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Final Report

EVALUATION OF AMBIENT SPECIES PROFILES, AMBIENT VERSUS MODELED NMHC:NO$_x$ AND CO:NO$_x$ RATIOS, AND SOURCE-RECEPTOR ANALYSES

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1 INTRODUCTION

BACKGROUND

The current regulatory approach to achieving ozone and related air quality standards is based on emissions estimation and modeling. In recent years, several studies have attempted to evaluate the emissions estimates and methods against ambient measurements by comparing non-methane organic compound (NMOC) species profiles, NMOC:NO$_x$ ratios, CO:NO$_x$ ratios, and using receptor modeling of NMOCs. Areas of interest have included the relative contributions of mobile, stationary, and biogenic sources, and evidence for underestimation of sources and/or missing sources. However, over the same time period the emission estimates have also been revised to reflect the latest information. In particular, EPA's MOBILE emission factor model has been updated (current version MOBILE5a) resulting in significant increases in estimated emission factors for NMOC, NO$_x$, and CO.

The objective of this study was to critically review the most relevant available literature on ambient species profiles, ambient versus emission model NMOC:NO$_x$ ratios and CO:NO$_x$ ratios, and receptor modeling of NMOCs. By design, the review did not include any "tunnel studies" (i.e., comparisons of tunnel-based estimates of mobile source emission factors with predictions of emission factor models such as MOBILE5a), although some studies did employ tunnels to obtain species profiles. Neither does this study attempt to systematically review uncertainties in emission inventories, although many uncertainties are discussed in the context of reviews.

The key issue to be addressed from the reviews is whether studies provide evidence that emissions of NMOCs and/or CO from one or more major source categories are underestimated and to what degree. For NMOCs, an associated issue is the composition of any emissions that are missing from current inventories. The validity of any such conclusions rests equally on the quality of both the ambient data and the emission inventories used in studies. The reviews focus on uncertainties in the NMOC and CO inventories because these are the issues most extensively addressed in the recent literature. However, NO$_x$ inventories are based on estimation methods similar to those used for NMOC and CO and also contain uncertainties. To evaluate each study, the reviews address the methodologies and assumptions used, uncertainties in measured values and source profiles, quality of emission inventories, and the potential effects of these factors on study conclusions.

SELECTION OF STUDIES

Twenty-five studies were identified for review in the EPA work assignment (the work assignment is included here as Appendix 1). In the initial phase of the project several additional studies were identified, and it was decided that six additional studies should be included in the review. Since the work plan level of effort was based on the assumption that 25 studies would be reviewed, it was necessary to remove six studies from the original list. Appendix 2 briefly describes the six additional studies included, followed by the six studies that were removed. During this study several new papers became available in published or preprint form, and other relevant studies were recommended to us. We were unable to expand the scope to include them in our review, but they are identified in Appendix 3.

STUDIES REVIEWED

The studies under review can be divided into four basic types: receptor modeling studies, source fingerprint studies, ratio studies, and mass balance studies. Of the 25 studies, 13 are receptor modeling studies, 6 deal primarily with source fingerprints, 5 are ambient ratio studies, and one is a mass balance study. These groupings are used throughout this report. Tables 1–4, at the end of this section, summarize key information about each of the 25 studies under review. Within each group of studies, the studies are listed in chronological order, based on publication and/or presentation date.

METHODOLOGY AND REPORT ORGANIZATION

Our approach to this study is mirrored in the report organization, as described below. Since 13 of the 25 studies reviewed employed receptor modeling, Section 2 provides an overview of the receptor modeling method. The critical reviews of studies form the core of this work and are presented in Section 3. Section 4 synthesizes the findings from the critical reviews.

Receptor Modeling Overview

Several receptor modeling techniques are applied in the studies reviewed in this work assignment. Section 2 presents a brief review of receptor modeling which explains, in simple terms, the basic modeling methodologies and the history of the development and application of the various modeling techniques. The receptor modeling techniques reviewed include Chemical Mass Balance (CMB), tracer analyses, and factor analysis methods. The underlying assumptions of each modeling technique are examined with regard to the model's applicability for specific types of application. The strengths and weaknesses (limitations) of each method are discussed relative to other modeling methodologies. This review provides a framework for evaluating the validity and technical merit of the results presented in the numerous studies.

