Sonoma Technology, Inc.

1360 Redwood Way, Suite C
Petaluma, CA 94954-1169
707/665-9900
FAX 707/665-9800
www.sonomatech.com

A PROPOSAL FOR COMPARISON OF AMBIENT MEASUREMENTS TO EMISSIONS REPRESENTATIONS FOR MODELING

In Response to CCOS RFP dated June 28, 2005
STI-705060

Prepared for:
California Air Resources Board
1001 I Street
Sacramento, CA 95814

Submitted by:
Sonoma Technology, Inc.
1360 Redwood Way, Suite C
Petaluma, CA 94954-1169

Technical Contact:
Stephen B. Reid
Air Quality Analyst

Business Contact:
Lyle R. Chinkin
Senior Vice President and General Manager

July 15, 2005

2. TECHNICAL APPROACH

2.1 SCOPE OF WORK

The scope of work provided in the RFP calls for the 11 tasks listed below. Key milestones include (1) a project kickoff meeting to present and refine the work plan; (2) reviewing available data and analysis approaches and presenting a plan for the TC's consideration at the end of Task 4 and before the bulk of the analyses is conducted; (3) depending on the TC's recommendations, conducting the analyses suggested in Tasks 5 through 10; and (4) preparing a Final Report and a peer-reviewed journal article. Each task is briefly described in the list below and in more detail in the following sections.

Task 1. Participate in a project kickoff meeting and submit a detailed draft work plan.

Task 2. Identify the air quality data that are available to support the analyses, including 1-hr and 3-hr speciated VOC data, as well as NO_x and carbon monoxide (CO) measurements.

Task 3. Acquire and evaluate ARB's current speciation database and assess the suitability of the ARB speciation profiles.

Task 4. Review and assess alternative evaluation approaches for the comparison of ambient and emissions data. Organize a one-day workshop at ARB offices in Sacramento to further discuss alternative analytical methods, available data, and the likelihood of deriving sound assessments of modeled emissions estimates.

Task 5. Perform VOC source apportionment by applying the selected analysis method to each valid CCOS VOC sample and selected CRPAQS samples using appropriate source composition profiles or speciation data.

Task 6. Integrate and synthesize the results from the ongoing CCOS Advanced Data Analysis Study and other pertinent studies that reconcile the emission inventory with ambient or other data.

Task 7. Compare and reconcile the spatial and temporal patterns in predicted VOC/NO_x and CO/NO_x ratios as represented by the gridded emission inventory with corresponding ratios from PAMS and CCOS supplemental monitoring sites.

Task 8. Compare and reconcile the spatial and temporal patterns in the predicted levels of VOC species with the corresponding ambient data.

Task 9. Assess the importance of the disparity of spatial scales between point ambient measurements and the spatial averaging of emissions used in air quality model inputs.

Task 10. Draw appropriate conclusions regarding potential biases and uncertainties that may exist in the CCOS emission inventory or the gridded representation of the inventory based on the previous tasks.

Task 11. Prepare interim and final reports. Present and discuss the findings of the study at a one-day CCOS TC meeting in Sacramento.

The work will be carried out in two phases. Phase 1 will provide information that is useful to those involved in SIP modeling activities in time for use in the preparation of the 2006 SIP updates for central and northern California. Work on Phase 1 will be documented in an interim report to be completed by January 31, 2006. All remaining analyses will be carried out in Phase 2, which will be completed (including the submittal of the final report and the manuscript for publication) within one year of initiating the study.

Task 1—Participate in the Project Kickoff Meeting

The STI project manager and other key personnel will participate in a one-day project kickoff meeting in Sacramento, California, which will take place within three weeks of the initiation of the study. The purposes of the meeting are (a) to collaborate with the CCOS TC and ARB staff to formulate plans for the completion of the proposed study and (b) to acquire information from ARB Technical Support Division staff about the current status of the CCOS emission inventory, including an assessment of source categories for which emission estimates are thought to be subject to the greatest uncertainties. ARB staff will provide information on the methods used for preparing the emission inventories for modeling (including the speciation and spatial distribution of the inventory) and will provide access to relevant ambient data with supporting information.

Based on the discussions and information gathered at the kickoff meeting, STI will prepare a detailed Work Plan that specifies the analyses to be performed during Phases 1 and 2 of the proposed project. (Phase 1 includes completion of an Interim Report.) Analysis methods will be selected on the bases of their suitability for meeting the purpose and goals of the project, their technical merit, and the timeliness with which they may be completed.

STI will prepare a draft version of the Work Plan for the TC's review and comment. In consideration of reviewers' feedback, STI will also prepare and submit a final work plan.

Task 2—Identify Available Air Quality Data

The objective of Task 2 is to identify locations with valid 1-hr or 3-hr speciated VOC, NO_x, CO, and meteorological data collected during the CCOS (summer 2000) and CRPAQS (winter 2000-2001) periods that will be used in later tasks. Proper evaluation of data availability, quality, and representativeness is vital for effective emission inventory reconciliation and source apportionment.

STI's approach will rely on its previous and current work conducting extensive validation of data in the CCOS database, and validating and evaluating PAMS VOC data collected in the SJV. Our familiarity with the data will make this task efficient and effective in determining the best sites for later analysis. We will determine what sites have sufficient data during the selected period, assess the validity of the data, and assess the likely sources affecting, and characteristics of (i.e., downwind, fresh urban, etc), the sites. Preliminary work has already been documented in communications with the CCOS TC and will be used in this task (see, for example, **Figure 2-1**). We will rely on our experience with emission inventory reconciliation, source apportionment, and VOC data analysis to help guide our selection of sites (Lurmann and Main, 1992; Main et

al., 1995, 1996; Chinkin et al., 1998; Main and Chinkin, 1998; Main et al., 1999a; Main et al., 1999b; Main, 2000; Chinkin et al., 2000; Main, 2001a, b; Brown and Hafner, 2002; Hafner and Roberts, 2002; Brown and Hafner, 2003c; Brown et al., 2004; Brown and Hafner, 2004; Zhao et al., 2004; Brown et al., 2005c; Kim et al., 2005).

Many considerations will be used in site selection:

- Objective of analysis (e.g., requiring a large data set for PMF or a data set with sufficient samples from all wind quadrants for emission inventory reconciliation).
- Monitoring objectives of a site (e.g., urban, rural, source-oriented, etc.).
- Ambient concentration levels well above instrument detection limits.
- Ambient concentration levels above a meaningful threshold, such as the following approximate thresholds which are often used as benchmarks: NO_x > 10 ppb; VOC > 50 ppbC, and CO > 150 ppb.
- Spatial distribution of sites (e.g., whether interest is focused on urban sites only or both urban and rural).
- Temporal distribution of the data (e.g., 1-hr or 3-hr data are needed for effective source apportionment and emission inventory reconciliation).

The deliverable for this task will be a technical memorandum describing the process to determine potential sites, and our recommendations on which sites will produce the most useful data for later analysis. We will include details of the number of samples available plus likely sources and characteristics affecting the sites. STI will prepare a draft version for the TC's review and comment. STI staff will review and discuss the memorandum with the CCOS TC through a conference call or face-to-face meeting. In consideration of reviewers' feedback, STI will revise the memorandum and deliver a final version.

Task 3—Review Chemical Speciation Profiles

The ARB maintains a database of organic gas and particulate matter (PM) speciation profiles, as well as a cross-reference table that indicates which total organic gas (TOG) or PM profile should be assigned to a given source category. Speciation profiles are also available from the EPA's Speciate 3.2 database, DRI, and other sources. STI recently reviewed ARB and EPA speciation databases for use in an emission inventory development study for the San Francisco Bay area. For Task 3, we will verify that we have the ARB's and EPA's most up-to-date libraries of speciation profiles. We will review the ARB's speciation profiles, profile-to-source category assignments, and available supporting literature and documentation. STI will perform a literature search to identify information more recent than the sources cited for the ARB's speciation profiles.

