, the California Regional Particulate Air Quality Study (CRPAQS), was deployed at selected locations in the valley [Solomon and Magliano, 1999; Brown et al., 2006; Rinehart et al., 2006; Turkiewicz et al., 2006; Chow et al., 2006a]. Two ATOFMS were operated continuously in Fresno and Angiola from November 30, 2000 to February 4, 2001 as part of the CRPAQS to study wintertime aerosol composition, transformations, mixing state, and source apportionment. The size and chemical composition of more than 2 million particles was acquired with ATOFMS at each site. The data collected between January 9th, 2001 and February 4th, 2001 will be scaled with reference APS scaling functions to study the effect of different scaling curves on ATOFMS scaling results. Particles with diameters $0.2 - 2.5 \,\mu\text{m}$ were the focus of this study.

Custom software was used to calibrate the mass spectra and extract ion peaks into peak lists. These peak lists were imported into a single particle mass spectrometry data analysis tool kit, YAADA, for extensive analysis [*Allen*, 2002]. The spectra were then classified with an adaptive resonance theory based clustering method (ART-2a) [*Song et al.*, 1999], which groups particles into clusters based on the existence and intensity of ion peaks in individual particle mass spectra. Single particle mass spectral information is converted into a weight matrix for classification. Two particles are considered to belong to the same cluster if the dot product of their weight matrices is higher than a predetermined threshold value, which was set to 0.8 for the current work. Upon applying ART-2a on the CRPAQS datasets, major particle types that accounted for 90% of total particles were isolated for further analysis. The majority of the single particle mass spectra contain information on both positive and negative ions, however, about 5.9% of the particles in Fresno study and 1.5% of the particles in Angiola study did not produce positive mass spectra. These particles were excluded from the classification step.

6.3.2 Reference Studies with APS Scaling Functions

APS scaling functions from five reference studies, including TexAQS, NC-CCS, CIFEX, UCSD Freeway, and APMEX were applied to the Fresno and Angiola ATOFMS measurements to study the impact of using multiple scaling functions.

TexAQS is a comprehensive research project to address the air pollution problems in the state of Texas, as a result of the high number of days in exceedance of the national 1-hour standard of ozone and fine particulate matter concentrations [*Sodeman*, 2004]. The goal of this study is to investigate ground level ozone and fine particulate matter in the Houston region and the east half of Texas to determine whether the pollutants are

from local sources or long-range transport. ATOFMS was operating continuously for 4 weeks from August 20 to September 15, 2000 at the La Porte airport, which is located 40 km east of downtown Houston. TexAOS measurements represent a polluted urban environment. The NC-CCS collected lab based ambient measurements at the EPA Human Studies Facility in Chapel Hill, NC in the summer of 2003. The main purpose of this study was to characterize the effect of the coarse particle concentrator on ambient particulate matter chemical composition and size distributions [Moffet et al., 2004]. During the first concentrator characterization study (NC-CCS-I), the ATOFMS was operated for 10 hours of switching between non-concentrated and concentrated ambient particles. ATOFMS was operated for 8 hours during the second concentrator characterization study (NC-CCS-II), a period when substantially higher (nearly 100%) ambient relative humidity (RH) was encounted which led to severe degradation in visibility. CIFEX was conducted in April 2004 at Trinidad Head, California to observe long range transport of Asian dust traveling across the Pacific Ocean [Holecek et al., 2007]. The sampling site is located on the coast of California about 60 miles south of the California-Oregon border. This study captured particles in a remote marine environment with occasional influence from local anthropogenic activities and long-range transport of Asian dust. The UCSD Freeway Study took place in the summer of 2004 where continuous ambient measurements were conducted with an ATOFMS for nearly 5 weeks inside a trailer at the University of California, San Diego [Toner et al., 2007]. The sampling site was only 10 meters away from a major freeway with heavy traffic. The purpose of this measurement was to study the instantaneous chemistry of vehicular emission particles under ambient conditions, to aid in source apportionment of particles

from vehicle emissions. Finally, during the APMEX, ambient ATOFMS sampling was conducted in October, 2004 at Hanimaadhoo, a very remote location near the north edge of the Maldives islands [*Spencer et al.*, 2007]. The main purpose of this study was to understand the atmospheric impact of anthropogenic activities.

6.3.3 The Calculation of the Scaling Functions in Reference Studies

The detailed APS scaling procedure is described in the recent paper by Qin and co-workers [Oin et al., 2006]. The same method is adapted here with minor modifications. Briefly, particle number counts were first tabulated from both APS and ATOFMS measurements for the following 12 size ranges: 0.300-0.523, 0.523-0.605, 0.605-0.699, 0.699-0.807, 0.807-0.933, 0.933-1.077, 1.077-1.243, 1.243-1.435, 1.435-1.655, 1.655-1.911, 1.911-2.207, and 2.207-2.547 µm. A scaling factor is calculated for each size bin by calculating the ratio of APS to ATOFMS particle counts for the corresponding size range. By plotting the scaling factors against the mid point of each size bin, a scaling curve can be obtained which is used to fit the scaling functions. Since the purpose of the current work is to test the applicability of scaling functions from reference studies to test studies, generating hourly scaling functions from reference studies for the object studies is not applicable. Thus, only one average scaling function is obtained from each reference study in the current work. For each reference study, time periods were removed if either APS or ATOFMS were offline. Since scaling curves can change substantially at different times of the day due to the variation in ambient particle concentrations and compositions, an average scaling curve for the same hour of the day throughout the whole study period was first calculated. The final scaling curve was obtained by averaging the mean scaling curves for each hour of the day. Similar to the

previous work by Qin et al., each scaling function is fitted separately for the size range below and above 1.783 µm which can be characterized with 5 parameters:

$$\phi_{APS} = \begin{cases} C_1 \cdot e^{C_2 \cdot D_a} & (when \ D_a < 1.783 \ um) \\ C_3 \cdot D_a^2 + C_4 \cdot D_a + C_5 & (when \ D_a \ge 1.783 \ um) \end{cases}$$
(1)

where C1 and C2 are the best-fit parameters determined by exponential regression of scaling factors over the size bins. The first function was extrapolated down to 0.2 μ m to obtain the scaling factors for the smallest particles detected by ATOFMS. C3, C4, C5 were obtained by second-order polynomial regression.

6.4 RESULTS AND DISCUSSION

6.4.1 Scaling Curves and Scaling Functions

The scaling curves for the reference studies: TexAQS, NC-CCS-I, NC-CCS-II, CIFEX, Freeway, APMEX, and Angiola are presented in Figure 6.1. Since APS measurements are available during the Angiola study, the Angiola APS scaling curve is also included along with the reference scaling curves. All scaling curves resemble a reverse check mark in the $PM_{2.5}$ (Da $\leq 2.5 \mu m$) size range with the lowest point at 1.783 μm for most curves. The exceptions are the NC-CCS curves which dip at 1.545 μm and the APMEX curve which dips at 2.059 μm . The scaling curves from all six studies are similar in shape but the absolute scaling factors can vary by several orders of magnitude. The APS scaling parameters for each study are listed in Table 1.



Figure 6.1 APS scaling curves for all studies, including TexAQS, NC-CCS-I, NC-CCS-II, CIFEX, Freeway, APMEX, and Angiola studies.

Study	C1	C2	C3	C4	C5
CIFEX	90538.75	-4.42	372.61	-1336.04	1245.93
Freeway	241360.23	-5.96	289.94	-1043.43	950.88
TexAQS	598326.07	-4.91	742.50	-2658.89	2423.82
Angiola	41576.86	-3.81	635.66	-2403.85	2287.07
NC-CCS-I	558422.02	-5.33	682.05	-2233.29	1905.64
NC-CCS-II	381091.24	-3.46	6250.30	-20892.62	18551.49
APMEX	66592.45	-3.48	1674.69	-6501.40	6420.04

Table 6.1 APS scaling parameters for all studies.

6.4.2 Major Particle Types in CRPAQS

Detailed discussions of the major particle types are provided in another paper by Qin and co-workers [Qin et al., 2007], and only a brief description is provided here. The majority of particles analyzed during the CRPAQS study were transformed, as indicated by the presence of secondary ammonium $(m/z \ 18)$ and nitrate $(m/z \ -46, -62 \ and -125)$ ion marker peaks in their mass spectra. OC represent particles mainly containing organic carbon with secondary ammonium and nitrate; biomass are organic carbon particles with very intense potassium peak; HMOC represent organic carbon particles that contain characteristic peaks between m/z 100 and 200 in both positive and negative spectra [Qin and Prather, 2006]; ECOC are particles containing both elemental carbon and organic carbon; EC represent elemental carbon particles with intense C_n^+/C_n^- peaks (n is integer); sea salt are freshly emitted sea salt particles with intense sodium and chloride peaks; aged sea salt are sea salt particles containing significant amount of nitrate and some organics; dust are inorganic mineral species mixed with nitrate and organic carbon; and NH₄NO₃-OC represent organic carbon particles but with huge amount of ammonium nitrate. All the aforementioned particle types are present in both the Fresno and Angiola studies. There are also particle types that are specific to each location.

Knowing the ATOFMS sample flow rate, the un-scaled particle type mass concentrations can be obtained from raw ATOFMS counts by assuming all particles are spherical with a density of 1.9 g/cm³ [Qin et al., 2006]. Figure 6.2 shows the un-scaled daily average particle type mass concentrations and mass fractions in the size range of 0.2-2.5 μ m. The size resolution is 0.1 μ m with the label representing the bin midpoint. The low mass concentration values within each bin (< 0.2 μ g/m³) illustrate the significant



Figure 6.2 Size-resolved un-scaled particle type mass concentrations and mass fractions for Fresno and Angiola. (a) un-scaled particle type mass concentrations in Fresno (b) un-scaled particle type mass fractions in Fresno (c) un-scaled particle type mass concentrations in Angiola (d) un-scaled particle type mass fractions in Angiola.

undercounting of particles by the ATOFMS as shown in Figure 6.2a and 6.2c. Without scaling, the ambient particle mass concentrations are centered near $1.5 - 1.9 \mu m$. These size-resolved mass concentration distributions are not indicative of the atmospheric concentrations, but reflect the preferential transmission of particles around 1.7 μm by the ATOFMS nozzle. This preferential transmission is one aspect that can be corrected using APS scaling functions. Since particle transmission efficiency mainly depends on size [Dahneke and Cheng, 1979], particles within the same size range are undercounted to the same extent. Therefore, the particle type mass fractions as a function of size shown in Figure 6.2b and 6.2d represent the true ambient particle fractions without scaling..

The major particle type mass fractions illustrate that carbonaceous particles dominate the submicron size range ($0.2 \le D_a < 1.0 \ \mu m$), however their fractions decrease substantially in the supermicron range ($1.0 \le D_a \le 2.5 \ \mu m$) as aged sea salt and dust particles becoming the dominant components. Figure 6.2 also show that despite the fact that carbonaceous particles (mainly organic carbon, elemental carbon, and biomass) account for more than 90% of the total mass in the submicron size range at both sites, the percentages of biomass and OC particles are much lower in Angiola. The combined mass fractions of carbonaceous particles are similar in Fresno and Angiola, however, a lower fraction of biomass and a higher fraction of K-ECOC are observed in Angiola due to particle aging [*Qin et al.*, 2007].

6.4.3 Scaled ATOFMS Mass Concentrations

Scaling causes a dramatic shift in the size distributions of major particle type mass concentrations compared to those shown in Figure 6.2a and 6.2c. Representative distributions after scaling are included in Figure 6.3. The y-axis represents the 24-hour



Figure 6.3 Fresno and Angiola size-resolved particle type mass concentrations scaled with TexAQS and APMEX scaling functions. (a) Fresno particle type mass concentrations with TexAQS APS scaling function (b) Fresno particle type mass concentrations with APMEX APS scaling function (c) Angiola particle type mass concentrations with TexAQS APS scaling function (d) Angiola particle type mass concentrations with APMEX APS scaling function.

average mass concentrations over the whole sampling duration; the x-axis shows the midpoint of each size bin with a resolution of 0.1 μ m. Figure 6.3a and 6.3c correspond to the scaled mass concentrations in Fresno and Angiola using the TexAQS APS scaling function. The total particulate mass concentration peaks between 0.5 - 0.6 μ m with carbonaceous species dominating the submicron size range. The mass concentrations of aged sea salt particles increase in the supermicron range. Applying scaling functions from Freeway, CIFEX, and NC-CCS-I studies results in similar size distributions to those in Figure 6.3a and 6.3c. Figure 6.3b and 6.3d represent the scaled mass concentration of major particle types using APMEX scaling function. Compared to the results in Figure 6.3a and 6.3c, the size distribution of APMEX scaled mass concentrations has an additional peak around 1.7 μ m as well as the peak between 0.5 - 0.6 μ m. The scaled mass concentrations calculated with the NC-CCS-II scaling function show similar distribution to that obtained with APMEX, except that the peak at 1.7 μ m is a little more intense.

One major factor that affects the supermicron scaling results is the shape of the scaling curve. As shown in Figure 6.1, neither APMEX nor NC-CCS-II scaling curves reach the minima within 1.655-1.911 μ m, which sets these scaling curves apart from most other curves. The minimum point on APMEX scaling curve is within 1.911-2.207 μ m, while that on NC-CCS-II is within 1.435-1.655 μ m. For these two curves, particles within 1.655-1.911 μ m no longer have the lowest scaling factors, thus the relative fractions of these particles increase significantly. Figure 6.2a and 6.2c show that majority of aged sea salt and dust particles fall within the size range of 1.6 – 2.0 μ m, thus these particles are impacted the most by a shift of scaling curve minimum. As a result, higher

mass concentrations of aged sea salt and dust particles are obtained for the supermicron size range with the APMEX and NC-CCS-II scaling functions. One exception to this trend is that the scaling curve of NC-CCS-I does not reach the minimum between 1.655-1.911 µm, although its scaling results are similar to those with TexAQS, CIFEX, and Freeway scaling functions. The reason for this exception is not known; however, it shows that the change in scaling curve shape does not necessarily correspond to a change in the scaling results. One thing worth to point out is that all the reference APS scaling curves are only similar in shape, the actual scaling factor values vary substantially for the same particle diameter. Thus, it is expected that the absolute scaled mass concentrations would also vary considerably depending on the APS scaling function used. This difference in mass concentrations is also illustrated in Figure 6.3 (a vs. b and c vs. d) where a different Y-axis scale is needed for the same study when using different scaling curves. Thus, comparing the absolute values of scaled particle type mass concentrations will not provide much insight on the true ambient concentrations.

6.4.4 APS Scaled Particle Mass Fraction

Although the mass concentrations obtained by scaling the test studies with APS scaling functions from reference studies do not reflect the real ambient concentrations, a remarkable consistency is observed in the mass fractions of individual particle types. The scaled major particle type mass fractions for the Fresno and Angiola studies are shown in Figure 6.4. Particles were segregated into submicron, supermicron and PM_{2.5} size ranges for finer comparisons. Each pie chart corresponds to the mass fractions obtained with the scaling function from a specific reference study as listed on top. Besides the reference



Figure 6.4 Fresno and Angiola individual particle type mass fractions for submicron, supermicron and PM2.5 range obtained with APS scaling functions from TexAQS, Freeway, CIFEX, NC-CCS, APMEX, and Angiola studies.

scaling functions, Angiola measurements are also scaled with co-located APS measurements for comparison purposes.

Surprising consistency can be observed in Figure 6.4 for the mass fractions of submicron particle types regardless of the scaling function used. In general, Fresno submicron particles consist 49% OC, 37% biomass, 4.5% Pos27, 3.3% ECOC, 1.5% dust, and 1.0% aged sea salt. The rest of the particle types account for less than 1% each in the mass fractions, and the unclassified particles account for 2.3% of total submicron mass. The standard deviations of each particle type mass fraction obtained with all 6 reference scaling functions are less than 9% of the average values, except for NH₄NO₃-OC which is 13%. Angiola scaled mass fractions are shown in Figure 6.4b. Scaled submicron particle type mass fractions also showed very good consistencies, with 16% OC, 37% K-ECOC, 22% ECOC, 6.8% Pos59, 5.0% biomass, 4.4% EC, and 1.1% NH₄NO₃-OC particle. Sea salt, aged sea salt, HMOC, NH₄NO₃, and dust account for less than 1% each, and the unclassified particles explain 6.1% of Angiola submicron mass. The mass fraction standard deviations are less than 4% of the corresponding average values, with the exception of 12% for aged sea salt, 11% for NH4NO3-OC, and 22% for NH4NO3 particles. In addition to the consistency in submicron particle type mass fractions acquired with various APS scaling functions, Figure 6.4b also illustrates that similar results are obtained when scaling Angiola submicron particles with co-located APS scaling function and with reference study scaling functions. Therefore, a resonably accurate estimation of the mass fractions of submicron particle types can be acquired by scaling ATOFMS measurements with scaling functions from other studies.

Compared to the submicron scaling results, supermicron particles contain lower fractions of carbonaceous particles and higher fractions of aged sea salt, dust and NH_4NO_3 rich particles. More variation is obtained for the supermicron mass fractions obtained by using various scaling functions. One major factor causing this variation is the shift in scaling curve minima as discussed in section 6.4.4. The change in the minimum of the scaling curve at larger sizes can significantly increase the relative amount of the particles between 1.655-1.911 μ m, into which most aged sea salt particles fall. This increase on aged sea salt mass fraction will then affect the mass fractions of other particle types. For Fresno particles in the supermicron size range, compared to utilizing other scaling functions, scaling with APMEX and NC-CCS-II leads to lower mass fractions of OC (22.5% instead of 25.8%), biomass (17.8% instead of 19.0%) and ECOC (4.2% instead of 5.1%) particles, and a higher fraction of aged sea salt particles (32.3% instead of 27.6%). Angiola scaled supermicron particle type mass fractions show similar patterns to those in Fresno. Moreover, the supermicron mass fractions obtained with co-located APS scaling function fall within the mass fraction range calculated with other scaling functions, showing that particle type mass fractions obtained with reference scaling functions are good estimates of the ambient aerosol concentrations.

The particle type mass concentrations for $PM_{2.5}$ is calculated by adding the mass concentrations of the corresponding types in the submicron and supermicron ranges. Although there appears to be more variations in the mass fractions, especially for the aged sea salt particles (varied from 3.4% to 16.1% in Fresno), it is mainly caused by the changes in the scaling curve minima, as mentioned earlier. Figure 6.3 clearly illustrates the difference caused by scaling curves. Scaling Fresno and Angiola data with APMEX scaling function generates a second peak near $1.5 - 1.9 \mu m$, in which most of the aged sea salt particles fall. This second peak is not present when scaling with the TexAQS scaling function. APMEX scaled mass concentrations contain a much higher fraction of the aged sea salt particles in the PM_{2.5} range (13.0% for Fresno and 9.8% for Angiola) compared to those scaled with TexAQS (4.6% for Fresno and 2.9% for Angiola), causing the variations observed in the PM_{2.5} mass fractions as shown in Figure 6.4.

6.5 CONCLUSIONS

ATOFMS measurements at two ambient sampling locations, Fresno and Angiola in California's San Joaquin Valley, are scaled with APS scaling functions to obtain quantitative information on individual particle type mass fractions. The effect of APS scaling functions on the results was investigated by taking the scaling functions from five different studies acquired under a wide range of ambient conditions. The Angiola measurements were also scaled using co-located APS measurements to evaluate the results obtained from reference scaling functions.

Although the mass concentrations of individual particle types can vary more than one order of magnitude depending on the scaling functions used, nearly identical particle type mass fractions are observed in the submicron size range regardless of the APS scaling functions used. More variations in the mass fractions is observed for the supermicron and $PM_{2.5}$ size ranges, mainly caused by the shift on the scaling curve minimum point. Lower mass fractions of carbonaceous particles (44.5% instead of 49.9%) and higher fractions of aged sea salt (32.3% instead of 27.6%) and dust (7.4% instead of 6.9%) particles are obtained in Fresno when scaling with APMEX and NC- CCS-II scaling functions compared to using other scaling functions. Even though the mass fractions in the supermicron and $PM_{2.5}$ range are not as consistent as those in the submicron region when scaling with different APS scaling functions, we can still obtain the particle type mass fractions in these size ranges with errors less than 19%. Similar trends are observed in Angiola particle type mass fractions as those in Fresno. When Angiola measurements are scaled with a co-located APS scaling function, the submicron particle type mass fractions are almost identical to those obtained with reference scaling functions. Therefore, to obtain quantitative information from ATOFMS measurements from a study that does not have co-located APS measurements, the APS scaling functions from other studies can be used to provide a very good estimate of submicron particle type mass fractions and a close estimate of supermicron and $PM_{2.5}$ mass fractions.

6.6 ACKNOWLEDGEMENT

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Chapter 7

7 Conclusions and Future Directions

7.1 CONCLUSIONS

Real-time single particle mass spectrometry (RTSPMS) has provided a new perspective on the understanding of ambient aerosols by providing size and chemical composition of individual particles [*Suess and Prather*, 1999; *Johnston*, 2000; *Noble and Prather*, 2000]. In contrast to the traditional bulk filter analysis, RTSPMS measures single particle size and chemical composition in real-time, acquiring information on aerosol mixing state. In particular, aerosol time-of-flight mass spectrometry (ATOFMS) analysis has been used extensively in ambient and laboratory settings to study aerosol size, chemical composition, mixing state, formation mechanisms, reaction pathways, and source apportionment. This technique has been proven to provide tremendous unique insight in aerosol aging and atmospheric processing.

Part of this dissertation has been focusing on utilizing ATOFMS to investigate ambient aerosol properties in several highly polluted regions in California, namely, the Fresno and Angiola area in the San Joaquin Valley (SJV) and the Riverside area in the Los Angeles (LA) basin. ATOFMS measurements were used to determine ambient aerosol chemical composition, mixing state, formation mechanisms and aging. These high time resolution measurements were able to capture instantaneous changes in ambient conditions, and illustrate distinct diurnal variations of specific particle types in both the SJV and eastern LA basin. ATOFMS can also be used to study the aging process; various degrees of aerosol aging have been observed under similar PM_{2.5} mass concentrations during the SJV studies, which is difficult for other methods to achieve. Another important element of this dissertation addresses the quantification methodologies of ATOFMS measurements. It has been demonstrated that to obtain quantitative information from the ATOFMS particle raw counts, aerodynamic particle sizer (APS) [*Wilson and Liu*, 1980] or micro-orifice uniform deposit impactor (MOUDI) [*Marple et al.*, 1986] measurements can be used to scale ATOFMS measurements to obtain quantitative ATOFMS aerosol mass concentrations during the SJV studies.

During the California Regional Particulate Air Quality Study (CRPAQS), ATOFMS measurements in Fresno and Angiola observed biomass burning particles and unique high mass organic compounds (HMOC). Detailed characterizations of these two types of particles, illustrating their size, composition, chemical associations, and temporal variations, were presented in Chapter 2. Between the two types, HMOC particles had larger size distributions, and are most likely humic-like substances (HULIS) formed through fog processing. Both biomass and HMOC particles displayed strong diurnal variations in Fresno with relatively low particle counts during the daytime, increasing dramatically in late afternoon, and eventually peaking at night. The diurnal variations are hypothesized to be caused by a combination of the following factors. The SJV wintertime inversion layers decrease at night, which helps to concentrate particles near the surface. Elevated nighttime residential heating activities lead to a direct increase in biomass emissions, which caused the nighttime spike of biomass particles observed by ATOFMS. The HMOC particles were formed by particle phase partition of the

semivolatile species from biomass emission under the nighttime low temperature, followed by aqueous phase processing due to the high relative humidity (RH). Therefore HMOC particle counts also peaked at night, consistent with the results from ATOFMS. In contrast, biomass particles in the rural Angiola area were mostly heavily transformed with diverse chemical compositions, and showed more of a gradual build-up over time. These observations suggest that the particle chemistry in urban Fresno area is controlled by local sources and that in the rural Angiola area is controlled by long range transport into the area. These results demonstrate that ATOFMS single particle measurements can be used to better understand how specific sources and meteorological conditions affect ambient particle concentrations hourly. Real-time information on the sizes and temporal variations of biomass and HMOC particles can be used as inputs for models to determine the factors that play the most significant roles in controlling the concentrations of organic compounds in the SJV [*Held et al.*, 2004].

The overall comparison between urban and rural ambient aerosols by ATOFMS measurements during the CRPAQS is described in Chapter 3. The observed differences between these two sites improved the understanding of the aerosol formation mechanisms and source apportionment in the SJV. Located in an urban center, Fresno aerosols were a mixture of fresh and aged particles. Most particle types in Fresno peaked at night; however, the ECOC and EC types peaked during the day mostly from local traffic emissions. The major particle types in the submicron size range ($0.2 \le D_a < 1.0 \mu m$) were carbonaceous and biomass, whereas those in the supermicron range ($1.0 \le D_a \le 2.5 \mu m$) were aged sea salt, biomass, OC, and/or NH₄NO₃-OC, depending on the meteorological conditions. The major PM_{2.5} components by mass were biomass, OC, and

NH₄NO₃-OC; high PM_{2.5} mass concentrations can be dominated by the relatively fresh biomass particles as well as the aged OC and NH₄NO₃-OC particles.

Rural Angiola particles were more aged than those in Fresno and contained higher amounts of ammonium nitrate, due to the influences from local agriculture and ranching activities. Major particle types peaked during the day. Since rural aerosols are transported from urban areas from aloft, they generally don't mix with particles near the surface until the daily inversion layers break around noon, causing the daytime peak. Low temperature and high RH at night were likely the key factors that caused the nighttime peaks of K-ECOC, HMOC and Pos59 particles. The Angiola submicron size range was dominated by ECOC, K-ECOC and OC particles, and the supermicron particles were alternately dominated by aged sea salt, or a mixture of K-ECOC, ECOC, NH₄NO₃-OC, and NH₄NO₃, depending on the meteorological conditions. Unlike Fresno, ammonium nitrate was the dominant factor leading to high PM_{2.5} mass concentrations in Angiola.

The studies at Fresno and Angiola also demonstrated the ability of ATOFMS to provide information on aerosol aging, which is difficult for other techniques to achieve. Even though similar high PM_{2.5} mass concentrations were observed in Fresno during the buildup and stagnant periods, the relatively fresh biomass particles account for the majority of the aerosol mass during buildup, whereas most of the PM_{2.5} during the stagnant period is made up from a combination of biomass, aged OC, and aged NH₄NO₃-OC particles. By identifying the major chemical components leading to the high PM_{2.5} mass concentrations, ATOFMS measurements can help to develop effective strategies to control the pollutants in the SJV.

Chapter 4 presented the results from another field campaign that was conducted in the summer and fall of 2005 as part of the Study of Organic Aerosols in Riverside (SOAR) to study seasonal variability of ambient aerosol composition and formation mechanisms in Riverside, CA. Although similar ATOFMS particle types were observed in both seasons, their temporal variations and formation mechanisms were quite different. In both seasons, the submicron size range was dominated by carbonaceous particles with sulfate and nitrate (>75%), and supermicron was dominated by aged sea salt, dust and carbonaceous particles, with the exception that dust particles were prevalent in both size ranges during Santa Ana periods. Most chemical classes in the summer displayed strong diurnal variations, with high carbonaceous number fractions appearing from night to morning and aged sea salt, dust, biomass, OC-vanadium and different types of carbonaceous particles peaking in the afternoon. The morning aerosols were emitted by local sources, such as vehicle emissions, whereas the afternoon peaks were due to the transport of Los Angeles morning aerosols, which were more aged due to photochemical reactions during transport. In contrast, the fall measurements showed distinct episodic changes on major particle type fractions that were greatly influenced by meteorological conditions. The supermicron size range contained a substantial fraction of carbonaceous particles during the buildup and high mass episodes, which were taken over by aged sea salt and dust particles during the scavenging period. The fall aerosols were less aged which could be partly attributed to a decrease in photochemical reactions due to weaker solar radiation, as well as lower ozone concentrations. The majority of the ambient particles contained secondary nitrate and sulfate with higher relative amounts of particle phase nitrate observed in the fall than in the summer. During both seasons, the beta

attenuation monitor measurements displayed similar temporal trends when compared to the ATOFMS total carbonaceous fractions, especially in the supermicron range, indicating that carbonaceous particles with sulfate and nitrate were the major component of the $PM_{2.5}$ mass concentrations.

Both Fresno and Riverside are polluted urban areas with distinct diurnal variations observed on the ATOFMS major particle types. However, the aerosol sources and formation mechanisms are rather different. In winter, the particles in Fresno were freshly emitted from local sources, and the major transformation mechanism was aqueous phase processing. The nighttime peak in particle concentrations was due to lower inversion layers and a rapid increase in direct emissions at night. In contrast, summer Riverside aerosols peaked in early afternoon due to the transport of particles emitted in the Los Angeles area, which undergo aging due to photochemical reactions during transport. Aerosols emitted locally in Riverside were observed; however, they were not the major components by mass.

Another important aspect of this work is to develop scaling methodologies to obtain quantitative information from ATOFMS measurements. In Chapter 5, two methods were developed and tested on the CRPAQS measurements. The basic idea is to scale ATOFMS measurements with either MOUDI size-segregated particle mass concentrations or APS size-segregated particle number concentrations to correct for ATOFMS undercounting due to the losses during particle transmission and ionization [*Dahneke and Cheng*, 1979]. ATOFMS mass concentrations can then be obtained from number counts by assuming a spherical shape and certain density. The main advantage of scaling with the MOUDI measurements is to obtain size segregated mass concentrations of individual chemical species, making it possible to derive relative sensitivity factors [Bhave et al., 2002]; the advantage of scaling with APS data is its ability of providing high time resolution measurements with finer size cut, which is aid in obtaining total mass concentration with high accuracy. When scaling ATOFMS measurements with MOUDI measurements for the Fresno data, the scaled high time resolution ATOFMS mass concentrations correlated well with independently measured beta attenuation monitor (BAM) mass concentrations ($R^2 = 0.79$). In this study, the absolute values of the scaled ATOFMS mass concentrations were ~70% of the BAM measurements over the same period. Since the MOUDI measurements were only available during a short time period, application of the scaling function of this period to the entire study resulted in underestimation for the periods without MOUDI data. Uncertainties were also introduced when increasing the time resolution from 5-8 hours (MOUDI time resolution) to 1 hour. APS scaling method was applied to the Angiola study due to the lack of such measurements in Fresno. Since the APS provides high temporal resolution of particle number concentrations, hourly correction factors were obtained by comparing ATOFMS counts with the APS, resulting in increased accuracy. By applying composition specific density values to different particle types to obtain mass concentrations, the scaled ATOFMS PM_{2.5} mass concentrations correlated extremely well with BAM measurements ($R^2 = 0.91$), and showed comparable absolute values. These scaling methods enabled ATOFMS to provide quantitative information when studying ambient aerosols.

When no co-located APS measurements were available like the Fresno study, it is possible to obtain quantitative information from ATOFMS measurements using the APS

scaling function from a different study. Chapter 6 illustrated that although correcting ATOFMS measurements with the scaling function from other studies may not generate representative mass concentrations, the relative mass fractions of individual particle types are very close to the real values. When scaling Fresno and Angiola ATOFMS data with APS scaling functions from six other studies, the relative mass fractions of major particle types were nearly identical for the submicron particles and were quite close for the supermicron particles for all six scaling functions. Moreover, very similar mass fractions were obtained when scaling Angiola ATOFMS measurements with co-located APS data and with APS scaling functions from other studies. These comparisons validated the fact that in the absence of co-located APS measurements, correcting ATOFMS measurement with scaling functions from different studies can provide very good estimates of major particle type mass fractions in the submicron range and close estimations in the supermicron range.

7.2 FUTURE DIRECTIONS

ATOFMS has been extensively used in ambient and laboratory studies and proven to provide irreplaceable new information and insight that greatly improves our understanding to aerosols. Nonetheless, there is still room for improvements in both the instrumentation and data analysis methodologies, which, after being incorporated, will demonstrate more significant advances of this method.

Instrument development and improvement has always been an important aspect of our research. A newer version of the ATOFMS has been built, which features significantly smaller dimensions and lighter weight than the previous version [*Gard et*
al., 1997] and will soon be able to conduct measurements on an airplane with a remote control system [*Holecek et al.*, (in preparation)]. Even simply upgrading the computer and data acquisition system for the ATOFMS used throughout this dissertation tripled the data collection rate in the typical urban environment from an average of 1 particle/second to 3.5 particles/second. Higher time resolution and more statistically reliable results can be obtained with the improvements. More studies are needed to test the new system and fully illustrate its advantages.

In recent studies, Moffet and Prather utilized single particle light scattering intensity in ATOFMS measurements to obtain the optical properties of each particle [*Moffet and Prather*, 2005]. Future development might also focus on modifying the light scattering region and incorporating multi-angle light scattering capabilities into the ATOFMS. This feature would enable the simultaneous measurements of single particle size, chemical composition, optical properties and shape parameters as a function of time, and aerosol mixing state. The additional information will help to improve the accuracy of current global climate models regarding the correlation between aerosol mixing state and radiative forcing. If the multi-angle light scattering system is incorporated into the aircraft ATOFMS, we will have the ability to study the chemical and physical properties of cloud droplets, which is vital for studying the cloud indirect effect on the global climate budget.

The initial efforts of obtaining quantitative information from ATOFMS measurements showed very promising results and demonstrated great potential as discussed in Chapter 5. The next step would be to obtain mass concentrations of specific chemical species. It is important to note that particle types and chemical species are two

different concepts, each particle type can contain a variety of chemical species, such as a combination of organic carbon, ammonium, nitrate, and sulfate. Since the area of the ATOFMS marker peak is related to the amount of a specific species on each particle. chemical species mass concentration can be calculated from peak areas [Bhave et al., 2002]. However, due to matrix effects [*Reilly et al.*, 2000], instrument response to the same species may vary depending on the ionization matrix. However, matrix effects could possibly be ignored for particles of the same type since they have similar chemical compositions. Therefore, instrument response to a certain chemical species should be relatively constant for particles of the same particle type. Thus the instrument sensitivity factors to certain chemical species for a given particle type can be derived by linear multivariate regression between ATOFMS marker peak area for each type and the mass concentrations of the corresponding species. Knowing the peak area and instrument sensitivity factors for each particle type, high time resolution mass concentration of specific chemical species can be obtained from ATOFMS measurements. The ultimate goal is to use these scaling procedures to obtain quantitative mass concentrations of particles from different sources in future ambient source apportionment studies.