Critical Reviews of Studies

In Section 3 each of the 25 studies is critically reviewed and evaluated. Each study was reviewed from two predetermined viewpoints: objective and skeptical. The skeptic is eager to find holes in the logic or execution of the study, and may not accept the basic premise or approach of the study. The objective reviewer is willing to consider the evidence presented on its own merits and may be swayed by a convincing, thorough investigation, but is not naive and will not be convinced if there are obvious flaws or omissions in a study. The extent to which the two reviews are similar, both unfavorable, divided, or both favorable (albeit grudgingly on the part of the skeptic) is an indication of the perceived strength of the study. The objective and skeptical reviews were written independently by two members of the study team; reviewers did not see the alternate viewpoint until after their own reviews were complete.

Two points about the critical reviews are emphasized:

- The critical reviews are preceded by a brief synopsis of the study intended to help orient readers. However, it was impossible for us to completely summarize each study either in the brief synopsis or the critical reviews. In many cases a complete understanding of both the study and the reviewers comments will require that the original work be consulted. *We strongly advocate that readers do obtain and consult copies of the original work since this is the appropriate context in which to read the critical reviews.* The most balanced view of each study will come from consideration of the author's viewpoint alongside both the objective and skeptical reviews.

- Understand that reviews were written from predetermined viewpoints, which is a departure from the normal peer-review process. In particular, the skeptic "wants to support the opinion that the study proves nothing that will have broad implications" (to quote from the work assignment). *Thus, viewpoints taken in reviews do not necessarily reflect the natural disposition of the reviewer toward the study.*

Synthesis of Critical Reviews

In Section 4, the individual assessments of the studies from both perspectives are synthesized and examined as a group. The synthesis examines the degree of consensus between the various studies, taking into account the assessments of methodologies and individual studies developed in the critical reviews. For the receptor modeling studies, three geographic areas are the subject of several studies by different research groups (Los Angeles, Chicago, Atlanta), and the results of these studies are compared. Finally, the overall evidence for underestimation of NMOC or CO emissions presented in the studies is summarized.

Table 1. VOC source apportionment/receptor modeling studies.

Researchers, Affiliation, Date	Location	Time	Sponsor	Approach	No. of profiles	No. of fitting species	Conclusions	Comments
Nelson et al., CSIRO (Australia), 1983	Sydney (3 sites)	early 1980's hourly 6 a.m. - noon	CSIRO	CMB/ mass balance	6	15	MV exh 36% of NMHC; gas evap 32%; solvents 23%	Good agreement with EI except gas evap higher than EI
Wadden, Univ. Ill., Uno and Wakamatsu, NIES (Japan), 1986	Tokyo (aloft)	1981 June (2 days) diurnal	NIES (Japan), USPHS	CMB/trajectory	4	14-17	MV 7% of 17 VOC species sum; refinery 26%	MV lower than EI; refinery higher
O'Shea and Scheff, Ill. Inst. of Tech., 1988	Chicago (1 site)	1985 weekdays 12-1 p.m.		CMB/trajectory	3	9	MV 61% of 9 VOC species sum	no comparison to EI
Aronian et al., Univ. Ill., 1989	Chicago (3 sites)	winter 8 am - noon	EPA	CMB	8	23	MV exh 35% of NMOC; gas vapor 5%; refineries 11%	good agreement with EI except refineries higher than EI
Lewis and Conner, EPA AREAL, 1992	Atlanta (1 site)	1990 30-min diurnal	EPA	CMB	1	10	MV exh 40-100% of NMOC	source profile from local tunnel study
Sweet and Vermette, Ill. St. Water Surv., 1992	Chicago, E. St. Louis	1986-1990 various seasons	Ill. DENR	factor analysis/ CMB	6	12	MV accounts for most toxics on average day, less on polluted day	no NMOC analysis
Kenski, Wadden, and Scheff, Univ. Ill., Lonneman, EPA, 1992	Atlanta (2 sites)	1984-86 summer 6-9 a.m.	EPA	CMB	4	29	MV exh 53% of NMOC; gas vapor 16%	MV exh lower than EI

