

**VALIDATION AND APPLICATION PROTOCOL FOR SOURCE APPORTIONMENT  
OF PHOTOCHEMICAL ASSESSMENT MONITORING STATIONS (PAMS) AMBIENT  
VOLATILE ORGANIC COMPOUND (VOC) DATA**

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Executive Summary Report

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**Title:** Validation And Application Protocol For Source Apportionment Of Photochemical Assessment Monitoring Stations (PAMS) Ambient Volatile Organic Compound (VOC) Data

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## **Objectives of the Research Project**

The objectives of this research project were to review the applicability of the Chemical Mass Balance (CMB) receptor modeling and available source composition profiles for estimating source contributions to ambient VOCs using data from the Photochemical Assessment Monitoring Station (PAMS) networks and to develop a protocol for validation of ambient and source composition input data and for evaluation and interpretation of model outputs.

## **Summary of Findings**

This document provides a protocol for applying the Chemical Mass Balance (CMB) receptor model to volatile organic compound (VOC) data from the Photochemical Assessment Monitoring Station (PAMS) networks and for evaluating and interpreting model outputs. The protocol provides recommended procedures for validating ambient VOC data, assigning uncertainties to ambient and source measurements, selecting and evaluating source composition profiles and fitting species, evaluating and validating model outputs, and analyzing and interpreting the CMB source contribution estimates and associated uncertainties. The CMB applications and validation protocol developed by Watson et al. (1998) was adapted here for application to PAMS and similar VOC data.

The guidance includes a current library of available source VOC composition profiles in CMB8-ready format and sample CMB Version 8 VOC source and ambient input data files. The profiles are contained in the file CMBProfilesLibrary.xls. This library is a compilation of source profiles that have been used by the Desert Research Institute in prior VOC source apportionment studies. They include profiles that were newly developed for specific studies, the literature, and from the California Air Resources Boards Modeling Emissions Data System (MEDS). Studies for which profiles were newly developed include the 1993 Coast Oxidant Assessment for Southeast Texas (Fujita et al., 1995b), 1995 Boston and Los Angeles VOC Source Apportionment Study (Fujita et al. 1997a), 1995/96 Washington Ozone Transport Study (Fujita et al., 1997c), 1996 El Paso/Juarez Ozone Study (Fujita, 2001; Seila et al., 2001), and 1998 Central Texas On-Road Hydrocarbon Study (1999a), 1999 VOC Source Signatures in Houston, (Fujita et al., 1999b), apportionment of 1994-97 South Coast Air Basin PAMS VOC data (Fujita and Campbell, 2003b), and the 2000 Weekend Ozone Observations in the South Coast Air Basin (Fujita et al. 2002; Fujita et al., 2003a). The document and supporting files are intended to facilitate and encourage the application of the CMB receptor model to PAMS VOC data by State and Local air pollution agencies as an evaluation of emissions inventories.

The profiles are expressed as weight fractions and are normalized to the sum of the 55 PAMS target hydrocarbons. The PAMS species typically account about 80 percent of the total ambient hydrocarbons in urban locations, and their sum is more reproducible among different laboratories than total NMHC or NMOC. Compounds other than the 55 Photochemical Assessment Monitoring Station (PAMS) target NMHCs that are individually identified are grouped into a category named "other". Compounds reported as "unknowns" are grouped into a category named "UNID". The profiles also include total NMHC (i.e., the sum of PAMS species + other + unid) normalized to sum of PAMS species. Although not measured in the PAMS program, methyl tert-butyl ether (MTBE) is included in the profiles because it is a major component in reformulated gasoline and in the exhaust of vehicles using RFG. By including MTBE in the profile, its ambient concentration can be predicted by CMB.

To assist with the selection of profiles, several sort fields are included such as category (source type), location and year. The list of profiles can be filtered by selecting values from any or all of these fields using the pull down menus on each heading. Up to four profiles can be compared graphically in a set of three column plots. Two of the plots contain the 55 PAMS species and all other organic species, respectively, for the selected profiles. A third plot shows a detailed comparison of the typical major species for the first two profiles selected. Running a macro in the source profile data file automatically generates the source profile, source selection and species selection files.