ATOFMS has enjoyed tremendous success since its invention nearly a decade ago. Deployed in numerous field campaigns, ATOFMS has proven to be an indispensable and unique technology that directly provides the sizes and chemical compositions of individual particles in real time. New improvements and features as briefly discussed above will further enhance the accuracy and expend the capability of the instruments. It is firmly believed that the information obtained by ATOFMS will play essential roles in

7.3 **REFERENCES**

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Appendix

A. Matlab Scripts for Scaling ATOFMS Measurements

A.1 SCRIPTS FOR SCALING WITH MOUDI

A.1.1 IMPORTMOUDI.m

% impactor_tableM will put multiple IOP information into one matlab file. % modify according to MOUDI data availability

AnalyteList = {'Mass','ClIon','NO3','SO4','NH4','NaIon','KIon','OC1','OC2', ... 'OC3','OC4','OCParo','OC','EC1','EC2','EC3','EC','CTotal','Na', ... 'Mg','Al','Si','P','S','Cl','K','Ca','Ti','V','Cr','Mn', ... 'Fe','Co','Ni','Cu','Zn','Ga','As','Se','Br','Rb', ... 'Sr','Y','Zr','Mo','Pd','Ag','Cd','In','Sn', ... 'Sb','Ba','La','Au','Hg','TI','Pb','U'}; % 58 species in total.

RawDataDir = 'Q:\CHUNKS\Fresno\quant\text\'; % put your directory name in quotes

MoiDaCut1 = [10.0 5.62 2.5 1.8 1.0 0.56 0.32 0.18 0.10 0.01]; MoiDaCut2 = [10.0 5.62 2.5 1.0 0.56 0.32 0.18 0.10 0.056 0.01];

EventCode(1,:) = 'Fresno-12150510'; EventStart(1) = datenum('15-Dec-00 05:00:00'); EventStop(1) = datenum('15-Dec-00 10:00:00');

EventCode(2,:) = 'Fresno-12160005'; EventStart(2) = datenum('16-Dec-00 00:00:00'); EventStop(2) = datenum('16-Dec-00 05:00:00');

EventCode(3,:) = 'Fresno-12161016'; EventStart(3) = datenum('16-Dec-00 10:00:00'); EventStop(3) = datenum('16-Dec-00 16:00:00');

EventCode(4,:) = 'Fresno-12170510'; EventStart(4) = datenum('17-Dec-00 05:00:00'); EventStop(4) = datenum('17-Dec-00 10:00:00');

EventCode(5,:) = 'Fresno-12171624'; EventStart(5) = datenum('17-Dec-00 16:00:00'); EventStop(5) = datenum('17-Dec-00 24:00:00');

EventCode(6,:) = 'Fresno-12181016'; EventStart(6) = datenum('18-Dec-00 10:00:00'); EventStop(6) = datenum('18-Dec-00 16:00:00');

EventCode(7,:) = 'Fresno-12260510'; EventStart(7) = datenum('26-Dec-00 05:00:00'); EventStop(7) = datenum('26-Dec-00 10:00:00'); EventCode(8,:) = 'Fresno-12271016'; EventStart(8) = datenum('27-Dec-00 10:00:00'); EventStop(8) = datenum('27-Dec-00 16:00:00');

EventCode(9,:) = 'Fresno-12271624'; EventStart(9) = datenum('27-Dec-00 16:00:00'); EventStop(9) = datenum('27-Dec-00 24:00:00');

EventCode(10,:) = 'Fresno-12280510'; EventStart(10) = datenum('28-Dec-00 05:00:00'); EventStop(10) = datenum('28-Dec-00 10:00:00');

EventCode(11,:) = 'Fresno-12281624'; EventStart(11) = datenum('28-Dec-00 16:00:00'); EventStop(11) = datenum('28-Dec-00 24:00:00');

EventCode(12,:) = 'Fresno-01041016'; EventStart(12) = datenum('04-Jan-01 10:00:00'); EventStop(12) = datenum('04-Jan-01 16:00:00');

EventCode(13,:) = 'Fresno-01050005'; EventStart(13) = datenum('05-Jan-01 00:00:00'); EventStop(13) = datenum('05-Jan-01 05:00:00');

EventCode(14,:) = 'Fresno-01060005'; EventStart(14) = datenum('06-Jan-01 00:00:00'); EventStop(14) = datenum('06-Jan-01 05:00:00');

EventCode(15,:) = 'Fresno-01061016'; EventStart(15) = datenum('06-Jan-01 10:00:00'); EventStop(15) = datenum('06-Jan-01 16:00:00');

EventCode(16,:) = 'Fresno-01070510'; EventStart(16) = datenum('07-Jan-01 05:00:00'); EventStop(16) = datenum('07-Jan-01 10:00:00');

EventCode(17,:) = 'Fresno-01071624'; EventStart(17) = datenum('07-Jan-01 16:00:00'); EventStop(17) = datenum('07-Jan-01 24:00:00');

EventCode(18,:) = 'Fresno-01311016'; EventStart(18) = datenum('31-Jan-01 10:00:00'); EventStop(18) = datenum('31-Jan-01 16:00:00');

EventCode(19,:) = 'Fresno-02010510'; EventStart(19) = datenum('01-Feb-01 05:00:00'); EventStop(19) = datenum('01-Feb-01 10:00:00');

EventCode(20,:) = 'Fresno-02020005'; EventStart(20) = datenum('02-Feb-01 00:00:00'); EventStop(20) = datenum('02-Feb-01 05:00:00');

EventCode(21,:) = 'Fresno-02021016'; EventStart(21) = datenum('02-Feb-01 10:00:00'); EventStop(21) = datenum('02-Feb-01 16:00:00');

EventCode(22,:) = 'Fresno-02030510'; EventStart(22) = datenum('03-Feb-01 05:00:00'); EventStop(22) = datenum('03-Feb-01 10:00:00');

```
EventCode(23,:) = 'Fresno-02031624';
EventStart(23) = datenum('03-Feb-01 16:00:00');
EventStop(23) = datenum('03-Feb-01 24:00:00');
```

% And so forth, for each of the IOPs (corresponding to each sheet of the Excel workbook).

```
% sampler codes
SamplerCode(1,:) = 'MX1';
SamplerCode(2,:) = 'MX2';
SamplerCode(3,:) = 'MX3';
SamplerCode(4,:) = 'MX4';
SamplerCode(5,:) = 'MX5';
SamplerCode(6,:) = 'MX6';
SamplerCode(7,:) = 'MX7';
SamplerCode(8,:) = 'MX8';
SamplerCode(9,:) = 'MX9'; % After-filter
% Array lengths
NumEvent = size(EventCode,1); % # of different evernts.
NumSampler = size(SamplerCode, 1); % # of different SamplerCodes, here is 9.
Site = cell(NumEvent*NumSampler,1);
% Construct MoiLabel, XIndex, DaMin/Max, Start, and Stop
for i = 1:NumEvent
 for j = 1:NumSampler
  idx = (i-1)*NumSampler + j;
  XIndex(i,j) = idx;
  Site{idx} = 'Fresno';
  MoiLabel(idx,:) = [EventCode(i,:) '-' SamplerCode(j,:)];
  DaMin(idx) = MoiDaCut1(j+1);
    DaMax(idx) = MoiDaCut1(j);
  else
    DaMin(idx) = MoiDaCut2(j+1);
    DaMax(idx) = MoiDaCut2(j);
  end
  Start(idx) = EventStart(i);
  Stop(idx) = EventStop(i);
 end
end
% Initialize data vectors
for k = 1:length(AnalyteList)
 eval(sprintf('%s = NaN*ones(length(MoiLabel),1);',AnalyteList{k}));
 eval(sprintf('%sStd = NaN*ones(length(MoiLabel),1);',AnalyteList{k}));
end
% Construct data vector for each species
for i = 1:NumEvent
 % Load raw data from text file
 iopcode = EventCode(i,8:15);
 InFile = sprintf('F%s.txt',iopcode);
 load('-ascii',fullfile(RawDataDir,InFile));
 eval(sprintf('rawdat = F%s;',iopcode));
 eval(sprintf('clear F%s;',iopcode));
 % store data in vectors
 idx = XIndex(i,:);
 odds = [1:2:2*NumSampler];
```

```
evens = [2:2:2*NumSampler];
```

```
for j = 1:NumSampler
  jdx = find(rawdat(:,odds(j)) < 2*(rawdat(:,evens(j))));
  kdx = find(rawdat(:,odds(j)) < 0);
  jdx = union(jdx, kdx);
  rawdat(jdx,[odds(j):evens(j)]) = NaN*ones(length(jdx),2);
end
for k = 1:length(AnalyteList)
  eval(sprintf('%s(idx) = rawdat(k,odds);',AnalyteList{k}));
  eval(sprintf('%sStd(idx) = rawdat(k,evens);',AnalyteList{k}));
```

```
end
end
```

% *** After this loop, use lines 39~43 of your current script to save the data. Your data vectors should now % be of length 207 (9*23) instead of 9. Each vector will contain all of the data (or standard error) from a % single analyte for the entire study period. These vectors can be read subsequently by the % COLLECT_IMPACTOR function of the quant package. ***

```
% Save results
DataFile = 'C:\yaada110\quant\refdata\fresno_impactor'; % insert your own file name
List1 = sprintf(', "%s'",AnalyteList{:});
List2 = sprintf(', "%sStd"',AnalyteList{:});
eval(sprintf('save(DataFile %s%s)', List1, List2));
save('-append',DataFile,'DaMin','DaMax','AnalyteList','Site','MoiLabel','Start','Stop');
```

A.1.2 QUANT_FRESNO.m

function quant_fresno(Task)

% QUANT_SCOS provides an example of how to use the YAADA Quant Package % Call as: QUANT_SCOS(Task)

% Task = 1 tabulate impactor measurements from each IOP

- % Task = 2 tabulate ATOFMS data for counting efficiency calculations
- % Task = 3 make diagnostic plot of unscaled ATOFMS vs. impactor mass conc
- % Task = 4 calculate particle detection efficiency coefficients
- % Task = 5 examine residual mass concentrations
- % Task = 6 plot scaled mass vs. impactor measurements
- % Task = 7 tabulate ATOFMS data for chemical sensitivity calculations
- % Task = 8 make diagnostic plots of peak areas vs. impactor chemical msmts
- % Task = 9 calculate chemical sensitivities

% Task = 10 examine residual chemical concentrations

- % Task = 11 plot scaled chemical conc vs. impactor measurements
- %

% Tasks must be executed in numerical order.

% Prakash V. Bhave May 02

global YAADA close all

IOPCode = {'Fresno-12150510','Fresno-12160005','Fresno-12161016','Fresno-12170510', ... 'Fresno-12171624','Fresno-12181016', 'Fresno-12260510','Fresno-12271016', ... 'Fresno-12271624','Fresno-12280510', 'Fresno-12281624', 'Fresno-01041016', ... 'Fresno-01050005','Fresno-01061016','Fresno-01070510', 'Fresno-01071624', ... 'Fresno-01311016','Fresno-02010510','Fresno-02020005', ... 'Fresno-02021016','Fresno-02030510','Fresno-02031624'... };

```
% MOICode = {'MX4','MX5','MX6'}; % Dec 15 - 18 IOP using MOI size cut 1 !!!
MOICode = {'MX3','MX4','MX5','MX6'}; % other IOPs using MOI size cut 2
%
      MX7
               MX6
                       MX5
                               MX4
                                       MX3
% MOI 1 0.18-0.32 0.32-0.56 0.56-1.00 1.00-1.80 1.80-2.50
% MOI_2 0.10-0.18 0.18-0.32 0.32-0.56 0.56-1.00 1.00-2.50
SpecList = {'Mass','NH4','NO3','SO4'};
TableFile = fullfile('Q:\CHUNKS\Fresno\quant\QuantFresno','QuantFresnoA.mat');
%-----%
% Tabulate impactor measurements
                                      %
%-----%
if Task == 1
ImpactorTable = collect_impactor(IOPCode,MOICode,SpecList);
save(TableFile,'ImpactorTable');
end
%-----%
% Tabulate ATOFMS data for counting efficiency calcs %
%-----%
if Task == 2
load(TableFile,'ImpactorTable');
HitSizeTable = collect_hitsize(InstCode,ImpactorTable);
save(TableFile,'-append','HitSizeTable');
end
%-----%
% Define RowID
                                %
%-----%
if Task > 2
load(TableFile,'ImpactorTable','HitSizeTable');
for i = 1:numrow(HitSizeTable)
   x(i) = length(cellextract(HitSizeTable(i).PID,1));
  y(i,:) = cellextract(ImpactorTable(i).Mass,1);
end
 % RowID = find(x > 0 & ~isnan(y(:,1))' & ...
      HitSizeTable(:).AirVolume > 0); clear x y
 %
 RowID = find(x > 100 \& \sim isnan(y(:,1))'); clear x y
 % RowID = find(x > 0); clear x y
% RowID = 1:numrow(HitSizeTable);
end
%-----%
% make diagnostic plots of unscaled ATOFMS mass conc %
% vs. impactor mass concentrations %
%-----%
if Task == 3
% [h1,h2] = plot_scatter(TableFile,'Mass',1);
% load(TableFile,'ImpactorTable','HitSizeTable');
%
% [h1,h2] = plot_scatter(TableFile,'Mass',1,RowID); axes(h1);
% xlabel('Impactor Measurement of Mass (\mug m^{-3})');
% ylabel('Unscaled ATOFMS Mass Concentration (ng m^{-3})');
% print(gcf,'-depsc','Q:/CHUNKS/Fresno/quant/figures/uMass4SO4.eps');
```

```
[h1,h2] = plot_scatter(TableFile, 'Mass', 3, RowID); axes(h1);
xlabel('Particle Diameter (\mum)');
ylabel('Inverse Particle Detection Efficiency (\Phi_{MOI})');
print(gcf,'-depsc','Q:/CHUNKS/Fresno/quant/figures/Phi4.eps');
end; % clear RowID
%-----%
% Calculate ATOFMS particle detection efficiencies
                                          %
%_____%
if Task == 4
load(TableFile,'ImpactorTable','HitSizeTable');
PhiTable = regress_impactor(ImpactorTable,HitSizeTable,'Mass','dapower', ...
         [4999 -3.236]); % Guess from Allen/etal:2000 Never put RowID here! Want Phi for all bins !!!
% Save PhiTable
save(TableFile,'-append','PhiTable');
end
%-----%
                                      %
% Examine residual mass concentrations
%_____%
if Task == 5
examine_residual(TableFile,0,RowID);
% examine_residual(TableFile,0);
end
%-----%
% Plot scaled ATOFMS data vs. impactor mass msmts
                                            %
%-----%
if Task == 6
  load(TableFile,'ImpactorTable','HitSizeTable');
  [h1,h2] = plot_scatter(TableFile,'Mass',2, RowID);
  axes(h1);
  xlabel('Impactor Measurement of Mass (\mug m^{-3})');
 ylabel('Scaled ATOFMS Mass Measurement (\mug m^{-3})');
  print(gcf,'-depsc','Q:/CHUNKS/Fresno/quant/figures/Mass4.eps');
end
%-----%
% Tabulate ATOFMS data for chemical sensitivity calcs %
%-----%
if Task == 7
load(TableFile,'PhiTable');
ResponseTable = collect_responseNEW(PhiTable);
save(TableFile,'-append','ResponseTable');
end
%-----%
% make diagnostic plots of ATOFMS peak areas vs.
                                           %
% impactor chemical measurements
                                      %
%-----%
if Task == 8
for i = 4:4
   [h1,h2] = plot_scatter(TableFile,SpecList{i}, 1); axes(h1);
%
%
   xlabel(['Impactor Measurement of ' SpecList{i} ' (\mug m^{-3})']);
```

ylabel(['ATOFMS ' SpecList{i} ' Response (ion signal \times 10^{-9} m^{-3})']); % print(gcf,'-depsc',sprintf('Q:/CHUNKS/Fresno/quant/figures/u%s4SO4.eps',SpecList{i})); % [h1,h2] = plot_scatter(TableFile,SpecList{i},3); axes(h1); xlabel('Particle Diameter (\mum)'); ylabel(['Inverse ' SpecList{i} ' Chemical Sensitivity (\Psi_{MOI})']); print(gcf,'-depsc',sprintf('Q:/CHUNKS/Fresno/quant/figures/Psi%s4.eps',SpecList{i})); end end %-----% % Calculate ATOFMS chemical sensitivities % %_____% if Task == 9load(TableFile,'ImpactorTable','PhiTable','ResponseTable'); DataTable = table(PhiTable,ResponseTable.RespNH4,ResponseTable.RespNO3,ResponseTable.RespSO4);Guess = [2.5e-10 2.4; ... 4.7e-10 2.4; ... 5.0e-10 2.4]; % 1st row for NH4, 2nd row for NO3 ScaledTable = regress_impactor(ImpactorTable,DataTable, ... {'NH4';'NO3';'SO4'},'dapower',Guess); save(TableFile,'-append','ScaledTable'); end %-----% % Examine residual species concentrations % %-----% if Task == 10examine_residual(TableFile,1); end %-----% % Plot scaled ATOFMS data vs. impactor chemical msmts % %-----% if Task == 11for i = 2:2figure [h1,h2] = plot_scatter(TableFile,SpecList{i},2); axes(h1): xlabel(['Impactor Measurement of 'SpecList{i} ' ($mug m^{-3})$ ']); ylabel(['Scaled ATOFMS ' SpecList{i} ' Measurement (\mug m^{-3})']); print(gcf,'-depsc',sprintf('Q:/CHUNKS/Fresno/quant/figures/%s4.eps',SpecList{i})); end end

return

A.1.3 ARRIVAL_RATE.m

```
% ARRIVAL RATE estimates particle arrival rates (ArrRat) given the time
required to record a miss (BTmiss)
% Written by: Prakash Bhave
% 28-May-2004 wrote Tasks 1&2
% 01-Jun-2004 wrote Task 3
% 02-Jun-2004 wrote Task 4
% Increment the Task variable to execute different steps of calculation
```

Task = 4;

```
InFile = 'O:\CHUNKS\Fresno\quantitation\Fresno busy';
OutFile = 'Q:\CHUNKS\Fresno\quantitation\arrival_rate2h.mat';
LengthPer = 7200; % length of sampling intervals [s]
SecPerDay = 3600*24;
CountBin = 0:10; % bins for #miss frequency distributions
%-----%
% Tabulate frequency distributions of number of misses %
% recorded during seconds when no hits were recorded %
% during that second nor the prior second
                                              %
%-----%
if Task == 1
% Load results of COLLECT BUSYDATA
load(InFile,'uTime','NumHit','NumMiss');
% Define date/time parameters and sampling intervals
StartTime = datenum('01-Dec-2000');
StopTime = datenum('04-Feb-2001');
lper = LengthPer/SecPerDay;
NumPer = floor((StopTime-StartTime)/lper);
etime = StartTime + NumPer*lper;
BinCut = split_bin(StartTime,etime,NumPer,'lin');
clear etime lper
% Initialize matrix of frequency distributions, FreqMiss
FreqMiss = zeros(NumPer,length(CountBin));
% Loop over each sampling interval
for i = 1:NumPer
 % "alltim" is vector of all seconds during sampling interval
 alltim = (BinCut(i)*SecPerDay):(BinCut(i+1)*SecPerDay);
 alltim = alltim(1:end-1)/SecPerDay;
 % Find all seconds when a particle was recorded
 uidx = range_search(uTime','=',BinCut(i:i+1));
 [x,ia] = intersect(alltim,uTime(uidx)); clear x
 % Tabulate #hits and #misses during each second of sampling interval
 nhit = zeros(size(alltim)):
 nmis = zeros(size(alltim));
 nhit(ia) = NumHit(uidx);
 nmis(ia) = NumMiss(uidx);
 clear alltim uidx ia
 % Find seconds with no hits recorded during 2 consecutive seconds
 h2count = nhit(1:end-1) + nhit(2:end);
 idx = 1 + find(h2count == 0);
 % Construct frequency distribution of #miss during seconds of interest
 FreqMiss(i,:) = hist(nmis(idx),CountBin); close
 disp(sprintf('Finished interval %s - %s',datestr(BinCut(i),0), ...
                        datestr(BinCut(i+1),13)));
 clear nhit nmis h2count idx
end
clear i NumPer SecPerDay StartTime StopTime
% Save frequency distributions and associated data
save(OutFile,'BinCut','CountBin','FreqMiss');
end
%-----%
```

% and a range of arrival rates, Lambda % %------% disp('Running C:\yaada110\quant\arrival_rate.m') if Task == 2 % "BTmiss" is time required to record a miss, from RATIO_METHOD BTmiss = 0.264; % "Lambda" is a vector of possible particle arrival rates [Hz] Lambda = 10.^[-2:.01:2]; NumFreq = length(Lambda);

% Initialize matrix of poisson w. busy time distributions, PBT PBT = zeros(NumFreq,length(CountBin));

```
% Loop over each possible particle arrival rate
for i = 1:NumFrea
 lamb = Lambda(i);
 % "arriv" is vector times when particles arrive at rate, Lambda(i)
 n = round(1.25*LengthPer*lamb);
 arriv = cumsum(exprnd(1/lamb,n,1)); clear n
 % "npart" is # of particle arrivals during sampling interval
 npart = max(find(arriv < LengthPer));</pre>
 % "detect" indicates if an arrival was recorded (1) or not (0)
 detect = ones(1, npart);
 for j = 1:npart
 % Arrivals within BTmiss secs after a detected particle go unrecorded
 if detect(j)
  jdx = range_search(arriv,'=(]',[arriv(j),arriv(j)+BTmiss]);
  detect(jdx) = 0;
 end
 clear jdx
 end
 % Save the arrival times of those scatters that are recorded
 arriv = arriv(find(detect));
 % Find the second when each arrival was recorded
 [x,idx] = unique(floor(arriv)); clear x
 % "PBT" is frequency distribution of # misses recorded per second
 PBT(i,:) = hist(diff([0;idx]),CountBin); close
 PBT(i,1) = LengthPer - sum(PBT(i,2:end)); % can't forget the zeros!
 disp(sprintf('Generated PBT for Lambda = %9.4f Hz',lamb));
 clear j arriv lamb npart detect idx
end
clear i NumFreq
% Save PBT distributions and associated data
save(OutFile,'-append','BTmiss','PBT','Lambda');
end
%-----%
% Determine particle arrival rate during each sampling %
% interval by minimizing the difference between the %
% real particle distribution and PBT distributions %
            -----%
%--
disp('Running C:\yaada110\quant\arrival_rate.m')
if Task == 3
load(OutFile,'CountBin','BinCut','FreqMiss','Lambda','PBT');
```

NumPer = length(BinCut) - 1; NumFreq = length(Lambda);

% Initialize sum squared residuals "ResSumSq" & arrival rate "ArrRat" ResSumSq = zeros(NumPer,NumFreq);

```
ArrRat = zeros(NumPer,1);
```

```
% Loop over each sampling interval and each possible arrival rate
for i = 1:NumPer
 for j = 1:NumFreq
 % Normalize PBT distribution to match # misses in sampling interval
 normalize = sum(FreqMiss(i,:).*CountBin) / sum(PBT(j,:).*CountBin);
 frequences = PBT(j,:) * normalize;
 % "ResSumSq" is sum of squared residuals between normalized PBT and
 % the real frequency distribution
 ResSumSq(i,j) = sum((FreqMiss(i,:) - freqmiss).^2);
 clear normalize freqmiss
 end; clear j
end; clear i
% Minimize ResSumSq to estimate true particle arrival rate "ArrRate"
for i = 1:NumPer
 if(sum(FreqMiss(i,2:end)))
 ArrRat(i) = geomean(Lambda(find(ResSumSq(i,:) == min(ResSumSq(i,:)))));
 end
end; clear i
% Save resulting distributions
save(OutFile,'-append','ResSumSq','ArrRat');
clear NumPer NumFreq
end
%-----%
% Plot the estimated particle arrival rate, the total %
% particle detection rate (hit+miss), and the hit %
% rate.
                                   %
%-----
                    -----%
disp('Running C:\yaada110\quant\arrival_rateTask4.m')
if Task == 4
load(InFile,'NumMiss','NumHit','uTime');
load(OutFile,'BinCut','ArrRat');
% Define date/time parameters
BinMid = mean([BinCut(1:end-1);BinCut(2:end)]);
NumPer = length(BinMid);
% Count number of hits and misses in each time period
nhit = zeros(NumPer,1); nmis = nhit;
oldid = 0;
for i = 1:NumPer
 uidx = (oldid+1):max(find(uTime <= BinCut(i+1)));</pre>
 if uidx
 oldid = uidx(end);
 nhit(i) = sum(NumHit(uidx));
 nmis(i) = sum(NumMiss(uidx));
 end: clear uidx
 disp(sprintf('Finished interval %s - %s',datestr(BinCut(i),0), ...
                         datestr(BinCut(i+1),13)));
end; clear oldid NumHit NumMiss uTime
% "DetRat" is particle detection rate [Hz]; "HitRat" is hit rate [Hz]
DetRat = (nmis+nhit)/LengthPer;
HitRat = nhit/LengthPer;
```

HitRatio = nhit ./(nhit + nmis); clear nhit nmis

```
% Save resulting distributions
save(OutFile,'-append','DetRat','HitRat');
%%% Plot results as a time series %%%
close all
Start = BinCut([1 NumPer/2]);
Stop = BinCut([NumPer/2 NumPer+1]);
for i = 1:2
subplot(2,1,i);
plot(BinMid,ArrRat,'k-'); hold on
plot(BinMid,DetRat,'r-');
plot(BinMid,HitRat,'b-');
set(gca,'XLim',[Start(i) Stop(i)],'YLim',[0 60]);
xlabel_date;
if i == 1
 legend('Arrival Rate', 'Detection Rate', 'Hit Rate', 2);
end
end
% Label y-axis
fullpage = axes('position',[0 0 1 1]);
set(fullpage,'Visible','off')
ht = text(0.05,0.5, 'ATOFMS Sampling Rates at Fresno Site [Hz]');
set(ht,'Rotation',90,'HorizontalAlignment','center');
% Format and save figure
set(gcf,'PaperOrientation','portrait','PaperPosition',[0 0 8.5 11])
PlotFN = '../Transfer_code/2004_0602/arrival_rate.eps';
print(gcf,'-depsc',PlotFN);
```

clear BinMid NumPer Start Stop i fullpage ht PlotFN end

clear Task InFile OutFile LengthPer SecPerDay CountBin

A.1.4 BT_HIT5.m

% BTHis estimates the busy time for recording hit particles (BTHIT) % given the time required to record a miss(BTMISS: 0.264s) % Written by: Xueying Qin % 17-Jun-2004 % 12-Jul-2004 modify Task = 2; InFile1 = 'Q:\CHUNKS\Fresno\quantitation\Fresno_busy'; InFile2 = 'Q:\CHUNKS\Fresno\quantitation\arrival_rate+2S'; InFile3 = 'Q:\CHUNKS\Fresno\quant\PBT\PBTHistPBT8_1h'; OutFile = 'Q:\CHUNKS\Fresno\quantitation\BTHITs\bthit5+2S.mat'; %------% % Tabulate frequency distributions of number of hits recorded during % % 30 seconds exclusive of miss particle busy time % %-----% if Task == 1

load(InFile1,'uTime','NumHit','NumMiss'); % Load results of COLLECT_BUSYDATA LengthPer = 3600; % length of sampling intervals [s] - SampleTimeBin, time resolution SecPerDay = 3600*24; % CountBin = 0:200; % bins for #hits frequency distributions

```
% Define date/time parameters and sampling intervals
StartTime = datenum('01-Dec-2000 0:00');
StopTime = datenum('04-Feb-2001 0:00');
HitTimeBin = 30;
                                    % collect # of hit particles every 30s
BTMISS = 0.290;
lper = LengthPer/SecPerDay;
                                        % 1/NumOfTimeBinPerDay
NumPer = floor((StopTime-StartTime)/lper); % Total # of SampleTimeBin for the whole study
etime = StartTime + NumPer*lper;
BinCut = split_bin(StartTime,etime,NumPer,'lin');
clear etime lper
% Initialize HitRatio and matrix of frequency distributions, FreqHit
HitRatio = zeros(1, NumPer);
FreqHit = zeros(NumPer,length(CountBin));
% Loop over each SampleTimeBin
for i = 1:NumPer
   alltim = (BinCut(i)*SecPerDay):(BinCut(i+1)*SecPerDay); %"alltim"-all seconds in this SampleTimeBin
   alltim = alltim(1:end-1)/SecPerDay;
   uidx = range_search(uTime','=',BinCut(i:i+1)); % Find all seconds when a particle was recorded
   [x,ia] = intersect(alltim,uTime(uidx)); clear x
   nhit = zeros(size(alltim)); % Tabulate #hits and #misses for each SampleTimeBin
  nmis = zeros(size(alltim));
  nhit(ia) = NumHit(uidx);
  nmis(ia) = NumMiss(uidx);
   if (sum(nhit)+sum(nmis))
     HitRatio(i) = sum(nhit) / (sum(nhit)+sum(nmis));
   end
   clear uidx ia alltim
   % Calculate time left for hits during each second exclusive of miss particles
   HitTime = 1 - nmis*BTMISS;
   % Calculate Hit particle counts for each 30 seconds (discard the last period of each 30 minutes if
% SumTime < 30s).
   TotalHitTime = cumsum(HitTime);
   TotalHitCount = cumsum(nhit):
   tHitTime = floor (TotalHitTime/HitTimeBin);
   [Time,uIdx] = unique(tHitTime);
   uIdx = uIdx(1:end-1);
   NewHitCount = diff([0,TotalHitCount(uIdx)]);
   clear Time uIdx
   % Construct frequency distribution of #his per 30-second for each 30 minutes
   FreqHit(i,:) = hist(NewHitCount,CountBin); close
   disp(sprintf('Finished interval %s - %s',datestr(BinCut(i),0), datestr(BinCut(i+1),13)));
  clear nhit nmis HitTime TotalHitTime TotalHitCount tHitTime NewHitCount
end
% Save frequency distributions and associated data
save(OutFile,'BinCut','CountBin','FreqHit','HitRatio','BTMISS','HitTimeBin');
clear i NumPer StartTime StopTime HitTimeBin BTMISS BinCut HitRatio uTime NumHit NumMiss
clear FreqHit
```

clear SecPerDay LengthPer CountBin

```
end
```

```
%------%
% Determine particle BTHIT during each sampling interval by minimizing the
                                                                              %
% difference between the real particle distribution and PBT distributions
                                                                         %
%
                                                 %
% here I excluded all the time period where no hits and misses were recorded
                                                                           %
% so that all the BTHIT obtained are valid
                                                               %
% PBTHist = A(151) x Lambda(201) x CountBin(201)
                                                                       %
%_-----
                                                         ----%
if Task == 2
load(OutFile,'CountBin','BinCut','FreqHit','HitRatio','HitTimeBin');
load(InFile2,'ArrRat');
load(InFile3,'PBTHist','A','Lambda');
% Effective Poisson arrival rate for Hits. ArrRatHit=0 if no hits and misses in a 30-min period
% arrival_rate*hit_rate*30 (30s interval for hits vs. 1s interval for misses)
ArrRatHit = (ArrRat .* HitRatio')*HitTimeBin;
NumPer = length(ArrRatHit) % 1560 bins
NumFreq = length(A) \% 151
% Initialize sum squared residuals "ResSumSq" & BTHIT
ResSumSq = zeros(NumPer,NumFreq); % 1560x151
BTHIT = zeros(NumPer, 1); \% 1560x1
% Loop over each sampling interval and each possible arrival rate
for i = 1:NumPer
   if ArrRatHit(i) == 0 | sum(FreqHit(i,2:end)) < 30
     ResSumSq(i,:) = NaN;
     BTHIT(i) = NaN;
  else
    SumLambdaSq = (Lambda - ArrRatHit(i)).^2; % pick PBT Lambda closest to ArrRatHit in each 30-min
    PBTLambdaIdx = find(SumLambdaSq(:) == min(SumLambdaSq));
    if length(PBTLambdaIdx) > 1
       PBTLambdaIdx = PBTLambdaIdx(1);
    end
    for j = 1:NumFreq
       normalize = sum(FreqHit(i,:).*CountBin) / sum(squeeze(PBTHist(j,PBTLambdaIdx,:))'.*CountBin);
% Normalize PBT # hits for each SampleTimeBin
       freqhit = squeeze(PBTHist(j,PBTLambdaIdx,:))' * normalize;
       \operatorname{ResSumSq}(i,j) = \operatorname{sum}((\operatorname{FreqHit}(i,j) - \operatorname{freqhit}).^2); \% "ResSumSq" - sum of squared residuals between
% normalized PBT and the real frequency distribution
       clear normalize freqhit
    end
    BTHIT(i) = HitTimeBin * mean(A(find(ResSumSq(i,:) == min(ResSumSq(i,:)))));
    disp(sprintf('Finished interval %s - %s',datestr(BinCut(i),0), datestr(BinCut(i+1),13)));
    clear j PBTLambdaIdx SumLambdaSq
  end
end
% Save resulting distributions
save(OutFile,'-append','ResSumSq','BTHIT', 'ArrRatHit');
clear ArrRatHit Idx NumPer NumFreq ResSumSq
```

```
clear CountBin BinCut FreqHit HitRatio ArrRat PBTHist A Lambda
end
```

A.1.5 BUSY_FOLDERFILL.m

function busy_foldfill(uTime,NumHit,NumMiss,AvgPos,BTmiss)
% BUSY_FOLDFILL plots the hit recording times versus folder position

```
% Call as: BUSY_FOLDFILL(uTime,NumHit,NumMiss,AvgPos,BTmiss)
% where
% uTime is a numeric vector of unique times when data were collected
%
       unique implies that there are no repeated entries in uTime
%
       i.e. uTime = unique(uTime)
% NumHit is a vector containing the number of hits recorded during
%
       each data collection period
% NumMiss is a vector containing the number of misses recorded during
%
       each data collection period
% AvgPos is a vector containing the average folder position of each
%
       hit saved during each data collection period
% BTmiss is the number of seconds required to record a miss (e.g. 0.186)
%
       this parameter may be estimated using BUSY_POISSON
%
% Note: Should run COLLECT_BUSYDATA before using this function
% Written by: Prakash Bhave 21-Feb-2003
% Revised by: Prakash Bhave 13-Oct-2003
% Set PlotDat = 0 in bins without data
%_____%
                                         %
             Check inputs
%
%_____%
if nargin \sim = 5
error('Call as BUSY_FOLDFILL(uTime,NumHit,NumMiss,AvgPos,BTmiss)');
end
if ~isvector(uTime) | ~isvector(NumHit) | ~isvector(NumMiss) | ...
 ~isnumeric(uTime) | ~isnumeric(NumHit) | ~isnumeric(NumMiss) | ...
 ~isvector(AvgPos) | ~isnumeric(AvgPos)
error('Expecting numeric vectors for uTime, NumHit, NumMiss, and AvgPos');
end
%-----%
%
      Define local variables %
%_____%
% Convert uTime to seconds
Time = round(uTime*24*3600);
Time = Time + 1 - \min(\text{Time});
% Calculate free time leftover after misses are recorded
FreeTime = 1 - NumMiss*BTmiss; clear NumMiss
% Fill data vectors with zeros when no particles were detected
NumTime = max(Time);
nHit = zeros(NumTime,1);
fTime = zeros(NumTime,1);
sPos = zeros(NumTime,1);
nHit(Time) = NumHit;
fTime(Time) = FreeTime;
sPos(Time) = NumHit.*AvgPos;
% Define averaging periods of interest
LengthPer = [1 2 5 10 15 30 60 300];
% Define folder-related parameters
MaxFolPos = 500; % Maximum spectra stored per folder
FolderInc = 50; % Desired resolution (must be a divisor of MaxFolPos)
```

Fpos = FolderInc:FolderInc:MaxFolPos;

%-----%

```
% Estimate the time required to record a hit, as fxn of Folder Position %
%-----
          -----%
clear PlotDat
% Loop over each averaging length
for i = 1:length(LengthPer)
NumSec = LengthPer(i);
disp(sprintf('Examining periods of length = %i seconds',NumSec));
% convert data vectors to matrices
StudyTime = NumTime - mod(NumTime,NumSec);
NumPer = StudyTime/NumSec;
XnHit = reshape(nHit(1:StudyTime), NumSec,NumPer);
XfTime = reshape(fTime(1:StudyTime),NumSec,NumPer);
XsPos = reshape(sPos(1:StudyTime), NumSec,NumPer);
% Calculate average folder position during each period
       = sum(XsPos,1)./sum(XnHit,1);
aPos
% Calculate ratio of FreeTime to NumHit during each period
BThEstim = sum(XfTime,1)./sum(XnHit,1);
% Loop over each increment of Folder Positions
for j = Fpos
 jdx = find(aPos > j-FolderInc & aPos <= j);
 if jdx
 NumJdx = length(jdx);
 junk = sort(BThEstim(jdx));
 PlotDat(i,j/FolderInc) = junk(ceil(0.01*NumJdx)); % lowest percentile
 clear jdx NumJdx junk
 else
 PlotDat(i,j/FolderInc) = NaN;
 end
end
clear NumSec StudyTime NumPer XnHit XfTime XsPos aPos BThEstim
end
%-----
                                            -----%
%
                   Plot Data
                                             %
%-----
      -----%
figure;
Symbol = 'osdv^<>ph'; Symbol = [Symbol Symbol];
Color = 'krgbcmy'; Color = [Color Color Color];
xTick = Fpos - FolderInc/2;
% Loop over each averaging length
for i = 1:length(LengthPer)
hp(i) = plot(xTick,PlotDat(i,:),[Color(i) Symbol(i)]); hold on
ltext{i} = sprintf('%i s Avg Time',LengthPer(i));
end
set(gca,'YLim',[0 1]);
legend(hp,ltext,4);
xlabel('Average Position of Spectrum in Folder');
ylabel(sprintf ...
   ('Estimate of Hit Recording Time [s]: assuming BT_{miss} = \%1.3f s', ...
    BTmiss));
title('Analysis of Folder Filling Times');
% Format the figure
set(gcf, 'PaperOrientation', 'landscape', 'PaperPosition', [0 0 11 8.5]);
```

% return

A.1.6 BUSY_POISSON.m

function busy_poisson(uTime,NumHit,NumMiss,Htext)

% use 'FresnoBusyPoisson' for Htext.