94081.80

Table 1. Concluded

Researchers, Affiliation, Date	Location	Time	Sponsor	Approach	No. of profiles	No. of fitting species	Conclusions	Comments
Harley et al., Caltech, 1992	Los Angeles (9 sites)	1986, 1987 summer 4-hr avg and diurnal	EPRI	CMB	6	15	MV exhaust 35% of NMOC; unburnt gas major factor missing from EI	restricted fitting species to non-reactive VOC
Gertler et al., DRI, 1993	Los Angeles (2 sites)	1987 SCAQS hourly	SCAQS	CMB	4	15-17	MV exh 60-70%	evap and refinery source could not be resolved
Kenski et al., Univ. Ill., 1993	Detroit Chicago Beaumont Atlanta Washington	1984-88 summer 6-9 a.m. and diurnal	EPA	CMB	7	29	MV exh: 14% BMT; 28% Det; 41% Chi; 53% Atl; 56% Wash	agreement with EI generally good
Lewis et al., EPA, 1993	Atlanta (1 site)	1990 30-min diurnal	EPA	CMB, source profiles from GRACE/SAFER	8	36	Total MV 63-80%, depending on def. of NMOC	
Scheff and Wadden, Univ. Ill., 1993	Chicago (3 sites)	1987 summer 8-12	EPA, NSF	CMB, trajectory	8	23	MV 21% of 23-species sum; refinery 7%; gas vapor 7%	59% unidentified; MV good agreement with EI
Mukund et al., Battelle, 1994	Columbus (6 sites)	1989 summer 6-9 a.m.	EPA	CMB	5	16	MV exh 34% of 16-species sum; gas vapor 19%	primary focus on toxics

Table 2. VOC source profile studies.

Researchers, Affiliation, Date	Objectives	Location	Data	Sponsor	Approach	Conclusions	Comments
Scheff et al., Ill. Inst. of Tech., 1989	develop VOC source fingerprints for CMB		source profiles from literature	EPA, NSF	lit. review	10 source profiles developed	MV exhaust profile from Sigsby; gas vapor profile from winter blend
VOC/PM Speciation Data System, EPA, 1991	library of source profiles		VOC and PM source profiles	EPA	lit. review and eval.; some new data generated	over 700 profiles	MV profiles have been updated since 1991
Doskey et al., Argonne, 1992	VOC source fingerprints	Chicago	source profiles generated	Ill. DENR	ambient VOC measurements in impacted areas	evap profiles are sensitive to season and grade of gasoline	used parking garage to obtain cold start and hot soak profiles
Goldan et al., NOAA, 1993	characterize biogenic emissions	Niwot Ridge, Colorado	ambient VOC in remote forested area	NOAA	ambient meas.	new biogenic species, emissions = isoprene	large meas. uncertainty
Korc and Chinkin, STI, 1993	review of VOC source profiles used in EI		VOC source profiles from EPA, CARB, and CIT	LADCO	lit review	replace EPA profiles for gas. evap. and surf. coating	used ambient data to identify possible problems with the profiles
Henry, USC, Lewis, EPA, and Conner, USC, 1994	development of VOC source profiles for CMB	Atlanta (1 site)	ambient NMOC	EPA	develop GRACE/SAFER method to extract source profiles from ambient data	develop city-specific profiles for "roadway", whole gasoline, and gasoline vapor	assumes acetylene is a tracer for MV exhaust

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Table 3. Ambient ratio studies.