Procedures for evaluating the validity of the application of CMB to PAMS VOC data includes: 1) determination of model applicability; 2) review of initial source contribution estimates; 3) examination of model outputs and performance measures; 4) identification of deviations from model assumptions; 5) identification and correction of model input errors; 6) verification of the consistency and stability of source contribution estimates; and 7) evaluation of the results of the CMB analysis with respect to other source assessment methods.

## **Publications and Presentations**

The results of several studies were used in the development of the application and validation protocol for VOC source apportionment and compilation of the VOC source composition library. The following is a list of relevant journal publications, reports and presentations. While some of the projects predate this study, most overlap this study in time and influenced the development of the protocol.

### Publications

- Fujita, E.M., J.G. Watson, J.C. Chow, and Z. Lu (1994). Validation of the Chemical Mass Balance Receptor Model Applied to Hydrocarbon Source Apportionment in the Southern California Air Quality Study. *Environ. Sci. Technol.* **28**(9).
- Fujita, E.M., J.G. Watson, J.C. Chow and K.L. Magliano (1995c). 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(21), 3019-3035.

- McDonald, J. D., B. Zielinska, E.M. Fujita, J.C. Sagebiel, J.C. Chow, and J.G. Watson (2000). Fine Particle and Gaseous Emission Rates from Residential Wood Combustion. *Environ. Sci. and Technol.*, 34: 2080-2091.
- Fujita E.M. (2001). Hydrocarbon Source Apportionment for the 1996 Paso del Norte Ozone Study. *Science of the Total Environment* 276, 171-184.
- Watson, J., J.C. Chow, and E. Fujita (2001). Review of Volatile Organic Compound Source Apportionment by Chemical Mass Balance. *Atmos. Environ.* 35:1567-1584.
- Fujita, E.M., D.E. Campbell, B. Zielinska, J.C. Sagebiel, J.L. Bowen, W. Goliff, W.R. Stockwell, and D.R. Lawson (2003a). Diurnal and Weekday Variations in Source Contributions of Ozone Precursors in California's South Coast Air Basin. *J. Air & Waste Manage. Assoc.* 53: 844-863.
- McDonald, J. D., B. Zielinska, E.M. Fujita, J.C. Sagebiel, J.C. Chow, and J.G. Watson Jacob (2003). Emissions from Charbroiling and Grilling of Chicken and Beef. *J. Air & Waste Manage. Assoc.* 53: 185-194.
- Fujita, E.M., G. Harshfield, and L.H. Sheetz (2003c). Performance Audits and Laboratory Comparisons for SCOS97-NARSTO Measurements of Speciated Volatile Organic Compounds. *Atmos. Environ.* in press.

### Reports

- Fujita, E.M., Z. Lu, J. Sagebiel, G. Harshfield, and B. Zielinska (1995a). Validation and Evaluation of the Coast Oxidant Assessment for Southeast Texas (COAST) Volatile Compound Data. Prepared for the Texas Natural Resource Conservation Commission. August 1995.
- Fujita, E.M., Z. Lu, J. Sagebiel, N.F. Robinson, and J. G. Watson (1995b). VOC Source Apportionment for the Coast Oxidant Assessment for Southeast Texas. Final report prepared for the Texas Natural Resource Conservation Commission, August 1995.
- Lawson, D.R., S. Diaz, E.M. Fujita, S.L. Wardenburg, R.E. Keislar, Z. Lu and D.E. Schorran (1996). Program for the Use of Remote Sensing Devices to Detect High-Emitting Vehicles. Final Report. Prepared for Technology Advancement Office, South Coast Air Quality Management District, Diamond Bar, CA, April 16, 1996.
- Fujita, E.M., Z. Lu, L. Sheetz, G. Harshfield, and B. Zielinska (1997a). Determination of Mobile Source Emission Source Fraction Using Ambient Field Measurements. Final Report prepared for the Coordinating Research Council, Atlanta, GA, July 1997.
- Fujita, E., Z. Lu, G. Harshfield, and B. Zielinska (1997b). NARSTO-Northeast: Hydrocarbon and Carbonyl Measurement Audits for the 1995 Field Study. Final Report prepared for the Electric Power Research Institute, Palo Alto, CA, July 1997
- Fujita, E.M., Z. Lu, L. Sheetz, G. Harshfield, T. Hayes, and B. Zielinska (1997c). Hydrocarbon Source Apportionment in Western Washington. Report prepared for the State of Washington Department of Ecology, Lacey, WA, September, 1997.