% BUSY_POISSON compares the ATOFMS Hit and Miss rates to a Poisson distrib.

% Call as BUSY_POISSON(uTime,NumHit,NumMiss,Htext) % where % uTime is a numeric vector of unique times when data were collected % unique implies that there no repeated entries in uTime % i.e. uTime = unique(uTime) % NumHit is a vector of length(uTime) containing the number of hits during % each data collection time % NumMiss is a vector of length(uTime) containing the number of misses during % each data collection time % Htext is the text string to put in the figure header (optional) % Written by: Prakash Bhave 16-Feb-2003 %-----% % Check inputs % %_____% if nargin $< 3 \mid$ nargin > 4error('Call as BUSY_POISSON(uTime,NumHit,NumMiss,Htext)'); end if ~isvector(uTime) | ~isvector(NumHit) | ~isvector(NumMiss) | ... ~isnumeric(uTime) | ~isnumeric(NumHit) | ~isnumeric(NumMiss) error('Expecting numeric vectors for uTime, NumHit, and NumMiss'); end if ~exist('Htext','var') Htext = ";elseif ~ischar(Htext) | ~isvector(Htext) error('Expecting a single character string for Htext'); end %-----.....% % % Analyze and Plot Data %_____% % Determine the amount of ATOFMS off-line time within the range of uTime dt = diff(uTime): if length(find(dt < 0)) error(sprintf('Detected %i unsorted PartID(s)',length(find(dt < 0)))); end OffLinePer = 120; % default = 2 minutes OffLineTime = sum(dt(find(dt*24*3600 > OffLinePer))); NumOnLine = ceil((uTime(end)-uTime(1)-OffLineTime)*24*3600); clear dt OffLinePer OffLineTime figure; set_font('Serif',12); % Loop over each plot (1st analyze Miss Rate, then Hit Rate) for iplot = 1:2subplot(2,1,iplot); switch iplot case 1 zerosec = [NumMiss(find(NumHit == 0)) zeros(1,NumOnLine-length(uTime))]; % seconds during which % no hits, only misses xtext = 'Number of Misses Per Second [k]'; ytext = 'Probability of k Misses Per Second'; ttext = 'Analysis of Miss Rate'; case 2

```
zerosec = [NumHit(find(NumMiss == 0)) zeros(1,NumOnLine-length(uTime))]; % seconds during which
% Calculate event occurances & Poisson probabilities
N = \text{length}(\text{zerosec}); \% \# \text{ of seconds during which only hits were detected, or only misses were detected}
                               % Mean Hit/Miss Rate, mean hit/sec for only hit seconds, or miss/sec for only
```

```
xmax = max(zerosec);
mu = mean(zerosec);
% misses seconds
sig = 1.96*std(zerosec)/sqrt(N); % 95% ConfInterval of Mean
for i = 0:xmax+3
 p(i+1) = exp(-mu)*mu^i/factorial(i); % Poisson probabilities
 pu(i+1) = exp(-(mu-sig))*(mu-sig)^i/factorial(i);
 pl(i+1) = exp(-(mu+sig))*(mu+sig)^i/factorial(i);
end
 for i = 0:xmax
 NumI = length(find(zerosec==i));
 q(i+1) = NumI/N;
                                      % Event occurances
 if NumI > 1
 qerr(i+1) = q(i+1)*1.96*sqrt(1/NumI + 1/N); % 95% errorbar
 else
 qerr(i+1) = q(i+1);
 end
 qu(i+1) = q(i+1) + qerr(i+1);
 ql(i+1) = max(q(i+1) - qerr(i+1), 1/N);
end
 % Plot data
he(:,1) = errorbar(0:xmax+3,p,(p-pl),(pu-p),'ro'); hold on
he(:,2) = errorbar(0:xmax,q,(q-ql),(qu-q),'kx');
set(he(2,:),'MarkerSize',10);
hl = line([0 xmax+3], [1/N 1/N]); set(hl, 'Color', 'b', 'LineStyle', '--');
ymin = 10^{floor}(\log 10(1/N));
% Format the plot
set(gca,'XTick',[0:xmax+3],'YScale','log','YLim',[ymin 1],'XLim',[-1 xmax+3])
xlabel(xtext);
ylabel(ytext);
title(ttext);
legend([he(2,:) hl],['Poisson (mu = ' sprintf('% 1.2f',mu) ')'], ...
     ['Actual (N = ' sprintf('%i',N) ')'], 'Observable threshold');
clear i p pu pl q qerr qu ql
end
% Format the figure, add header
set(gcf, 'PaperOrientation', 'portrait', 'PaperPosition', [0 0 8.5 11]);
axes('Position',[0 0 1 1],'Visible','off');
ht = text(0.1,0.965,Htext,'HorizontalAlignment','left', ...
           'FontSize',16,'FontWeight','bold');
```

A.1.7 BUSY_SCALE.m

% no misses, only hits

end

xtext = 'Number of Hits Per Second [k]': ytext = 'Probability of k Hits Per Second';

ttext = 'Analysis of Hit Rate';

function BusyTime = busy_scale(CountMiss,CountHit,AvgHitPos,Param) % BUSY_SCALE calculates the time spent processing detected particle data % Call as BusyTime = BUSY_SCALE(CountMiss,CountHit,AvgHitPos,Param) % where % CountMiss is the number of missed particles in the period % CountHit is the number of hit particles in the period

```
% AvgHitPos is average position in folder of the hit particles
% Param is a vector of parameters in the form [a b c]
%
% BusyTime (seconds) is calculated as
% BusyTime = a * (CountMiss + CountHit) + b * CountHit
%
          + c * (CountHit.*AvgHitPos)
% YAADA - Software Toolkit to Analyze Single-Particle Mass Spectral Data
%
% Copyright (C) 1999-2002 California Institute of Technology
% Copyright (C) 2001-2002 Arizona State University
%
% Jonathan O. Allen 03 Jan 00
if nargin \sim = 4
 error('Call as BusyTime = BUSY_SCALE(CountMiss,CountHit,AvgHitPos,Param)');
end
if ~isvector(CountMiss)
 error('Expecting vector for CountMiss');
end
if ~isvector(CountHit)
 error('Expecting vector for CountHit');
end
if ~isvector(AvgHitPos)
 error('Expecting vector for AvgHitPos');
end
if ~isvector(Param)
 error('Expecting vector for Param');
end
% calculate busy time in seconds
BusyTime = Param(1) * (CountMiss + CountHit) + Param(2) * CountHit ...
```

```
+ Param(3) * (CountHit.*AvgHitPos);
```

A.1.8 CALC_HITRATIO.m

function [HitRatio,PosRatio,NegRatio] = calc_hitratio(Da,Spec)
% CALC_HITRATIO calculates the ratio of Hits/(Hits+Misses) as a fxn of Da
% Call as: [HitRatio,PosRatio,NegRatio] = CALC_HITRATIO(Da,Spec)
% where
% Da is a vector of particle diameters (output of GET_COLUMN)
% Spec is a vector of spectrum types (Neg=0, Pos=1, Dual=2; Miss=NaN)
% HitRatio is a vector of Hit Ratios (#Hit/#Sized) for each Da value
% PosRatio is a vector of #PosSpec/#Sized for each Da value
% Written by: Prakash Bhave 21-Aug-2002
% Revised by Prakash Bhave 25-Aug-2002
% added PosRatio and NegRatio as optional output arguments

% $\,$ used moving average method instead of bin & interpolate method $\,$

% Check inputs if ~isvector(Da) | ~isvector(Spec) error('Expecting vectors for Da and Spec'); elseif length(Da) ~= length(Spec) error('Da and Spec must be the same length'); end

```
% Construct vectors of Hit, PosSpec, and NegSpec (1 if true, 0 if false)
Hit = \sim isnan(Spec);
Pos = zeros(size(Spec));
Neg = zeros(size(Spec));
Pos(find(Spec == 1 | Spec == 2)) = 1;
Neg(find(Spec == 0 | Spec == 2)) = 1;
% Calculate HitRatios using a moving average algorithm
HalfAvg = 250;
if HalfAvg > round(length(Spec)/10)
 warning('Insufficient data in TimeBin - HitRatios are less reliable');
 HalfAvg = round(length(Spec)/10);
end
SizeRes = 100: % nearest 1/100th of micron
[sDa,sortid] = sort(Da);
[uDa,uniqid] = unique(round(sDa(~isnan(sDa))*SizeRes)); uniqid = [0;uniqid];
HitRatio = NaN*ones(size(Spec)); PosRatio = HitRatio; NegRatio = HitRatio;
for i = 2:length(uniqid)-1
 idx = sortid([uniqid(i-1)+1:uniqid(i)]);
 midx = round(median(uniqid(i-1)+1:uniqid(i)));
 if midx < 2*HalfAvg
  havg = floor(midx/2);
 elseif midx > sum(~isnan(Da)) - 2*HalfAvg
  havg = floor((sum(~isnan(Da))-midx)/2);
 else
  havg = HalfAvg;
 end
 fillidx = [midx-havg:midx+havg];
 HitRatio(idx) = sum(Hit(sortid(fillidx)))/length(fillidx);
 PosRatio(idx) = sum(Pos(sortid(fillidx)))/length(fillidx);
 NegRatio(idx) = sum(Neg(sortid(fillidx)))/length(fillidx);
end
```

A.1.9 COLLECT_BUSYDATA.m

```
function collect_busydata(Task,DataFN)
% I use 'Q:\CHUNKS\Fresno\quantitation\Fresno_busy' for my data.
% COLLECT_BUSYDATA estimate busy time coefficients using ambient data
% Call as: COLLECT_BUSYDATA(Task,DataFN)
% where
% Task = 1 to collect particle data into vectors
   Task = 2 to calculate #Hits, #Misses, AvgHitPos during each second
%
%
        of the study. This task is time-consuming. Allow
%
        about 6 hours for 1 month of data (on a 700 MHz PC).
%
        Also, reserve at least 2GB free space in your YAADA user
        directory for temporary files, "*000.mat". These temporary
%
%
        files are to be deleted after completing Task 2.
%
% DataFN name of file where data are to be stored (use single quotes).
%
       DataFN should be different for each data set. For example,
%
       perhaps use 'Angiola_busy' for the Angiola data.
%
% Note: Tasks must be executed sequentially.
      Running Task 1 will overwrite the results of Task 2.
%
```

```
% Written by: Prakash Bhave 21-Aug-2002
```

- % originally written for Bakersfield data analysis
- % Revised by: Prakash Bhave 09-Feb-2003
- % adapted and documented for general use
- % Revised by: Prakash Bhave 16-Feb-2003

% removed Task 3, renamed from ESTIMATE_BUSY to COLLECT_BUSYDATA

global YAADA INST CL_PART PART

```
%--- Collect all particle data in vectors ---%
if Task == 1
Time = []; Velocity = []; Da = []; PosInFolder = []; Hit = [];
for i = 1:numrow(CL_PART)
 load_chunk(CL_PART(i).ChunkName,'PART');
  Time
           = [Time
                        PART(:).Time];
  Velocity = [Velocity PART(:).Velocity];
  PosInFolder = [PosInFolder PART(:).PositionInFolder];
  Da
          = [Da
                      PART(:).Da];
 Hit
          = [Hit
                     PART(:).Hit];
end
save(DataFN,'Time','Velocity','Da','PosInFolder','Hit');
% QA: Check for unsorted PartIDs
idx = find(Time(2:end) < Time(1:end-1));
if length(idx)
 disp(sprintf('*** Detected %i unsorted PartID(s) ***',length(idx)));
 for i = 1:length(idx)
 disp('Examine timestamps of PartIDs in the vicinity of:');
 disp(datestr(Time(idx(i)-2:idx(i)+4)));
 end
 error('Stop: need to adjust timestamp(s) or delete PartID(s)');
end
end
```

%--- Collect HitCount, MissCount, and AvgPos, for each second of study ---%

```
if Task == 2
load(DataFN,'Time','PosInFolder','Hit')
[uTime,uIdx] = unique(Time);
uIdx = [0 uIdx];
 for II = [0:10000:length(uTime)]
 for i = II+1:min(II+10000,length(uTime))
 numhit(i-II) = sum(Hit(uIdx(i)+1:uIdx(i+1)));
  nummiss(i-II) = uIdx(i+1) - uIdx(i) - numhit(i-II);
  if numhit(i-II) == 0
   avgpos(i-II) = 0;
  else
   avgpos(i-II) = sum(Hit(uIdx(i)+1:uIdx(i+1))).* ...
        PosInFolder(uIdx(i)+1:uIdx(i+1)))/numhit(i-II);
 end
 disp(i);
 end
 if II == 0
 NumHit = numhit; NumMiss = nummiss; AvgPos = avgpos;
 else
 load(sprintf('%i.mat',II-10000));
 NumHit = [NumHit numhit];
 NumMiss = [NumMiss nummiss];
 AvgPos = [AvgPos avgpos];
 end
 tempfile = fullfile(YAADA.UserDir,sprintf('%i.mat',II));
```

save(tempfile,'NumHit','NumMiss','AvgPos'); clear i *vg* *um* tempfile end load(sprintf('%i.mat',II)); save(DataFN,'-append','uTime','NumHit','NumMiss','AvgPos'); end

return

A.1.10 COLLET_HITSIZE.m

function HitSizeTable = collect_hitsize(InstCode,ImpactorTable) % COLLECT_HITSIZE collects ATOFMS data for counting efficiency calculations % Call as HitSizeTable = collect_hitsize(InstCode,ImpactorTable) % where % InstCode is an ATOFMS instrument code (or a cell array if InstCodes) % ImpactorTable is output from COLLECT_IMPACTOR % % HitSizeTable contains the following columns: % Column Name Type Description % % SampleCode Word Unique identifier for particle ensemble (primary key) % InstCode Word ATOFMS Instrument code Cell Particle identifiers in the ensemble % PID % HitCount Single Number of hit particles in time bin % MissCount Single Number of missed particles in time bin % AvgHitPos Double Average position of hit particles in folder % IOPTime Double Length of sampling period (d) % OffLineTime Double Time instrument was off-line (d) % BusyTime Double Time instrument was busy (d) % BusyScale Cell Inverse fraction time instrument busy or off-line % AirVolume Double Air volume sampled during time period (m3) % Da Cell Measured particle aerodynamic diameter (um) Neg=0, Pos=1, Dual=2; Miss=NaN % Spectrum cell % HitRatio cell #Hit/#Sized for given particle diameter SpecGrav Cell Assumed particle specific gravity % Dp Cell Estimated particle physical diameters (um) % Cell Estimated particle volumes (um³) % PartVol % PartMass Cell Estimated particle masses (ug) % % The columns of type Cell in HitSizeTable are vectors with one % element for each particle ``hit" by ATOFMS during the IOP. % YAADA - Software Toolkit to Analyze Single-Particle Mass Spectral Data % % Copyright (C) 1999-2002 California Institute of Technology % Copyright (C) 2001-2002 Arizona State University % % Prakash V. Bhave 16 May 02 % modified by PVB 29 Jul 02 % uses COLLECT PARTBIN % modified by PVB 24 Sep 02 (for AAAR 2002) % assumed ATOFMS measures Dst instead of Da % changed Dp, PartVol, and PartMass accordingly % modified by PVB 31 Oct 02 (for T96 quantitative model eval) % switched Dp definition back to using the da2dp conversion % switched back to constant density, to reproduce T96 Riverside results % modified by PVB 5 Oct 03 % compatibility with COLLECT_PARTBIN in Yaada v1.10

% modified by PVB 18 Apr 04
% modified interface w. COLLECT_PARTBIN to include BusyPeriod
% changed BusyScale column to cell type

global YAADA PARTBIN

```
% Check inputs
if nargin \sim = 2
 error('Call as COLLECT_HITSIZE(InstCode,ImpactorTable)');
end
if ~isa(ImpactorTable,'table')
 error('Expecting table object for ImpactorTable');
end
if ~iscell(InstCode)
if ~isword(InstCode)
 error('Expecting word for InstCode');
end
elseif length(InstCode) ~= numrow(ImpactorTable)
error('length of InstCode must match number of rows of ImpactorTable');
end
%-----%
% Collect ATOFMS data by size and time
                                                     %
% Calculate air volume sampled by ATOFMS during each IOP
                                                             %
% Estimate single particle diameters, volumes, and masses
                                                         %
%-----%
% Construct arrays of study names, instrument codes, and sample codes
SampleCode = ImpactorTable(:).SampleCode;
[StudyID,Sidx] = get_studyname(SampleCode);
if ~iscell(InstCode);
 % Assume all data are from same ATOFMS instrument
 InstCode = fillcell(1,numrow(ImpactorTable),InstCode);
end
% Loop over each field study
for i = 1:length(StudyID)
 if isempty(strmatch(StudyID{i},YAADA.StudyName,'exact'));
  opendb(StudyID{i});
 end
 idx = find(Sidx == i);
 % Loop over each ATOFMS instrument
 InstList = unique(InstCode);
 for j = 1:length(InstList)
  jdx = strmatch(InstList{j},InstCode);
  RowID = intersect(idx, jdx);
  % use COLLECT_PARTBIN to bin ATOFMS data
  Start = ImpactorTable(RowID).Start;
  Stop = ImpactorTable(RowID).Stop;
  DaMin = ImpactorTable(RowID).DaMin;
  DaMax = ImpactorTable(RowID).DaMax;
  for k = 1:length(Start)
   instcode{k} = InstList{j};
  end; clear k
  collect_partbin(instcode,Start,Stop,DaMin,DaMax,[],1,2/24/60,15/24/60);
  clear instcode Start Stop DaMin DaMax
  % loop over each time/size bin
  NumEnsemb = numrow(PARTBIN);
  Dp
         = cell(1,NumEnsemb);
  PartVol = cell(1,NumEnsemb);
```

```
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```

```
PartMass = cell(1,NumEnsemb);
  for k = 1:NumEnsemb
   da = cellextract(PARTBIN(k).Da,1);
   sg = cellextract(PARTBIN(k).SpecGrav,1);
   Dp\{k\} = da2dp_lookup(da,sg);
                                         % um
   PartVol{k} = pi / 6 * Dp{k}.^3;
                                         % um^3
   PartMass{k} = 1e-6 * PartVol\{k\}.* sg; % convert um3(g/cc) to ug
   clear da sg
  end; clear NumEnsemb k
  % append particle dp, volume, and mass estimates to PARTBIN
  DpCol = column('Dp','Estimated physical (Stokes) diameter','um', ...
             'cell',0,0,Dp);
  VolumeCol = column('PartVol','Estimated particle volume','um^3', ...
             'cell',0,0,PartVol);
  MassCol = column('PartMass','Estimated particle mass','ug', ...
             'cell',0,0,PartMass);
  PARTBIN = table(PARTBIN,DpCol,VolumeCol,MassCol);
  clear Dp PartVol PartMass DpCol VolumeCol MassCol
  % rename PARTBIN to avoid overwriting
  eval(sprintf('%s%s_Table = PARTBIN;',upper(StudyID{i}),InstList{j}));
 end; clear j jdx
end; clear i idx
```

```
%_____%
%
    Aggregate all data into a single table
                                            %
%_____%
% Initialize Variables
NumRow = numrow(ImpactorTable);
HitCount = zeros(1,NumRow);
MissCount = zeros(1,NumRow);
AvgHitPos = zeros(1,NumRow);
IOPTime = zeros(1,NumRow);
OffLineTime = zeros(1,NumRow);
BusyTime = zeros(1,NumRow);
BusyScale = cell(1,NumRow);
AirVolume = zeros(1,NumRow);
PID
       = cell(1,NumRow);
[PID{:}] = deal(partid([]));
       = cell(1,NumRow);
Da
Spectrum = cell(1,NumRow);
HitRatio = cell(1,NumRow);
SpecGrav = cell(1,NumRow);
Dp
      = cell(1,NumRow);
PartVol = cell(1,NumRow);
PartMass = cell(1,NumRow);
% Fill in the data columns
for i = 1:NumRow
 eval(sprintf('PARTBIN = %s%s_Table;',upper(StudyID{Sidx(i)}),InstCode{i}));
 j = get_pbidx(InstCode{i},ImpactorTable(i).Start,ImpactorTable(i).Stop, ...
              ImpactorTable(i).DaMin, ImpactorTable(i).DaMax);
 HitCount(i) = PARTBIN(j).HitCount;
 MissCount(i) = PARTBIN(j).MissCount;
 AvgHitPos(i) = PARTBIN(j).AvgHitPos;
 IOPTime(i) = ImpactorTable(i).Stop - ImpactorTable(i).Start;
 OffLineTime(i) = PARTBIN(j).OffLineTime;
 BusyTime(i) = PARTBIN(j).BusyTime;
 BusyScale{i} = cellextract(PARTBIN(j).BusyScale,1);
 AirVolume(i) = PARTBIN(j).AirVolume;
          = cellextract(PARTBIN(j).PID,1);
 PID{i}
```

```
= cellextract(PARTBIN(j).Da,1);
 Da{i}
 Spectrum{i} = cellextract(PARTBIN(j).Spectrum,1);
 HitRatio{i} = cellextract(PARTBIN(j).HitRatio,1);
 SpecGrav{i} = cellextract(PARTBIN(j).SpecGrav,1);
% SpecGrav{i} = ImpactorTable(i).SpecGrav;
 Dp{i}
             = cellextract(PARTBIN(j).Dp,1);
 PartVol{i} = cellextract(PARTBIN(j).PartVol,1);
 PartMass{i} = cellextract(PARTBIN(j).PartMass,1);
 clear j
end
% Construct HitSizeTable
SampCol = column('SampleCode','Particle ensemble identifier', ...
          ",'Word',1,0,SampleCode);
InstCol = column('InstCode','ATOFMS instrument code','','Word',0,0,InstCode);
PIDCol = column('PID', 'Particle identifiers in ensemble', '', 'cell', 0, 0, PID);
HitCol = column('HitCount','Number of hit particles in time bin', ...
          ",'single',0,0,HitCount);
MissCol = column('MissCount', 'Number of missed particles in time bin', ...
           ",'single',0,0,MissCount);
AvgPCol = column('AvgHitPos','Average position of hit particles in folder', ...
          ",'double',0,0,AvgHitPos);
TiopCol = column('IOPTime','Length of sampling period', ...
          'd','double',0,0,IOPTime);
OffCol = column('OffLineTime', 'Time instrument was off-line', ...
          'd', 'double', 0, 0, OffLineTime);
BusyCol = column('BusyTime','Time instrument was busy', ...
          'd', 'double', 0, 0, BusyTime);
BsCol = column('BusyScale','Scale Factor for Instrument Off-Line and Busy Time', ...
          ",'cell',0,0,BusyScale);
AvolCol = column('AirVolume','Air volume that ATOFMS sampled', ...
          'm3','double',0,0,AirVolume);
DaCol = column('Da','Aerodynamic diameter','um','cell',0,0,Da);
SpecCol = column('Spectrum', 'Neg=0, Pos=1, Dual=2; Miss=NaN', ...
             ",'cell',0,0,Spectrum);
HRCol = column('HitRatio','Probability of Hit|Sized', ...
          ",'cell',0,0,HitRatio);
SgCol = column('SpecGrav','Estimated particle specific gravity', ...
           'g/cc','cell',0,0,SpecGrav);
DpCol = column('Dp','Estimated physical (Stokes) diameter', ...
          'um'.'cell'.0.0.Dp):
PvolCol = column('PartVol','Estimated particle volume', ...
          'um^3','cell',0,0,PartVol);
MassCol = column('PartMass','Estimated particle mass','um3', ...
          'cell',0,0,PartMass);
HitSizeTable = table('HitSizeTable',SampCol,InstCol,PIDCol,HitCol,MissCol, ...
                      AvgPCol,TiopCol,OffCol,BusyCol,BsCol,AvolCol,DaCol,SpecCol, ...
            HRCol,SgCol,DpCol,PvolCol,MassCol);
HitSizeTable.name = 'HitSizeTable';
return
```

A.1.11 COLLECT_IMPACTOR.m

function ImpactorTable = collect_impactor(EventCode,MOICode,SpecList)
% COLLECT_IMPACTOR tabulates impactor data from selected IOPs
%
% Call as ImpactorTable = COLLECT_IMPACTOR(EventCode,MOICode,SpecList)
% where

```
% EventCode is cell array of IOP codes (e.g. {'T96-103', 'T96-C03', 'T96-D03'})
% MOICode is cell array of impactor sampler codes (e.g. {'MX5','MX6','MX7'})
% SpecList is cell array of chemical species (e.g. {'Mass','NH4','NO3'})
%
% ImpactorTable is a table object with the following columns:
% Column Name Type Description
%
   _____
% SampleCode Word Unique identifier for particle ensemble (primary key)
% SampleDesc Text Description of particle ensemble
% EventCode Word Identifier for sampling event
% Start
            Time Start of sampling period
% Stop
             Time End of sampling period
% DaMin
              Double Minimum aerodynamic diameter in particle ensemble
               Double Maximum aerodynamic diameter in particle ensemble
% DaMax
% SpecList{1} Cell Impactor measurement of SpecList{1} (ug/m3)
                       Impactor measurement of SpecList{2} (ug/m3)
% SpecList{2} Cell
%
   SpecList{3} Cell
                       Impactor measurement of SpecList{3} (ug/m3)
%
    etc
% YAADA - Software Toolkit to Analyze Single-Particle Mass Spectral Data
%
% Copyright (C) 1999-2002 California Institute of Technology
% Copyright (C) 2001-2002 Arizona State University
%
% Prakash V. Bhave 16 May 2002
% Check inputs
if nargin \sim = 3
error('Call as ImpactorTable = COLLECT_IMPACTOR(EventCode,MOICode,SpecList)');
end
if ~iscell(EventCode) | ~iscell(MOICode) | ~iscell(SpecList)
error('Expecting cell arrays for EventCode, MOICode, and SpecList');
end
% Load impactor data
idx = 0;
for i = 1:length(EventCode)
 StudyName(i,:) = strtok(EventCode{i},'-');
 MOIDataFN = sprintf('quant/refdata/%s_impactor',lower(StudyName(i,:)));
 load(MOIDataFN)
 for j = 1:length(MOICode)
  idx = idx + 1;
  % Find matching sample label in database
  label = sprintf('%s-%s',EventCode{i},MOICode{j});
  Lidx = strmatch(label,MoiLabel,'exact');
  if isempty(Lidx)
   error(sprintf('Unknown sample label %s',label));
  elseif ~isscalar(Lidx)
   error(sprintf('Multiple indices matching %s',label));
  end;
  MoiCode{idx} = label;
  MoiDesc{idx} = sprintf(\%s, \%s, \%s, \%s, \%s, \%s, \%1.2f-\%1.2f, um', ...
           Site{Lidx}, ...
           datestr(Start(Lidx),1),datestr(Start(Lidx),15), ...
                datestr(Stop(Lidx),1),datestr(Stop(Lidx),15), ...
                     DaMin(Lidx), DaMax(Lidx));
  MoiEvent{idx} = EventCode{i};
  MoiStart(idx) = Start(Lidx);
  MoiStop(idx) = Stop(Lidx);
  MoiDaMin(idx) = DaMin(Lidx);
```

```
MoiDaMax(idx) = DaMax(Lidx);
  for k = 1:length(SpecList)
   eval(sprintf('Moi%s{idx} = [%s(Lidx) %sStd(Lidx)];', ...
           SpecList{k},SpecList{k},SpecList{k}));
  end
  clear label
 end
end
%--- create ImpactorTable ---%
CodeCol = column('SampleCode','Code for sampling event', ...
              ",'Word',1,0,MoiCode);
DescCol = column('SampleDesc', 'Description of sampling event', ...
              ",'Text',0,0,MoiDesc);
EventCol = column('EventCode', 'Code for sampling event', ...
              ",'Word',1,0,MoiEvent);
StartCol = column('Start','Start of sampling period','d','Time',0,0,MoiStart);
StopCol = column('Stop', 'Stop of sampling period', 'd', 'Time', 0, 0, MoiStop);
DaMinCol = column('DaMin','Minimum aerodynamic particle size','um', ...
           'Double',0,0,MoiDaMin);
DaMaxCol = column('DaMax','Maximum aerodynamic particle size','um', ...
           'Double',0,0,MoiDaMax);
MainColList = 'CodeCol,DescCol,EventCol,StartCol,StopCol,DaMinCol,DaMaxCol';
for k = 1:length(SpecList)
 SpecColLabel = sprintf("'%s concentration and SD"',SpecList{k});
 eval(sprintf('%sCol = column("%s",%s,"ug/m3","Cell",0,0,Moi%s);', ...
         SpecList{k},SpecList{k},SpecColLabel,SpecList{k}));
end
SpecColList = sprintf(',%sCol',SpecList{:});
eval(sprintf('ImpactorTable = table("ImpactorTable",%s%s);',MainColList,SpecColList));
```

A.1.12 COLLECT_PARTBIN.m

function collect_partbin(InstCode,Start,Stop,DaMin,DaMax,PartBinFileName, ... HitOnly,OffLinePeriod,BusyPeriod) % COLLECT PARTBIN creates tables of particle data binned on time and Da % Call as COLLECT_PARTBIN(InstCode,Start,Stop,DaMin,DaMax,PartBinFileName, ... % HitOnly,OffLinePeriod) % where % InstCode cell vector of instrument codes % Start vector of time bin starts % Stop vector of time bin ends vector of minimum aerodynamic diameters (um) % DaMin vector of maximum aerodynamic diameters (um) % DaMax % PartBinFileName name of file to write PARTBIN table % HitOnly collect only data from hit particles if true % OffLinePeriod time instrument is considered off-line if no particles are detected in OffLinePeriod % length of subintervals for BusyScale calculations (d) % BusyPeriod % The InstCode, Start, Stop, DaMin, and DaMax vectors define each bin. % These vectors must have the same length. PERMUTE_PARTBIN can be used % to create these vectors. % % PartBinFileName is optional; file is written to default PartBin file % (partbin.mat in YAADA.StudyDir) if PartBinFileName is empty. % HitOnly is optional and defaults to true.

- %
- % The output of COLLECT_PARTBIN is a PARTBIN table saved to a file.
- % PARTBIN tables have these columns
- % Column Name Type Description
- % ------ -----
- % PartBinID double Unique serial number for instrument-time-size bin
- % InstCode word Instrument for bin
- % Start time Start time for bin
- % Stop time Stop time for bin
- % DaMin double Minimum aerodynamic diameter of bin
- % DaMax double Maximum aerodynamic diameter of bin
- % PID cell Particle identifiers in bin
- % SpecGrav cell Particle specific gravity
- % Da cell Particle aerodynamic diameter (um)
- % Hit cell Hit=1, Miss=0
- % Spectrum cell Neg=0, Pos=1, Dual=2; Miss=NaN
- % HitRatio cell #Hit/#Sized for given particle diameter
- % MissCount double Number of missed particles in time bin
- % HitCount double Number of hit particles in time bin
- % AvgHitPos double Average position in folder of hit particles % in time bin
- % OffLineTime double Time instrument was off-line in timebin
- % BusyTime double Time instrument was busy in time bin
- % BusyScale cell Inverse fraction of time instr is busy or off-line
- % AirVolume double Amount of air sampled during bin (m3) %

% The columns of type Cell in PARTBIN tables are vectors with one % element for each particle in the bin.

%

% See also PERMUTE_PARTBIN, CALC_HITRATIO

% YAADA - Software Toolkit to Analyze Single-Particle Mass Spectral Data %

- % Copyright (C) 1999-2000 California Institute of Technology
- % Copyright (C) 2001-2002 Arizona State University

% Jonathan O. Allen 31 Oct 00

% Require explicit Start, Stop, DaMin, DaMax

- % Allow discontinuous Da bins
- % Use global PARTBIN
- % Added HitOnly option
- % Removed calculated values (Dp, Volume, nStar, mStar)
- % Added AirVolume (from P. Bhave)
- % JOA 2002-06-10

% Force explicit bin definition with InstCode, Start, Stop, DaMin,

- % DaMax vectors.
- % JOA 2002-08-09
- % Added columns: Hit, Spectrum, and HitRatio
- % Prakash Bhave 2003-10-05

% Changed BusyScale column to cell type, so that it may vary within an IOP % Prakash Bhave 2004-04-18

% Changed definition of AirVolume from actual sampling volume to total sampling volume for each IOP % Xueying Qin 2004-04-28

global YAADA INST PARTBIN