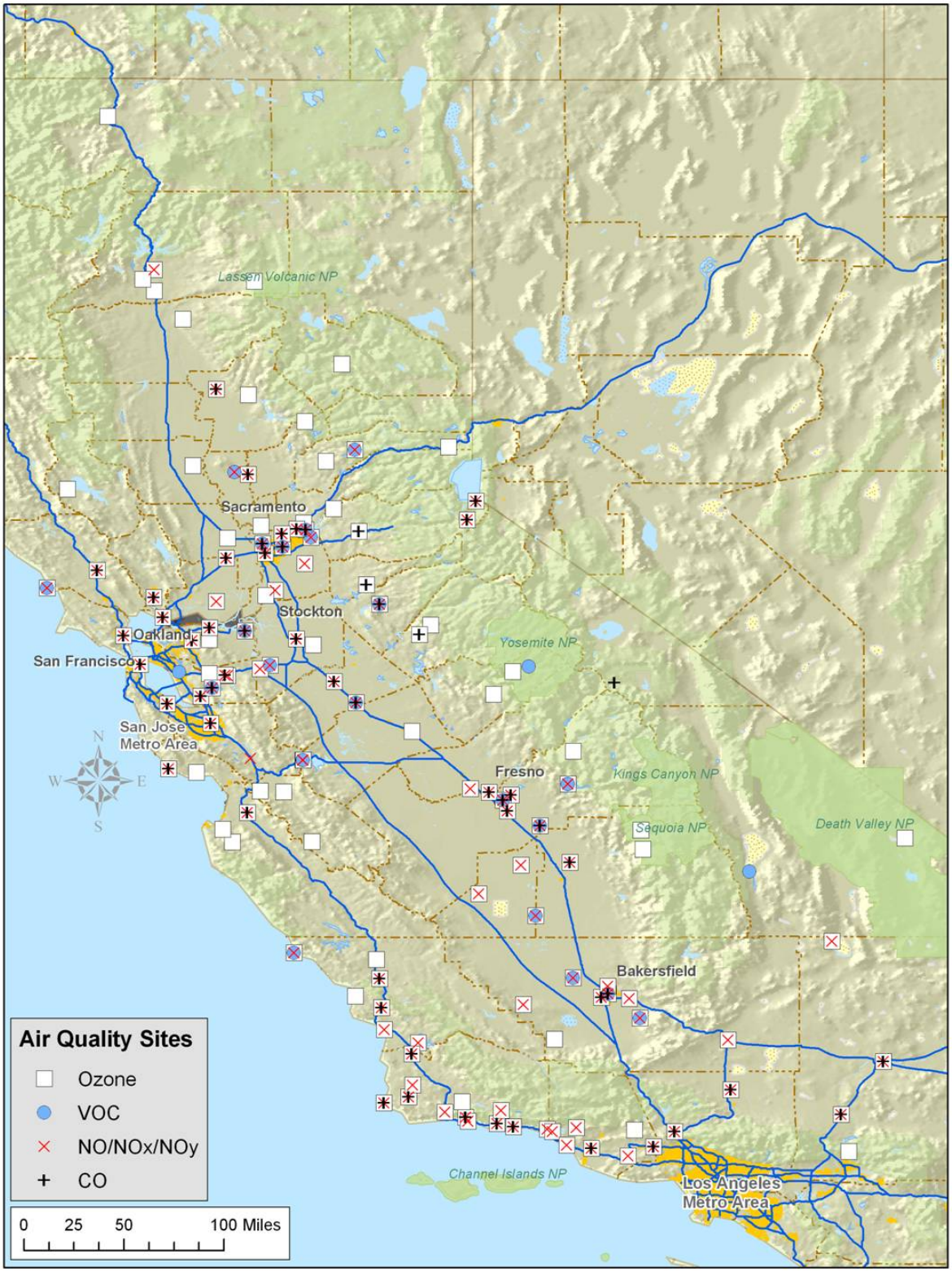

Figure 2-1. Map of sites with available air quality data.

In assessing the suitability of ARB's speciation profiles, STI will rank the importance of the profiles based on the mass of emissions associated with source categories assigned to each profile, as well as the reactivity of the individual compounds in each profile. In addition, a secondary ranking will be performed based on the age of the profile. Supporting references cited for the ARB's and EPA's speciation profile databases, such as those listed in Section 1.3.4, include some publications dating back to the 1970s and 1980s. Speciation profiles based on these older literature sources should receive special attention for a literature review to determine whether more complete or superior measurements are available.

With input from the CCOS TC, STI will develop a set of criteria for evaluating individual speciation profiles, including the vintage of the profile and its underlying source tests, the number of tests conducted, the number of chemicals measured, and applicability of the profile to California.

Based on this analysis, STI will prepare a technical memorandum summarizing and recommending speciation profiles that should be applied for photochemical modeling and for receptor-based data analyses (e.g., source apportionment). In addition, the memorandum will provide recommendations for updating or improving the available speciation profiles. A draft version of the memorandum will be prepared for the TC's review and comment. STI will revise the memorandum based on feedback from the CCOS TC.

Task 4—Evaluate Alternative Data Analysis Methods

The purpose of Task 4 is to solidify the technical approaches and analyses to be conducted throughout the remainder of the project. In consultation with the CCOS TC, STI will establish a list of technical questions and issues of concern. STI staff members will apply their data analyses expertise, as well as their familiarity with air quality and meteorological conditions in the SJV to consider alternative analytical approaches that would be best suited to address each technical question. STI will ascertain the suitability of available data to support possible approaches and will consider relevant studies that have been previously completed or are currently underway.

STI will organize a one-day workshop in Sacramento to discuss the technical questions of concern, present the merits and disadvantages and details of the likely technical approaches to proposed data analyses, and solicit input and feedback from ARB staff members, the CCOS TC, and other interested parties. For the purposes of estimating costs, we have assumed that the workshop will be held at ARB's facilities in Sacramento, which will be made available at no cost to the project.

STI will document the foundations of the CCOS gridded emission inventories, such as emissions modeling version numbers of OFFROAD, EMFAC, CEIDARS, and CEFS, and/or supplemental information (such as the methods used, if any, to incorporate day-specific emissions data).

STI will prepare a technical memorandum that documents the workshop proceedings and summarizes the merits and disadvantages of suggested alternative data analysis methods. The memorandum will describe the specific analyses proposed to be performed for the remainder of

the study and highlight the analyses that will be completed by January 31, 2006. Software, databases, and/or input and output files to be used or produced during the study will be documented (all of which will be delivered at the conclusion of the study). STI will prepare a draft version for the TC's review and comment. In consideration of reviewers' feedback, STI will revise the memorandum and deliver a final version.

Task 5—Perform VOC Source Apportionment

The objective of Task 5 is to apply source apportionment tools (often called receptor models) to ambient data collected during CCOS (summer 2000) and CRPAQS (winter 2000-2001) to (1) evaluate source profiles and (2) determine relative source contributions to total VOC mass. These results will then be compared to the emission inventory to aid in improving source profiles and identify important source types. Analysis of results will include evaluation of the differences in results for episodes and cleanout/rainout periods, as well as the effect of local meteorology and carryover of emissions on source apportionment. Results will also be put into context with the extent of reaction and photochemical age of the ambient VOCs. Results from this task will help the CCOS TC understand (1) if there are gross biases between source profiles observed in the ambient data and those used in the emission inventory, (2) differences between source allocations from source apportionment in the ambient data and the distribution in the emission inventory, and (3) the degree of photochemistry seen in the ambient data and implications of these findings to photochemical model performance evaluation.