- Watson, J.G., Robinson, N.F., Lewis, C.W., Coulter, C.T., Chow, J.C., Fujita, E.M., Conner, T.L., Pace, T.G. (1998a). CMB8 applications and validation protocol for PM<sub>2.5</sub> and VOCs. Report No. 1808.2D1, Desert Research Institute, Reno, NV.
- Watson, J., E. Fujita, J.C. Chow, B. Zielinska, L. Richards, W. Neff, and D. Dietrich (1998b). Northern Front Range Air Quality Study. Final report prepared for Colorado State University, Fort Collins, CO, June 30, 1998.
- Fujita, E., and Z. Lu (1998a). Analysis of Data From the 1995 NARSTO-Northeast Study. Volume III: Chemical Mass Balance Receptor Modeling. Final report prepared for Coordinating Research Council, Atlanta, GA, July 1998.
- Fujita, E. (1998b). Emission Source Profiles Applicable to CMB Receptor Modeling of Texas PAMS VOC Data. TNRCC Contract No. 98 80078200. Final report prepared for the Texas Natural Resource Conservation Commission, Austin, TX, November 1998.
- Fujita, E., J.G. Watson, J.C. Chow, N. Robinson, L. Richards, and N. Kumar (1998c). Northern Front Range Air Quality Study. Volume C: Source Apportionment and Simulation Methods and Evaluation. Final report prepared for Colorado State University, Fort Collins, CO, June 30, 1998.
- Fujita, E.M., R.E. Keislar, J.L. Bowen, W. Goliff, F. Zhang, L.H. Sheetz, M.D. Keith, J.C. Sagebiel, and B. Zielinska (1999a). 1998 Central Texas On-Road Hydrocarbon Study. Final report prepared for the Texas Department of Transportation, Austin, TX under subcontract to PBS&J, Austin, TX, March, 1999.
- Fujita, E. (1999b). VOC Source Signatures in Houston, TX Phase 1: Sample Collection. Prepared for the Texas Natural Resource Conservation Commission (Contract No. 980069300) under subcontract to MCNC-North Carolina Supercomputing Center, Research Triangle Park, NC, August, 1999.
- Fujita, E.M., H. Moosmuller, M.C. Green, J.L. Bowen, Leon Dolislager, Ash Lashgari, Nehzat Motallebi, Randy Pasek, and Jim Pederson (1999c). SCOS97-NARSTO 1997 Southern California Ozone Study and Aerosol Study: Volume IV Summary of Quality Assurance. Prepared for the California Air Resource Board, Sacramento, CA December, 1999.
- Fujita, E., W. Goliff, J. Sagebiel, F. Zhang, L.H. Sheetz, M.D. Keith, and B. Zielinska (2001). VOC Source Signatures in Houston, TX. Prepared for the Texas Natural Resource Conservation Commission (Contract No. 980069300) under subcontract to MCNC-North Carolina Supercomputing Center, Research Triangle Park, NC, February, 2001.
- Fujita, E.M., D.E. Campbell, W. Stockwell, R. Keislar, B. Zielinska, J.C. Sagebiel, W. Goliff, M. Keith, and J.L. Bowen (2002). Weekend/Weekday Ozone Observations in the South Coast Air Basin Volume II: Analysis of Air Quality Data. Final report prepared by the Desert Research Institute, Reno, NV for the National Renewable Energy Laboratory, Golden, CO, and the Coordinating Research Council, April 2002.
- Fujita, E. and D. Campbell (2003b). PAMS Data Analysis for Southern California Volume VII: Source Apportionment of Volatile Organic Compounds. Final report prepared for the South Coast Air Quality Management District, Diamond Bar, CA, June 20, 2003