```
if nargin < 5 \mid nargin > 9
 errmsg = ['Call as COLLECT_PARTBIN(InstCode,Start,Stop,DaMin,' ...
     'DaMax,PartBinFileName,HitOnly,OffLinePeriod)'];
 error(errmsg); clear errmsg
end
if ~iscell(InstCode)
 error('Expecting cell vector of InstCode');
end
% time bin inputs
if ~(isvector(Start) & isnumeric(Start))
 error('Expecting vector of Matlab times for Start');
end
if ~(isvector(Stop) & isnumeric(Stop))
 error('Expecting vector of Matlab times for Stop');
end
% Da bin inputs
if ~isvector(DaMin)
 error('Expecting vector for DaMin');
end
if ~isvector(DaMax)
 error('Expecting vector for DaMax');
end
% verify vectors are same length
NumBin = length(Start);
if length(InstCode) ~= NumBin
 error('Size of InstCode and Start vectors must match');
end
if length(Stop) ~= NumBin
 error('Start and Stop vectors not same size');
end
if length(DaMin) ~= NumBin
 error('Start and DaMin vectors not same size');
end
if length(DaMax) ~= NumBin
 error('Start and DaMax vectors not same size');
end
if ~exist('OffLinePeriod','var')
 % if no particles in OffLinePeriod, then assume instrument is off-line
 % default 2 min
 OffLinePeriod = 2/24/60;
elseif ~isscalar(OffLinePeriod)
 error('Expecting scalar for OffLinePeriod');
end
if ~exist('BusyPeriod','var')
 % default entire time bin
 BusyPeriod = [];
elseif ~isscalar(BusyPeriod)
 error('Expecting scalar for BusyPeriod');
end
if ~exist('PartBinFileName','var')
 PartBinFileName = fullfile(YAADA.StudyDir,'partbin');
elseif isempty(PartBinFileName)
```

```
PartBinFileName = fullfile(YAADA.StudyDir,'partbin');
end
if ~exist('HitOnly','var')
 HitOnly = 1;
else
 HitOnly = bool2num(HitOnly);
 if length(HitOnly) > 1
  error('Expecting scalar for HitOnly');
 end
end
if YAADA.Verbose
 t0 = now:
end
% allocate memory
PartBinID = 1:NumBin;
% busy time columns
HitCount2 = zeros(1,NumBin);
MissCount2 = zeros(1,NumBin);
AvgHitPos2 = zeros(1,NumBin);
OffLineTime2 = zeros(1,NumBin);
BusyTime2 = zeros(1,NumBin);
BusyScale2 = cell(1,NumBin);
AirVolume2 = zeros(1,NumBin);
% particle data columns
PID2
         = cell(1,NumBin);
[PID2{:}] = deal(partid([]));
Spectrum2 = cell(1,NumBin);
SpecGrav2 = cell(1,NumBin);
HitRatio2 = cell(1,NumBin);
Da2
         = cell(1,NumBin);
Hit2
         = cell(1,NumBin);
LastInstCode = ' ';
LastStart = 0;
LastStop = 0;
for bi = 1:NumBin
 % search on new InstCode-Time combinations
 if ~(strcmp(InstCode{bi},LastInstCode) & LastStart == Start(bi) & LastStop == Stop(bi))
  LastInstCode = InstCode{bi};
  LastStart = Start(bi);
  LastStop = Stop(bi);
  % search on particles in time range
  Query = sprintf('InstCode == %s and Time = [%f %f]',InstCode{bi},Start(bi),Stop(bi));
  PID = run_query(Query,'part',0);
  if length(PID)
   % get data from PART
   [Hit,Time,PositionInFolder,Da,SpecGrav,Velocity] = ...
      get_column(PID,'Hit','Time','PositionInFolder','Da','SpecGrav','Velocity');
   % get data from SPEC
```

```
Spectrum = NaN*ones(size(Hit));
NegPID = run_query(PID(find(Hit)), 'Polarity == 0', 'PART', 0);
PosPID = run_query(PID(find(Hit)), 'Polarity == 1', 'PART',0);
[DualPID,idx] = intersect(PID,intersect(NegPID,PosPID));
Spectrum(idx) = 2; clear idx
[x,idx] = intersect(PID,setdiff(PosPID,DualPID));
Spectrum(idx) = 1; clear x idx
[x,idx] = intersect(PID,setdiff(NegPID,DualPID));
Spectrum(idx) = 0; clear x idx
clear NegPID PosPID DualPID
%%%%% busy time scaling %%%%%
% find off-line time
dt = [Time; Stop(bi)]-[Start(bi); Time];
OffLineTime = sum(dt(find(dt >= OffLinePeriod)));
% get busy time parameters, sample flow from INST
IID = unique(instid(PID));
if length(IID) > 1
        warning('Multiple InstID for %s between %s and %s; First BusyTimeFunction used', ...
      InstCode{ti},datestr(Start(bi)),datestr(Stop(bi)));
end
InstIdx = search(INST.instid,'==',IID(1));
BusyTimeFcn = upper(char(INST(InstIdx,'BusyTimeFunction')));
BusyTimeParam = INST(InstIdx, 'BusyTimeParam');
BusyTimeParam = BusyTimeParam{:};
SampleFlow = INST(InstIdx,'SampleFlow');
% calculate busy time
HitIdx = find(Hit);
% count hits and misses for time period
% HitCount, MissCount, AvgHitCount are for time bin
HitCount = length(HitIdx);
MissCount = length(PID) - HitCount;
if HitCount
 % PositionInFolder only relevant for hit particles
 AvgHitPos = mean(PositionInFolder(HitIdx));
else
 AvgHitPos = 0;
end
switch BusyTimeFcn
 case 'BUSY_SCALE'
  BusyTime = busy_scale(MissCount,HitCount,AvgHitPos,BusyTimeParam);
  % convert s to d
  BusyTime = BusyTime / 24 / 3600;
 otherwise
  error(sprintf('Unknown busy time function %s',BusyTimeFcn));
end
% calculate busy time scaling factor
BusyScale = NaN * ones(size(Da));
if isempty(BusyPeriod)
 bs = (Stop(bi) - Start(bi)) ./ (Stop(bi) - Start(bi) - OffLineTime - BusyTime);
 BusyScale = bs * ones(size(Da));
else
 % calculate different BusyScale for each subinterval
 NumSubInt = ceil((Stop(bi) - Start(bi)) / BusyPeriod );
```

```
bStop = Start(bi) + NumSubInt * BusyPeriod;
   SubIntCut = split_bin(Start(bi),bStop,NumSubInt,'lin'); clear bStop
   for j = 1:NumSubInt
    SubIdx = range_search(Time,'=',[SubIntCut(j) SubIntCut(j+1)]);
    dtsub = [Time(SubIdx); SubIntCut(j+1)]-[SubIntCut(j); Time(SubIdx)];
    SubOffLineTime = sum(dtsub(find(dtsub >= OffLinePeriod))); clear dtsub
    SubHitCount = length(find(Hit(SubIdx)));
    SubMissCount = length(SubIdx) - SubHitCount;
    if SubHitCount
     SubAvgHitPos = mean(PositionInFolder(intersect(HitIdx,SubIdx)));
    else
     SubAvgHitPos = 0;
    end
    switch BusyTimeFcn
     case 'BUSY_SCALE'
       SubBusyTime = busy_scale(SubMissCount,SubHitCount,SubAvgHitPos,BusyTimeParam);
       % convert s to d
       SubBusyTime = SubBusyTime / 24 / 3600;
      otherwise
       error(sprintf('Unknown busy time function %s',BusyTimeFcn));
    end
    bs = BusyPeriod ./ (BusyPeriod - SubOffLineTime - SubBusyTime);
    BusyScale(SubIdx) = bs; clear bs
   end
  end
  % calculate volume of air sampled while on-line (convert from m3/s to m3/d)
  AirVolume = (Stop(bi) - Start(bi))*SampleFlow*24*3600; % total sampling time x flowrate
  %%% Calculate Hit Ratios %%%
  HitRatio = calc_hitratio(Da,Spectrum);
  [SortedDa, SortDaIdx] = sort(Da);
 end
end
if length(PID)
 % segregate hit particles by Da
 % [PIDDa,DaIdx] = bin_on_column(PID,'Da',[DaMin DaMax],[],[],'log');
 % in-line bin_on_column using Da
 % find particles in Da Bin (DaIdx)
 Idx = range_search(SortedDa,'=[)',[DaMin(bi) DaMax(bi)]);
 si = SortDaIdx(Idx);
 [PIDDa,sii] = sort(PID(si));
 DaIdx = si(sii);
 if HitOnly
  DaIdx = intersect(HitIdx,DaIdx);
 end
 if length(DaIdx)
  PID2{bi} = PID(DaIdx);
  Da2{bi} = Da(DaIdx);
         Hit_{bi} = Hit(DaIdx);
         Spectrum2{bi} = Spectrum(DaIdx);
         SpecGrav2{bi} = SpecGrav(DaIdx);
  HitRatio2{bi} = HitRatio(DaIdx);
  BusyScale2{bi} = BusyScale(DaIdx);
```

end

```
% HitCount2, MissCount2, AvgHitCount2 are for time bin
HitCount2(bi) = HitCount;
MissCount2(bi) = MissCount;
AvgHitPos2(bi) = AvgHitPos;
% busy time values are for time bin
OffLineTime2(bi) = OffLineTime;
BusyTime2(bi) = BusyTime;
AirVolume2(bi) = AirVolume;
else
% For time periods with no hits, OffLineTime is equal to the time period
OffLineTime2(bi) = Stop(bi) - Start(bi);
end
end
```

```
% make PARTBIN table
```

```
PartBinIDCol = column('PartBinID','Instrument-Time-Size identifier',",'double',1,0,PartBinID);
InstCodeCol = column('InstCode','Instrument Code',",'word',0,0,InstCode);
StartCol = column('Start','Bin start time','d','time',0,0,Start);
StopCol = column('Stop','Bin stop time','d','time',0,0,Stop);
DaMinCol = column('DaMin','Minimum aerodynamic diameter','um','double',0,0,DaMin);
DaMaxCol = column('DaMax','Maximum aerodynamic diameter','um','double',0,0,DaMax);
```

PIDCol = column('PID', 'Matching particle identifiers', ", 'cell', 0, 0, PID2);

```
SpectrumCol = column('Spectrum', 'Neg=0, Pos=1, Dual=2; Miss=NaN', ...
                      ",'cell',0,0,Spectrum2);
         SpecGravCol = column('SpecGrav','Specific gravity',",'cell',0,0,SpecGrav2);
         DaCol = column('Da','Aerodynamic diameter','um','cell',0,0,Da2);
         HitCol = column('Hit','Hit=1,Miss=0',",'cell',0,0,Hit2);
         HitRatioCol = column('HitRatio','P(Hit|Sized)',",'cell',0,0,HitRatio2);
         NHitCol = column('HitCount','Number of Hit Particles','','double',0,0,HitCount2);
         NMissCol = column('MissCount', 'Number of Missed Particles','', 'double', 0, 0, MissCount2);
         AvgHitPosCol= column('AvgHitPos','Average Position of Hit Particles in Folder',",'double',0,0,AvgHitPos2);
         OffLineTimeCol = column('OffLineTime', 'Time Instrument On-Line', 'd', 'double', 0, 0, OffLineTime2);
         BusyTimeCol = column('BusyTime','Time Instrument Busy','d','double',0,0,BusyTime2);
         BusyScaleCol
                          =
                               column('BusyScale','Scale
                                                           Factor
                                                                      for
                                                                            Instrument
                                                                                           Off-Line
                                                                                                               Busy
                                                                                                        and
Time',",'cell',0,0,BusyScale2);
```

AirVolumeCol = column('AirVolume','Volume of Air Sampled','m3','double',0,0,AirVolume2);

PARTBIN

table ('PartBin', PartBinIDCol, InstCodeCol, StartCol, StopCol, DaMinCol, DaMaxCol, PIDCol, SpecGravCol, DaCol, HitCol, SpectrumCol, HitRatioCol, NHitCol, NMissCol, AvgHitPosCol, OffLineTimeCol, BusyTimeCol, BusyScaleCol, AirVolumeCol);

save(PartBinFileName,'PARTBIN');

if YAADA.Verbose
t1 = now;
disp(sprintf('Particle data binned in %f s',(t1-t0)*24*3600));
disp(' ');
end

return

A.1.13 COLLECT_RESPONSE.m

function ResponseTable = collect_response(DataTable)
% COLLECT_RESPONSE collects ATOFMS data for chemical sensitivity calculations
```
% Call as ResponseTable = COLLECT_RESPONSE(DataTable)
% where
% DataTable contains at least the following columns:
% Column Name Type Description
% -----
% SampleCode Word Unique identifier for particle ensemble (primary key)
% PID
            Cell Particle identifiers in the ensemble
% Da
           Cell Measured particle aerodynamic diameter (um)
% ResponseTable has the columns of DataTable plus the following
% Column Name Type Description
% -----
% RespNH4 Cell ATOFMS response to NH4 (peak area)
% RespNO3 Cell ATOFMS response to NO3 (peak area)
% The columns of type Cell in ResponseTable are vectors with one
% element for each particle ``hit" by ATOFMS during the sampling period
% See also COLLECT_HITSIZE, REGRESS_IMPACTOR
% YAADA - Software Toolkit to Analyze Single-Particle Mass Spectral Data
% Copyright (C) 1999-2002 California Institute of Technology
% Copyright (C) 2001-2002 Arizona State University
% Prakash V. Bhave 16 May 2002
global YAADA
% Check inputs
if nargin \sim = 1
 error('Call as ResponseTable = COLLECT_RESPONSE(DataTable)');
if ~isa(DataTable,'table')
 error('Expecting table object for DataTable');
%_____%
      Collect ATOFMS responses to individual species
                                                      %
    -----%
% Accept sample codes from different field studies
SampleCode = DataTable(:).SampleCode;
[StudyID,Sidx] = get_studyname(SampleCode);
% Loop over each field study
for i = 1:length(StudyID)
 if isempty(strmatch(StudyID{i},YAADA.StudyName,'exact'));
  opendb(StudyID{i});
 idx = find(Sidx == i);
 % Collect sample codes and PartIDs related to the given study
 pid = \{\}; sc = \{\};
 for j = 1:length(idx)
  pid{j} = cellextract(DataTable(idx(j)).PID,1);
  sc{j} = char(DataTable(idx(j)).SampleCode);
 end; clear idx
```

% Collect ATOFMS responses to NH4 and NO3 if i == 1

[rnh4,rno3,UnsortedTable] = species_response(pid,sc); else

% Combine results from different studies

%

%

%

%

%

end

end

%

%----

end

```
[rnh4,rno3,OutTable] = species_response(pid,sc);
UnsortedTable = sort(merge(UnsortedTable,OutTable));
clear OutTable
end
clear pid sc rnh4 rno3
end
% Sort ResponseTable so that primary keys match with DataTable
idx = [];
for i = 1:numrow(DataTable)
idx(i) = strmatch(DataTable(i).SampleCode,UnsortedTable(:).SampleCode);
end
ResponseTable = UnsortedTable(idx);
clear UnsortedTable
```

A.1.14 DAPOWER.m

```
function YHat = dapower(Beta,RegressTbl)
% DAPOWER reconstructs ATOFMS data as a*Da^b
% Call as YHat = DAPOWER(Beta,RegressTbl)
% Scaling factor = a * Da^b.
% YAADA - Software Toolkit to Analyze Single-Particle Mass Spectral Data
%
% Copyright (C) 1999-2002 California Institute of Technology
% Copyright (C) 2001-2002 Arizona State University
% Jonathan O. Allen 10 Jun 98
% Prakash V. Bhave 30 Apr 02
% Check inputs
if ~isa(RegressTbl,'table')
 error('Expecting table object for RegressTbl');
end
% Initialize variables
NumEnsemb = numrow(RegressTbl);
YHat
        = zeros(NumEnsemb,1);
% Determine regression coefficients and scaled values
for i = 1:NumEnsemb
 Da = cellextract(RegressTbl(i,'da'),1);
 Multip = cellextract(RegressTbl(i,'Multiplier'),1);
 YHat(i) = nansum(Multip .* Beta(1).* Da .^ Beta(2));
end
```

return

A.1.15 ESTIMATE_PARTMASS.m

function [PartMass,PartMassTable] = estimate_partmass(PID,Da,Rho,SampleCode)
% ESTIMATE_PARTMASS estimates mass of each individual particle
% Call as PartMass = ESTIMATE_PARTMASS(PID,Da,Rho)
% where
% PID is a cell array of PartID lists
% Da is a cell array of aerodynamic diameters (um)
% Rho is the assumed particle density (g/cc)

```
% PartMass is a cell array of estimated particle masses (ug)
%
% If user wishes to retain intermediate results, can also be called as:
% [PartMass,PartMassTable] = ESTIMATE_PARTMASS(PID,Da,Rho,SampleCode)
% where
% SampleCode is a cell array of particle ensemble identifiers
% PartMassTable is a table object with the following columns:
% Column Name Type Description
%
% SampleCode Word Unique identifier for particle ensemble (primary key)
% PID
             Cell Particle identifiers in the ensemble
% Da
             Cell Measured particle aerodynamic diameter (um)
% Density
              Cell Assumed particle density (g/cc)
% Dp
             Cell Estimated particle physical diameter (um)
% PartVol
              Cell Estimated particle volume (um<sup>3</sup>)
   PartMass Cell Estimated particle mass (ug)
%
%
% The columns of type Cell in PartMassTable are vectors with one
% element for each particle ``hit" by ATOFMS during the IOP.
% YAADA - Software Toolkit to Analyze Single-Particle Mass Spectral Data
%
% Copyright (C) 1999-2002 California Institute of Technology
% Copyright (C) 2001-2002 Arizona State University
%
% Prakash V. Bhave 16 May 02
% Check inputs
if nargin == 3
if nargout ~= 1
 error('Call as PartMass = ESTIMATE_PARTMASS(PID,Da,Rho)');
end
if ~iscell(PID) | ~iscell(Da)
 error('Expecting cell arrays for PID and Da');
end
elseif nargin == 4
if nargout \sim = 2
 error('Call as [PartMass,PartMassTable] = ESTIMATE_PARTMASS(PID,Da,Rho,SampleCode)');
end
if ~iscell(SampleCode) | ~iscell(PID) | ~iscell(Da)
 error('Expecting cell arrays for SampleCode, PID, and Da');
end
else
error('Invalid number of input arguments');
end
if ~isscalar(Rho) | ~isnumeric(Rho)
error('Expecting numeric scalar for Rho');
end
% Initialize variables
NumEnsemb = length(PID);
Density = cell(1,NumEnsemb);
Dp
       = cell(1,NumEnsemb);
PartVol = cell(1,NumEnsemb);
PartMass = cell(1,NumEnsemb);
% Estimate Dp, PartVol, and PartMass
for i = 1:NumEnsemb
 if isempty(PID\{i\}) == 0
  if length(PID\{i\}) ~= length(Da\{i\})
```

```
\label{eq:intro:constraint} \begin{array}{l} error(sprintf('PID\{\%s\} \mbox{ and } Da\{\%s\} \mbox{ must be of the same length',i,i)}; \\ end \\ Density\{i\} = Rho * ones(size(Da\{i\})); & \% \mbox{ g/cm^3} \\ Dp\{i\} = da2dp\_lookup(Da\{i\},Density\{i\}); & \mbox{ um} \\ PartVol\{i\} = pi / 6 * Dp\{i\}.^3; & \% \mbox{ um}^3 \\ PartMass\{i\} = 1e-6 * PartVol\{i\} \mbox{ .* Density}\{i\}; & \mbox{ convert um3(g/cc) to ug} \\ end \\ end \end{array}
```

```
if nargin == 4
 % Make PartMassTable
 CodeCol = column('SampleCode','Code for sampling event', ...
            ",'Word',1,0,SampleCode);
 PIDCol = column('PID', 'Particle identifiers', '', 'cell', 0, 0, PID);
 DaCol = column('Da','Measured aerodynamic diameter','um','cell',0,0,Da);
 DensCol = column('Density','Estimated particle density','g/cc', ...
             'cell',0,0,Density);
 DpCol = column('Dp','Estimated physical (Stokes) diameter','um', ...
             'cell',0,0,Dp);
 VolumeCol = column('PartVol','Estimated particle volume','um^3', ...
            'cell',0,0,PartVol);
 MassCol = column('PartMass','Estimated particle mass','ug', ...
            'cell',0,0,PartMass);
 PartMassTable = table('PartMassTable',CodeCol,PIDCol,DaCol,DensCol, ...
               DpCol,VolumeCol,MassCol);
 PartMassTable.name = 'PartMassTable';
end
```

A.1.16 EXAMINE_RESIDUAL.m

```
function examine_residual(TableFN,ChemFlag,RowID)
% EXAMINE_RESIDUAL searches for biases in the scaling functions
% Call as EXAMINE_RESIDUAL(TableFN,ChemFlag,RowID)
% where
% TableFN is the name of file containing all data tables
% ChemFlag is 0 to examine mass residuals (Default)
%
          1 to examine chemical species residuals
% RowID is an optional input; vector of indices to data points of interest
% YAADA - Software Toolkit to Analyze Single-Particle Mass Spectral Data
%
% Copyright (C) 1999-2002 California Institute of Technology
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%
% Prakash V. Bhave - revision history
% 16 May 2002 original code
% 13 Mar 2004 due to revision of REGRESS_IMPACTOR, nuwrow(PhiTable) now
%
          equals numrow(ImpactorTable). Changed call to TABULATE_RESIDUAL
%
          accordingly
% Check inputs
if nargin > 3
error('Call as EXAMINE_RESIDUAL(TableFN,ChemFlag)');
end
load(TableFN);
if ~exist('ChemFlag','var')
ChemFlag = 0;
```

```
end
if ~exist('RowID','var')
RowID = 1:numrow(ImpactorTable);
end
% Make ResidTable
if ~ChemFlag
 ResidTable = tabulate_residual(ImpactorTable(RowID),PhiTable(RowID));
else
 ResidTable = tabulate_residual(ImpactorTable(RowID),ScaledTable(RowID));
end
save(TableFN,'-append','ResidTable');
%_____%
   Correlation of residuals with impactor analytes
%
                                                       %
%----
      -----%
% Collect impactor data for each analyte
if ~(exist('AllMoiData','var') & exist('AllMoiStd','var') & ...
   exist('MoiSpecList','var'))
 [AllMoiData,AllMoiStd,MoiSpecList] = moimatrix(ImpactorTable(:).SampleCode);
 save(TableFN,'-append','AllMoiData','AllMoiStd','MoiSpecList');
end
% Residuals vs. impactor analyte concentrations
MoiData = AllMoiData(RowID,:);
MoiStd = AllMoiStd(RowID,:);
ColIdx = strmatch('Resid',ResidTable.Collist);
for j = 1:length(ColIdx)
 ColName = cellextract(ResidTable.Collist',ColIdx(j));
 eval(sprintf('YVec = ResidTable(:).%s;',ColName));
 YVec = YVec(:);
 % Residuals vs. each impactor analyte
 for i = 1:size(MoiData,2)
  XVec = MoiData(:,i);
  ErrVec = 2*MoiStd(:,i);
  idx = find(~isnan(XVec));
  [R2,Strong] = r2strong(XVec(idx),YVec(idx));
  if Strong
   figure; clf
   set(gcf, 'PaperOrientation', 'landscape', 'PaperPosition', [0 0 11 8.5])
   % Scatter plot
   h1 = axes('Position',[.136 .176 0.5 .647]);
   axes(h1); box on;
   [hr,Symbol,Color] = plot_residual(ImpactorTable(RowID), ...
                     [XVec ErrVec], YVec, idx);
   % Label plot
   axes(hr); lim = axis;
   text(lim(1)+0.05*(lim(2)-lim(1)), 0.9*lim(4), sprintf('R^2 = \%1.2f', R2));
   hx = xlabel(sprintf('Impactor Measurement of %s (\\mug m^{-3})', ...
         MoiSpecList{i}));
   hy = ylabel(sprintf('Residual Aerosol %s Concentration (\\mug m^{-3})',...
         ColName(6:end)));
   % Legend
   h2 = axes('Position', [.705.1760.204.647]);
   axes(h2); box on;
   legend_symbol(ImpactorTable(RowID),idx,Symbol,Color);
  end
  clear idx
 end
end
```

A.1.17 IMPORT_APNM.m

```
function Conc = import_apnm(TimeCut,MaxFrac);
% IMPORT_APNM imports NO3 data from Automated Particle Nitrate Monitor
% Call as: Conc = IMPORT_APNM(TimeCut,MaxFrac);
% where
% TimeCut is a vector of time divisions in numeric form
% MaxFrac is maximum APNM off-line fraction (defaults to 0.5)
%
% Example:
% TimeCut = split_bin(datenum('06-Jan-1999'),datenum('03-Feb-1999'),672);
% Conc = import_apnm(TimeCut,0.25);
%
% In the above example, the period from Jan6 - Feb3 is split into 672
% equally spaced time intervals. This corresponds to 672 1-hour periods.
% Then, the average NO3 concentration is calculated for each hour when the
% APNM was offline for no more than 0.25 hours (15 minutes).
%
% See also SPLIT_BIN
% Written by: Prakash Bhave 01-Aug-2002
%--- Check inputs ---%
if ~isnumeric(TimeCut) | ~isvector(TimeCut)
 error('Expecting numeric vector of time divisions for TimeCut');
end
if ~exist('MaxFrac','var')
 MaxFrac = 0.5;
elseif ~isscalar(MaxFrac) | ~isnumeric(MaxFrac)
 error('Expecting numeric scalar for MaxFrac');
elseif MaxFrac > 1 | MaxFrac < 0
 error('MaxFrac must be between 0 and 1');
end
%---- Load APNM data ---%
DataFile = 'Q: \ CHUNKS \ Fresno \ Art2a Results \ JAN \ 090204 \ VF08 \ PartType \ UnClass \ Final Class \ test Fres.txt';
load(DataFile,'-ascii');
RawDat = testFres; clear DataFile testFres
NumRow = size(RawDat,1);
NO3 = RawDat(:,end);
tStart = datenum(RawDat(:,3),RawDat(:,2),RawDat(:,1), ...
          RawDat(:,4),RawDat(:,5),RawDat(:,6));
tStop = datenum(RawDat(:,9),RawDat(:,8),RawDat(:,7), ...
          RawDat(:,10),RawDat(:,11),RawDat(:,12));
clear RawDat
%--- Check time bins ---%
TimeBinSize = (TimeCut(end)-TimeCut(1))/(length(TimeCut)-1);
if max(tStop-tStart) >= TimeBinSize
 error('APNM sampling periods should be less than 1 timebin long');
end
Start = TimeCut(1:end-1);
Stop = TimeCut(2:end);
NumPer = length(Start);
%--- Find sampling periods that overlap more than one time bin ---%
```

```
for i = 1:NumRow
idx = max(find(Start < tStart(i)));
if Stop(idx) > tStart(i) & Stop(idx) < tStop(i)
    overlap = [overlap;i];
end
end
```

```
%--- Split the sampling periods that overlap multiple time bins ---%
for i = 1:length(overlap)
 idx = overlap(i);
 mid = Start(find(Start > tStart(idx) & Start < tStop(idx)));</pre>
 tStart(NumRow+i) = mid;
 tStop(NumRow+i) = tStop(idx);
 NO3(NumRow+i) = NO3(idx);
 tStop(idx)
               = mid:
end
[tStart,order] = sort(tStart);
tStop = tStop(order);
NO3 = NO3(order);
clear order
%--- Calculate Avg NO3 conc for each time bin ---%
Conc = NaN*ones(NumPer,1);
for i = 1:NumPer
 % Find off-line time
 idx = find(tStart >= Start(i) & tStop <= Stop(i));</pre>
 OffT(i) = Stop(i) - Start(i) - sum(tStop(idx) - tStart(idx));
 % Create vector of NO3 concentrations
 if OffT(i)/TimeBinSize < MaxFrac
  Conc(i) = sum(NO3(idx).*(tStop(idx) - tStart(idx)))/TimeBinSize;
 end
```

end return

A.1.18 LEGEND_SCATTER.m

```
function legend_scatter(DataTable,Idx,Symbol,Color)
% LEGEND_SCATTER makes the legend for scatter plots
% Called as LEGEND_SCATTER(DataTable,Idx,Symbol,Color)
% where
% DataTable is a table object with at least the following columns:
% Column Name Type Description
%
  ----- ----
                 ____
% SampleCode Word Unique identifier for particle ensemble (primary key)
% EventCode Word Identifier for sampling event
% DaMin
              Double Minimum aerodynamic diameter in particle ensemble
% DaMax
              Double Maximum aerodynamic diameter in particle ensemble
% Idx is a vector of indices to data points which are plotted
% Symbol is a string of MATLAB recognized plotting symbols (e.g. 'os^dp<hv>')
% Color is a n*3 matrix of color definitions
% YAADA - Software Toolkit to Analyze Single-Particle Mass Spectral Data
%
% Copyright (C) 1999-2002 California Institute of Technology
% Copyright (C) 2001-2002 Arizona State University
%
```

% Prakash V. Bhave 30 Apr 02

```
% Check inputs
if nargin \sim = 4
 error('Call as LEGEND_SCATTER(DataTable,Idx,Symbol,Color)');
end
if ~isa(DataTable,'table')
 error('Expecting table object for DataTable');
end
if ~isvector(Idx) | length(Idx) > numrow(DataTable)
 error('Idx must be a vector with length less than numrow(DataTable)');
end
% Get sampling periods and size bins
[Code,uidx] = unique(DataTable(:,'EventCode'));
[y,idx] = sort(uidx);
for i = 1:length(Code)
 EventCode{i} = Code{idx(i)};
end; clear y i idx Code
DaMin = unique(DataTable(:,'DaMin'));
DaMax = unique(DataTable(:,'DaMax'));
% Define dimensional variables
NumSym = length(Symbol);
NumEvent = length(unique(DataTable(Idx,'EventCode')));
NumBin = length(DaMin);
if NumBin > size(Color,1)
 error('Too many size bins for given color scheme');
end
% Define plotting parameters
box on; hold on
xmax = 10;
ymax = NumEvent + 1;
yhead = 2.5;
set(gca,'XTick',[],'YTick',[])
set(gca,'XLim',[0 xmax],'YLim',[0.5 ymax + yhead])
fontsize = 10;
marksize = 12;
if NumBin == 2
xpos = [.02 .77 .87 .65]*xmax;
elseif NumBin == 3
xpos = [.02 .72 .82 .92 .65]*xmax;
else
error('Must expand the definition of xpos');
end
% Plot EventCodes and symbols
event = ' ';
eidx = 0;
symbols = [Symbol Symbol]; % add more if this is not enough
for i = 1:length(Idx)
 i1 = Idx(i);
 if isempty(strmatch(event,DataTable(i1,'EventCode')))
  event = DataTable(i1,'EventCode');
  eidx = eidx+1;
  eid2 = strmatch(event,EventCode,'exact');
  ypos = ymax - eidx;
  ht(i1) = text(xpos(1),ypos,DataTable(i1,'EventCode'));
  set(ht(i1),'FontSize',fontsize);
 end
```

```
damin = DataTable(i1,'DaMin');
  if damin == DaMin(j)
   hp(eidx,j) = plot(xpos(j+1),ypos,symbols(eid2));
   set(hp(eidx,j),'MarkerSize',marksize,'MarkerEdgeColor',[0 0 0], ...
             'MarkerFaceColor',Color(j,:));
  end
  if eidx > NumSym
   hp2(eidx-NumSym,j) = plot(xpos(j+1),ypos,['w' symbols(eid2)]);
   set(hp2(eidx-NumSym,j),'MarkerSize',0.6*marksize, ...
           'MarkerEdgeColor',[0 0 0],'MarkerFaceColor',[1 1 1]);
  end
 end
end
% Write column headings
for j = 1:NumBin
 BinText = sprintf('%1.2f - %1.2f \\mum',DaMin(j),DaMax(j));
 htt(j) = text(xpos(j+1),ymax-.16*yhead,sprintf('%s',BinText));
 set(htt(j),'FontSize',fontsize);
end
set(htt(:),'FontSize',fontsize,'Rotation',90,'HorizontalAlignment','Left');
htt(NumBin+1) = text(0.01*xmax,ymax-.1*yhead,'EventCode');
set(htt(end),'FontSize',fontsize);
```