For example, STI recently conducted source apportionment analyses of ambient monitoring data at two sites in California's South Coast Air Basin (SoCAB) and compared the results with emission inventories provided by the South Coast Air Quality Management District. The TNMOC composition at a selected site from the emission inventory is shown in **Figure 2-2**, and the composition determined by source apportionment analysis is shown in **Figure 2-3**. The results show that reasonable agreement exists between the relative contribution by source type derived from ambient data and the emission inventory, but that on-road mobile sources may be somewhat underestimated in the emission inventory.

Our approach is to use the strengths of two prominent and complementary receptor models supported by EPA—CMB and PMF—to both evaluate the source profiles in the context of the ambient data and attempt to reconcile the source profiles with the ambient data. CMB will be applied with source profiles used in photochemical modeling to evaluate how these source profiles fit the ambient data. The expectation is that the VOC mass associated with secondary formation will not be well fit by the model, and that some sources may not be clearly identified or their profiles may not be accurate. To complement CMB source apportionment, we propose to use PMF and ambient data only (i.e., no explicit source profiles) to obtain a set of profiles, likely including a measure of secondary and "carryover" mass. PMF output will assist us in identifying any additional sources and their profiles that account for a significant part of the mass. Using this dual-model approach, we will gain a better understanding of the source profiles, their effectiveness in representing the ambient data, and what changes can be made to the profiles to improve photochemical model performance.

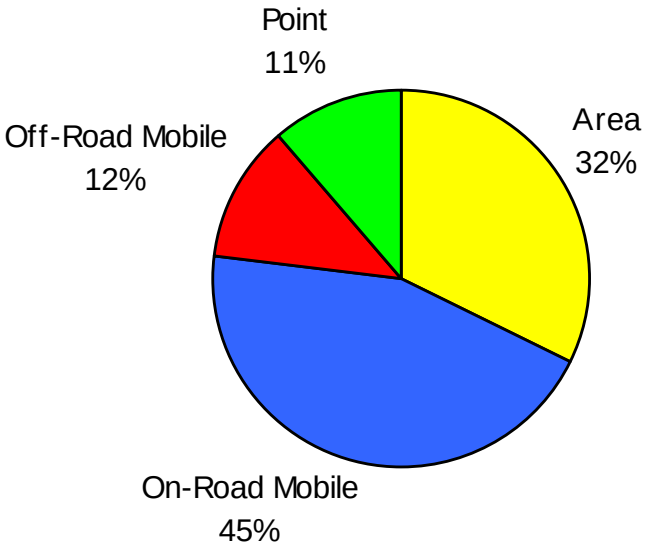

Figure 2-2. TNMOC composition at the Hawthorne site, 0500-1000 PST, by emission inventory source category (kg/hr).

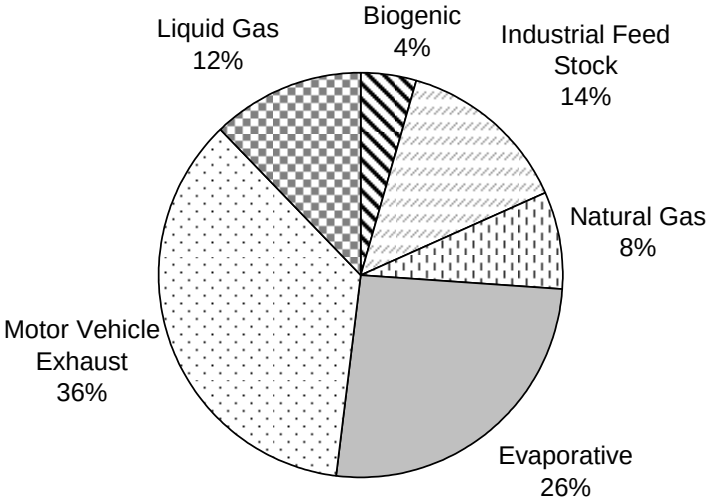

Figure 2-3. TNMOC composition at the Hawthorne site, 0500-1000 PST, by source apportionment factor.

The deliverables from this task will be a better understanding of the sources of VOC ozone precursors, how well the source profiles account for the ambient VOC mass, our relative confidence in the source profiles, the degree of secondary formation and air mass age of the VOC samples, and an understanding of the representativeness of the sites. We will include recommendations that can be directly used in photochemical modeling and in the reconciliation of the emission inventory tasks.

Assumptions and Biases in the Receptor Models

The CMB and PMF models both have underlying assumptions and biases that have been well-documented and discussed in the literature (Paatero and Tapper, 1994; Fujita et al., 1995; Watson et al., 2001; Watson et al., 2002; Yarwood et al., 2005). These assumptions and biases are important to understand in the context of SIP modeling.

A strength of CMB is that it can be applied to a single sample, but one of the key assumptions of CMB is that all significant sources have been identified and their profiles are well-characterized. By using source profiles that are used in the photochemical model in CMB application, we can better understand how these profiles fit the ambient data. However, CMB will not be able to identify additional sources or account for secondary formation effectively.

PMF has many assumptions similar to those in CMB, and while it requires a large data matrix (i.e., at least 100 samples of speciated VOC data), it does not need an *a priori* assumption of sources and their profiles, since it uses only the ambient data to create the optimal combination of profiles and their contributions to total mass. However, it is possible to incorporate known profiles into a PMF analysis and thus, identify those others for which there may not be good *a priori* knowledge. This enables the identification of additional sources that may not be well-characterized by CMB, because they are not included or have incorrect profiles. Additionally, PMF results often include a "secondary" component, which can be used to effectively quantify the contribution of secondary VOC to the total mass. In the context of CMB results, PMF results can be used to evaluate the effectiveness of the source profiles, and whether additional sources need to be considered. PMF results can also be used with various estimates of air mass age to better quantify the affect of photochemical processing on total VOC mass.

Both CMB and PMF results will be analyzed by wind direction, for episode-versus-nonepisode differences, on cleanout or rain days, and by time of day. We will use non-parametric regression (Henry et al., 2002) and conditional probability function (CPF) with wind direction data to help identify the location of nearby sources of air pollution and quantitatively explore the relationship between apportioned sources and wind direction (Henry et al., 2002; Kim and Hopke, 2004a, b, c). Because 24-hr VOC data are too averaged to compare to meteorological parameters and do not capture the important diurnal trends of VOC sources, 3-hr data will be used in this source apportionment effort. Using such data in the non-parametric regression will permit the sub-apportionment of the source contributions to different wind directions and potentially to more specific sources.

How biases and assumptions are addressed differs between the models. By using both receptor models, CCOS will not have to rely on results from only one approach, and can be more confident in the results assessing the source profiles, the degree of secondary formation, and the representativeness of the sites. These results will also help explain discrepancies that may be evident from the emission inventory reconciliation in separate tasks.

Extent of Reaction and Photochemical Age of the Air Mass

Data analysis in addition to source apportionment will be needed to understand the photochemical age of the ambient hydrocarbons. Extensive work identifying the extent of

reaction using Mapper software has been recently conducted by Charles Blanchard for CCOS, and we will build on available results. We will use multiple ratios of ambient hydrocarbons to assess the extent of reaction of selected ambient air samples (described below), and combine these ratios with their ozone formation reactivities (Carter, 1994; Carter and Lurmann, 1991) to evaluate what the profiles may have been without photochemical reactions. We may stratify data by time of day to obtain several classes of reactivity regimes that can then be modeled separately, depending on time and budget (Kim et al., 2005). We will then compare the extent of reaction and air mass age results to source apportionment results to understand the effectiveness of the receptor models to quantify the age of the air mass. Findings will be used to understand the implications for the possible modification of source profiles and to identify candidate sites for model evaluation.