Researchers, Affiliation, Date	Objectives	Location	Time	Data	Sponsor	Approach	Conclusions	Comments
Baugues, EPA, 1986	develop EKMA inputs, assess MV component	30 cities	1984-85 summer avg 6-9 a.m.	ambient NMOC and NO_x	EPA	acetylene as MV tracer; used NMOC:acetylene = 27 for MV	MV 18-88% of NMOC; lowest in Houston; higher than EI	EI not adjusted for time of day or species meas.
Lonneman et al., EPA, 1989	develop EKMA inputs	Los Angeles, Long Beach, Claremont	1987 summer (5 days) 6-9, 12-3, and 3-6	ambient NMOC and NO_y (SCAQS)	EPA	ambient $NMOC:NO_y$ at source and receptor sites	$NMOC:NO_y$ lower at receptor site	no comparison to EI $NMOC:NO_x$
Baugues, EPA, 1991	EI validation	16 cities	1985	ambient NMOC and NO_x	EPA	adjust EI to provide best comparison with ambient $NMOC:NO_x$	EI ratios average 23% lower than ambient	rule effectiveness assumptions have large effect
Fujita et al., CARB, 1992	EI validation	Los Angeles (8 sites)	1987 summer, fall avg. 7-8 a.m.	SCAQS ambient NMOC, CO, NO_x	CARB	comparison of ambient and EI $NMOC:NO_x$ and $CO:NO_x$ ratios	ambient ratios higher than EI; MV emis. underest.	speciated VOC data used qualitatively
Korc et al., STI, 1993	EI validation	Chicago, Gary, Milwaukee	1991 summer 7-9 a.m.	LMOS ambient NMOC, CO, NO_x	LADCO	ambient $NMOC:NO_x$ and $CO:NO_x$ ratios and VOC mass fractions	ambient ratios higher than EI; MV emis. underest.	speciated VOC compared to speciated EI

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Table 4. Mass balance (urban flux) study.

Researchers, Affiliation, Date	Objectives	Location	Time	Data	Sponsor	Approach	Conclusions	Comments
Gillani and White, Wash. Univ., 1989	mass balance method for NO_x EI validation	St. Louis Baltimore	1975 1980	MISTT NEROS II	EPA	calc. urban NO_x flux from aircraft meas.	good agree. w/EI for NO_x in St. Louis; need isolated city	VOC data inadequate

2 RECEPTOR MODELING

Various receptor modeling techniques have been applied to estimate source contributions to ambient volatile organic compound (VOC) concentrations in the studies evaluated. This section presents a brief review of receptor modeling, defining the basic modeling methodologies and the history of the development and application of the three modeling techniques: tracer analysis, Chemical Mass Balance (CMB), and factor analysis methods. The underlying assumptions of each modeling technique are examined with regard to the model's applicability for specific types of application. The strengths and weaknesses (limitations) of each method are discussed relative to other modeling methodologies. This review provides a framework for evaluating the validity and technical merit of the results presented in the numerous studies.

WHAT ARE AIR QUALITY MODELS?

Air quality models relate pollutant emissions to atmospheric concentrations. They are often used to determine the impact on air quality due to changing emission patterns (resulting from growth and/or control). Air quality models are also used to determine source contributions to ambient concentrations. If the pollutants are inert (nonreactive in the atmosphere), then a linear air quality model may be developed, in which these contributions are additive.

If the composition of source emissions remains constant, then the linear air quality model is the following:

$$C_{ik} = \sum_{j=1}^{M} A_{ij} * D_{jk} * E_{jk} \qquad \text{(Eq. 1)}$$

which states that the ambient concentration of component i during the kth time interval (C_{ik}) equals the sum of the product of the fractional amount of component i in the emissions from source j (A_{ij}), the atmospheric dispersion of emissions from source j during time k (D_{jk}), and the total emission rate of all components from source j corresponding to time interval k (E_{jk}). The summation is over M total sources.

For a source model, or "dispersion" model, the values of A_{ij}, D_{jk}, and E_{jk} are measured (or estimated) and the model computes the component concentrations, C_{ik}. Receptor models start with measured component concentrations (C_{ik}) and source compositions (A_{ij}) and then compute the products $D_{jk}E_{jk}$. The receptor model is rewritten as:

$$C_{ik} = \sum_{j=1}^{M} A_{ij} * S_{jk} \qquad i=1,N \qquad \text{(Eq. 2)}$$

which states that the concentration of component i equals the sum of the products of the composition fractions (A_{ij}) and the total contribution of source j (S_{jk}). If the total number of components measured is N, the summations result in a set of N equations. This set of equations constitutes the basis of receptor models, including the Chemical Mass Balance (CMB) model (Watson 1982).