```
% Make column and row header lines
lim = axis;
hl(1) = line([lim(1),lim(2)],[ymax-.2*yhead ymax-.2*yhead]);
hl(2) = line([xpos(5) xpos(5)],[lim(3),lim(4)]);
set(hl(:),'Color',[.5 .5 .5]);
```

A.1.19 LEGEND_SYMBOL.m

function legend_symbol(DataTable,Idx,Symbol,Color) % LEGEND_SYMBOL makes the legend for scatter plots % Called as LEGEND_SYMBOL(DataTable,Idx,Symbol,Color) % where % DataTable is a table object with at least the following columns: % Column Name Type Description % -----% SampleCode Word Unique identifier for particle ensemble (primary key) % EventCode Word Identifier for sampling event % DaMin Double Minimum aerodynamic diameter in particle ensemble % DaMax Double Maximum aerodynamic diameter in particle ensemble % Idx is a vector of indices to data points which are plotted % Symbol is a string of MATLAB recognized plotting symbols (e.g. 'os^dp<hv>') % Color is a n*3 matrix of color definitions

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%

% Prakash V. Bhave 30 Apr 02

% Added symbols for NumEvent > 2*length(Symbol)

% Allowed different MoiBinCuts for different IOPs

% Prakash V. Bhave 15 Sep 2003

```
% Allow up to 7 different particle size intervals
% Prakash V. Bhave 5 Oct 2003
% Check inputs
if nargin \sim = 4
 error('Call as LEGEND_SYMBOL(DataTable,Idx,Symbol,Color)');
end
if ~isa(DataTable,'table')
 error('Expecting table object for DataTable');
end
if ~isvector(Idx) | length(Idx) > numrow(DataTable)
 error('Idx must be a vector with length less than numrow(DataTable)');
end
% Get sampling periods and size bins
[Code,uidx] = unique(DataTable(:,'EventCode'));
[y,idx] = sort(uidx);
for i = 1:length(Code)
 EventCode{i} = Code{idx(i)};
end; clear y i idx Code
SizeInts = unique([DataTable(:).DaMin;DataTable(:).DaMax]','rows');
DaMin = SizeInts(:,1); DaMax = SizeInts(:,2);
NumBin = size(SizeInts,1); clear SizeInts
% Define dimensional variables
NumSym = length(Symbol);
NumEvent = length(unique(DataTable(Idx,'EventCode')));
if NumBin > size(Color,1)
 error('Too many size bins for given color scheme');
end
% Define plotting parameters
box on; hold on
xmax = 10;
ymax = NumEvent + 1;
yhead = 2.5;
set(gca,'XTick',[],'YTick',[])
set(gca,'XLim',[0 xmax],'YLim',[0.5 ymax + yhead])
if NumBin < 5
 fontsize = 10;
 marksize = 14;
else
 fontsize = 8;
 marksize = 12;
end
if NumBin == 2
xpos = [.02 .77 .87 .65]*xmax;
elseif NumBin == 3
xpos = [.02 .72 .82 .92 .65]*xmax;
elseif NumBin == 4
xpos = [.02 .69 .78 .87 .96 .65]*xmax;
elseif NumBin == 5
xpos = [.02 .64 .72 .80 .88 .96 .60]*xmax;
elseif NumBin == 6
xpos = [.02 .62 .69 .76 .83 .90 .97 .59]*xmax;
elseif NumBin == 7
xpos = [.02 .61 .67 .73 .79 .85 .91 .97 .58]*xmax;
else
error('Must expand the definition of xpos');
```

end

```
% Plot EventCodes and symbols
event = ' ';
eidx = 0;
symbols = [Symbol Symbol]; % add more if this is not enough
for i = 1:length(Idx)
 i1 = Idx(i);
 if isempty(strmatch(event,DataTable(i1,'EventCode')))
  event = DataTable(i1,'EventCode');
  eidx = eidx+1;
  eid2 = strmatch(event,EventCode,'exact');
  ypos = ymax - eidx;
% ht(i1) = text(xpos(1),ypos,DataTable(i1,'EventCode'));
  dnum1 = DataTable(i1,'Start');
  dnum2 = DataTable(i1,'Stop');
  dtext = [datestr(dnum1,3) '' datestr(dnum1,7) ', ' datestr(dnum1,10)];
dtext = [datestr(dnum1,3) '' datestr(dnum1,7) ', ' ...
%
        datestr(dnum1,15) '-' datestr(dnum2,15)];
  ht(i1) = text(xpos(1),ypos,dtext);
  set(ht(i1),'FontSize',fontsize);
 end
 for j = 1:NumBin
  damin = DataTable(i1,'DaMin');
  damax = DataTable(i1,'DaMax');
  if damin == DaMin(j) & damax == DaMax(j)
   hp(eidx,j) = plot(xpos(j+1),ypos,symbols(eid2));
   set(hp(eidx,j),'MarkerSize',marksize,'MarkerEdgeColor',[0 0 0], ...
             'MarkerFaceColor',Color(j,:));
   if eidx > NumSym
     if eidx \leq 2*NumSym
      hp2(eidx-NumSym,j) = plot(xpos(j+1),ypos,['w' symbols(eid2)]);
      set(hp2(eidx-NumSym,j),'MarkerSize',0.6*marksize, ...
              'MarkerEdgeColor',[0 0 0],'MarkerFaceColor',[1 1 1]);
     else
     set(hp(eidx,j),'MarkerFaceColor',[1 1 1]);
      hp2(eidx-2*NumSym,j) = plot(xpos(j+1),ypos,['w' symbols(eid2)]);
      set(hp2(eidx-2*NumSym,j),'MarkerSize',0.6*marksize, ...
              'MarkerEdgeColor',[0 0 0],'MarkerFaceColor',Color(j,:));
     end
   end
  end
 end
end
% Write column headings
for j = 1:NumBin
 BinText = sprintf('%1.2f - %1.2f \\mum',DaMin(j),DaMax(j));
 htt(j) = text(xpos(j+1),ymax-.16*yhead,sprintf('%s',BinText));
end
set(htt(:),'FontSize',fontsize,'Rotation',90,'HorizontalAlignment','Left');
%set(htt(:),'FontSize',fontsize*1.25,'Rotation',90, ...
         'HorizontalAlignment','Left');
%
%htt(NumBin+1) = text(0.01*xmax,ymax-.1*yhead,'EventCode');
%htt(NumBin+1) = text(0.01*xmax,ymax-.1*yhead,'IOP Date');
%set(htt(end),'FontSize',fontsize);
% Make column and row header lines
\lim = axis:
```

```
hl(1) = line([lim(1),lim(2)],[ymax-.2*yhead ymax-.2*yhead]);
```

hl(2) = line([xpos(end) xpos(end)],[lim(3),lim(4)]); set(hl(:),'Color',[.5 .5 .5]);

return

A.1.20 MOIMATRIX.m

```
function [OutDat,OutStd,SpecList] = moimatrix(SampleCode)
% MOIMATRIX constructs a matrix of impactor measurements
% Call as [OutDat,OutStd,SpecList] = MOIMATRIX(SampleCode)
% where
% SampleCode is a cell array of particle ensemble identifiers
% OutDat is a 2D matrix of impactor measurements
%
         one row for each SampleCode
%
         one column for each analyte
% OutStd is a 2D matrix of impactor standard errors
% SpecList is a cell array of analytes corresponding to columns of OutDat
% YAADA - Software Toolkit to Analyze Single-Particle Mass Spectral Data
%
% Copyright (C) 1999-2002 California Institute of Technology
% Copyright (C) 2001-2002 Arizona State University
%
% Prakash V. Bhave 30 Apr 02
% Check inputs
if nargin \sim = 1
error('Call as [OutDat,SpecList] = MOIMATRIX(SampleCode)');
end
if ~iscell(SampleCode)
error('Expecting cell array for SampleCode');
end
% Make a list of all species which were measured by impactors
SpecList = \{\};
NumRow = length(SampleCode);
for i = 1:NumRow
 StudyName(i,:) = strtok(SampleCode{i},'-');
% MOIDataFN = sprintf('./quant/refdata/%s_impactor',lower(StudyName(i,:)));
 MOIDataFN = sprintf('quant/refdata/%s_impactor',lower(StudyName(i,:)));
 load(MOIDataFN,'AnalyteList');
 SpecList = union(SpecList,AnalyteList);
 StdList = \{\};
 for j = 1:length(SpecList)
  StdList{j} = [SpecList{j} 'Std'];
 end
end
% Assemble data matrix
NumSpec = length(SpecList);
OutDat = NaN * ones(NumRow,NumSpec);
OutStd = NaN * ones(NumRow,NumSpec);
for i = 1:NumRow
% MOIDataFN = sprintf('./quant/refdata/%s_impactor',lower(StudyName(i,:)));
 MOIDataFN = sprintf('quant/refdata/%s_impactor',lower(StudyName(i,:)));
 load(MOIDataFN,'AnalyteList','MoiLabel');
 idx = strmatch(SampleCode{i},MoiLabel);
 for j = 1:NumSpec
  spec = SpecList{j};
```

```
jdx = strmatch(spec,AnalyteList,'exact');
if ~isempty(jdx)
eval(sprintf('load(MOIDataFN,''%s'');',AnalyteList{jdx}));
eval(sprintf('OutDat(i,j) = %s(idx);',AnalyteList{jdx}));
eval(sprintf('load(MOIDataFN,''%sStd'');',AnalyteList{jdx}));
if exist([spec 'Std'],'var')
eval(sprintf('OutStd(i,j) = %sStd(idx);',AnalyteList{jdx}));
end
end; clear jdx
end; clear idx
clear AnalyteList MoiLabel
end
return
```

A.1.21 PBT8.m

```
% generate PBT distribution for 30 seconds periods PBTHist dimention: A x Lambda x CountBin
%
% Written by: Xueying Qin
% 23-Jun-2004
% 24-Jun-2004 modify smoothing, average PBT instead of arriv
% 28-Jun-2004 modify RANGE_SEARCH, shorten the time need to remove hits that arrive within BThit of
% another hit
% 06-Jul-2004 modify NumTerms, change it from a fixed # 10 to ceil(A*lamb*5)
% 07-Jul-2004 replace WHILE loop with FOR loop
% 12-Jul-2004 add "0" Counts to the histgram, this is important expecially when A and Lambda are small
% 19-Jul-2004 initialize Lambda values by taking ArrRatHit with 2 significant figures
tic
Task = 2;
CollectTime = 1; % PBT distribution for every 1s
NumOfPoints = CollectTime*1800; % total # of points in Poission distribution - here is 1800 points
CountBin = 0.200; % bins for #miss frequency distributions
Smoothing = 10;
        = 'Q:\CHUNKS\Fresno\quantitation\arrival_rate1h';
InFile1
InFile2 = 'Q:\CHUNKS\Fresno\quantitation\bt_hit5_1h';
OutFile = 'Q:\CHUNKS\Fresno\quant\PBT\PBT8_1h';
%-----% TASK 2 -----%
    Generate PBT histograms for a range value of BTHit, A;
%
                                                           %
% and a range of arrival rates, Lambda for every 30s time bin
                                                          %
%_-----%
if Task == 2
load(InFile1,'ArrRat');
                        % "Lambda" is a vector of possible particle arrival rates [Hz]
load(InFile2, 'HitRatio', 'HitTimeBin');
ArrRatHit = (ArrRat .* HitRatio')*HitTimeBin;
length(ArrRatHit)
ArrRatHit = ArrRatHit(find(ArrRatHit));
rndoff = zeros(size(ArrRatHit));
minlog = floor(log10(min(ArrRatHit(find(ArrRatHit)))));
maxlog = ceil(log10(max(ArrRatHit)));
for i = minlog:maxlog
 ii = 10^{i};
 temp = ArrRatHit/ii;
```

```
idx = find(temp > 1 & temp <= 10);
rndoff(idx) = ii*round(temp(idx)*10)/10;
clear ii temp idx
end
```

```
Lambda = unique(rndoff);
A = [0:0.01:1]/HitTimeBin; % "BTHit" is time required to record a hit
NumFreq = length(Lambda);
NumBTHit = length(A);
```

% Initialize matrix of poisson w. busy time distributions, PBT PBTHist = zeros(NumBTHit, NumFreq,length(CountBin));

```
% Loop over each possible particle arrival rate
for i = 1:NumBTHit
  BThit = A(i);
  for j = 1:NumFreq
    lamb = Lambda(j);
    n = round(1.25*NumOfPoints*lamb);
    PBT = zeros(Smoothing,length(CountBin));
    for k = 1:Smoothing % smooth PBT by calculating 10 times and take the average
       arriv = cumsum(exprnd(1/lamb,n,1));
         % "arriv" is vector times when particles arrive at rate, Lambda(i)
       npart = max(find(arriv < NumOfPoints));</pre>
         % "npart" is # of particle arrivals during sampling interval
       detect = ones(1, length(arriv)); % "detect" indicates if an arrival was recorded (1) or not (0)
       % Go over every particle groups, but only once for each particle
       m1=1;
                                  % remove particles that arrive within BThit of the previous particle
       for m = 2:npart
         if (arriv(m)-arriv(m1)) \le BThit
            detect(m)=0;
         else
            m1 = m;
         end
       end
       clear m m1
       arriv = arriv(find(detect(1:npart))); % only consider particles that arrives within NumOfPoints period
       [x.idx] = unique(floor(arriv/CollectTime)): clear x
       PBT(k,:) = hist(diff([0;idx]),CountBin); close
       PBT(k,1) = NumOfPoints - sum(PBT(k,2:end));
    end
    PBTHist(i,j,:) = mean(PBT,1);
    clear k PBT
    disp(sprintf('Generated PBT for Lambda = %9.4f Hz and BTHit = %9.4f S', lamb, BThit));
    clear arriv lamb detect npart x idx
  end
  clear BTHit j
end
clear i NumFreq NumBTHit
% Save PBT distributions and associated data
save(OutFile,'A','Lambda','PBTHist');
```

end

toc

A.1.22 PEAKMATRIX.m

function OutDat = peakmatrix(ScaledTable,ResponseTable) % PEAKMATRIX constructs a matrix of scaled ATOFMS measurements % Call as OutDat = PEAKMATRIX(ScaledTable,ResponseTable) % where % ScaledTable is the output of REGRESS_IMPACTOR % ResponseTable is the output of SPECIES_RESPONSE is a 2D matrix of scaled peak areas % OutDat % 1 row for each SampleCode, 1 column for each m/z ratio % YAADA - Software Toolkit to Analyze Single-Particle Mass Spectral Data % % Copyright (C) 1999-2002 California Institute of Technology % Copyright (C) 2001-2002 Arizona State University % % Prakash V. Bhave 30 Apr 02 % Check inputs if nargin $\sim = 2$ error('Call as PEAKMATRIX(ScaledTable,ResponseTable)'); end if ~isa(ScaledTable,'table') | ~isa(ResponseTable,'table') error('Expecting table objects for ScaledTable and ResponseTable'); end % Assemble data matrix NumRow = numrow(ScaledTable); NumMZ = 250; OutDat = NaN * ones(NumRow,NumMZ); for i = 1:NumRow phi = cellextract(ScaledTable(i).Phi,1); pkarea = cellextract(ResponseTable(i).PeakArea,1); for mz = 1:NumMZ OutDat(i,mz) = sum(phi.*pkarea(:,mz)); end end

return

A.1.23 PLOT_RESIDUAL.m

- % Y is a vector of residual concentrations
- % X is a vector of sample-specific data (i.e. Temperature, SO4, RH, etc.)
- % Idx is a vector of indices to data points which are to be plotted
- % ha is a handle to the resulting plot

```
% YAADA - Software Toolkit to Analyze Single-Particle Mass Spectral Data
%
% Copyright (C) 1999-2002 California Institute of Technology
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%
% Prakash V. Bhave 30 Apr 02
%---- Check Inputs ---%
if nargin ~= 4
 error('Call as PLOT_RESIDUAL(DataTable,X,Y,Idx)');
end
if ~isa(DataTable,'table')
 error('Expecting table object for DataTable');
end
NumRow = numrow(DataTable);
if size(X,1) ~= NumRow | size(Y,1) ~= NumRow
 error('Lengths of X and Y must be same length as DataTable');
end
if ~isvector(Idx) | length(Idx) > NumRow
 error('Idx must be a vector with length less than numrow(DataTable)');
end
%---- Get Sampling Periods and Size Bins ---%
[EventStart,uidx] = unique(DataTable(:,'Start'));
DaMin = unique(DataTable(:,'DaMin'));
NumEvent = length(EventStart);
NumBin = length(DaMin);
%---- Plotting Symbols and Colors ---%
Symbol = 'os^dp<hv>';
Color = [1 \ 0 \ 0; ... \% red
     0 1 0; ... % green
     0 0 1; ... % blue
     1 0 1; ... % magenta
     0 1 1; ... % cyan
   .66 .66 .66; ... % gray
     0 0 0]; % black
if NumBin > size(Color,1)
 error('Too many size bins for current color scheme');
end
%---- Plot the Data Points and Error Bars ---%
for i1 = 1:length(Idx)
 i = Idx(i1);
 idx1 = find(EventStart == DataTable(i,'Start'));
 idx2 = find(DaMin == DataTable(i,'DaMin'));
 plot_symbol(i,X,Y,idx1,idx2,Symbol,Color)
 clear idx1 idx2
end
%---- Make plot symmetrical about line at R = 0 ----%
\lim = axis;
\lim(1) = 0;
Amax = max([abs(lim(3)) abs(lim(4))]);
\lim(3) = -Amax;
\lim(4) = Amax;
axis square
axis(lim);
hline = line([lim(1) lim(2)], [0 0]);
```

```
set(hline,'Color',[.5 .5 .5]);
```

ha = gca;return

A.1.24 PLOT_SCATTER.m

function [h1,h2] = plot_scatter(DataFN,Analyte,PlotNum,RowID)

% PLOT_SCATTER produces scatter plots for comparing ATOFMS with impactor data

% Call as ha = PLOT_SCATTER(DataFN,Analyte,PlotNum,RowID)

% where[h1,h2] = plot_scatter(DataFN,Analyte,PlotNum,RowID)

- % DataFN is the name of the file containing the data tables
- % Analyte is the aerosol component of interest (e.g. 'Mass', 'NO3', etc.)
- % PlotNum is 1 to plot unscaled mHit vs. impactor data
- % 2 to plot scaled mHit vs. impactor data
- 3 to plot MOI/mHit vs. Da %
- % 4 to plot MOI/mSized vs. Da
- % 5 to plot scaled mSized vs. impactor
- % 6 to plot Estimated Phi vs. MOI/mHit
- % 7 to plot Estimated Eta1 vs. MOI/mSized
- % 8 to plot Estimated Phi (Eta1/HR) vs. MOI/mHit
- % 9 to plot MOI/mHit/HR vs. Da
- % 10 to plot mSized/MOI vs. Da
- % 11 to plot HR vs. Da
- % RowID is a vector of row indices to the data of interest (defaults to [:])

% YAADA - Software Toolkit to Analyze Single-Particle Mass Spectral Data %

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- %

% Prakash V. Bhave - revision history

- % 1 Jul 2002 original code for UCR NH4/NO3 quant paper
- % 30 Jul 2002 revised for application to other studies
- % 05 Aug 2002 revised to allow overlapping sampling periods
- % 21 Aug 2002 added phi and eta plots
- % 23 Sep 2003 allowed different MoiBinCuts for different IOPs
- % 5 Oct 2003 extended color scheme to allow up to 7 particle size intervals
- % 16 Oct 2003 fixed bug in RowID selection from DataTable

% 13 Mar 2004 plot only RowID data when PlotNum = 1 or 2

% 27 Apr 2004 replaced div by AirVolume with mult by BusyScale

% 28 Apr 2004 changed definition of AirVolume and added it back in

%--- Check inputs ---%

```
if exist(DataFN,'file') ~= 2
```

```
error(sprintf('%s not found in MATLAB"s search path',DataFN));
end
```

if ~isword(Analyte)

```
error('Expecting word for Analyte');
```

end

if ~isscalar(PlotNum) | ~isinteger(PlotNum)

error('Expecting scalar integer for PlotNum');

elseif PlotNum < 1 | PlotNum > 11

error('PlotNum out of range');

end

if exist('RowID','var')

if ~isvector(RowID) | ~isinteger(RowID)

error('Expecting vector of integers for PlotNum');

end end

```
%--- Load and rename data tables ---%
load(DataFN,'ImpactorTable')
RefTable = ImpactorTable;
switch PlotNum
case {1,3,9}
 if strmatch(upper(Analyte),'MASS','exact')
 load(DataFN,'HitSizeTable')
 DataTable = HitSizeTable;
 else
 load(DataFN,'PhiTable','ResponseTable')
 eval(sprintf('DataTable = table(PhiTable,ResponseTable.Resp%s);',Analyte));
 end
case {2,6}
 if strmatch(upper(Analyte),'MASS','exact')
 load(DataFN,'PhiTable')
 DataTable = PhiTable;
 else
 load(DataFN,'ScaledTable')
 DataTable = ScaledTable;
 end
case {4,10}
 if strmatch(upper(Analyte), 'MASS', 'exact')
 load(DataFN,'MissSizeTable')
 DataTable = MissSizeTable;
 else
 error(sprintf('Invalid option PlotNum = %i and Analyte = %s', ...
           PlotNum,Analyte));
 end
case {5,7,8}
 if strmatch(upper(Analyte),'MASS','exact')
 load(DataFN,'EtaTable')
 DataTable = EtaTable;
 else
 error(sprintf('Invalid option PlotNum = %i and Analyte = %s', ...
           PlotNum,Analyte));
 end
case 11
 if strmatch(upper(Analyte), 'MASS', 'exact')
 load(DataFN,'HitSizeTable','MissSizeTable')
  SizeDa = MissSizeTable(:).Da;
  SizeCol = column('SizeDa','Da of sized particles',",'Cell',0,0,SizeDa);
  DataTable = table(HitSizeTable,SizeCol);
 else
  error(sprintf('Invalid option PlotNum = %i and Analyte = %s', ...
           PlotNum,Analyte));
 end
end
% Select only the rows of interest
if ~exist('RowID','var')
 RowID = 1:numrow(RefTable);
end
RefTable = RefTable(RowID);
if PlotNum <= 3
 DataTable = DataTable(RowID);
end
```

%--- Extract impactor data from RefTable ---% NumRow = numrow(RefTable); MOI = NaN*ones(NumRow,2);

```
eval(sprintf('MOI(i,:) = cellextract(RefTable(i).%s,1);',Analyte));
end
if size(MOI,2) == 2
 MOI(:,2) = MOI(:,2) * 2; % plot MOI +/- 2 SD
end
%---- Extract ATOFMS data from DataTable ---%
switch PlotNum
case 1
 X = MOI;
 Score = zeros(NumRow,1);
 for i = 1:NumRow
 if strmatch(upper(Analyte), 'MASS', 'exact')
  Score(i) = sum(cellextract(DataTable(i).PartMass,1) ...
          .* cellextract(DataTable(i).BusyScale,1))/DataTable(i).AirVolume;
   Y = Score*1e3;
  else
   phi = cellextract(DataTable(i).Phi,1);
   eval(sprintf('resp = cellextract(DataTable(i).Resp%s,1);',Analyte));
   bs = cellextract(DataTable(i).BusyScale,1);
   Score(i) = sum(phi.*resp.*bs)/DataTable(i).AirVolume;
   clear phi resp
   Y = Score/1e9;
 end
 end
case {2,5}
 X = MOI;
 Y = NaN*ones(NumRow,2);
 for i = 1:NumRow
 eval(sprintf('temp = cellextract(DataTable(i).YHat%s,1);',Analyte));
  if length(temp) == 1
  Y(i,1) = temp;
  elseif length(temp) == 2
  Y(i,:) = temp;
  end
 clear temp
 end
case {3,4,10}
 X = sqrt(RefTable(:).DaMin .* RefTable(:).DaMax)';
 Score = zeros(NumRow,1);
 for i = 1:NumRow
  if strmatch(upper(Analyte), 'MASS', 'exact')
   Score(i) = sum(cellextract(DataTable(i).PartMass,1) ...
          .* cellextract(DataTable(i).BusyScale,1))/DataTable(i).AirVolume;
  else
   phi = cellextract(DataTable(i).Phi,1);
   eval(sprintf('resp = cellextract(DataTable(i).Resp%s,1);',Analyte));
   bs = cellextract(DataTable(i).BusyScale,1);
   Score(i) = sum(phi.*resp.*bs)/DataTable(i).AirVolume;
   clear phi resp
 end
 end
 if PlotNum == 10
 Y = Score./MOI(:,1);
 else
 Y = MOI(:,1)./Score;
 end
case 6
 Score = zeros(NumRow,1);
```

for i = 1:NumRow

```
for i = 1:NumRow
 if strmatch(upper(Analyte),'MASS','exact')
  Score(i) = sum(cellextract(DataTable(i).PartMass,1) ...
          .* cellextract(DataTable(i).BusyScale,1))/DataTable(i).AirVolume;
  Y(i) = sum(cellextract(DataTable(i).PartMass,1).* ...
         cellextract(DataTable(i).Phi,1))/ ...
       sum(cellextract(DataTable(i).PartMass,1));
 else
  error(sprintf('Invalid option PlotNum = %i and Analyte = %s', ...
           PlotNum,Analyte));
 end
end
X = MOI(:,1)./Score; Y = Y';
case 7
Score = zeros(NumRow.1):
 for i = 1:NumRow
 if strmatch(upper(Analyte),'MASS','exact')
  Score(i) = sum(cellextract(DataTable(i).PartMass,1) ...
          .* cellextract(DataTable(i).BusyScale,1))/DataTable(i).AirVolume;
  Y(i) = sum(cellextract(DataTable(i).PartMass,1) .* ...
         cellextract(DataTable(i).Eta,1))/ ...
       sum(cellextract(DataTable(i).PartMass,1));
 else
 error(sprintf('Invalid option PlotNum = %i and Analyte = %s', ...
           PlotNum,Analyte));
 end
end
X = MOI(:,1)./Score; Y = Y';
case 8
Score = zeros(NumRow,1);
for i = 1:NumRow
 if strmatch(upper(Analyte),'MASS','exact')
  Score(i) = sum(cellextract(DataTable(i).PartMass,1) .* ...
           cellextract(DataTable(i).Hit,1) .* ...
           cellextract(DataTable(i).BusyScale,1))/DataTable(i).AirVolume;
  Y(i) = sum(cellextract(DataTable(i).PartMass,1) .* ...
         cellextract(DataTable(i).Eta,1) .* ...
         cellextract(DataTable(i).Hit,1) ./ ...
         cellextract(DataTable(i).HitRatio,1)) / ...
       sum(cellextract(DataTable(i).PartMass,1) .* ...
         cellextract(DataTable(i).Hit,1));
 else
 error(sprintf('Invalid option PlotNum = %i and Analyte = %s', ...
           PlotNum,Analyte));
 end
 end
X = MOI(:,1)./Score; Y = Y';
case 9
X = sqrt(RefTable(:).DaMin .* RefTable(:).DaMax)';
Score = zeros(NumRow,1);
for i = 1:NumRow
 if strmatch(upper(Analyte), 'MASS', 'exact')
  Score(i) = sum(cellextract(DataTable(i).PartMass,1)./ ...
           cellextract(DataTable(i).HitRatio,1) .* ...
            cellextract(DataTable(i).BusyScale,1))/DataTable(i).AirVolume;
 else
  phi = cellextract(DataTable(i).Phi,1);
  eval(sprintf('resp = cellextract(DataTable(i).Resp%s,1);',Analyte));
  bs = cellextract(DataTable(i).BusyScale,1);
  Score(i) = sum(phi.*resp.*bs)/DataTable(i).AirVolume;
```

```
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```

```
clear phi resp
 end
 end
 Y = MOI(:,1)./Score;
case 11
 X = sqrt(RefTable(:).DaMin .* RefTable(:).DaMax)';
 for i = 1:NumRow
 NumHit(i) = length(cellextract(DataTable(i).Da,1));
 NumSized(i) = length(cellextract(DataTable(i).SizeDa,1));
 end
 Y = NumHit./NumSized; Y = Y';
end
%--- Get sampling period and size bin info ---%
[EventCode,uidx] = unique(RefTable(:,'EventCode'));
[xx,i] = sort(uidx); EventCode = EventCode(i); clear xx i uidx
NumEvent = length(EventCode);
SizeInts = unique([RefTable(:).DaMin;RefTable(:).DaMax]','rows');
DaMin = SizeInts(:,1); DaMax = SizeInts(:,2);
NumBin = size(SizeInts,1); clear SizeInts
%---- Plotting Formats ---%
close all
set(gcf,'PaperOrientation','landscape','PaperPosition',[0 0 11 8.5])
set(gca,'Visible','off');
set_font('Times',16)
%set_font('Helvetica',12)
Symbol = 'os^dp<hv>';
Color = [1 \ 0 \ 0; ... \% red
     0 1 0; ... % green
     0 0 1; ... % blue
     1 0 1; ... % magenta
     0 1 1; ... % cyan
   .66 .66 .66; ... % gray
     0 0 0]; % black
if NumBin > size(Color,1)
 error('Too many size bins for current color scheme');
end
hold on:
h1 = axes('Position',[.136.1760.5.647]);
h2 = axes('Position', [.705.1760.204.647]);
%---- Plot the Data Points and Error Bars ---%
axes(h1); box on;
for i = 1:NumRow
 idx1 = strmatch(cellextract(RefTable(i,'EventCode'),1),EventCode,'exact');
 idx2 = find(DaMin == RefTable(i,'DaMin') & DaMax == RefTable(i,'DaMax'));
 plot_symbol(i,X,Y,idx1,idx2,Symbol,Color)
 clear idx1 idx2
end
%--- Set Axis Limits and Draw 1:1 Lines ---%
\lim = axis;
axis square
switch PlotNum
case 1
 \lim(1) = 0; \lim(3) = 0; axis(\lim);
case {2,5}
 Amax = max(lim([2 4]));
 axis([0 Amax 0 Amax]);
```

```
h11(1) = line([0 Amax],[0 Amax]);
 h11(2) = line([0 Amax], [0 0.5*Amax]);
 h11(3) = line([0 0.5*Amax], [0 Amax]);
 set(h11(:),'LineStyle','--','Color',[.5.5.5])
case {3,4,9,10}
 \lim(1) = \min(\operatorname{RefTable}(:).\operatorname{DaMin})-0.01;
 \lim(2) = \max(\operatorname{RefTable}(:).\operatorname{DaMax})+0.01;
 \lim(3) = 10^{floor}(\log 10(\operatorname{nanmin}(Y)));
 lim(4) = 10^{ceil}(log10(nanmax(Y)));
 axis(lim);
 set(h1,'XScale','log','YScale','log');
 set(h1,'XTick',round(100*union(RefTable(:).DaMin,RefTable(:).DaMax))/100);
case {6,7,8}
 \lim(1) = 10^{floor}(\log 10(\min([\min(X) \min(Y)]))); \lim(3) = \lim(1);
 \lim(2) = 10^{\operatorname{ceil}}(\log 10(\max([\max(X) \max(Y)]))); \lim(4) = \lim(2);
 axis(lim);
 set(h1,'XScale','log','YScale','log');
 h11(1) = line(lim(1:2), lim(1:2));
 set(h11(:),'LineStyle','--','Color',[.5.5.5])
case 11
 lim(1) = min(RefTable(:).DaMin)-0.01;
 \lim(2) = \max(\operatorname{RefTable}(:).\operatorname{DaMax})+0.01;
 \lim(3) = 0; \lim(4) = 0.25;
 axis(lim);
 set(h1,'XScale','log','YScale','lin');
 set(h1,'XTick',round(100*union(RefTable(:).DaMin,RefTable(:).DaMax))/100);
end
%---- Label Plot with the R^2 Value ---%
\lim = axis:
R2 = r2strong(X(:,1),Y(:,1));
if strmatch(get(gca,'XScale'),'log') & strmatch(get(gca,'YScale'),'log')
 loglim = log10(lim);
 text(10^(loglim(1)+0.05*(loglim(2)-loglim(1))), ...
     10^(loglim(3)+0.95*(loglim(4)-loglim(3))), ...
     sprintf('R^2 = %1.2f',R2));
else
 text(0.05*lim(2), 0.95*lim(4), sprintf('R^2 = \%1.2f', R2));
end
```

```
%--- Make Legend ---%
axes(h2); box on;
legend_symbol(RefTable,[1:length(RowID)],Symbol,Color);
```

A.1.25 PLOT_SYMBOL.m

function plot_symbol(i,X,Y,idx1,idx2,Symbol,Color)
% PLOT_SYMBOL puts a colored symbol with error bars at a designated point
% See PLOT_SCATTER to understand the input requirements
% YAADA - Software Toolkit to Analyze Single-Particle Mass Spectral Data
% Copyright (C) 1999-2002 California Institute of Technology
% Copyright (C) 2001-2002 Arizona State University
% Prakash V. Bhave 30 Jul 2002

```
% Added symbols for NumEvent > 2*length(Symbol)
% Prakash V. Bhave 15 Sep 2003
% Error bars
if size(X,2) == 2
 plot([X(i)-X(i,2),X(i)+X(i,2)],[Y(i),Y(i)],'k-'); hold on
end
if size(Y,2) == 2
 plot([X(i),X(i)],[Y(i)-Y(i,2),Y(i)+Y(i,2)],'k-'); hold on
end
% Data points
if idx1 <= length(Symbol);
 hp(i) = plot(X(i), Y(i), ['k' Symbol(idx1)]); hold on
 set(hp(i),'MarkerSize',16,'MarkerFaceColor',Color(idx2,:));
% set(hp(i),'MarkerSize',10,'MarkerFaceColor',Color(idx2,:));
elseif idx1 \leq 2*length(Symbol);
 symb = Symbol(idx1 - length(Symbol));
 hp(i) = plot(X(i), Y(i), ['k' symb]); hold on
 set(hp(i),'MarkerSize',16,'MarkerFaceColor',Color(idx2,:));
% set(hp(i),'MarkerSize',10,'MarkerFaceColor',Color(idx2,:));
 hp2(i) = plot(X(i), Y(i), ['k' symb]); hold on
 set(hp2(i),'MarkerSize',6,'MarkerFaceColor',[1 1 1]);
else
 symb = Symbol(idx1 - 2*length(Symbol));
 hp(i) = plot(X(i), Y(i), ['k' symb]); hold on
```

```
set(hp(i),'MarkerSize',16,'MarkerFaceColor',[1 1 1]);
 hp2(i) = plot(X(i), Y(i), ['k' symb]); hold on
 set(hp2(i),'MarkerSize',6,'MarkerFaceColor',Color(idx2,:));
end
```

A.1.26 R2STRONG.m

function [R2,Strong] = r2strong(XVec,YVec,alpha) % R2STRONG determines if an R2 value provides "strong evidence" for correlation % Call as [R2,Strong] = R2STRONG(XVec,YVec,alpha) % where % XVec and YVec are vectors of data to be compared % alpha is the level of significance (OPTIONAL: defaults to 0.025) % R2 is the squared correlation coefficient of XVec, YVec % Strong is 1 if the correlation provides "strong evidence"; 0 otherwise % % Conditions for strong evidence are described in Supporting Information % section of Bhave, et al. 2002 % YAADA - Software Toolkit to Analyze Single-Particle Mass Spectral Data % % Copyright (C) 1999-2002 California Institute of Technology % Copyright (C) 2001-2002 Arizona State University % Prakash V. Bhave - revision history % 30 Apr 2002 original code % 13 Mar 2004 revised R2 calculation to ignore NaN values

% Check inputs

if nargin $< 2 \mid$ nargin > 3

```
error('Call as R2STRONG(XVec,YVec,alpha)');
end
if ~isvector(XVec) | ~isvector(YVec)
error('Expecting vectors for XVec and YVec');
elseif length(XVec) ~= length(YVec)
error('XVec and YVec must have same length');
else
idx = find(~isnan(XVec)&~isnan(YVec));
XVec = XVec(idx); YVec = YVec(idx);
end
if ~exist('alpha','var')
 alpha = .025;
elseif ~isnumeric(alpha) | ~isscalar(alpha)
error('Expecting numeric scalar for alpha');
elseif alpha >= 0.5 \mid alpha \leq 0
error('alpha must be between 0 and 0.5');
end
% Calculate R2 value
if length(XVec) < 3
R2 = NaN; Strong = 0;
return
end
Corr = corrcoef(XVec,YVec);
R2 = Corr(1,2)^2; clear Corr
% Calculate critical R2 value
df = length(XVec) - 2;
Ttest = tinv(1-alpha,df);
R2crit = (Ttest^2/df)/(1+Ttest^2/df); clear df Ttest
% Check if a single value is responsible for the correlation
if R2 > R2crit
% Calculate critical R2 value for N-1 element vector
df = length(XVec) - 3;
if df == 0
 Strong = 0; return
end
Ttest = tinv(1-alpha,df);
r2crit = (Ttest^2/df)/(1+Ttest^2/df); clear df Ttest
% Loop over input vectors, removing one element at a time
 AllIdx = 1:length(XVec);
 for i = AllIdx
 xvec = XVec(setdiff(AllIdx,i));
 yvec = YVec(setdiff(AllIdx,i));
 % calculate r2 value
 corr = corrcoef(xvec,yvec);
 r2 = corr(1,2)^2;
 if r2 < r2crit
  Strong = 0; return
% Strong = 1; disp(i);
 else
  Strong = 1;
 end
end
else
Strong = 0;
end
return
```

A.1.27 RATIO_METHOD.m

% RATIO_METHOD estimates BusyTime parameters using ATOFMS malfunctioning periods

%

% Written by: Prakash Bhave

16-May-2004 %

% Load data from COLLECT_BUSYDATA

% clear all

% load Fresno_busy Hit Time PosInFolder

% Define time periods when ATOFMS instrument malfunctioned FunnyTime = { ...

```
[datenum('16-Jan-2001 21:50:00') datenum('17-Jan-2001 02:00:00')]; ...
[datenum('28-Jan-2001 03:35:00') datenum('28-Jan-2001 11:15:00')]; ...
[datenum('31-Jan-2001 04:30:00') datenum('31-Jan-2001 08:45:00')]; ...
[datenum('01-Feb-2001 07:50:00') datenum('01-Feb-2001 10:40:00')]; ...
[datenum('02-Feb-2001 06:10:00') datenum('02-Feb-2001 10:00:00')]; ...
};
```

% FunnyTime = { ...