A number of hydrocarbons are used as indicators of ozone formation potential and tracers of various urban emissions. Assuming that the ratio of these species of interest in the emission inventory are relatively constant throughout the day, the relative abundance of the more reactive species (olefins and reactive aromatics such as xylenes) should decrease with time during the daylight hours, as they are reacted away via photochemistry. The relative abundance of less reactive species such as paraffins and less reactive aromatics (such as benzene) will, therefore, appear to increase. The ratios of more reactive species concentrations to less reactive species concentrations can, therefore, be used as indicators of the relative changes in air mass composition and age. Analysis of such ratios on an hourly basis shows the diurnal variations in air mass age. This analysis may also be used to investigate the presence of fresh emissions or the presence of unique regional sources of particular hydrocarbons. Commonly used ratios include xylenes to benzene (X/B), toluene to benzene (T/B), and acetylene to ethene (A/E) (Nelson and Quigley, 1983; Main, 2001a; Chan et al., 2002; Roberts et al., 2002; Brown and Hafner, 2004). Age of air mass in hours can also be estimated and used in this analysis.

Data

We propose to perform PMF and CMB on ambient 1-hr or 3-hr data from up to two sites, though the scope and budget may change given the results of Tasks 1 through 4. We will work with CCOS to choose appropriate sites for this and other tasks, such as an urban site impacted by fresh emissions and a downwind site that has maximum ozone concentrations (and aged VOCs). Collocated NO_x, ozone, and surface meteorology data will also be required. We will focus on summer 2000, particularly the various intensive operational period (IOP) days, though we will incorporate non-episode periods to isolate characteristics of fresh emissions. We may also perform CMB analysis on selected samples taken during CRAPQS if sufficient data are available and the results would further the understanding of emission sources. STI is currently performing validation of the CCOS database, is familiar with the data, and will require minimal time to evaluate the data for source apportionment. We will also build on our analyses of PAMS data for the SJV, and may utilize the STI-validated data from these sites for our analysis.

Task 6—Integrate the Results of Previous Research

Agreement of ambient- and emission inventory-derived ratios of hydrocarbons to NO_x for the SJV have generally been within a factor of 2 since the early 1990s. For example, Magliano

et al. (1993) and Haste et al. (1998) calculated ambient- and emission inventory-derived ratios of hydrocarbons to NO_x for Fresno, California. Magliano et al. and Haste et al. found ambient-derived ratios to be roughly 2 times greater than emission inventory-derived ratios. (Magliano et al. analyzed an SJV inventory acquired from the ARB between 1990 and 1993, while Haste et al. analyzed an analogous inventory acquired in 1997.) Since the time that the Magliano et al. and Haste et al. analyses were completed, the ARB has incorporated extensive improvements and revisions to its emission inventory for the SJV. STI is currently evaluating the ARB's most up-to-date inventory for the SJV (acquired in 2005). Preliminary results of comparisons of ambient- and emission-derived ratios for Fresno show a marked improvement (e.g., ambient hydrocarbons-to-NO_x are only 1.5 times greater than emission inventory-derived ratios).

While no reports from the CCOS Advanced Data Analysis study (I-8) have yet been issued that are relevant to this study, STI will keep in contact with contractors involved in the ongoing study and acquire results if they become available within the period of performance for this study. In addition, STI will acquire the results of other pertinent studies (e.g., CCOS modeling studies and CRPAQS emission reconciliation and SCAQMD reconciliation studies) that reconcile the emission inventory with ambient or other data. These results will be evaluated and integrated into the findings from the proposed study.

Preliminary results from more recent studies (Raffuse and Chinkin, 2005; Chinkin et al., 2005) indicate that while overall emission estimates seem to be improving, issues still remain with emission speciation profiles and spatial and temporal allocation factors. In another example, an evaluation of modeling performance for a September 16-20, 2000, ozone episode (Tesche et al., 2004) showed that diagnostic sensitivity runs focused on increased VOC emissions (anthropogenic and/or biogenic) yielded significant improvement in predicted ozone concentrations at the ground and aloft across the CCOS region, thus possibly indicating that there are likely to be uncertainties in either the VOC mass or speciation in the existing emission inventory. In the early stages of our study, these results will be evaluated and used to guide and focus our analyses. In the later stages of our proposed study, these results will be summarized and integrated into the findings.

Task 7—Perform Emission Inventory Reconciliation with Pollutant Ratios

In cooperation with the CCOS TC, STI will select the ambient air quality monitoring sites that will be included in the inventory reconciliation analyses. Considerations will include geographic locations, likelihood of influence by nearby emissions sources, or the quantity of ambient data above defined concentration thresholds (which tend to be caused by fresh emissions). STI will process ambient air quality and meteorological data into formats required by the analyses. In addition, STI will prepare seasonal wind rose plots to determine the potential influences of meteorology (e.g., diurnal variations in wind speed and direction) on the analyses.

STI will process and prepare the CCOS emission inventories for use (which we will have in-house for the related CCOS Model Aloft Improvement study led by Mr. Neil Wheeler) and will verify that they meet the following specifications:

- The inventory should be spatially, temporally, and chemically resolved to the finest level of detail possible (i.e., gridded, weekly, hourly, and speciated emissions).
- The inventory should encompass the selected ambient monitoring sites.
- The inventory should include emissions estimates for VOC, CO, NO_x, and individual chemical species (i.e., not carbon-bond or isomer groups). The ability to accurately match chemical species from the inventory to ambient air quality measurements is critical. Inventoried chemical species are often grouped into carbon-bond or isomer groups, which render individual species comparisons impossible. The most appropriate inventory for this analysis should include individual chemical species.

STI will calculate and compare emission inventory- and ambient-derived ratios of VOC/NO_x, CO/NO_x, and individual chemical species and will prepare the ratios for days and hours when the ambient data meet specified selection criteria. We will refine our comparisons by calculating emission inventory-based ratios for grid quadrants corresponding to the prevailing upwind direction. In addition, we will evaluate the effects of elevated point sources by comparing ambient- and emission inventory-derived ratios with and without contributions from elevated point sources.

STI recently performed this type of ratio analysis for four ambient site locations in the SoCAB using ambient data collected from 2000 to 2002. Summaries of PAMS site- and emission inventory-derived weekday HC/NO_x and CO/NO_x ratios for the full grid analysis zone and by wind quadrant are shown in **Figures 2-4 and 2-5**. The ratio comparisons for the full grid analysis zone indicates that the ambient weekday PAMS HC/NO_x ratio was a factor of 1.2 higher than the emission inventory-derived ratio, while the ambient weekday CO/NO_x ratio was a factor of 1.3 higher than the emission inventory-derived ratio.

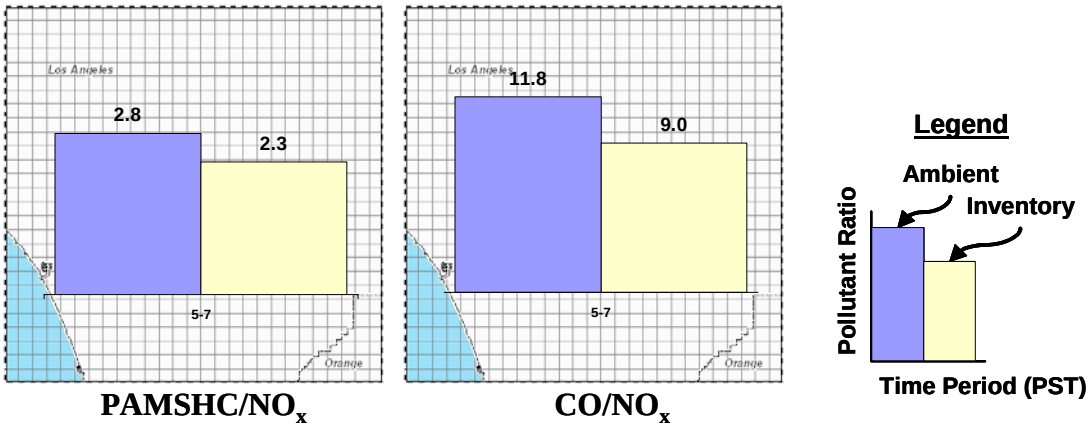

Figure 2-4. Los Angeles North Main ambient- and emission inventory-derived PAMS HC/NO_x and CO/NO_x ratios for the full analysis zone extent from 0500-0700 PST for 2001.