## Presentations

- Fujita, E.M. (1996). Determination of Mobile Source Emission Source Fraction Using Ambient Field Measurements. Presented at the Sixth CRC On-Road Vehicle emissions workshop, San Diego, CA, March 18-20, 1996.
- Fujita, E.M., W.A. Lonneman, A. Van Arsdale and A. Oi (1996). Narsto-NE Hydrocarbon Laboratory Comparison. Presented at the A&WMA Conference and Courses: Measurement of Toxic and Related Air Pollutants, RTP, NC, May 7-9, 1996.
- Fujita, E.M., Z. Lu, N.F. Robinson and J.G. Watson (1996). Application of Chemical Mass Balance Model to Coastal Oxidant Assessment for Southeast Texas Volatile Organic Compound Data. To be presented at the Air & Waste Management Association 89th Annual Meeting, Nashville, TN, June 23-28, 1996.
- Fujita, E.M., B. Zielinska, L.H. Sheetz, G. Harshfield, and E. Urberna (1996). Hydrocarbon and Carbonyl Audits for NARST-Northeast 1996 Field Study. Presented at the First NARSTO-Northeast Data Analysis Symposium and Workshop, Norfolk, VA, 10-12 December, 1996.
- Fujita, E.M., Z. Lu, L.H. Sheetz, G. Harshfield, and B. Zielinska (1997). Determination of Mobile Source Fraction Using Ambient Data. Presented at the Seventh CRC Mobile Source Emission Workshop, San Diego, CA, 9-11 April 1997.
- Fujita, E., J. Shire, G. Harshfield, E. Urberna, and B. Zielinska (1997). Performance Audits for Measurements of Carbonyl Compounds during the NARSTO-Northeast 1996 Summer Ozone Study. Presented at the American Geophysical Union 1997 Fall Meeting, San Francisco, CA, 8-12 Dec. 1997
- Fujita, E. and J.G. Watson (1998). Validation and Applications Protocol for Source Apportionment of Volatile Organic Compounds and Fine Particles. Presented at EPA/A&WMA 18th Symposium on Measurement of Toxic and Related Air Pollutants, Cary, NC, 1-3 September, 1998.
- Fujita, E., T. Hayes, R. Keislar, W. Goliff, L. Sheetz, M. Keith, J. Sagebiel, and B. Zielinska, C. Harder, S. Torpey, D. Castro, L. Moon, R. Ramon, and E. Collins (1999). 1998 On-Road Hydrocarbon Study. Presented at the 9th CRC On-Road Vehicle Emissions Workshop, San Diego, CA, 20-22 April, 1999.
- Fujita, E., (1999). Hydrocarbon source apportionment for the 1996 Paso del Norte Ozone Study. Presented at A&WMA 92nd Annual Meeting & Exhibition, St. Louis, MO, 20-24 June, 1999.
- Fujita, E., (2001). SCOS97-NARSTO: Quality Assurance Issues. Presented at the SCOS97-NARSTO Data Analysis Conference, Diamond Bar, CA February 13-15, 2001.
- Fujita, E., (2001). Source Attribution of Ambient Hydrocarbons in the South Coast Air Basin. Presented at the SCOS97-NARSTO Data Analysis Conference, Diamond Bar, CA February 13-15, 2001.
- Fujita, E., R. Keislar, and W. Stockwell (2001). Weekend/Weekday Ozone Observations in the South Coast Air Basin – Phase 2 Field Study. Presented at the 11th CRC On-Road Vehicle Emissions Workshop, San Diego, CA, 26-28 March, 2001.
- Fujita, E.M., W.R. Stockwell, D.E. Campbell, and D.R. Lawson (2002). OHVT Weekend/Weekday Ozone Study In The South Coast Air Basin. Presented at the 8th Diesel Engine Emission Reduction (DEER) Workshop, San Diego, CA, August 25-29, 2002.

Fujita, E.M. (2003). Source Receptor Analysis for VOC and fine PM; Source Identification and Apportionment. Presented at the Integrated Program on Urban, Regional and Global Air Pollution, Workshop on Mexico Emissions Inventory, Mexico City , February 25-26, 2003 .

### **Supplemental Keywords**

Chemical Mass Balance  
receptor model  
source apportionment  
source attribution  
source composition profiles  
volatile organic compounds (VOC)  
Photochemical Assessment Monitoring Stations (PAMS)

### **Relevant Web Sites**

This document, the CMBProfilesLibrary file and a self-extracting zipfile ( SoCAB.exe) containing sample CMB input files with ambient and source VOC datasets for California's South Coast Air Basin are available at the Desert Research Institute web site at <http://www.dri.edu/People/ericf/>. Specific questions and comments regarding this document and sample datasets may be addressed to Dr. Eric Fujita at [ericf@dri.edu](mailto:ericf@dri.edu). The CMB software is available at the TTN web site at <http://www.epa.gov/scram001/tt23.htm>. Questions regarding the CMB software should be directed to Dr. John Watson at DRI at [johnw@dri.edu](mailto:johnw@dri.edu).