[datenum('16-Jan-2001 22:00:00') datenum('17-Jan-2001 03:00:00')]; ... %

[datenum('28-Jan-2001 03:00:00') datenum('28-Jan-2001 12:00:00')]: ... %

% [datenum('31-Jan-2001 04:30:00') datenum('31-Jan-2001 08:45:00')]; ...

% [datenum('01-Feb-2001 07:50:00') datenum('01-Feb-2001 10:40:00')]; ...

% [datenum('02-Feb-2001 06:10:00') datenum('02-Feb-2001 10:00:00')]; ... };

```
%
```

% Define constants and plotting parameters close all Colors = 'bgrcmyk'; BinLength = .1/24; % 6 minutes Smoothing = .5/24; % 30-min moving average SecPerDay = 3600*24;MISRT = []; BTMIS = [];

```
% Loop over each instrument malfunction episode
for i = 1:length(FunnyTime)
 timerange = FunnyTime{i};
 start = floor(timerange(1));
 stop = ceil(timerange(2));
 idx = range_search(Time','=',[start stop]);
 funtime = Time(idx);
 funhit = Hit(idx);
 funpos = PosInFolder(idx); clear idx
```

```
% Loop over subintervals within each period; get #hits, #misses, avg folder pos
numbin = floor((stop-start)/BinLength)
 [bincut,binmid] = split_bin(start,stop,numbin,'lin');
 for j = 1:numbin
 jdx = range_search(funtime', '=', bincut(j:j+1));
  numhit(j) = sum(funhit(jdx));
  nummis(j) = length(jdx)-numhit(j);
  if numhit(j)
   avgpos(j) = sum(funpos(jdx).*funhit(jdx))/numhit(j);
  else
```

```
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```

```
avgpos(j) = NaN;
end
clear jdx
end
```

```
% Smooth acquisition rates using a moving average filter
smohit = numhit;
smomis = nummis;
npt = round((Smoothing/BinLength)/2);
for j = (1+npt):(numbin-npt)
smohit(j) = mean(smohit(j-npt:j+npt));
smomis(j) = mean(smomis(j-npt:j+npt));
end; clear j
```

```
% Interpolate across the malfunctioning episode
funidx = find(bincut >= timerange(1) & bincut < timerange(2));
kdx = setdiff([1:numbin],funidx);
esthit = interp1(binmid(kdx),smohit(kdx),binmid);
estmis = interp1(binmid(kdx),smomis(kdx),binmid);
clear kdx
```

```
% Calculate ratio of excess misses to lost hits during malfunction
xmis = nummis-estmis;
xhit = esthit-numhit;
ratio = xmis(funidx)./xhit(funidx);
% Plot the ratio versus average folder position
figure(1);
plot(avgpos(funidx),ratio,[Colors(i) 'o']); hold on
```

```
% Estimate time required to record a miss
btmis = (numhit-esthit)./(numhit.*estmis - esthit.*nummis);
btmis = BinLength*SecPerDay*btmis(funidx);
% Plot this estimate versus #miss/seconds
figure(2); hold on
plot(nummis(funidx)/(BinLength*SecPerDay),btmis,[Colors(i) 'o']);
```

```
% Plot time series of #hit, #miss during malfunctioning date(s)
figure;
plot(binmid,numhit/(BinLength*SecPerDay),'kx'); hold on
plot(binmid,smohit/(BinLength*SecPerDay),'k-')
plot(binmid,esthit/(BinLength*SecPerDay),'k.')
plot(binmid,nummis/(BinLength*SecPerDay),'rx')
plot(binmid,smomis/(BinLength*SecPerDay),'r-')
plot(binmid,estmis/(BinLength*SecPerDay),'r.')
hleg = legend({'Actual Hits'; 'Averaged Hits'; 'Estimated Hits'; ...
'Actual Misses';'Averaged Misses';'Estimated Misses'});
set(hleg,'FontSize',12);
ylabel('Particle Detection Rate [Hz]');
xlabel_timedate;
```

```
% Aggregate resulting data into a single vector
MISRT = [MISRT nummis(funidx)/(BinLength*SecPerDay)];
i
```

BTMIS = [BTMIS; btmis'];

clear timerange start stop fun* numbin bin* num* smo* est* x* avgpos npt clear ratio btmis end; clear i

% Format figures

```
figure(1);
set(gca,'YLim',[-20 30]);
xlabel('Average Folder Position of Hit Particles');
ylabel('Ratio of Misses Gained to Hits Lost');
for i = 1:length(FunnyTime)
  LegText{i} = datestr(min(floor(FunnyTime{i})),1);
end
hleg = legend(LegText);
set(hleg,'FontSize',12);
```

```
figure(2);
xlim = get(gca,'XLim');
set(gca,'XLim',[2.5 xlim(2)]);
set(gca,'YLim',[0.5]);
ylabel('Estimated Miss Recording Time [s]');
xlabel('Missed Particle Detection Rate [Hz]');
hleg = legend(LegText);
set(hleg,'FontSize',12);
```

```
% Display important results to screen
disp('Estimate of Miss Recording Time [s]');
disp(sprintf(' Mean = %5.4f',mean(BTMIS(find(MISRT>3)))));
disp(sprintf(' Sigma = %5.4f',std(BTMIS(find(MISRT>3)))));
disp(sprintf(' N = %d',length(find(MISRT>3))));
```

A.1.28 REGRESS_IMPACTOR.m

function OutTable = regress_impactor(RefTable,DataTable,Analyte,Model,Guess)
% REGRESS_IMPACTOR compares ATOFMS and impactor data by nonlinear regression
%

- % To calculate particle detection efficiencies, call as:
- % PhiTable = REGRESS_IMPACTOR(RefTable,HitSizeTable,'Mass',Model,Guess)

% where

- % RefTable is the output of COLLECT_IMPACTOR
- % HitSizeTable is the output of COLLECT_HITSIZE
- % Model is the regression model (e.g. 'dapower')
- % Guess are the initial guesses of the parameter values
- % PhiTable is a table object with the following columns:
- % Column Name Type Description

% -----

- % SampleCode Word Unique identifier for particle ensemble (primary key)
- % AirVolume Double Air volume sampled during time period (m3)
- % PID Cell Particle identifiers in the ensemble
- % Da Cell Measured particle aerodynamic diameter (um)
- % PartMass Cell Estimated masses of individual particles (ug)
- % Phi Cell Scaled ATOFMS counts
- % YHatMass Cell Scaled ATOFMS Mass concentration w/CI (ug/m3)

%

- % Two steps are required to calculate NH4 and NO3 senstivities:
- % 1. First run REGRESS_IMPACTOR with Analyte = 'Mass' to obtain PhiTable.
- % 2. Then, run REGRESS_IMPACTOR again by calling as:

% where

- % Guess must contain 2 rows (1st row for NH4, 2nd row for NO3)
- % PhiTable is described above
- % ScaledTable has columns of PhiTable plus the following:
- % Column Name Type Description
- % -----
- % YHatNH4 Cell Scaled ATOFMS NH4 concentration w/CI (ug/m3)

% YHatNO3 Cell Scaled ATOFMS NO3 concentration w/CI (ug/m3) % YAADA - Software Toolkit to Analyze Single-Particle Mass Spectral Data % % Copyright (C) 1999-2002 California Institute of Technology % Copyright (C) 2001-2002 Arizona State University % % Prakash V. Bhave - revision history % 30 Apr 2002 original code % 30 Oct 2002 revised for compatibility with MATLAB Rel.12 changed "nlinfit" to "nlinfit_table" % % 13 Mar 2004 redefined RegIdx to exclude data when MOIConc=NaN % PhiTable is generated with same # of rows as RefTable % 27 Apr 2004 replaced div by AirVolume with mult by BusyScale % 28 Apr 2004 changed definition of AirVolume and added it back in % Check inputs if nargin $\sim = 5$ error('Five input arguments are required. See help text.'); end if ~isa(RefTable,'table') | ~isa(DataTable,'table') error('Expecting table objects for RefTable and DataTable'); elseif ~cellcmp(RefTable(:).SampleCode,DataTable(:).SampleCode) error('SampleCodes in RefTable and DataTable must be identical'); end if ~iscell(Analyte) junk = Analyte; clear Analyte Analyte{1} = junk; clear junk end for i = 1:length(Analyte) if isempty(strmatch(upper(Analyte{i}),upper(RefTable.Collist),'exact')) error(sprintf('%s must be a column of RefTable', Analyte{i})); end end if isempty(strmatch(upper(Analyte{1}),'MASS')) & ... isempty(strmatch('phi',lower(DataTable.Collist),'exact')) error('Must calculate Phi before chemical sensitivities can be determined'); end [ModelName,ModelExt] = strtok(Model,'_'); if exist(ModelName) $\sim = 2$ error(sprintf('Invalid Model: %s',Model)); end if ~isnumeric(Guess) error('Expecting numeric for Guess'); elseif length(Analyte) ~= size(Guess,1) error('Guess must have one row for each Analyte'); end % Initialize variables NumEnsemb = length(RefTable(:).SampleCode); % Loop over each analyte for i = 1:length(Analyte) analyte = Analyte $\{i\}$; % Extract impactor data from RefTable MOIConc = zeros(NumEnsemb,2); for j = 1:NumEnsemb eval(sprintf('MOIConc(j,:) = cellextract(RefTable(j).%s,1);',analyte)); end

RegIdx = find(~isnan(MOIConc(:,1)));

```
% Calculate multiplying factor for each individual particle
if strmatch(upper(analyte), 'MASS', 'exact')
 for j = 1:NumEnsemb
   partmass = cellextract(DataTable(j).PartMass,1);
   hitratio = cellextract(DataTable(j).HitRatio,1);
   busyscale = cellextract(DataTable(j).BusyScale,1);
   if strmatch(ModelExt,'_sized','exact')
    Multiplier{j} = (partmass.*busyscale./hitratio) / DataTable(j).AirVolume;
   else
    Multiplier{j} = (partmass.*busyscale) / DataTable(j).AirVolume;
   end
 end
 clear partmass
else
 for j = 1:NumEnsemb
 phi = cellextract(DataTable(j).Phi,1);
 eval(sprintf('resp = cellextract(DataTable(j).Resp%s,1);',analyte));
 busyscale = cellextract(DataTable(j).BusyScale,1);
 Multiplier{j} = (phi .* resp .* busyscale) / DataTable(j).AirVolume;
 clear phi resp
% Tried normalizing data to give equal weight to low-NO3 size/time bins
% if ModelName == 'no3matrix'
% Multiplier{j} = Multiplier{j}/MOIConc(j,1);
% MOIConc(j,:) = [1 0];
% end
 end
end
% Make RegTable for regression calculations
CodeCol = column('SampleCode','Code for particle ensemble', ...
           ",'Word',1,0,RefTable(:).SampleCode);
DaCol = column('Da','Aerodynamic diameter','um','cell',0,0, ...
           DataTable(:).Da);
HRCol = column('HitRatio','Hit ratio',",'cell',0,0, ...
           DataTable(:).HitRatio);
MultCol = column('Multiplier','multiplier','ug/m3','cell',0,0,Multiplier);
RegTable = table('RegTable',CodeCol,DaCol,HRCol,MultCol);
% Futile attempt to quantify matrix effects on NO3 sensitivity (Sep-2002)
% if ModelName == 'no3matrix'
% RegTable = table(RegTable,DataTable.Matrix);
% end
RegTable.name = 'RegTable';
RegTable = RegTable(RegIdx);
% Run nonlinear regression
[BetaHat Resid Jacobian] = nlinfit_table(RegTable,MOIConc(RegIdx,1), ...
                ModelName,Guess(i,:));
BetaCI = nlparci(BetaHat,Resid,Jacobian);
[YHat,YHatErr] = table_nlpredci(ModelName,RegTable,BetaHat,Resid,Jacobian);
for j = 1:length(BetaHat)
 Coef(j,1) = BetaHat(j);
 Coef(j,2) = BetaCI(j,2) - BetaHat(j);
end
disp(sprintf('Calculated regression coefficients for %s',analyte));
if length(BetaHat) == 2
 disp(sprintf('preexponent = \%0.6g + ... \%0.6g',Coef(1,:)));
 disp(sprintf(' exponent = %1.4f +/- %1.4f',Coef(2,:)));
else
```

```
format long; disp(Coef); format
% Make OutTable
if strmatch(upper(analyte),'MASS')
switch lower(Model)
 case {'dapower','logda2','logda3','hrpower','daslide'}
  for j = 1:NumEnsemb
   da
             = cellextract(DataTable(j).Da,1);
   hr
             = cellextract(DataTable(j).HitRatio,1);
   if strmatch('dapower', Model, 'exact')
    Phi{j}
               = \operatorname{Coef}(1,1) * \operatorname{da} \land \operatorname{Coef}(2,1);
   elseif strmatch('logda2',Model,'exact')
              = \exp(\operatorname{Coef}(1,1)^*(\log(\operatorname{da})).^2 + \operatorname{Coef}(2,1)^*\log(\operatorname{da})...
    Phi{j}
                                  + \text{Coef}(3,1));
   elseif strmatch('logda3',Model,'exact')
    Phi{j}
               = \exp(\operatorname{Coef}(1,1)*(\log(\operatorname{da})).^3 + \operatorname{Coef}(2,1)*(\log(\operatorname{da})).^2 + \dots
                 Coef(3,1)*log(da) + Coef(4,1));
   elseif strmatch('hrpower', Model, 'exact')
              = 1./hr .^ Coef(1);
    Phi{j}
   elseif strmatch('daslide', Model, 'exact')
    phi(find(da \le 1)) = Coef(1);
    phi(find(da > 1)) = Coef(1)*da(find(da > 1)).^Coef(2);
    Phi{j} = phi'; clear phi
   end
   if intersect(RegIdx,j)
    [junk x] = intersect(RegIdx,j); clear junk
    YHatMass{j} = [YHat(x),YHatErr(x)]; clear x
   else
    YHatMass{j} = [NaN NaN]; % YHatMass = NaN when MOIConc = NaN
   end
  end
  PhiCol = column('Phi', 'Scaled ATOFMS counts', ", 'Cell', 0, 0, Phi);
  YHatCol = column('YHatMass', 'Scaled ATOFMS Mass concentration w/CI', ...
               'ug/m3','Cell',0,0,YHatMass);
  OutTable = table(DataTable,PhiCol,YHatCol);
  OutTable.name = 'PhiTable';
 case {'dapower_sized','logda2_sized','logda3_sized'}
  for j = 1:NumEnsemb
   da
             = cellextract(DataTable(j).Da,1);
               = cellextract(DataTable(i).PartMass.1):
   mass
   hr
             = cellextract(DataTable(j).HitRatio,1);
   if strmatch('dapower', Model)
    Eta{j}
              = \operatorname{Coef}(1,1) * \operatorname{da} \land \operatorname{Coef}(2,1);
    Phi{j} = Eta{j}./hr;
   elseif strmatch('logda2',Model)
               = \exp(\operatorname{Coef}(1,1)*(\log(\operatorname{da})).^{2} + \operatorname{Coef}(2,1)*\log(\operatorname{da})...
    Eta{j}
                                  + \text{Coef}(3,1));
    Phi{j} = Eta{j}./hr;
   elseif strmatch('logda3',Model)
                = \exp(\operatorname{Coef}(1,1)*(\log(\operatorname{da})).^3 + \operatorname{Coef}(2,1)*(\log(\operatorname{da})).^2 + \dots
    Eta{j}
                 Coef(3,1)*log(da) + Coef(4,1));
    Phi{j} = Eta{j}./hr;
   end
   YHatMass{j} = [YHat(j), YHatErr(j)];
  end
  PhiCol = column('Phi', 'Scaled ATOFMS counts', ", 'Cell', 0, 0, Phi);
  EtaCol = column('Eta', 'Scaled ATOFMS counts', ", 'Cell', 0, 0, Eta);
```

YHatCol = column('YHatMass','Scaled ATOFMS Mass concentration w/Cl', ...

'ug/m3','Cell',0,0,YHatMass);

end

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```
OutTable = table(DataTable,PhiCol,EtaCol,YHatCol);
  OutTable.name = 'EtaTable';
 end
else
 for j = 1:NumEnsemb
  if ismember(j,RegIdx)
    jdx = find(RegIdx == j);
    YHatSpec{j} = [YHat(jdx), YHatErr(jdx)];
   else
    YHatSpec{j} = [NaN NaN];
   end
 end
 eval(['YHatCol = column(' sprintf("'YHat%s",',analyte) ...
      "Scaled ATOFMS ' sprintf('%s',analyte) ' concentration w/CI", ' ...
          "ug/m3","Cell",0,0,YHatSpec);']);
 if i == 1
  OutTable = table(DataTable,YHatCol);
 else
   OutTable = table(OutTable,YHatCol);
 end
 OutTable.name = 'ScaledTable';
end
end
```

A.1.29 SAMPLE_AIRVOL.m

```
function AirVolTable = sample_airvol(InstCode,Start,Stop,NumBin)
% SAMPLE_AIRVOL calculates the air volume sampled by ATOFMS during specified
%
          time periods. Off-line time and busy time are calculated
%
          in the process.
% Call as AirVolTable = SAMPLE_AIRVOL(InstCode,Start,Stop,NumBin)
% where InstCode is an ATOFMS instrument code or cell array of InstCodes
%
      Start is beginning of the study period (numeric scalar)
%
            is end of the study period (numeric scalar)
      Stop
      NumBin is number of individual time bins
%
%
% Can also be called as: AirVolTable = SAMPLE_AIRVOL(InstCode,Start,Stop)
% where Start and Stop are vectors containing the StartTime and StopTime of
%
     each time period of interest (e.g. IOPs)
%
% AirVolTable is a table with this form:
% Column Name Type
                           Description
%
       _____ ___
%
   Start
                     Start of time bin (primary key)
            Time
%
   Stop
             Time
                     Stop of time bin
% HitCount Single number of hit particles in time bin
% MissCount Single
                        number of missed particles in time bin
% AvgHitPos Double
                         average position of hit particles in folder
% OffLineTime Double
                          time instrument was off-line (d)
% BusyTime Double
                         time instrument was busy (d)
   AirVolume Double
                         Air volume sampled during time bin (m3)
%
% YAADA - Software Toolkit to Analyze Single-Particle Mass Spectral Data
%
% Copyright (C) 1999-2002 California Institute of Technology
% Copyright (C) 2001-2002 Arizona State University
```

- % Jonathan O. Allen 21 Jul 00
- % Prakash V. Bhave 26 Apr 02
- % Modifications by PVB
- % If no particles are hit, OffLineTime = length of time bin
- % Issue warning if BusyTime + OffLineTime exceeds SamplingTime
- % If time periods are consecutive, search ATOFMS data only once (for speed)
- % Start and Stop can be input as vectors
- % OffLinePeriod is hardcoded as 2 minutes
- % Added calculation of AirVolume, the air volume sampled by ATOFMS
- % Renamed function from SCALE_TIME to SAMPLE_AIRVOL
- % Renamed BusyTable to AirVolTable (sampled air volume is now the end result)
- % Allow cell array input for InstCode

global YAADA INST tic;

```
% Check inputs
if nargin == 4
 if ~isscalar(NumBin) | ~isnumeric(NumBin)
  error('Expecting numeric scalar for NumBin');
 end
 if ~isscalar(Start) | ~isnumeric(Start) | ~isscalar(Stop) | ~isnumeric(Stop)
  error('Expecting numeric scalars for Start and Stop');
 end
elseif nargin == 3
 if length(Start) ~= length(Stop)
  error('Start and Stop must be of the same length');
 end
 if ~isempty(find(Stop <= Start))
  error('StartTime must be less than StopTime');
 end
else
 error('Call as AirVolTable = SAMPLE_AIRVOL(InstCode,Start,Stop,NumBin)');
end
if ~iscell(InstCode)
if ~isword(InstCode)
 error('Expecting word for InstCode');
else
 InstCode = fillcell(1,length(Start),InstCode);
end
elseif length(InstCode) ~= length(Start)
error('InstCode and Start must be same length');
end
% Define BinStart, BinStop, NumBin, LengthPer
if length(Start) > 1
 ConsecFlag = 0;
 NumBin = length(Start);
 BinStart = Start;
 BinStop = Stop;
else
 ConsecFlag = 1;
 BinCut = split_bin(Start,Stop,NumBin,'lin');
 BinStart = BinCut(1:end-1);
 BinStop = BinCut(2:end);
end
LengthPer = BinStop - BinStart;
```

% Initialize variables

```
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```

```
HitCount = zeros(1,NumBin);
MissCount = zeros(1,NumBin);
AvgHitPos = zeros(1,NumBin);
% Collect PartIDs in a cell array
if ConsecFlag
 Query = sprintf('InstCode == %s and Time = [%f %f]', ...
            InstCode{1},BinStart(1),BinStop(NumBin));
 PartID = run_query(Query,'part',0);
 if length(PartID) \sim = 0
  PID = bin_on_column(PartID,'Time',BinCut);
 else
  PID\{1\} = PartID;
 end
 clear PartID BinCut
else
 for t = 1:NumBin
  Query = sprintf('InstCode == %s and Time = [%f %f]', ...
            InstCode{t},BinStart(t),BinStop(t));
  PID{t} = run_query(Query,'part',0);
 end
end
% Collect data for busy and off-line scaling
for t = 1:NumBin
 if length(PID\{t\}) ~= 0
 % get instrument specific information
  IID = unique(instid(PID{t}));
  if length(IID) > 1
   warning('Multiple InstID for %s between %s and %s', ...
        InstCode,datestr(BinStart(t)),datestr(BinStop(t)));
  end
             = search(INST.instid,'==',IID(1));
  InstIdx
  BusyTimeFcn = upper(char(INST(InstIdx, 'BusyTimeFunction')));
  BusyTimeParam = cellextract(INST(InstIdx, 'BusyTimeParam'),1);
  SampleFlow = INST(InstIdx).SampleFlow;
  % get particle data from database
  [Time,Hit,PosInFolder] = get_column(PID{t},'Time','Hit','PositionInFolder');
  % count hits and misses, calculate AvgHitPos
  HitCount(t) = sum(Hit);
  MissCount(t) = length(PID{t}) - HitCount(t);
  AvgHitPos(t) = mean(PosInFolder(find(Hit)));
  % calculate off-line time
  OffLinePeriod = 2/60/24; % default 2 min
  dt = [Time; BinStop(t)]-[BinStart(t); Time];
  OffLineTime(t) = sum(dt(find(dt >= OffLinePeriod)));
  % calculate busy time
  switch BusyTimeFcn
   case 'BUSY SCALE'
    % convert s to d
    BusyTime(t) = busy_scale(MissCount(t),HitCount(t),AvgHitPos(t),...
                   BusyTimeParam) / 24 / 3600;
   otherwise
    error(sprintf('Unknown busy time function %s',BusyTimeFcn));
  end
```

```
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```

```
else
 OffLineTime(t) = LengthPer(t);
 BusyTime(t) = 0;
 end
 % check whether BusyTime + OffLineTime exceeds SamplingTime
 if BusyTime(t) + OffLineTime(t) > LengthPer(t)
  warning(sprintf ...
      ('BusyTime + OffLineTime during period %i exceeds Sampling Time',t));
 end
 % calculate sampled air volume
 SampleTime = LengthPer(t) - OffLineTime(t) - BusyTime(t); % days
 AirVolume(t) = (SampleFlow*24*3600)*SampleTime; % convert to m3/s to m3/d
end
% make AirVolTable table
StartCol = column('Start','Start time of bin','d','Time',1,0,BinStart);
StopCol = column('Stop','Stop time of bin','d','Time',0,0,BinStop);
HitCol = column('HitCount','Number of Hit Particles', ...
           ",'single',0,0,HitCount);
MissCol = column('MissCount', 'Number of Missed Particles', ...
           ",'single',0,0,MissCount);
AvgPosCol = column('AvgHitPos', ...
           'Average Position of Hit Particles in Folder', ...
           ".'double',0,0,AvgHitPos);
OffCol = column('OffLineTime','Time Instrument Off-Line', ...
           'd', 'double', 0, 0, OffLineTime);
BusyCol = column('BusyTime','Time Instrument Busy', ...
           'd','double',0,0,BusyTime);
VolumeCol = column('AirVolume','Air Volume that ATOFMS Sampled', ...
           'm3','double',0,0,AirVolume);
AirVolTable = table('AirVolTable',StartCol,StopCol,HitCol,MissCol, ...
            AvgPosCol,OffCol,BusyCol,VolumeCol);
% report the elapsed time
if YAADA.Verbose
 t = toc;
 disp(sprintf('Calculated the air volume sampled by ATOFMS in %f s',t));
```

disp(' '); end

return

A.1.30 SPECIES_RESPONSE.m

function [RespNH4,RespNO3,ResponseTable] = species_response(PID,SampleCode)
% SPECIES_RESPONSE collects ATOFMS instrument response to NH4 and NO3
% Call as [RespNH4,RespNO3] = SPECIES_RESPONSE(PID)
% where
% PID is a cell array of PartID lists
% RespNH4 is a cell array of ATOFMS responses to NH4
% RespNO3 is a cell array of ATOFMS responses to NO3
% If user wishes to retain intermediate results, can also be called as:
% [RespNH4,RespNO3,ResponseTable] = SPECIES_RESPONSE(PID,SampleCode)
% where
% SampleCode is a cell array of particle ensemble identifiers
% ResponseTable is a table object with the following columns:

```
% Column Name Type Description
%
       ----- ----
% SampleCode Word Unique identifier for reference sample (primary key)
% PID
            Cell Particle identifiers matching reference sample
% Area18
             Cell Peak Area at m/z 18 [NH4+]
% Area30
            Cell Peak Area at m/z 30 [NO3-]
% ElevNoise Cell Peaks to ignore due to "elevated noise" (0 or 1)
% RespNH4 Cell ATOFMS response to NH4
% RespNO3
               Cell ATOFMS response to NO3
%
% The columns of type Cell in ResponseTable are vectors with one
% element for each particle ``hit" by ATOFMS during the IOP.
% YAADA - Software Toolkit to Analyze Single-Particle Mass Spectral Data
%
% Copyright (C) 1999-2002 California Institute of Technology
% Copyright (C) 2001-2002 Arizona State University
% Prakash V. Bhave 29 Apr 02
global YAADA
tic;
% Check inputs
if nargin == 1
if nargout \sim = 2
 error('[RespNH4,RespNO3] = SPECIES_RESPONSE(PID)');
end
if ~iscell(PID)
 error('Expecting cell array for PID');
end
elseif nargin == 2
if nargout \sim = 3
 error('[RespNH4,RespNO3,ResponseTable] = SPECIES_RESPONSE(PID,SampleCode)');
end
if ~iscell(SampleCode) | ~iscell(PID)
 error('Expecting cell arrays for SampleCode and PID');
end
if length(SampleCode) \sim =  length(PID)
 error('PID and SampleCode must be of the same length');
end
else
error('Invalid number of input arguments');
end
% Initialize variables
NumEnsemb = length(PID);
Area18 = cell(1,NumEnsemb);
Area30 = cell(1,NumEnsemb);
ElevNoise = cell(1,NumEnsemb);
RespNH4 = cell(1,NumEnsemb);
RespNO3 = cell(1,NumEnsemb);
% Collect ATOFMS instrument responses (ignore negative spectra)
for i = 1:NumEnsemb
 if isempty(PID\{i\}) == 0
  [negarea,posarea] = get_int_spectrum(PID{i},31,'Area',2,'sum');
  [negbs,posbs] = get_int_spectrum(PID{i},4,'BlowScale',2,'max');
  ElevNoise{i} = max(posbs(:,1:3),[],2);
  % Zero the responses from spectra with elevated noise levels
```

```
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```

```
noise_idx = find(ElevNoise{i});
  resp18 = posarea(:,18); Area18{i} = resp18;
  resp30 = posarea(:,30); Area30{i} = resp30;
  resp18(noise_idx) = 0;
  resp30(noise_idx) = 0;
  RespNH4\{i\} = resp18;
  RespNO3\{i\} = resp30;
  clear posarea posbs neg*
 end
end
if nargin == 2
% Make ResponseTable
 CodeCol
              = column('SampleCode','Code for sampling event', ...
               ",'Word',1,0,SampleCode);
 PIDCol
             = column('PID', 'Particle identifiers',", 'cell',0,0,PID);
 Area18Col
              = column('Area18','Peak areas at m/z 18 [NH4+]', ...
               'peak area', 'cell', 0, 0, Area 18);
 Area30Col
              = column('Area30','Peak areas at m/z 30 [NO3-]', ...
               'peak area', 'cell', 0, 0, Area 30);
 ElevNoiseCol = column('ElevNoise','Elevated noise in each spectrum', ...
               ",'cell',0,0,ElevNoise);
 RespNH4Col = column('RespNH4','ATOFMS response to NH4', ...
               'peak area','cell',0,0,RespNH4);
 RespNO3Col = column('RespNO3','ATOFMS response to NO3', ...
               'peak area','cell',0,0,RespNO3);
 ResponseTable = table('ResponseTable',CodeCol,PIDCol,Area18Col, ...
               Area30Col,ElevNoiseCol,RespNH4Col,RespNO3Col);
 ResponseTable.name = 'ResponseTable';
end
% report the elapsed time
if YAADA.Verbose
 t = toc;
```