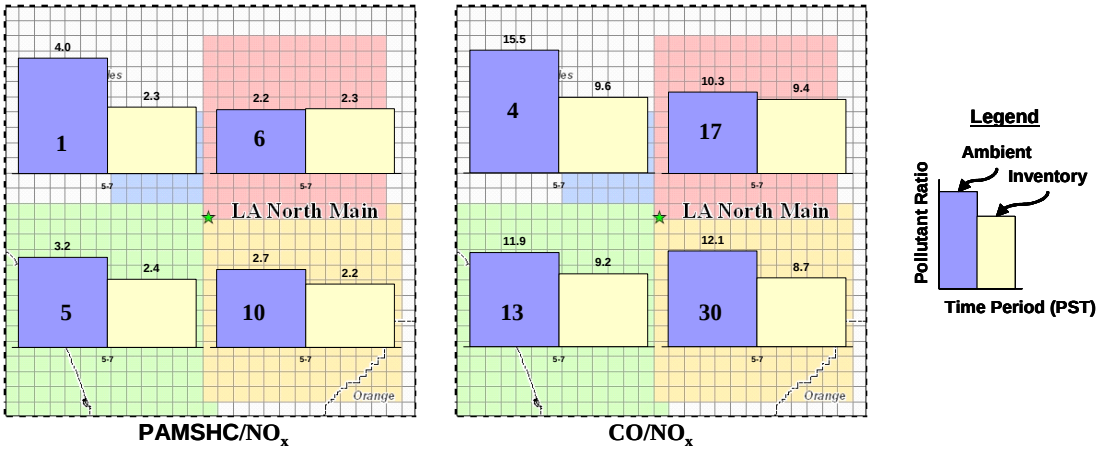

Figure 2-5. Los Angeles North Main ambient- and emission inventory-derived weekday PAMS HC/NO_x and CO/NO_x ratios by wind quadrant from 0500-0700 PST for 2001. Values in the ambient ratio column indicate number of samples.

In addition, STI will compare model-derived VOC-to-NO_x and CO-to-NO_x ratios with both ambient- and inventory-derived ratios. STI proposed to perform model-to-ambient comparisons of these ratios under the Model Aloft Improvement project, so there is likely to be some overlap between these two studies that results in increased efficiencies. As comparisons are performed, significant discrepancies between modeled and measured values will be documented, and inventory-derived values will be analyzed to determine whether these discrepancies are more likely to result from biases in the emission inventory or problems with other model inputs or mechanisms. This analysis may point to possible modeling issues that can be addressed in the parallel Model Aloft Improvement study.

To perform these comparisons, STI will calculate inventory-derived VOC-to-NO_x and CO-to-NO_x ratios for comparison with CMAQ/CAMx model-derived ratios. The emission inventory-derived ratios will be calculated across the entire gridded CCOS modeling domain. Ground-level and elevated sources will be treated separately. The model-derived ratios will be calculated as the average modeled concentrations for the three-dimensional grid cells at ground-level or at elevation. (Grid cells at elevation will be selected according to the stack heights and plume rises of nearby elevated emissions sources.) These analyses will require extensive use of GIS-enabled spatial analysis techniques (see Section 1.3.3) and will help ensure that model results are adequately representing pollutant ratios predicted by the gridded emission inventory.

We understand that gridded emission files are available for each day of an ozone episode that occurred between July 29 and August 4, 2000, but that gridded emission estimates for an ozone episode that occurred in September 2000 may need to be updated and new gridded emission files may need to be prepared for other days during summer 2000. STI has extensive experience in preparing gridded, model-ready emission files using emissions modeling systems such as SMOKE and EPS2.0, having recently prepared model-ready emission files for the large geographic regions such as Gulf Coast of the United States, a nine-state region in the Midwestern United States, and an industrial city in the State of Qatar.

We will prepare summaries and graphical illustrations of findings. Specific areas of the inventory warranting further investigation and specific recommendations for inventory improvements will be identified.

Task 8—Perform Emission Inventory Reconciliation with Speciated VOCs

Further investigation of the CCOS emission inventory will be conducted by comparing the relative amounts of individual hydrocarbons in the ambient data and in the emission inventory, including comparisons of spatial and temporal patterns in the predicted levels of VOC species with the corresponding ambient data.

For example, in the emission inventory reconciliation study STI recently performed for the SoCAB, individual species ratios were computed for a select number of chemical compounds (or compound groups): acetylene/benzene, ethylene/acetylene, benzene/xylenes, benzene/toluene, CO/benzene, total aromatics/PAMS HC, and total biogenic species (isoprene)/ PAMS HC. These species were selected as markers of gasoline exhaust (acetylene, ethylene, aromatic hydrocarbons) and biogenic emissions (isoprene). Comparisons were made for the full extent grid analysis zone surrounding each monitoring site and for each individual wind quadrant within the analysis zone. For the ambient data, average and median ratios were calculated. For the emission inventory data, average and inverse distance weighted (IDW) average ratios were calculated, which weight the emissions less as the distance away from the ambient monitor increases. **Table 2-1** shows the ambient- and emission inventory-derived chemical species ratios for one ambient site in 2001.

In addition to comparison of individual species ratios, a comparison of ambient- and emission inventory-derived compositions of total non-methane organic carbon (TNMOC) can also be undertaken. In a recent emission inventory reconciliation study for the Houston-Galveston area of Texas, STI compared the ambient- and emission inventory-derived relative compositions of 26 individual species that were detected and identified by the ambient measurement system. This analysis was conducted by hour of day and by wind quadrant (because of the known differences between quadrants dominated by mobile sources and those dominated by industrial sources), and these comparisons enabled STI to evaluate how representative the speciation of the emission inventory was of the TNMOC composition detected by the ambient monitoring sites.

Figure 2-6 shows comparisons of ambient- and emission inventory-derived TNMOC compositions by wind quadrant at a selected monitoring site in the Houston-Galveston area. Note that the emission inventory-derived compositions of benzene were significantly higher than the ambient-derived compositions when the winds were from the east (Quadrants 1 and 2). Examination of the gridded emission inventory indicated that the sources of these emissions were chemical manufacturing operations, raising the possibility that the chemical speciation profiles used to speciate the point source inventory were over-representing the relative amount of benzene.

Table 2-1. Los Angeles North Main emission inventory (EI)/ambient species ratios comparison for weekdays in 2001.