```
disp(sprintf('Collected ATOFMS responses in %f s',t));
disp(' ');
end
```

A.1.31 TABLE_NLPREDCI.m

function [ypred, delta] = table_nlpredci(model,inputs,x,f,J)
%TABLE_NLPREDCI Confidence intervals for nonlinear least squares prediction.

- % where model input is a table.
- % [YPRED, DELTA] = NLPREDCI(MODEL, INPUTS, X, F, J) returns predictions,
- % YPRED, and 95% confidence interval delta on the nonlinear least
- % squares prediction X, given the residuals, F, and the Jacobian, J.
- %
- % The confidence interval calculation is valid for systems where the
- % length of F exceeds the length of X and J has full column rank at X.
- %
- % NLPREDCI uses the outputs of NLINFIT for its inputs.
- % Example:
- % [x,f,J] = nlinfit(input,output,model,xinit);
- % [yp, ci[= nlpredci(model,input,x,f,J);
- %
- % See also NLINFIT.
```
% Bradley Jones 1-28-94
% Copyright (c) 1993-98 by The MathWorks, Inc.
% $Revision: 2.9 $ $Date: 1998/07/10 14:45:54 $
% Prakash Bhave 7-30-01
% length(inputs) replaced with numrow(inputs)
%initialization
if nargin < 5
 error('Requires five inputs. Usage: [P, D] = NLPREDCI(MODEL, INPUTS, X, F, J)');
end;
f = f(:);
[m,n] = size(J);
if m \le n
 error('The number of observations must exceed the number of parameters.');
end;
if length(x) \sim = n
 error('The length of X must equal the number of columns in J.')
end;
% approximation when a column is zero vector
temp = find(max(abs(J)) == 0);
if ~isempty(temp)
 J(temp,:) = J(temp,:) + sqrt(eps);
end;
%calculate covariance
[Q, R] = qr(J,0);
Rinv = R eye(size(R));
evalstr = [model, '(x, inputs)'];
ypred = eval(evalstr);
delta = zeros(numrow(inputs),length(x));
for i = 1:length(x)
 change = zeros(size(x));
 change(i) = sqrt(eps)*x(i);
 evalstr1 = [model,'(x+change,inputs)'];
  predplus = eval(evalstr1);
  delta(:,i) = (predplus - ypred)/(sqrt(eps)*x(i));
end
E = delta * Rinv;
delta = sqrt(sum(E.*E,2));
v = m-n;
rmse = sqrt(sum(f.*f)/v);
% Calculate confidence interval
delta = delta .* rmse * tinv(0.975,v);
```

A.1.32 TABULATE_RESIDUAL.m

function ResidTable = tabulate_residual(ImpactorTable,ScaledTable)
% TABULATE_RESIDUAL constructs a table of residual concentrations
% Call as ResidTable = TABULATE_RESIDUAL(ImpactorTable,ScaledTable)

```
% where
% ImpactorTable is the output of COLLECT_IMPACTOR
% ScaledTable is the output of REGRESS_IMPACTOR (may also use PhiTable)
%
% ResidTable is a table object with the following columns:
% Column Name Type Description
% -----
% SampleCode Word Unique identifier for particle ensemble (primary key)
% ResidMass Double Residual Mass concentration (ug/m3)
% ResidNH4 Double Residual NH4 concentration (ug/m3)
% etc. for all species that have been quantified
% YAADA - Software Toolkit to Analyze Single-Particle Mass Spectral Data
%
% Copyright (C) 1999-2002 California Institute of Technology
% Copyright (C) 2001-2002 Arizona State University
% Prakash V. Bhave 30 Apr 02
% Check inputs
if nargin \sim = 2
error('Call as TABULATE_RESIDUAL(ImpactorTable,ScaledTable)');
end
if ~isa(ImpactorTable,'table') | ~isa(ScaledTable,'table')
error('Expecting table objects for ImpactorTable and ScaledTable');
elseif ~cellcmp(ImpactorTable(:).SampleCode,ScaledTable(:).SampleCode)
error('SampleCodes in ImpactorTable and ScaledTable must be identical');
end
% Make a list of ATOFMS analytes which have been quantified
SpecList = \{\};
idx = strmatch('YHat',ScaledTable.Collist);
NumAnalyte = length(idx);
for i = 1:NumAnalyte
 temp = cellextract(ScaledTable.ColList',idx(i));
 SpecList = {SpecList{:},temp(5:end)}; clear temp
end; clear i idx
% Calculate residual concentrations for each analyte
NumRow = numrow(ImpactorTable);
for i = 1:NumAnalyte
 analyte = SpecList\{i\};
 eval(sprintf('Y = ImpactorTable(:).%s;',analyte));
 eval(sprintf('YHat = ScaledTable(:).YHat%s;',analyte));
 for j = 1:NumRow
  resid = Y{j} - YHat{j}; resid = resid(1); % ignore error bounds
  eval(sprintf('Resid%s(j) = resid;',analyte)); clear resid
 end; clear j
 clear Y YHat
end; clear i
% Construct ResidTable
CodeCol = column('SampleCode','Particle ensemble identifier', ...
          ",'Word',1,0,ImpactorTable(:).SampleCode);
ResidTable = table('ResidTable',CodeCol);
for i = 1:NumAnalyte
 analyte = SpecList\{i\};
 eval(['ResidCol = column(' sprintf("'Resid%s",',analyte) ....
    "'Residual ' sprintf('%s',analyte) ' concentration", ' ...
```

ResidTable = table(ResidTable,ResidCol); end ResidTable.name = 'ResidTable';

return

A.1.33 TIMERES_BUSY.m

- % TIMERES_BUSY calculates the busytime scaling factors during a Fresno IOP.
- % Modify i to select a specific IOP
- % Modify NumPer to change the temporal resolution
- %
- % Written by Prakash Bhave 04-04-2004
- % adapted from COLLECT_PARTBIN

```
% Get IOP start and stop times
load Q:\CHUNKS\Fresno\quant\test ImpactorTable
StartTime = unique(ImpactorTable(:).Start);
StopTime = unique(ImpactorTable(:).Stop);
```

OffLinePeriod = .5/60/24; % 30 seconds

i = 6; % Choose an IOP (1,2,3,4,5, or 6) Query = sprintf('InstCode == JKE and Time = [%f %f]',StartTime(i),StopTime(i));

% Get particle data PID = run_query(Query,'part',0); [Hit,Time,Position] = get_column(PID,'Hit','Time','PositionInFolder');

```
% Select temporal resolution of BusyTime calcs
% NumPer = 1;
NumPer = round((StopTime(i) - StartTime(i))*24*12); % 5 minute periods
% NumPer = round((StopTime(i) - StartTime(i))*24*4); % 15 minute periods
% NumPer = 1; % Whole IOP in 1 period
[BinCut,BinMid] = split_bin(StartTime(i),StopTime(i),NumPer,'lin');
```

clear BusyScale BusyTime OffLineTime

```
for ii = 1:NumPer
idx = range_search(Time,'=',[BinCut(ii) BinCut(ii+1)]);
```

% calculate off-line time dt = [Time(idx); BinCut(ii+1)]-[BinCut(ii); Time(idx)]; OffLineTime(ii) = sum(dt(find(dt >= OffLinePeriod)));

```
BusyTimeFcn = upper(char(INST(1,'BusyTimeFunction')));
BusyTimeParam = cellextract(INST(1,'BusyTimeParam'),1);
SampleFlow = INST(1,'SampleFlow');
```

% calculate busy time HitIdx = find(Hit(idx));

```
% count hits and misses for time period
% HitCount, MissCount, AvgHitCount are for time bin
HitCount = length(HitIdx);
MissCount = length(idx) - HitCount;
if HitCount
% PositionInFolder only relevant for hit particles
AvgHitPos = mean(Position(idx(HitIdx)));
```

```
else
  AvgHitPos = 0;
 end
 switch BusyTimeFcn
  case 'BUSY_SCALE'
   BusyTime(ii) = busy_scale(MissCount,HitCount,AvgHitPos,BusyTimeParam);
   % convert s to d
   BusyTime(ii) = BusyTime(ii) / 24 / 3600;
  otherwise
   error(sprintf('Unknown busy time function %s',BusyTimeFcn));
 end
 % calculate busy time scaling factor
 BusyScale(ii) = (BinCut(ii+1) - BinCut(ii)) ./ ...
           (BinCut(ii+1) - BinCut(ii) - OffLineTime(ii) - BusyTime(ii));
end
BusyScale;
% Plot busyscale
% close all;
figure,
plot(BinMid,BusyScale,'bo');
ylabel('BusyScale');
% xlabel_timedate([get(gca,'xlim') NaN NaN],0);
set(gca, 'xtick', StartTime(i):(StopTime(i) - StartTime(i))/16:StopTime(i));
set(gca, 'xticklabel', datestr(get(gca, 'xtick'),15));
xlabel('Time');
title(sprintf('Fresno BusyScale IOP%d with 5-minute time interval.', i))
```

A.2 SCRIPTS FOR SCALING WITH APS AND SMPS

A.2.1 APS_SCALING_PART_1.m

% Thomas Rebotier, February 2007

 $scalingFileName = input(Please enter the path and name of the file used to save scaling information(n>(example: C:\\Soar1) \n>','s');$

fprintf(1, 'Saving current Matlab workspace in the file preScalingContext\n\n'); save preScalingContext

fprintf(1, 'About to run getAllAPSfiles. \nMake sure the APS files are correct. \nDetails Below. Example in scaling/APD_directory_example');

help getAllAPSfiles

 $APSdir = input('Now enter the directory name of the APS file directory\n(example: C:\SOAR1_APS) (n>',s');$

[X,Y,Z] = getAllAPSfiles(APSdir);

fprintf(1, 'about to run getAtofmsScaleData. Details Below.'); help getAtofmsPIDScaleData ExtraQuery = input('Now enter the PID or nothing (defaults to all hits), then hit ENTER\n>','s'); [mytimes, Da, atofmsBin, U] = getAtofmsPIDScaleData(Y, ExtraQuery, 1);

fprintf(1, 'about to bin Atofms data, average APS data, \nand compute ratio matrix. Details below.'); help discreteScaling

timeSlice = str2num(input('Enter the duration of a time slice, in hours. \forall Usually, just type "1"\n>','s'));

timeShift = str2num(input('Enter how many hours AHEAD of the ATOFMS computer he APS computer is. \forall Usually, just type "0"(n>','s'));

X = X - timeShift/24;

threshold = str2num(input('Enter the lowest number of particles desired to take a \nparticular time slice into account. Usually, just $100(n^{-1}, s')$;

[scalingMatrix, scalingTimes, allTimes, atofmsBins, apsAvg, xremove] = discreteAPSScaling(atofmsBin, mytimes, X, U, Z, timeSlice, threshold);

 $flowRate = str2num(input('Enter the volume correction factor, either as an absolute \nnumber (about 60,000) or as the ATOFMS liter/minute(n>','s'));$

if(flowRate<100)
flowRate = 60000*flowRate;
end
scalingMatrix = scalingMatrix * flowRate;
finiteindex = sum(isfinite(scalingMatrix),2);
remove = find(finiteindex==0);
scalingMatrix(remove,:) = [];</pre>

scalingTimes(remove) = [];

fprintf(1, 'Part 1 of the import is over. \nPLEASE INSPECT THE RATIO MATRIX, called scalingMatrix. \nYou need to remove lines that only have NaNs or Inf. \nremove them also from "scalingTimes", the variable that keeps track of \nwhat times the scaling curves correspond to, and possibly from other \nvariables (Bin, Da, etc...) if you plan on using these later');

fprintf(1, 'Once you are satisfied with the scaling \nmatrix, run part 2 of the script');

A.2.2 APS_SCALING_PART_2.m

% Thomas Rebotier, February 2007

hiY = max(find(U < 2.5))+1;

 $hiY = str2num(input(['To only work on PM 2.5 we must keep only the first ' int2str(hiY) ' bins. \nEnter this number below or change it if you want to scale over fewer or more bins\n>'],'s'));$

fprintf(1, 'about to run fitScalingModel. Details Below.'); help fitAPSScalingModel [crosspoint, polys1, residual1, ss1, polys2, residual2, ss2] = fitAPSScalingModel(Y, scalingMatrix, hiY);

plotAll = input('Do you want to plot all the scaling curves and compute the correlations? (n(answer "y" or "n" only please)(n>','s');

if (plotAll == 'y' | plotAll == 'Y' | plotAll == 'Yes' | plotAll == 'YES' | plotAll == 'yes')

 $plotDirectory = input('Create a directory to put all the figures in, \name here. Figures will be saved as TIFF.\name{number} (a batch converter) to turn them to GIFs for \nimport into GIF animators\n>','s');$

plotScaling(Y, hiY, scalingMatrix, crosspoint, polys1, polys2, scalingTimes, plotDirectory);

end

save(scalingFileName, 'scalingTimes', 'crosspoint', 'polys1', 'polys2', 'U', 'scalingMatrix','flowRate'); input(' We have now generated all scaling information. \nTo play around with the guts of the scaling and keep all \nintermediary variables abort this script now','s');

clear

load preScalingContext
load(scalingFileName);

A.2.3 DISCRETEAPSSCALING.m

% Thomas Rebotier, February 2007

function [scalingMatrix, scalingTimes, allTimes, atofmsBins, apsAvg, xremove] = discreteAPSScaling(atofmsBin, mytimes, X, U, Z, timeSlice, threshold)

% function [scalingMatrix, scalingTimes, atofmsBins, apsAvg] = discreteScaling(atofmsBin, mytimes, X, Y, Z, timeSlice, threshold)

```
% Computes the ratio of APS counts to binned atofms counts
```

% atofmsBin the vector of particle bins

```
% X Z the output of getAllAPSfiles
```

- % U from getAtofmsScaleData
- % TimeSlice is in hours, defaults to 1
- % threshold is how many paticles it takes to keep that hour, defaults to 100

```
if(~exist('timeSlice','var'))
  timeSlice = 1;
end
```

```
if(~exist('threshold','var'))
threshold = 100;
end
```

% Step 1: get scaling matrix for all times in APS dataset

```
lowtime = min(X);
hitime = max(X);
firstday = fix(X);
lastday = fix(X);
allAMShours = fix(24*X/timeSlice);
firsthour = min(allAMShours);
lasthour = max(allAMShours);
allhours = fix(24*mytimes/timeSlice);
atofmsBins = zeros(lasthour-firsthour+1, length(U)-1);
apsAvg = zeros(lasthour-firsthour+1, length(U)-1);
scalingTimes = zeros(lasthour-firsthour+1, 1);
```

```
for mytime = firsthour:lasthour
    i = mytime-firsthour+1;
    scalingTimes(i) = mytime * timeSlice/24;
    currentParts = find(allhours==mytime);
    currentAB = atofmsBin(currentParts);
    for mybin=1:(length(U)-1)
        atofmsBins(i, mybin) = length(find(currentAB==mybin));
    end
        apsAvg(i,:) = mean( Z(find(allAMShours==mytime),:), 1);
    end
```

scalingMatrix = apsAvg ./ atofmsBins ;

% Step 2: keep only PM2.5 and times with enough particles

```
remove = find(U >= 2.5);
if length(remove) > 1
  remove(1)=[];
end
remove(end)=[];
scalingMatrix(:,remove) = [];
```

```
smallerBins = atofmsBins;
smallerBins(:,remove)=[];
totalParts = sum(smallerBins,2);
xremove = find(totalParts < threshold);
scalingMatrix(xremove,:) = [];
allTimes = scalingTimes;
scalingTimes(xremove) = [];
```

return

A.2.4 DISCRETESMPSSCALING.m

% Thomas Rebotier, February 2007 function [scalingMatrix, scalingTimes, allTimes, atofmsBins, SMPSAvg, xremove] = discreteSMPSScaling(atofmsBin, mytimes, X, U, Z, timeSlice, threshold) % function [scalingMatrix, scalingTimes, atofmsBins, SMPSAvg] = discreteScaling(atofmsBin, mytimes, X, Y, Z, timeSlice, threshold) % Computes the ratio of SMPS counts to binned atofms counts % atofmsBin the vector of particle bins % X Z the output of getAllSMPSfiles % U from getAtofmsScaleData % TimeSlice is in hours, defaults to 1 % threshold is how many paticles it takes to keep that hour, defaults to 100 if(~exist('timeSlice','var')) timeSlice = 1;end if(~exist('threshold','var')) threshold = 100;end % Step 1: get scaling matrix for all times in SMPS dataset lowtime = min(X); hitime $= \max(X);$ firstday = fix(X);lastday = fix(X);allAMShours = fix(24*X/timeSlice);firsthour = min(allAMShours); lasthour = max(allAMShours); allhours = fix(24*mytimes/timeSlice); atofmsBins = zeros(lasthour-firsthour+1, length(U)-1); SMPSAvg = zeros(lasthour-firsthour+1, length(U)-1); scalingTimes = zeros(lasthour-firsthour+1, 1); for mytime = firsthour:lasthour

```
i = mytime-firsthour+1;
scalingTimes(i) = mytime * timeSlice/24;
currentParts = find(allhours==mytime);
currentAB = atofmsBin(currentParts);
for mybin=1:(length(U)-1)
    atofmsBins(i, mybin) = length(find(currentAB==mybin));
end
SMPSAvg(i,:) = mean( Z(find(allAMShours==mytime),:), 1);
```

```
end
```

scalingMatrix = SMPSAvg ./ atofmsBins ;

```
% % % % Step 2: keep only bins > 40 nm (Jake's lowest) and times with enough particles
% % %
% % % remove = find(U <= 40);
% % % % if length(remove) > 1
% % % % remove(1)=[];
% % % % remove(end)=[];
% % % % scalingMatrix(:,remove) = [];
```

```
smallerBins = atofmsBins;
% % smallerBins(:,remove)=[];
totalParts = sum(smallerBins,2);
xremove = find(totalParts < threshold);
scalingMatrix(xremove,:) = [];
allTimes = scalingTimes;
scalingTimes(xremove) = [];
return
```

A.2.5 FITAPSSCALINGMODEL.m

% Thomas Rebotier, February 2007 function [crosspoint, polys1, residual1, ss1, polys2, residual2, ss2] = fitAPSScalingModel(Y, scalingMatrix,

```
hiY);
```

% function [crosspoint, polys1, residual1, ss1, polys2, residual2, ss2] = fitAPSScalingModel(Y, scalingMatrix, hiY);

% Fits the log of the scaling matrix by two curves: a cubic for low Da bins % and a quadric for high Da bins.

```
if(~exist('hiY','var'))
  hiY = length(Y);
end
crosspoint = zeros(size(scalingMatrix,1),1);
residual = zeros(size(scalingMatrix,1),1);
\log SM = \log(scalingMatrix)/\log(10);
for i=1:size(scalingMatrix,1)
  [lowval, low] = min(scalingMatrix(i,:));
  crosspoint(i) = Y(low);
  lowline = scalingMatrix(i,1:low);
  lowidx = find(isfinite(lowline));
  % IF IT IS PRESENT, EMPHASIZE FIRST BIN BY DUPLICATING POINT (weight 4)
  if(lowidx(1)==1)
       lowidx = [1 \ 1 \ 1 \ lowidx];
  end
  highline = scalingMatrix(i,low:hiY);
  highidx = find(isfinite(highline));
  x1=Y(lowidx);
  if(lowidx(1)==1)
     x1(1)=0.5*(x1(1)+0.3);
     % IF IT IS PRESENT, EMPHASIZE FIRST BIN BY DUPLICATING POINT (weight 4)
     x1(2)=x1(1);
     x1(3)=x1(1);
     x1(4)=x1(1);
  end
  x2=Y(low-1+highidx);
  y=logSM(i,1:hiY);
  s1=0;
  s2=0;
  if(length(lowidx)>9)
         [poly1,s1] = polyfit(x1, y(lowidx), 5);
  else
     if(length(lowidx)>7)
         [poly1,s1] = polyfit(x1, y(lowidx), 4);
     else
       if(length(lowidx)>5)
```

```
[poly1,s1] = polyfit(x1, y(lowidx), 3);
       else
          if(length(lowidx)>3)
                    [poly1,s1] = polyfit(x1, y(lowidx), 2);
          else
            if(length(lowidx)>1)
                    [poly1,s1] = polyfit(x1, y(lowidx), 1);
            else
               if(length(lowidx)>0)
                    [poly1,s1] = polyfit(x1, y(lowidx), 0);
               end
            end
          end
       end
     end
  end
  if(length(highidx>2))
          [poly2,s2] = polyfit(x2, y(low-1+highidx), 2);
  else
     if(length(highidx>1))
                      [poly2,s2] = polyfit(x2, y(low-1+highidx), 1);
     else
       if(length(highidx>0))
                              [poly2,s2] = polyfit(x2, y(low-1+highidx), 0);
       end
     end
  end
  polys1(i,1:length(poly1)) = poly1;
  ss1{i} = s1;
  residual1(i) = s1.normr;
  polys2(i,1:length(poly2)) = poly2;
  ss2{i} = s2;
  residual2(i) = s2.normr;
end
```

A.2.6 FITSMPSSCALINGMODEL.m

if(lowidx(1)==1)

end s1=0;

x1(1)=0.5*(x1(1)+0.3);

```
% Thomas Rebotier, February 2007
function [polys, residual, ss] = fitSPMSScalingModel(Y, scalingMatrix, hiY);
% function [crosspoint, polys1, residual1, ss1, polys2, residual2, ss2] = fitSPMSScalingModel(Y,
scalingMatrix, hiY);
% Fits the log of the scaling matrix by one curves of degree 4.
if(~exist('hiY','var'))
hiY = length(Y);
end
residual = zeros(size(scalingMatrix,1),1);
logSM = log(scalingMatrix)/log(10);
for i=1:size(scalingMatrix,1)
lowline = scalingMatrix(i,:);
lowidx = find(isfinite(lowline));
x1=Y(lowidx);
y=logSM(i,1:hiY);
```

```
if(length(lowidx)>5)
          [poly1,s1] = polyfit(x1, y(lowidx), 5);
  else
     if(length(lowidx)>4)
          [poly1,s1] = polyfit(x1, y(lowidx), 4);
     else
       if(length(lowidx)>3)
          [poly1,s1] = polyfit(x1, y(lowidx), 3);
       else
          if(length(lowidx)>2)
                    [poly1,s1] = polyfit(x1, y(lowidx), 2);
          else
            if(length(lowidx)>1)
                    [poly1,s1] = polyfit(x1, y(lowidx), 1);
            else
               if(length(lowidx)>0)
                    [poly1,s1] = polyfit(x1, y(lowidx), 0);
               end
            end
          end
       end
     end
          end
  polys(i,1:length(poly1)) = poly1;
  ss{i} = s1;
  residual(i) = s1.normr;
end
```

A.2.7 GETALLAPSFILES.m

```
% Thomas Rebotier, February 2007
function [X,Y,Z] = getAllAPSfiles(dirname)
% function [X,Y,Z] = getAllAPS files (dirname)
% loads APS text files from the directory dirname
% files must be csv text files
% ALL AND ONLY THE DATA FILES MUST INCLUDE AN UNDERSCORE IN THEIR NAME
% returns Julian time in X, size bin centers in Y except Y(1) is bin upper
% bound, and data in Z.
%
% (c) T Rebotier, ucsd, 2006
% credit to John Holecek for getAPSfile
myfiles = dir(dirname);
% Now process files one by one
for i=1:length(myfiles)
  [T,R] = strtok(myfiles(i).name,'_');
  if(length(R)>0)
                   [x,y,z] = getAPSmatrix([dirname '\' myfiles(i).name]);
     if(~exist('X','var'))
       X = x;
       \mathbf{Y} = \mathbf{y};
       Z = z;
     else
                             X = [X; x];
                             Z = [Z; z];
     end
         end
end
```

return

A.2.8 GETALLSMPSFILES.m

% Thomas Rebotier, February 2007 function [X,Y,Z] = getAllSMPSfiles(dirname) % function [X,Y,Z] = getAllSMPS files (dirname) % loads SMPS text files from the directory dirname % files must be csv text files % ALL AND ONLY THE DATA FILES MUST INCLUDE AN UNDERSCORE IN THEIR NAME % returns Julian time in X, size bin centers in Y except Y(1) is bin upper % bound, and data in Z. % % (c) T Rebotier, ucsd, 2006 % credit to John Holecek for original getAPSfile myfiles = dir(dirname); % Now process files one by one for i=1:length(myfiles) [T,R] = strtok(myfiles(i).name,'_'); if(length(R)>0) [x,y,z] = getSMPSmatrix([dirname '\' myfiles(i).name]); if(~exist('X','var')) X = x; $\mathbf{Y} = \mathbf{y};$ Z = z;else if(size(Z,2) = size(z,2))X = [X; x];Z = [Z; z];end end end end return

A.2.9 GETAPSMATRIX.m

```
%%% retrieve APS matrix information
%%% 05 April 2004
%%% X = juliantime; Y = binmidpoints; Z = data
function [X,Y,Z] = getAPSmatrix(filename)
```

```
filestream = fopen(filename, 'r');
```

```
cnt = 0;
while(feof(filestream) == 0)
lstring = fgets(filestream);
if(lstring==-1)
break;
end
%% get size bins in APS data
if(strncmp('Sample #', lstring, 8))
bstring = lstring;
for i=1:5 %%% Read off first 5 columns for size bins, including <0.523 size bin
[a bstring] = strtok(bstring, ',');
```

```
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```

```
end:
     % Grab <.523 size bin
     Y0 = str2num(strtok(a, <'));
     Y = str2num(strtok(bstring, 'E'));%E marks end of size bins and beginning of text -- Event 1 ...
     Y = [Y0 Y];
  end;
   %% get data for each size bin
  if length(str2num(strtok(lstring, ','))) == 1
     cnt = cnt + 1;
     bstring = lstring;
     [a bstring] = strtok(bstring, ',');
     %% Parse date and time and convert to julian time
     [datestamp, bstring] = strtok(bstring, ',');
     [timestamp, bstring] = strtok(bstring, ',');
     [blank,bstring] = strtok(bstring, ',');% skip column
     % do not skip <523 size bin
     %[blank,bstring] = strtok(bstring, ',');% skip column
     X(cnt) = datenum(datestamp) + datenum(timestamp);
     for i=1:length(Y)
       [d bstring] = strtok(bstring, ',');
        Z(cnt,i) = str2num(d);
     end;
  end:
end:
\mathbf{X} = \mathbf{X'}:
fclose(filestream);
```

A.2.10 GETATOFMSPIDSCALEDATA.m

```
function [mytimes, Da, Bin, U] = getAtofmsPIDScaleData( Y, PIDin, unit)
%function [mytimes, Da, Bin, U] = getAtofmsPIDScaleData(Y, PIDin, unit)
% Gives Da converted to micron or nanometers depending on unit: micron =1 nano =2
% and the APS/SMPS bin according to the bins Y
% Y(1) is an upper bound, so S(:,1) is the counts of parts < Y(1)
% Y(i) i>1 is a bin center for a geometric bin size progression, so
% the other bounds are computed as the geometric mean of Y(i) and Y(i+1)
% PIDname allows to get scaling for a particular subset of particles
% without this parameter, the routine calls a run_query of all hits.
% RETURNS: particle time, Da, bin #, separators U. Bin of 0 is smaller than .3microns
% and bin # larger than the # of given bins is larger Da than allowed
% Thomas Rebotier, February 2007
u = (log(Y(end)) - log(Y(2))) / (length(Y)-2);
U = Y(1) * exp( u * (0:(length(Y)-1)));
U = [0.3 U];
if(~exist('PIDname','var'))
  ExtraQuery = 'Hit == 1';
  PID = run_query(ExtraQuery);
else
  if(length(PIDin) == 0)
     ExtraQuery = 'Hit == 1';
                   PID = run_query(ExtraQuery);
  else
     PID = PIDname;
  end
end
```

```
fprintf(1,'Got PID of %d particules\n', length(PID));
mytimes = get_column(PID,'Time');
fprintf(1,'Got TIMES\n');
Da = get_column(PID, 'Da');
fprintf(1,'Got Da\n');
% Converts Da to microns
t = min(100, length(PID));
testme = median(Da(1:t));
if(testme > 50 & unit == 1) % Da originally in nanometers must be in microns
  Da = Da/1000;
end
if(testme < 50 & unit == 2) % Da originally in microns must be in nanometers
  Da = Da*1000;
end
Bin = zeros(length(PID),1);
for col = 1:length(U)
  islarger = Da > U(col);
  Bin = Bin + islarger;
end
```

```
return
```

A.2.11 GETATOFMSSCALEDATA.m

```
function [mytimes, Da, Bin, U] = getAtofmsScaleData(Y, ExtraQuery, unit)
% function [mytimes, Da, Bin, U] = getAtofmsScaleData(Y, ExtraQuery, unit)
% Gives Da converted to (unit==1)microns or (unit==2) nanamoeters
% and the APS bin according to the bins Y
% Y(1) is an upper bound, so S(:,1) is the counts of parts < Y(1)
% Y(i) i>1 is a bin center for a geometric bin size progression, so
% the other bounds are computed as the geometric mean of Y(i) and Y(i+1)
% ExtraQuery allows to get scaling for a particular subset of particles
% for example 'polarity = 1 AND polarity = 2'
% for all other queries, and by default (no specified extra query) there is
% a default hit=1 clause.
% RETURNS: particle time, Da, bin #, separators U. Bin of 0 is smaller than .3microns
% and bin # larger than the # of given bins is larger Da than allowed
% Thomas Rebotier, February 2007
u = (log(Y(end)) - log(Y(2))) / (length(Y)-2);
U = Y(1) * exp( u * (0:(length(Y)-1)));
U = [0.3 U];
if(~exist('ExtraQuery','var'))
  ExtraQuery = 'Hit == 1';
else
  if(length(ExtraOuery) > 0)
     ExtraQuery = [ '( 'ExtraQuery ') AND Hit == 1'];
  else
     ExtraQuery = 'Hit == 1';
  end
```

end

PID = run_query(ExtraQuery); fprintf(1,'Got PID of %d particules\n', length(PID));

```
mytimes = get_column(PID,'Time');
fprintf(1,'Got TIMES\n');
Da = get_column(PID,'Da');
fprintf(1,'Got Da\n');
% Converts Da to microns
t = min(100, length(PID));
testme = median(Da(1:t));
if(testme > 50 & unit == 1) % Da originally in nanometers must be in microns
  Da = Da/1000;
end
if(testme < 50 & unit == 2) % Da originally in microns must be in nanometers
  Da = Da*1000:
end
Bin = zeros(length(PID),1);
for col = 1:length(U)
  islarger = Da > U(col);
  Bin = Bin + islarger;
end
return
```

A.2.12 GETSMPSMATRIX.m

```
%%% retrieve SMPS matrix information
%%% 05 April 2004
\%\%\% X = juliantime; Y = binmidpoints; Z = data
function [X,Y,Z] = getSMPSmatrix(filename)
filestream = fopen(filename, 'r');
cnt = 0;
while(feof(filestream) == 0)
  lstring = fgets(filestream);
  if(lstring==-1)
     break;
  end
   %% get size bins in SMPS data
  if(strncmp('Sample #', lstring, 8))
     bstring = lstring;
     for i=1:4 %%% Read off first 4 columns for size bins, excluding first size bin
       [a bstring] = strtok(bstring, ',');
     end;
     Y = str2num(strtok(bstring, 'S'));%S for 'Scan-up' marks end of size bins and beginning of text ...
  end;
  %% get data for each size bin
  if length(str2num(strtok(lstring, ','))) == 1
     cnt = cnt + 1;
     bstring = lstring;
     [a bstring] = strtok(bstring, ',');
     %% Parse date and time and convert to julian time
     [datestamp, bstring] = strtok(bstring, ',');
     [timestamp, bstring] = strtok(bstring, ',');
     [blank,bstring] = strtok(bstring, ',');% skip column
```

```
X(cnt) = datenum(datestamp) + datenum(timestamp);
```

```
for i=1:length(Y)
     [d bstring] = strtok(bstring, ',');
     Z(cnt,i) = str2num(d);
    end;
end;
end;
X = X';
fclose(filestream);
```

A.2.13 GRAPHAPS_SCALINGPERF.m

function graphAPS_ScalingPerf(crosspoint, polys1, polys2, scalingTimes, mytimes, Da, X, timeSlice, scalingFactor)

%function graphAPS_ScalingPerf(crosspoint, polys1, polys2, scalingTimes, mytimes, Da, X, timeSlice, scalingFactor)

% computes the scaled ATOFMS for each hour (or time slice) and compares it

% to the number from APS; graphs the result and gives the correlation outliers removed.

% Thomas Rebotier, February 2007

```
if(~exist('timeSlice','var'))
           timeSlice = 1;
         end
         lowtime = min(X);
         hitime = \max(X);
         firstday = fix(X);
         lastday = fix(X);
         allAMShours = fix(24*X/timeSlice);
         firsthour = min(allAMShours);
         lasthour = max(allAMShours);
         allhours = fix(24*mytimes/timeSlice);
         apsAvg = zeros(lasthour-firsthour+1, 1);
         scalingTimes = zeros(lasthour-firsthour+1, 1);
         APScount = zeros(lasthour-firsthour+1, 1);
         for mytime = firsthour:lasthour
            i = mytime-firsthour+1;
           currentParts = find(allhours==mytime);
           currentDa = Da(currentParts);
            currenttimes = mytimes(currentParts);
            APScount(i)=0;
            for part=1:length(currentDa)
              APScount(i) = APScount(i) + scaleAPS_Part(crosspoint, polys1, polys2, scalingTimes, currentDa(part),
currenttimes(part));
           end
            apsAvg(i,:) = sum(mean( Z(find(allAMShours==mytime),:), 1));
         end
         APScount = APScount/scalingFactor;
         figure
         plot(APSavg);
         hold on
         plot(apsAvg,'r');
         % remove outliers from off-line ATOFMS
         R2 = corr(APSavg, apsAvg)^2;
         text(length(scalingTimes)/2, 20, ['R2 = ' num2str(R2, '%7.5f')]);
```

return

function r = corr(x,y)

```
c = corrcoef(x,y);
r = c(1,2);
```

end

A.2.14 GRAPHSMPS_SCALINGPERF.m

```
function graphSMPS_ScalingPerf(polys, scalingTimes, mytimes, Da, X, timeSlice, scalingFactor)
         % function graphSMPS_ScalingPerf(polys, scalingTimes, mytimes, Da, X, timeSlice, scalingFactor)
         % computes the scaled ATOFMS for each hour (or time slice) and compares it
         % to the number from SMPS; graphs the result and gives the correlation outliers removed.
         % Thomas Rebotier, February 2007
         if(~exist('timeSlice','var'))
           timeSlice = 1;
         end
         lowtime = min(X);
         hitime = \max(X);
         firstday = fix(X);
         lastday = fix(X);
         allAMShours = fix(24*X/timeSlice);
         firsthour = min(allAMShours);
         lasthour = max(allAMShours);
         allhours = fix(24*mytimes/timeSlice);
         SMPSAvg = zeros(lasthour-firsthour+1, 1);
         scalingTimes = zeros(lasthour-firsthour+1, 1);
         SMPScount = zeros(lasthour-firsthour+1, 1);
         for mytime = firsthour:lasthour
           i = mytime-firsthour+1;
           currentParts = find(allhours==mytime);
           currentDa = Da(currentParts);
           currenttimes = mytimes(currentParts);
           SMPScount(i)=0;
           for part=1:length(currentDa)
              SMPScount(i) = SMPScount(i)
                                                        scaleSMPS_Part(polys,
                                                                                 scalingTimes,
                                                                                                  currentDa(part),
                                                   +
currenttimes(part));
           end
           SMPSAvg(i,:) = sum(mean(Z(find(allAMShours==mytime),:), 1));
         end
         SMPScount = SMPScount/scalingFactor;
         figure
         plot(SMPSavg);
         hold on
         plot(SMPSAvg,'r');
         % remove outliers from off-line ATOFMS
         R2 = corr(SMPSavg, SMPSAvg)^2;
         text(length(scalingTimes)/2, 20, ['R2 = ' num2str(R2,'%7.5f')]);
         return
         function r = corr(x,y)
                  c = corrcoef(x,y);
                  r = c(1,2);
         end
```

A.2.15 PLOTSCALING.m

```
% Thomas Rebotier, February 2007
function plotScaling(Y, hiY, scalingMatrix, crosspoint, poly1, poly2, scalingTimes, plotDirectory)
Y2=Y;
Y2(1) = (Y(1)+0.3)/2;
x=Y2(1:hiY);
\log SM = \log(scalingMatrix)/\log(10);
figure;
for i=1:size(scalingMatrix,1)
         i1 = find(x<=crosspoint(i));</pre>
          i2 = find(x>=crosspoint(i));
  plot(x,scalingMatrix(i,:),'r')
  hold on
  YYY2 = (log(10)*polyval(poly2(i,:),Y2(i2)));
  YYY(i2) = YYY2;
  YYY1 = (\log(10)*polyval(poly1(i,:),Y2(i1)));
  YYY(i1) = YYY1;
  if(i1(end) = i2(1))
     YYY(i2(1)) = (YYY1(end) + YYY2(1))/2;
     YYY1(end) = YYY(i2(1));
     YYY2(1) = YYY(i2(1));
  end
  plot(x,exp(YYY));
  scalingModelCorrelation(i) = corr(YYY', logSM(i,1:size(YYY,2))')^2;
% scalingModelCorrelation1(i) = corr(YYY1', logSM(i,i1)')^2;
% scalingModelCorrelation2(i) = corr(YYY2', logSM(i,i2)')^2;
  j=0;
  for k=2:2:24
    j=j+1;
     xlabel{j}=num2str(Y2(k), '\%3.1f');
  end
  set(gca, 'YLim', [5 100000]);
  set(gca, 'XScale', 'log');
  set(gca, 'YScale', 'log');
  set(gca, 'XTick', x(2:2:24), 'XTickLabel', xlabel);
  text(0.6, 60000, datestr(scalingTimes(i)));
  text(1.6, 60000, ['R2 = ' num2str(scalingModelCorrelation(i),'%5.3f')]);
%
    set(gca, 'Y2Tick', (1:4));
          savename = [plotDirectory '/hour' num2str(i,'%03d') ];
          print('-dtiff', savename);
  hold off
end
function r = corr(x,y)
         c = corrcoef(x,y);
          r = c(1,2);
```

```
end
```

A.2.16 PLOTSMPSSCALING.m

```
% Thomas Rebotier, February 2007
function plotSMPSScaling(Y, scalingMatrix, poly, scalingTimes, plotDirectory)
logSM = log(scalingMatrix)/log(10);
figure;
for i=1:size(scalingMatrix,1)
plot(Y,scalingMatrix(i,:),'r')
hold on
YYY = (log(10)*polyval(poly(i,:),Y));
```

```
plot(Y,exp(YYY));
  scalingModelCorrelation(i) = corr(YYY', logSM(i,1:size(YYY,2))')^2;
  i=0;
  for k=1:15:length(Y)
     j=j+1;
     xlabel{i}=num2str(Y(k), '\%3.0f');
  end
  set(gca, 'YLim', [100 10000000]);
  set(gca, 'XScale', 'log');
  set(gca, 'YScale', 'log');
  set(gca, 'XTick', Y(1:15:end), 'XTickLabel', xlabel);
  set(gca, 'XMinorTick', 'off');
  text(0.6, 60000, datestr(scalingTimes(i)));
  text(1.6, 60000, ['R2 = ' num2str(scalingModelCorrelation(i),'%5.3f')]);
          savename = [plotDirectory '/hour' num2str(i,'%03d') ];
          print('-dtiff', savename);
  hold off
end
function r = corr(x,y)
          c = corrcoef(x,y);
          r = c(1,2);
```

```
end
```

A.2.17 SCALEAPS_PART.m

```
% Thomas Rebotier, February 2007
function apsNumber = scaleAPS_Part(crosspoint, polys1, polys2, scalingTimes, Da, particleTime);
if(particleTime>=scalingTimes(1))
  rightScale = max(find(scalingTimes<particleTime));
else
  rightScale = 1;
  fprintf('Warning: particle obtained before APS scaling sample\n');
end
if( Da < crosspoint(rightScale) )
  apsNumber = (polyval(polys1(rightScale,:), Da));
end
if( Da > crosspoint(rightScale) )
  apsNumber = (polyval(polys2(rightScale,:), Da));
end
if( Da == crosspoint(rightScale) )
  apsNumber = 0.5 * (polyval(polys1(rightScale,:), Da)+polyval(polys2(rightScale,:), Da));
end
```

apsNumber = exp(log(10)*apsNumber);

return

A.2.18 SCALEAPS_PID.m

function [timeVector, scaledCounts, scaledConcentration, Mass] = scaleAPS_PID(skipMissingCurve, crosspoint, polys1, polys2, scalingTimes, PID, flowRate, density, timeSlice, startTime, finishTime) %function [timeVector, scaledCounts, scaledConcentration, Mass] = scaleAPS_PID(skipMissingCurve, crosspoint, polys1, polys2, scalingTimes, PID, flowRate, density, timeSlice, startTime, finishTime) %computes the scaled number of particles and mass for a given PID % % The user only need to change PID, density, timeSlice, startTime, and finishTime, the rest of the variables stay as they are.

%

% skipMissingCurve == 0 makes the program use the last curve when the right

% one is missing; = 1 makes the program ignore particles when the curve is

% missing

% crosspoint, polys1, polys2, scalingTimes come from the automatic scaling

% PID is the PID. For a cell array of PIDs, call scalePID over and over

% timeSlice is 1 for hourly temporals, 24 for daily temporals, etc.

% startTime and finishTime are matlab time variables

% Particles outside the specified times are NOT counted

% Absent a start time, the stretch is whatever the PID has

% Absent a finish time, the stretch is from start time to the last particle

%Particles with undefined Da are removed.

%Returns:

% timeVector is the starting time of each time slice

% scaledCounts the APS particle count in the time slice

% mass the mass temporal assuming a density of 1 and a spherical partical

% it is returned in MICROGRAMS (10e-9 Kg)

% (no shape factor)

% Thomas Rebotier, February 2007

```
all_Time = get_column(PID,'Time');
all_Da = get_column(PID,'Da');
```

keep = find((all_Da>0.02) & (all_Da<20000)); all_Time = all_Time(keep); all_Da = all_Da(keep);

```
if(~exist('density','var'))
  density = 1;
end
```

if(~exist('timeSlice','var')) timeSlice = 1;

end

```
if(exist('startTime', 'var'))
startPart = min(find(all_Time >= startTime));
else
startPart = 1;
```

```
startTime = all_Time(1);
end
```

nu

```
if(exist('finishTime', 'var'))
finishPart = max(find(all_Time <= finishTime));
else
finishPart = length(all_Time);
finishTime = all_Time(end);</pre>
```

```
end
```

```
startTime = timeSlice * floor(24*startTime/timeSlice) /24 ;
finishTime = timeSlice * ceil(24*finishTime/timeSlice) /24 ;
slices = floor( (finishTime-startTime)*24/timeSlice + 1);
timeVector = timeSlice*floor(startTime*24/timeSlice)/24 + ((1:slices)-1)*timeSlice/24;
scaledCounts = zeros(slices, 1);
scaledConcentration = zeros(slices, 1);
Mass = zeros(slices, 1);
warning =0;
warningB =0;
```

```
for i=startPart:finishPart
            particleTime = all_Time(i);
            Da = all_Da(i);
            if(Da > 35)
              micronDa = Da / 1000;
            else
              micronDa = Da;
            end
            slice = floor( (particleTime - startTime)*24/timeSlice + 1);
                   if(particleTime>=scalingTimes(1))
              rightScale = max(find(scalingTimes<particleTime));
                   else
              warning = warning +1;
              rightScale = 1;
                   end
            deltaT = particleTime-scalingTimes(rightScale);
            if(deltaT<timeSlice/24 & particleTime>=scalingTimes(1))
              warningB = warningB+1;
            end
                   if (skipMissingCurve == 0 \mid (\text{deltaT} \ge 0 \& \text{deltaT} < \text{timeSlice}/24))
                             if( Da < crosspoint(rightScale) )
                 apsNumber = (polyval(polys1(rightScale,:), Da));
                             end
                             if( Da > crosspoint(rightScale) )
                 apsNumber = (polyval(polys2(rightScale,:), Da));
                             end
                             if( Da == crosspoint(rightScale) )
                 apsNumber = 0.5 * (polyval(polys1(rightScale,:), Da)+polyval(polys2(rightScale,:), Da));
                             end
                             apsNumber = exp(log(10)*apsNumber);
              scaledCounts(slice) = scaledCounts(slice) + apsNumber;
              % apsNumber is the dimensonless ratio of APS particle counts to ATOFMS counts
              % flowRate is the volumetric correction, usually about 60,000
              scaledConcentration(slice) = scaledConcentration(slice) + apsNumber / flowRate;
              Mass(slice) = Mass(slice) + apsNumber * density * (1/6) * pi * micronDa^3 / flowRate;
            end
         end
         if( skipMissingCurve == 0 )
            if (warning > 0)
              fprintf(1,'Warning: %d particles were obtained before the smps was run. First smps scaling curve is
then used\n', warning);
            end
            if (warningB > 0)
              fprintf(1,'Warning: %d particles hit in time slices without curve have used prior curves.\n', warningB);
            end
         else
            if (warning > 0)
              fprintf(1,'Warning: %d particles hit before the smps was run have been skipped.\n', warning);
            end
            if (warningB > 0)
              fprintf(1, 'Warning: %d particles hit in time slices without curve have been skipped.\n', warningB);
            end
         end
```

return

A.2.19 SCALEAPS_PIDBINS.m

```
function [timeVector, scaledCounts, scaledConcentration, Mass] = scaleAPS_PIDbins(skipMissingCurve,
crosspoint, polys1, polys2, scalingTimes, U, PID, flowRate, density, timeSlice, startTime, finishTime)
         %function [timeVector, scaledCounts, scaledConcentration, Mass] = scaleAPS_PIDbins(skipMissingCurve,
crosspoint, polys1, polys2, scalingTimes, U, PID, flowRate, density, timeSlice, startTime, finishTime)
         % computes the scaled number of particles and mass for a given PID
         % skipMissingCurve == 0 makes the program use the last curve when the right
         % one is missing; = 1 makes the program ignore particles when the curve is
         % missing
         % crosspoint, polys1, polys2, scalingTimes and U come from the automatic
         % scaling, but U can be manually altered, it defines the bin boundaries
         %Typically you may want to remove U values larger than 2.5 microns.
         % PID is the PID. For a cell array of PIDs, call scalePID over and over
         % timeSlice is 1 for hourly temporals, 24 for daily temporals, etc.
         % startTime and finishTime are matlab time variables
         % Particles outside the specified times are NOT counted
         % Absent a start time, the stretch is whatever the PID has
         % Absent a finish time, the stretch is from start time to the last particle
         %Particles with undefined Da or Da larger than U(end) are removed.
         %Returns:
         % timeVector is the starting time of each time slice
         % scaledCounts the APS particle count in the time slice
         % mass the mass temporal assuming a density of 1 and a spherical partical
         % it is returned in MICROGRAMS (10e-9 Kg)
         % (no shape factor)
         % Thomas Rebotier, February 2007
         all_Time = get_column(PID,'Time');
         all_Da = get_column(PID,'Da');
         keep = find( (all_Da>U(1)) \& (all_Da<U(end)));
         all_Time = all_Time(keep);
         all_Da = all_Da(keep);
         if(~exist('density','var'))
           density = 1;
         end
         if(~exist('timeSlice','var'))
           timeSlice = 1;
         end
         if(exist('startTime', 'var'))
            startPart = min(find(all_Time >= startTime));
         else
            startPart = 1;
            startTime = all_Time(1);
         end
         if(exist('finishTime', 'var'))
            finishPart = max(find(all Time <= finishTime));
         else
            finishPart = length(all_Time);
            finishTime = all_Time(end);
         end
         startTime = timeSlice * floor(24*startTime/timeSlice) /24 ;
         finishTime = timeSlice * ceil(24*finishTime/timeSlice) /24;
         slices = floor( (finishTime-startTime)*24/timeSlice + 1);
```

```
timeVector = timeSlice*floor(startTime*24/timeSlice)/24 + ((1:slices)-1)*timeSlice/24;
         scaledCounts = zeros(slices, length(U)-1);
         scaledConcentration = zeros(slices, length(U)-1);
         Mass = zeros(slices, length(U)-1);
         warning =0;
         warningB =0;
         for i=startPart:finishPart
            particleTime = all_Time(i);
            Da = all_Da(i);
            if(Da > 35)
              micronDa = Da / 1000;
            else
              micronDa = Da:
            end
            slice = floor( (particleTime - startTime)*24/timeSlice + 1);
                   if(particleTime>=scalingTimes(1))
              rightScale = max(find(scalingTimes<particleTime));
                   else
              warning = warning +1;
              rightScale = 1;
                   end
            deltaT = particleTime-scalingTimes(rightScale);
            if(deltaT<timeSlice/24 & particleTime>=scalingTimes(1))
              warningB = warningB+1;
            end
                   if (skipMissingCurve == 0 \mid (\text{deltaT} \ge 0 \& \text{deltaT} < \text{timeSlice}/24))
                             if( Da < crosspoint(rightScale) )
                 apsNumber = (polyval(polys1(rightScale,:), Da));
                             end
                             if( Da > crosspoint(rightScale) )
                 apsNumber = (polyval(polys2(rightScale,:), Da));
                             end
                             if( Da == crosspoint(rightScale) )
                 apsNumber = 0.5 * (polyval(polys1(rightScale,:), Da)+polyval(polys2(rightScale,:), Da));
                             end
                             apsNumber = exp(log(10)*apsNumber);
              sizebin = max(find(U<=Da));</pre>
              if(length(sizebin)>0)
                 scaledCounts(slice,sizebin) = scaledCounts(slice,sizebin) + apsNumber;
              end
              % apsNumber is the dimensonless ratio of APS particle counts to ATOFMS counts
              % flowRate is the volumetric correction, usually about 60,000
              scaledConcentration(slice,sizebin) = scaledConcentration(slice,sizebin) + apsNumber / flowRate;
              Mass(slice,sizebin) = Mass(slice,sizebin) + apsNumber * density * (1/6) * pi * micronDa^3 / flowRate;
            end
         end
         if( skipMissingCurve == 0 )
            if (warning > 0)
              fprintf(1,'Warning: %d particles were obtained before the smps was run. First smps scaling curve is
then used\n', warning);
            end
            if (warningB > 0)
              fprintf(1,'Warning: %d particles hit in time slices without curve have used prior curves.\n', warningB);
            end
         else
            if (warning > 0)
```

fprintf(1,'Warning: %d particles hit before the smps was run have been skipped.\n', warning); end

```
if (warningB > 0)
```

 $fprintf(1, 'Warning: \%d \ particles \ hit \ in \ time \ slices \ without \ curve \ have \ been \ skipped.\n', \ warningB); end$

end

return

A.2.20 SCALEPID.m

function [timeVector, scaledCounts, Mass] = scalePID(crosspoint, polys1, polys2, scalingTimes, PID, flowRate, density, timeSlice, startTime, finishTime)

%function [timeVector, scaledCounts, Mass] = scalePID(crosspoint, polys1, polys2, scalingTimes, PID, flowRate, density, timeSlice, startTime, finishTime);

%computes the scaled number of particles and mass for a given PID

%

% The user only need to change PID, density, timeSlice, startTime, and finishTime, the rest of the variables stay as they are.

%

% crosspoint, polys1, polys2, scalingTimes come from the automatic scaling

% PID is the PID. For a cell array of PIDs, call scalePID over and over

% timeSlice is 1 for hourly temporals, 24 for daily temporals, etc.

% startTime and finishTime are matlab time variables

% Particles outside the specified times are NOT counted

% Absent a start time, the stretch is whatever the PID has

% Absent a finish time, the stretch is from start time to the last particle

%Particles with undefined Da are removed.

%Returns:

% timeVector is the starting time of each time slice

% scaledCounts the APS particle count in the time slice

% mass the mass temporal assuming a density of 1 and a spherical partical

% it is returned in MICROGRAMS (10e-9 Kg)

% (no shape factor)

```
% Thomas Rebotier, February 2007
```

```
all_Time = get_column(PID,'Time');
all_Da = get_column(PID,'Da');
```

```
keep = find( (all_Da>0.02) & (all_Da<20000));
all_Time = all_Time(keep);
all_Da = all_Da(keep);
```

```
if(~exist('density','var'))
  density = 1;
end
```

ena

```
if(~exist('timeSlice','var'))
timeSlice = 1;
```

end

```
if(exist('startTime', 'var'))
  startPart = min(find(all_Time >= startTime));
else
  startPart = 1;
  startTime = all_Time(1);
end
```

end

if(exist('finishTime', 'var'))

```
finishPart = max(find(all_Time <= finishTime));</pre>
else
  finishPart = length(all_Time);
  finishTime = all_Time(end);
end
slices = floor( (finishTime-startTime)*24/timeSlice + 1);
timeVector = startTime + ((1:slices)-1)*timeSlice/24;
scaledCounts = zeros(slices, 1);
Mass = zeros(slices, 1);
warning =0;
for i=startPart:finishPart
  particleTime = all_Time(i);
  Da = all_Da(i);
  if(Da > 35)
     micronDa = Da / 1000;
  else
     micronDa = Da;
  end
  slice = floor( (particleTime - startTime)*24/timeSlice + 1);
          if(particleTime>=scalingTimes(1))
     rightScale = max(find(scalingTimes<particleTime));
          else
     warning = warning +1;
     rightScale = 1;
          end
          if( Da < crosspoint(rightScale) )
     apsNumber = (polyval(polys1(rightScale,:), Da));
          end
          if( Da > crosspoint(rightScale) )
     apsNumber = (polyval(polys2(rightScale,:), Da));
          end
          if( Da == crosspoint(rightScale) )
     apsNumber = 0.5 * (polyval(polys1(rightScale,:), Da)+polyval(polys2(rightScale,:), Da));
          end
          apsNumber = exp(log(10)*apsNumber);
  scaledCounts(slice) = scaledCounts(slice) + apsNumber;
  % apsNumber is the dimensonless ratio of APS particle counts to ATOFMS counts
  % flowRate is the volumetric correction, usually about 60,000
  Mass(slice) = Mass(slice) + apsNumber * density * (1/6) * pi * micronDa^3 / flowRate;
end
```

if(warning > 0) fprintf(1,'Warning: %d particles were obtained before the APS was run. First APS scaling curve is then used', warning);

end

return

A.2.21 SCALESMPS_PART.m

% Thomas Rebotier, February 2007 function smpsNumber = scaleSMPS_Part(polys, scalingTimes, Da, particleTime);

```
if(particleTime>=scalingTimes(1))
rightScale = max(find(scalingTimes<particleTime));
else</pre>
```

rightScale = 1;

fprintf('Warning: particle obtained before smps scaling sample\n');

end

smpsNumber = (polyval(polys(rightScale,:), Da));

smpsNumber = exp(log(10)*smpsNumber);

return

A.2.22 SCALESMPS_PID.m

function [timeVector, scaledCounts, scaledConcentration, Mass] = scaleSMPS_PID(skipMissingCurve, polys, scalingTimes, PID, flowRate, density, timeSlice, startTime, finishTime)

%function [timeVector, scaledCounts, scaledConcentration, Mass] = scaleSMPS_PID(skipMissingCurve,

polys, scalingTimes, PID, flowRate, density, timeSlice, startTime, finishTime) %computes the scaled number of particles and mass for a given PID

%

% The user only need to change PID, density, timeSlice, startTime, and finishTime, the rest of the variables stay as they are.

%

% skipMissingCurve == 0 makes the program use the last curve when the right

% one is missing; == 1 makes the program ignore particles when the curve is

% missing

% polys and scalingTimes come from the automatic scaling

% PID is the PID. For a cell array of PIDs, call scalePID over and over

% timeSlice is 1 for hourly temporals, 24 for daily temporals, etc.

% startTime and finishTime are matlab time variables

% Particles outside the specified times are NOT counted

% Absent a start time, the stretch is whatever the PID has

% Absent a finish time, the stretch is from start time to the last particle

% Particles with undefined Da are removed.

%Returns:

% timeVector is the starting time of each time slice

% scaledCounts the smps particle count in the time slice

% mass the mass temporal assuming a density of 1 and a spherical partical

% it is returned in MICROGRAMS (10e-9 Kg)

% (no shape factor)

% Thomas Rebotier, February 2007

```
all_Time = get_column(PID,'Time');
all_Da = get_column(PID,'Da');
```

```
keep = find( (all_Da>0.02) & (all_Da<20000));
all_Time = all_Time(keep);
all_Da = all_Da(keep);
```

```
if(~exist('density','var'))
density = 1;
```

end

if(~exist('timeSlice','var'))
timeSlice = 1;

end

```
if(exist('startTime', 'var'))
startPart = min(find(all_Time >= startTime));
else
startPart = 1;
```

```
startTime = all_Time(1);
         end
         if(exist('finishTime', 'var'))
            finishPart = max(find(all_Time <= finishTime));
         else
            finishPart = length(all_Time);
            finishTime = all_Time(end);
         end
         startTime = timeSlice * floor(24*startTime/timeSlice) /24 ;
         finishTime = timeSlice * ceil(24*finishTime/timeSlice) /24 ;
         slices = floor( (finishTime-startTime)*24/timeSlice + 1);
         timeVector = timeSlice*floor(startTime*24/timeSlice)/24 + ((1:slices)-1)*timeSlice/24;
         scaledCounts = zeros(slices, 1):
         scaledConcentration = zeros(slices, 1);
         Mass = zeros(slices, 1);
         warning =0;
         warningB =0;
         for i=startPart:finishPart
            particleTime = all_Time(i);
            Da = all_Da(i);
            if(Da > 35)
              nanoDa = Da;
            else
              nanoDa = Da * 1000;
            end
            slice = floor( (particleTime - startTime)*24/timeSlice + 1);
                   if(particleTime>=scalingTimes(1))
              rightScale = max(find(scalingTimes<particleTime));
                   else
              warning = warning +1;
              rightScale = 1;
                   end
            deltaT = particleTime-scalingTimes(rightScale);
            if(deltaT<timeSlice/24 & particleTime>=scalingTimes(1))
              warningB = warningB+1;
            end
                   if (skipMissingCurve == 0 \mid (\text{deltaT} \ge 0 \& \text{deltaT} < \text{timeSlice}/24))
              smpsNumber = (polyval(polys(rightScale,:), Da));
                             smpsNumber = exp(log(10)*smpsNumber);
              scaledCounts(slice) = scaledCounts(slice) + smpsNumber;
              % smpsNumber is the dimensonless ratio of smps particle counts to ATOFMS counts
              % flowRate is the volumetric correction, usually about 60,000
              scaledConcentration(slice) = scaledConcentration(slice) + smpsNumber / flowRate;
              Mass(slice) = Mass(slice) + smpsNumber * density * (1/6) * pi * (nanoDa/1000)^3 / flowRate;
            end
         end
         if( skipMissingCurve == 0 )
            if (warning > 0)
              fprintf(1,'Warning: %d particles were obtained before the smps was run. First smps scaling curve is
then used\n', warning);
            end
            if (warning B > 0)
              fprintf(1,'Warning: %d particles hit in time slices without curve have used prior curves.\n', warningB);
            end
         else
            if (warning > 0)
```

fprintf(1,'Warning: %d particles hit before the smps was run have been skipped.\n', warning); end

```
if (warning B > 0)
```

fprintf(1,'Warning: %d particles hit in time slices without curve have been skipped.\n', warningB); end

end

return

A.2.23 SCALESMPS_PIDBINS.m

function [timeVector, scaledCounts, scaledConcentration, Mass] = scaleSMPS_PIDbins(skipMissingCurve, polys, scalingTimes, U, PID, flowRate, density, timeSlice, startTime, finishTime)

%function [timeVector, scaledCounts, scaledConcentration, Mass] = scaleSMPS_PIDbins(skipMissingCurve, polys, scalingTimes, U, PID, flowRate, density, timeSlice, startTime, finishTime)

% computes the scaled number of particles and mass for a given PID

```
% skipMissingCurve == 0 makes the program use the last curve when the right
```

% one is missing; == 1 makes the program ignore particles when the curve is

% missing

% polys, scalingTimes and U come from the automatic

% scaling, but U can be manually altered, it defines the bin boundaries

% PID is the PID. For a cell array of PIDs, call scalePID over and over

% timeSlice is 1 for hourly temporals, 24 for daily temporals, etc.

% startTime and finishTime are matlab time variables

% Particles outside the specified times are NOT counted

% Absent a start time, the stretch is whatever the PID has

% Absent a finish time, the stretch is from start time to the last particle

%Particles with undefined Da or Da larger than U(end) are removed.

%Returns: % timeVector is the starting time of each time slice

% scaledCounts the smps particle count in the time slice

% mass the mass temporal assuming a density of 1 and a spherical partical

% it is returned in MICROGRAMS (10e-9 Kg)

% (no shape factor)

% Thomas Rebotier, February 2007

```
all_Time = get_column(PID,'Time');
all_Da = get_column(PID,'Da');
```

```
keep = find( (all_Da>U(1)) & (all_Da<U(end)));
all_Time = all_Time(keep);
all_Da = all_Da(keep);
```

```
if(~exist('density','var'))
  density = 1;
end
```

```
. . . . . .
```

if(~exist('timeSlice','var'))
 timeSlice = 1;

end

```
if(exist('startTime', 'var'))
startPart = min(find(all_Time >= startTime));
else
startPart = 1;
startTime = all_Time(1);
end
```

```
if(exist('finishTime', 'var'))
  finishPart = max(find(all_Time <= finishTime));
  finishPart = length(all_Time);
  finishTime = all_Time(end);
startTime = timeSlice * floor(24*startTime/timeSlice) /24 ;
finishTime = timeSlice * ceil(24*finishTime/timeSlice) /24 ;
slices = floor( (finishTime-startTime)*24/timeSlice + 1);
timeVector = timeSlice*floor(startTime*24/timeSlice)/24 + ((1:slices)-1)*timeSlice/24;
scaledCounts = zeros(slices, length(U)-1);
scaledConcentration = zeros(slices, length(U)-1);
Mass = zeros(slices, length(U)-1);
warning =0:
warningB = 0;
for i=startPart:finishPart
  particleTime = all_Time(i);
  Da = all_Da(i);
  if(Da > 35)
     nanoDa = Da;
    nanoDa = Da * 1000;
  slice = floor( (particleTime - startTime)*24/timeSlice + 1);
         if(particleTime>=scalingTimes(1))
     rightScale = max(find(scalingTimes<=particleTime));
          else
     warning = warning +1;
     rightScale = 1;
          end
  deltaT = particleTime-scalingTimes(rightScale);
  if(deltaT<timeSlice/24 & particleTime>=scalingTimes(1))
     warningB = warningB+1;
          if (skipMissingCurve == 0 \mid (\text{deltaT} \ge 0 \& \text{deltaT} < \text{timeSlice}/24))
     smpsNumber = (polyval(polys(rightScale,:), Da));
                   smpsNumber = exp(log(10)*smpsNumber);
     sizebin = max(find(U<=Da));
     if(length(sizebin)>0)
       scaledCounts(slice,sizebin) = scaledCounts(slice,sizebin) + smpsNumber;
     end
     % smpsNumber is the dimensonless ratio of smps particle counts to ATOFMS counts
     % flowRate is the volumetric correction, usually about 60,000
     scaledConcentration(slice,sizebin) = scaledConcentration(slice,sizebin) + smpsNumber / flowRate;
     Mass(slice,sizebin) = Mass(slice,sizebin) + smpsNumber * density * (1/6) * pi * (nanoDa/1000)^3 /
```

```
flowRate:
```

end

end

else

end

else

end

end

```
if( skipMissingCurve == 0 )
```

```
if (warning > 0)
```

fprintf(1, Warning: %d particles were obtained before the smps was run. First smps scaling curve is then usedn', warning);

```
end
if (warningB > 0)
```

fprintf(1,'Warning: %d particles hit in time slices without curve have used prior curves.\n', warningB); end

```
else
    if (warning > 0)
        fprintf(1,'Warning: %d particles hit before the smps was run have been skipped.\n', warning);
    end
    if (warningB > 0)
        fprintf(1,'Warning: %d particles hit in time slices without curve have been skipped.\n', warningB);
    end
end
```

return

A.2.24 SMPS_SCALING_PART_1.m

```
% Thomas Rebotier, February 2007
         scalingFileName = input('Please enter the path and name of the file used to save scaling
information\n>(example: C:\\Soar1) \n>','s');
         fprintf(1, 'Saving current Matlab workspace in the file preScalingContext\n\n');
         save preScalingContext
         fprintf(1, 'About to run getAllSMPSfiles. \nMake sure the SMPS files are correct. \nDetails Below. Example
in scaling/APD_directory_example');
         help getAllSMPSfiles
         SMPSdir = input(Now enter the directory name of the SMPS file directory(nexample: C:)(SOAR1_SMPS))
n>', s');
         [X,Y,Z] = getAllSMPSfiles(SMPSdir);
          fprintf(1, 'about to run getAtofmsScaleData. Details Below.');
         help getAtofmsPIDScaleData
         ExtraQuery = input('Now enter the PID or nothing (defaults to all hits), then hit ENTER\n>','s');
         if(length(ExtraQuery)>0)
            eval(['PIDin = ' ExtraQuery ';']);
            [mytimes, Da, atofmsBin, U] = getAtofmsPIDScaleData(Y, ExtraQuery, 2);
         else
            [mytimes, Da, atofmsBin, U] = getAtofmsPIDScaleData(Y, ", 2);
         end
         fprintf(1, 'about to bin Atofms data, average SMPS data, \nand compute ratio matrix. Details below.');
         help discreteScaling
         timeSlice = str2num(input('Enter the duration of a time slice, in hours. \nUsually, just type "1"\n>','s'));
         timeShift = str2num(input('Enter how many hours AHEAD of the ATOFMS computer the SMPS computer is.
nUsually, just type "0"(n>','s'));
          X = X - timeShift/24;
         threshold = str2num(input('Enter the lowest number of particles desired to take a \nparticular time slice into
account. Usually, just 100\n>','s'));
          [scalingMatrix,
                              scalingTimes,
                                                 allTimes,
                                                                atofmsBins,
                                                                                  SMPSAvg,
                                                                                                  xremove]
                                                                                                                  =
discreteSMPSScaling(atofmsBin, mytimes, X, U, Z, timeSlice, threshold);
          flowRate = str2num(input('Enter the volume correction factor, either as an absolute \number (about 60,000)
or as the ATOFMS liter/minute\n>','s'));
         if(flowRate<100)
            flowRate = 60000*flowRate;
         end
         scalingMatrix = scalingMatrix * flowRate;
         finiteindex = sum(isfinite(scalingMatrix),2);
         remove = find(finiteindex==0);
         scalingMatrix(remove,:) = [];
         scalingTimes(remove) = [];
```

Yfiniteindex = sum(isfinite(scalingMatrix),1); Yremove = find(Yfiniteindex==0); scalingMatrix(:, Yremove) = []; Y(Yremove) = []; U(Yremove+1) =[];

fprintf(1, 'Part 1 of the import is over. \nPLEASE INSPECT THE RATIO MATRIX, called scalingMatrix. \nYou need to remove lines that only have NaNs or Inf. \nremove them also from "scalingTimes", the variable that keeps track of \nwhat times the scaling curves correspond to, and possibly from other \nvariables (Bin, Da, etc...) if you plan on using these later');

fprintf(1, 'Once you are satisfied with the scaling \nmatrix, run part 2 of the script');

A.2.25 SMPS_SCALING_PART_2.m

% Thomas Rebotier, February 2007 hiY = length(Y);

% $hiY = str2num(input(['To only work on PM 2.5 we must keep only the first ' int2str(hiY) ' bins. \nEnter this number below or change it if you want to scale over fewer or more bins\n>'],'s'));$

fprintf(1, 'about to run fitScalingModel. Details Below.'); help fitSMPSScalingModel [polys, residual, ss] = fitSMPSScalingModel(Y, scalingMatrix, hiY);

plotAll = input('Do you want to plot all the scaling curves and compute the correlations? (n(answer "y" or "n" only please)(n>','s');

if (plotAll == 'y' | plotAll == 'Y' | plotAll == 'Yes' | plotAll == 'YES' | plotAll == 'yes')

plotDirectory = input('Create a directory to put all the figures in, \nand enter its name here. Figures will be saved as TIFF.\n Use "abc" (a batch converter) to turn them to GIFs for \nimport into GIF animators\n','s');

plotSMPSScaling(Y, scalingMatrix, polys, scalingTimes, plotDirectory);

end

save(scalingFileName, 'scalingTimes', 'polys', 'U', 'scalingMatrix','flowRate');

input(' We have now generated all scaling information. \nTo play around with the guts of the scaling and keep all \nintermediary variables abort this script now','s');

clear

load preScalingContext
load(scalingFileName);