	Acetylene/Benzene		Ethylene/Acetylene		Benzene/Xylene		Benzene/Toluene		CO/Benzene		Isoprene/PAMSHC		Total Aromatics/PAMSHC	
Site	EI	Ambient	EI	Ambient	EI	Ambient	EI	Ambient	EI	Ambient	EI	Ambient	EI	Ambient
All	0.97	1.50	2.12	1.53	0.34	0.36	0.25	0.26	174.8	185.4	0.0011	0.0021	0.217	0.182
WD[a] 1	1.00	1.55	2.08	1.57	0.34	0.36	0.26	0.27	182.5	185.0	0.0011	0.0019	0.217	0.191
WD[a] 2	0.92	1.48	2.14	1.57	0.35	0.36	0.24	0.25	170.3	185.4	0.0010	0.0022	0.221	0.182
WD[a] 3	0.99	1.67	2.13	1.43	0.34	0.35	0.25	0.26	169.4	180.0	0.0011	0.0021	0.216	0.180
WD[a] 4	1.00	1.38	2.07	1.64	0.34	0.36	0.27	0.30	180.7	220.8	0.0011	0.0025	0.211	0.196

[a] WD = wind direction

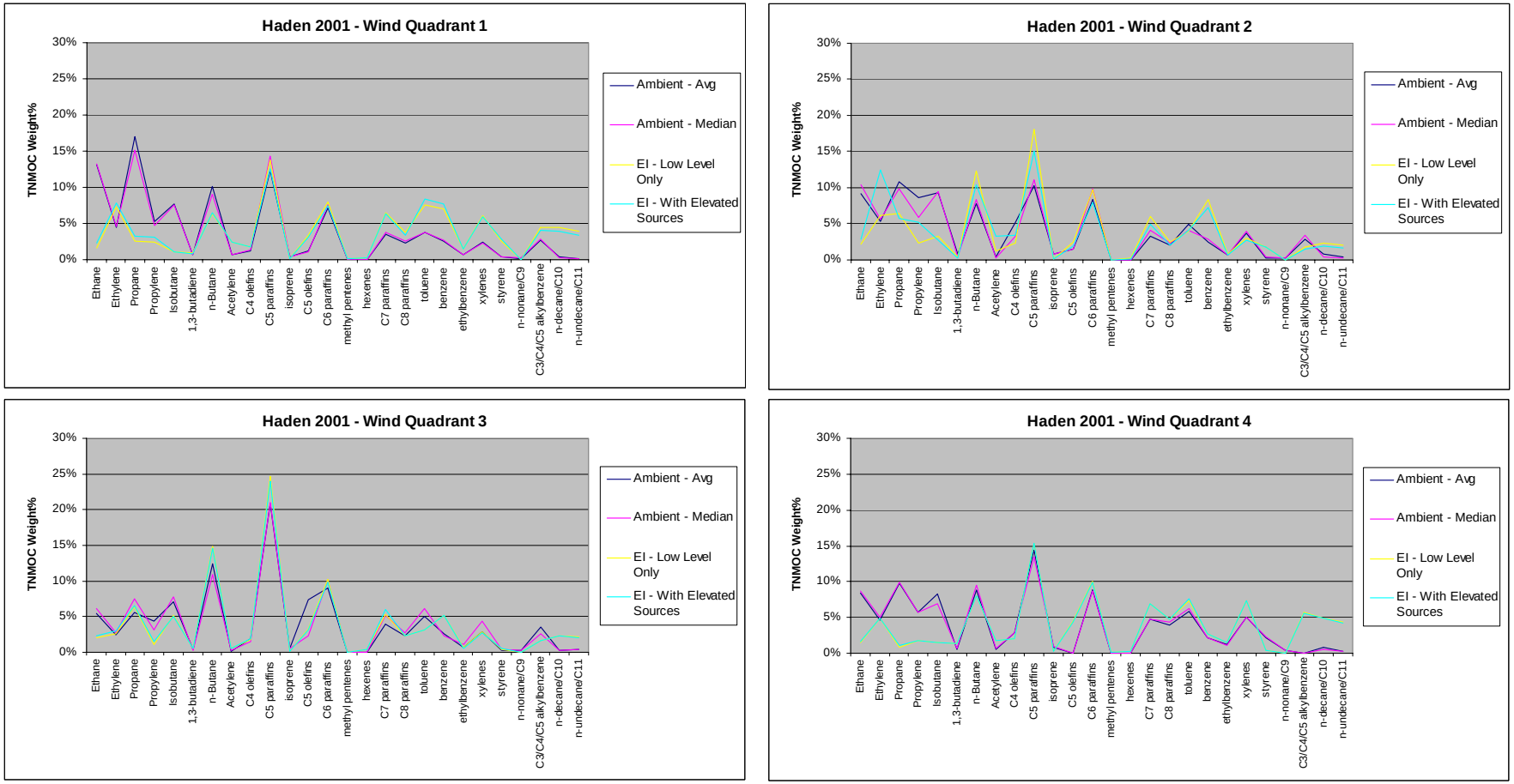

Figure 2-6. Comparison of the 0500 to 0900 CST ambient- and emission inventory-derived relative compositions of individual species by wind quadrant for the Houston, Texas, area Haden Rd. site in 2001.

Task 9—Assess Sources of Uncertainty or Bias

As a component of each data analysis, STI will characterize the potential sources of uncertainty or bias and the degree to which each analysis is likely to be impacted by these effects. For example, the difference in the spatial scales of the gridded emission inventory (2 km × 2 km) and ambient measurements (collected at a single point) can complicate intercomparison of estimated emissions with ambient air quality data in Tasks 7 and 8. The zone of influence on an air quality monitoring site varies with time depending on wind direction, atmospheric mixing, and carryover of aged pollutants. STI ordinarily considers meteorological conditions when selecting the specific inventory grid cells and elevated point sources to be included in the analysis. In addition, STI normally selects ambient and emission inventory data that represent time periods when emission rates are high and chemical reaction rates are low, such as the morning hours. These approaches tend to improve the comparability of the emission inventory to ambient data. The proper use of these strategies will be documented and their apparent effectiveness at strengthening the Tasks 7 and 8 analyses will be characterized.

A number of underlying assumptions in source apportionment have the potential to make results more uncertain. By using both the PMF and CMB receptor models, CCOS will not have to rely on results from only one approach and can be more confident in the results assessing the source profiles, the degree of secondary formation, and the representativeness of the sites. We will highlight and discuss any evident biases and assess the results' uncertainties.

Task 10—Identify Potential Biases and Uncertainties in the CCOS Emission Inventory

The objective of Task 10 is to integrate and synthesize the findings of the individual analyses performed during this project in order to present a coherent, corroborative set of conclusions; to place them in the context of independently completed studies (whether published or concurrent with the proposed work); and to explain apparent inconsistencies (if any) in the findings produced by different analytical approaches.

Our technical approach relies on the completion of all preceding tasks. The Task 10 Leader and project Principal Investigator will meet with the Task Leaders of each preceding task to discuss and review results. They will draw together the results to formulate the overarching conclusions and conceptual models of the reasons why preliminary CCOS photochemical modeling results appear to greatly differ from ambient observations. The themes to be covered in this synthesis and integration will focus in particular on potential problems with the emission inventories, including chemical speciations, temporal patterns, or other aspects. A synthesis discussion will be prepared for inclusion in the Interim or Final Reports discussing the apparent strengths and weaknesses of the CCOS emission inventories.

Task 11—Prepare Interim and Final Reports

By January 31, 2006, STI will prepare an interim report documenting the initial findings of this study. This report will summarize the findings tentatively established as interim products, including the level of correlation that should be expected between emissions estimates and ambient concentrations based on current methods, the extent to which ambient measurements

can be used to identify and evaluate divergences from emissions estimates, and which, if any, emissions estimates may be subject to significant biases based on comparison with ambient measurements.

When the technical analyses are completed, STI will prepare a draft final report documenting the technical approach, findings, and conclusions of the study, as well as a draft manuscript suitable for publication in a peer-reviewed journal summarizing the results of the study. The study findings will also be presented at a one-day CCOS TC meeting in Sacramento, California. Based on comments provided by the TC, STI will prepare and submit a final report and prepare a final version of the manuscript that will be submitted to an appropriate journal for review and publication. The manuscript will be prepared in the style required by the selected journal and focus on the most important findings of the study and their implications.

9. REFERENCES

Brown S.G. and Hafner H.R. (2002) Prescribed data analyses for Massachusetts PAMS sites. Technical memorandum prepared for Department of Environmental Protection, Lawrence, MA, by Sonoma Technology, Inc., Petaluma, CA, STI-902133-2263-TM, October.

Brown S.G. and Hafner H.R. (2003a) Exploratory source apportionment of Houston's Clinton Drive auto-GC 1998-2001 data. Final report prepared for Texas Commission on Environmental Quality, Austin, TX, by Sonoma Technology, Inc., Petaluma, CA, STI-900700-2317-FR, May.

Brown S.G. and Hafner H.R. (2003b) Source apportionment of Detroit pilot city air toxics data. Presented at the *National Workshop on Air Toxics Monitoring, Chicago, IL, May 13-14* (STI-902530-2371).

Brown S.G. and Hafner H.R. (2003c) Source apportionment of VOCs in the Houston, Texas, area. Presented at the *NARSTO Workshop on Innovative Methods for Emission-Inventory Development and Evaluation, Austin, TX, October 14-16* (STI-2356).

Brown S.G. and Hafner H.R. (2004) Source apportionment of VOCs in the Houston, Texas, area using positive matrix factorization. Paper no. 353 presented at the *Air & Waste Management Association's 97th Annual Conference and Exhibition, Indianapolis, IN, June 22-25* (STI-2415).

Brown S.G., Reid S.B., Roberts P.T., Buhr M.P., and Funk T.H. (2004) Reconciliation of the VOC and NO_x emission inventory with ambient data in the Houston, Texas region. Paper for *13th International Emission Inventory Conference "Working for Clean Air in Clearwater", Clearwater, FL, June 8-10* (STI-2525).

Brown S.G., Frankel A., and Hafner H.R. (2005a) South Coast Air Quality Management District PAMS Data Analysis - Tasks 4b and 4c, principal component analysis and source apportionment of PAMS VOC data. Draft technical memorandum prepared for the South Coast Air Quality Management District, Diamond Bar, CA, by Sonoma Technology, Inc., Petaluma, CA, STI-904046-2723-TM, March.

Brown S.G., Frankel A., Hafner H.R., Roberts P.T., and Anderson D.A. (2005b) Source apportionment of $PM_{2.5}$ in Phoenix, Arizona, with positive matrix factorization. Poster prepared for the *2005 Particulate Matter Supersites Program and Related Studies: An AAAR International Specialty Conference, February 7-11, Atlanta, GA* (STI-2687).

Brown S.G., Frankel A., Raffuse S.M., and Hafner H.R. (2005c) Source apportionment of $PM_{2.5}$ at a rural site in Louisiana using positive matrix factorization. (To be submitted).

Brown S.G., Frankel A., Raffuse S.M., Hafner H.R., and Anderson B.A. (2005d) Source apportionment of $PM_{2.5}$ at Hercules-Glade, Missouri, using positive matrix factorization. (to be submitted).

California Air Resources Board (2004a) Speciation profiles and size fractions. Available on the Internet at <http://www.arb.ca.gov/ei/speciate/htm>.

California Air Resources Board (2004b) Speciation profiles and size fractions--Citations for organic gas and PM speciation profiles (Excel). Available on the Internet at <http://www.arb.ca.gov/ei/speciate/speciate.htm>.

Carter W.P.L. and Lurmann F.W. (1991) Evaluation of a detailed gas phase atmospheric reaction mechanism using environmental chamber data. *Atmos. Environ.* **25A**, 2771-2806.

Carter W.P.L. (1994) Development of ozone reactivity scales for volatile organic compounds. *J. Air & Waste Manag. Assoc.* **44**, 881-899.

Chan C.Y., Chan L.Y., Wang X.M., Liu Y.M., Lee S.C., Zou S.C., Sheng G.Y., and Fu J.M. (2002) Volatile organic compounds in roadside microenvironments of metropolitan Hong Kong. *Atmos. Environ.* **36**, 2039-2047.

Chinkin L.R., Main H.H., Reiss R., Roberts P.T., and Romanow S. (1998) Analysis of PAMS data to evaluate reformulated gasoline effects. Presented at the *8th Coordinating Research Council (CRC) On-Road Vehicle Emissions Workshop, San Diego, CA, April 20-23*.

Chinkin L.R., Funk T.H., Main H.H., and Roberts P.T. (2000) PAMS data analysis for Southern California. Volume VI: use of PAMS data to evaluate a South Coast Air Basin emission inventory. Report prepared for the South Coast Air Quality Management District, Diamond Bar, CA, by Sonoma Technology, Inc., Petaluma, CA, STI-997528-1916-FR, November.

Chinkin L.R., Penfold B.M., Brown S.G., and Hafner H.R. (2005) Emission inventory evaluation and reconciliation in the South Coast Air Basin. Draft final report prepared for South Coast Air Quality Management District, Diamond Bar, CA, by Sonoma Technology, Inc., Petaluma, CA, STI-904045-2728-DFR, April.

DaMassa J., Tanrikulu S., Magliano K., Ranzieri A.J., and Niccum L. (1996) Performance evaluation of SAQM in Central California and attainment demonstration for the August 3-6, 1990 ozone episode. Report prepared by Technical Support Division, California Air Resources Board, Sacramento, CA, February.

Fujita E.M., Croes B.E., Bennett C.L., Lawson D.R., Lurmann F.W., and Main H.H. (1992) Comparison of emission inventory and ambient concentration ratios of CO, NMOG, and NO_x in California's South Coast Air Basin. *J. Air & Waste Manag. Assoc.* **42**, 264-276.

Fujita E.M., Watson J.G., Chow J.C., and Magliano K.L. (1995) Receptor model and emissions inventory source apportionments of nonmethane organic gases in California's San Joaquin Valley and San Francisco Bay Area. *Atmos. Environ.* **29**, 3019-3035.

Hafner H.R. and Roberts P.T. (2002) Recommendations for the PAMS network in the Northeast and Mid-Atlantic states. Presented at the *Symposium on Air Quality Measurement Methods and Technology, San Francisco, CA, November 13* (STI-900860-2231).

Hafner H.R. and Brown S.G. (2003) Review of Detroit DRUM impactor data. Technical memorandum prepared for the Lake Michigan Air Directors Consortium, Des Plaines, IL by Sonoma Technology, Inc., Petaluma, CA, STI-902910, February.

Haste T.L., Chinkin L.R., Kumar N., Lurmann F.W., and Hurwitt S.B. (1998) Use of ambient data collected during IMS95 to evaluate a regional emission inventory for the San Joaquin Valley. Final report prepared for the San Joaquin Valleywide Air Pollution Study Agency, c/o the California Air Resources Board, Sacramento, CA, by Sonoma Technology, Inc., Petaluma, CA, STI-997211-1800-FR, July.

Henry R.C. (1997) History and fundamentals of multivariate air quality receptor models. *Chemometrics and Intelligent Laboratory Systems* **37**, 525-530.

Henry R.C., Chang Y.-S., and Spiegelman C.H. (2002) Locating nearby sources of air pollution by nonparametric regression of atmospheric concentrations on wind direction. *Atmos. Environ.* **36**, 2237-2244.

Kim E. and Hopke P.K. (2004a) Comparison between conditional probability function and nonparametric regression for fine particle source directions. *Atmos. Environ.* **38**, 4667-4673.

Kim E. and Hopke P.K. (2004b) Source apportionment of fine particles at Washington, DC utilizing temperature resolved carbon fractions. *J Air Waste Manag Assoc* **54**, 773-785.

Kim E. and Hopke P.K. (2004c) Improving source identification of fine particles in a rural northeastern US area utilizing temperature resolved carbon fractions. *J. Geophys. Res* **109**, D09204.

Kim E., Brown S.G., Hafner H.R., and Hopke P.K. (2005) Characterization of non-methane volatile organic compounds sources in Houston during 2001 using Positive Matrix Factorization. *Atmos. Environ.* (in press).

Korc M.E., Jones C.M., Chinkin L.R., Main H.H., Roberts P.T., and Blanchard C. (1995) Use of PAMS data to evaluate the Texas COAST emission inventory. Final report prepared for U.S. Environmental Protection Agency, Research Triangle Park, NC, by Sonoma Technology, Inc., Santa Rosa, CA, Work assignment 2-95, EPA Contract No. 68D30020, STI-94520-1558-FR, December.

Lurmann F.W. and Main H.H. (1992) Analysis of the ambient VOC data collected in the Southern California Air Quality Study. Report prepared for the California Air Resources Board, Sacramento, CA, by Sonoma Technology, Inc., Santa Rosa, CA, STI-99120-1161-FR, Contract No. A823-130, February.

Magliano K.L., Lurmann F.W., and Watson J.G. (1993) Reconciliation of emissions inventory and ambient data in the San Joaquin Valley and the San Francisco Bay Area. Paper No. 93-WP-100.08 presented at the *Air & Waste Management Association 86th Annual Meeting, Denver, CO, June 14-18*.

Main H.H., Chinkin L.R., and Roberts P.T. (1995) Analysis of PAMS and NARSTO-Northeast ambient air quality data. Work assignment 5-95. Data analysis plan prepared for the U.S. Environmental Protection Agency, Research Triangle Park, NC, by Sonoma Technology, Inc., Santa Rosa, CA, EPA Contract No. 68D30020, STI-94550-1526-DA, June.

Main H.H., Chinkin L.R., and Roberts P.T. (1996) Analysis of VOC data in support of pollutant transport studies in Shasta County, California. In *Measurement of Toxic and Related Air Pollutants. Proceedings of an Air & Waste Management/U.S. Environmental Protection Agency International Specialty Conference, Raleigh-Durham, NC, May 7-9*, 67-74, Air & Waste Management, Pittsburgh, PA (STI-1581).

Main H.H. and Chinkin L.R. (1998) Example photochemical assessment monitoring station (PAMS) data analysis for Ventura County. Final report prepared for Ventura County Air Pollution Control District, Ventura, CA by Sonoma Technology, Inc., Santa Rosa, CA, STI-997450-1795-FR, March.

Main H.H., Chinkin L.R., Chamberlin A.H., and Hyslop N.M. (1999a) PAMS data analysis for Southern California. Volume I: characteristics of hydrocarbon data collected in the South Coast Air Quality Management District from 1994 to 1997. Report prepared for the South Coast Air Quality Management District, Diamond Bar, CA by Sonoma Technology, Inc., Petaluma, CA, STI-997521-1899-DFR, September.

Main H.H., Hurwitt S.B., and Roberts P.T. (1999b) Spatial and temporal characteristics of California PAMS and long-term trend site VOC data (1990-1997). Report prepared for the U.S. Environmental Protection Agency, Research Triangle Park, NC, by Sonoma Technology, Inc., Petaluma, CA, STI-998241-1883-FR, May. Available on the Internet at <http://www.arb.ca.gov/aaqm/qmosprog/pams/sti_voc.pdf> last accessed March 11, 2005.

Main H.H. (2000) Spatial and temporal characteristics of VOC data: 1998 Atlanta, Georgia, PAMS sites. Prepared for Georgia Department of Natural Resources, Atlanta, GA by Sonoma Technology, Inc., Petaluma, CA, STI-999433-2044-TM, November.

Main H.H. and Roberts P.T. (2000) PAMS data analysis workbook: illustrating the use of PAMS data to support ozone control programs. Prepared for the U.S. Environmental Protection Agency, Research Triangle Park, NC, by Sonoma Technology, Inc., Petaluma, CA, STI-900243-1987-FWB, September.

Main H.H. (2001a) PAMS analysis for Southern California: characteristics of VOC data 1994-1997. Presented at the *SCOS97-NARSTO Data Analysis Conference, Los Angeles, CA, February 13-15* (STI-2054).

Main H.H. (2001b) Prescribed data analysis for the Phoenix, Arizona, PAMS site 1999-2000. Final report prepared for the Arizona Department of Environmental Quality, Phoenix, AZ, by Sonoma Technology, Inc., Petaluma, CA, STI-901074-2103-FR, November.

Nelson P.F. and Quigley S.M. (1983) The m, p-xylenes: ethylbenzene ratio, a technique for estimating hydrocarbon age in ambient atmospheres. *Atmos. Environ.* **17**, 659-662.

Paatero P. and Tapper U. (1994) Positive matrix factorization: a non-negative factor model with optimal utilization of error estimates of data values. *Environmetrics* **5**, 111-126.

Paatero P. (2000) User's guide for positive matrix factorization programs PMF2 and PMF3, part 1: tutorial. Prepared by University of Helsinki, Finland, February.

Raffuse S.M. and Chinkin L.R. (2005) Emission inventory reconciliation in the San Joaquin Valley. Technical memorandum prepared for the California Air Resources Board, Sacramento, CA, by Sonoma Technology, Inc., Petaluma, CA, STI-902327-2751-TM, May.

Roberts P.T., Brown S.G., Main H.H., Buhr M.P., Hyslop N.P., MacDonald C.P., Roney J., Knoderer C.A., and Miller D. (2002) Preliminary VOC, olefin, and conceptual model results for Houston. Presented to the Texas Natural Resource Conservation Commission, Austin, TX, April 4.

San Joaquin Valley Air Pollution Control District (2004) San Joaquin Valley Air Basin plan demonstrating attainment of federal 1-hour ozone standards. October.

Sonoma Technology, Inc. (2004) California Regional Particulate Air Quality Study. Available on the Internet at <http://www.sonomatechdata.com/crpaqsmetrep/>.

Tesche T.W., McNally D.E., Wilkinson J.G., Jeffries H.E., Kumra Y., Emery C., Yarwood G., and Souten D.R. (2004) Evaluation of the 16-20 September 2000 ozone episode for use in 1-hr SIP development in the California Central Valley. Draft final report prepared by Alpine Geophysics, LLC, Ft. Wright, KY, February.

Thuillier R.H. and Ranzieri A. (1995) SARMAP--Lessons Learned. *Air &Waste Management Association's International Specialty Conference, San Diego, CA, 7-12 November 1993*, Regional Photochemical Measurement and Modeling Studies, Volume 3, Other Topics Related to Regional Studies, A.J. Ranzieri and P.A. Solomon, eds., Air & Waste Management Association,, Pittsburgh, PA.

Watson J.G., Chow J.C., and Fujita E.M. (2001) Review of volatile organic compound source apportionment by chemical mass balance. *Atmos. Environ.* **35**, 1567-1584.

Watson J.G., Zhu T., Chow J.C., Engelbrecht J., Fujita E.M., and Wilson W.E. (2002) Receptor modeling application framework for particle source apportionment. *Chemosphere* **49** (9), 1093-1136.

Yarwood G., Morris R., Rao S., Lau S., Fujita E., Campbell D., and White W. (2005) Evaluating VOC receptor models using grid-model simulations. Final report prepared for the Coordinating Research Council, Alpharetta, GA, by ENVIRON International Corp., Novato, CA; Desert Research Institute, Reno, NV, and University of California, Davis, CA, CRC project A-34, April.

Zhao W., Hopke P.K., and Karl T. (2004) Source identification of volatile organic compounds in Houston, TX. *Environmental Science and Technology* **38**, 1338-1347.