RECEPTOR MODELS

Receptor modeling tools, developed in the 1970's for air quality applications (Miller et al. 1972, Friedlander 1973), were first applied to estimate source contributions to atmospheric particulate matter (PM) concentrations (Watson 1979, Cooper and Watson 1980, Gordon 1980). Since that time, many researchers have used receptor modeling techniques for source apportionments of air pollutants, mostly for PM, and the majority using CMB or a combination of CMB and other receptor modeling tools, such as factor analysis. Three international specialty conferences dealing exclusively with receptor models were sponsored by the Air Pollution Control Association (APCA; currently AWMA) in the 1980's, and the proceedings of these conferences (Dattner and Hopke 1982, Pace 1985, Watson 1989) attest to the evolution of receptor models from research oddities to reliable environmental management tools. Numerous other critical examinations and reviews of receptor modeling techniques have been published (see for example, Hopke 1985). The U.S. EPA has developed a PC-based version of the CMB model (Watson et al. 1990), which is recommended for use in PM_{10} State Implementation Plan analyses.

Receptor modeling techniques have been widely used to apportion observed air pollutant concentrations to contributing sources. Unlike dispersion (or "source-to-receptor") models, which determine concentrations by numerically simulating the physical processes affecting the transport of emissions, statistical (or "receptor") models infer source contributions from properties of ambient air observed at the receptor. Receptor models succeed in determining source contributions by relating specific attributes of the ambient air to similar attributes of the sources. Usually these attributes consist of the concentrations of chemical components; however, the attributes are not limited to chemical species measurements and may include any measurable property of the emission source, such as particle shape (morphology).

Receptor models have been applied in the past to determine the contributions to ambient PM concentrations from such sources as motor vehicles, woodburning, geological dust (including soil dust, road dust, and construction activities), fuel oil combustion, marine (sea salt), and various industrial activities. Receptor models have also been used to apportion VOC concentrations (the focus of this work assignment) to such sources as gasoline vapor (evaporation), motor vehicle exhaust, petroleum refineries, graphic arts,

architectural coating (painting), dry cleaning, wastewater treatment, and industrial solvent evaporation.

Various forms of receptor models are described below. The major underlying assumptions are presented for each modeling methodology, and the strengths and limitations of each approach are discussed. It is important to note that the limitations of receptor models are generally related to the degree to which the assumptions are violated. The fulfillment of an assumption is usually a question of degree rather than of yes or no. Often small deviations from the basic assumptions can be tolerated within the goals of the application.

There are two assumptions that are common to all receptor models:

> **Assumption 1.** The compositions of source emissions are constant (i.e., the values of A_{ij} are measurable and non-varying).

> **Assumption 2.** Components do not react with each other (i.e., they add linearly).

A third assumption is also common to many receptor modeling techniques:

> **Assumption 3.** The number of sources (or source types) contributing to a receptor is known (equal to M).

The modeling methods presented below require that Assumption 3 be satisfied, with the exception that factor analysis techniques may be applied when the number of sources is unknown.

TRACER ANALYSIS

The simplest receptor modeling technique is known as "tracer" analysis, in which an observed tracer is used to estimate the contribution of pollutant mass from a specific source (or source type). A "tracer" usually refers to some element or chemical compound that is known to be emitted from a particular source type. The presence of an inert tracer, unique to only one source or source type, is a direct indication of the contribution of pollutants from that source. For example, when lead was used in motor vehicle fuel, the presence of particulate lead in an air sample could be used to indicate the contribution of motor vehicle activity, since almost all emitted lead was associated with vehicles using leaded gasoline. Acetylene has historically been used as a tracer compound for motor vehicles (Lonneman et al. 1974) when VOC component measurements are available.

In this case, the contribution of source type j (S_{jk}) can be determined by simply dividing the observed concentration of the tracer component that is associated with source j (C_{tk}) by the fractional amount of tracer component t present in the emissions from source j (A_{tj}). An additional assumption (in addition to Assumptions 1, 2 and 3) is required for the tracer analysis method:

Assumption 4. Each source type j has one component t, or "tracer," in its composition such that A_{tj} equals zero for all other sources.

The strength of tracer analysis is that if a tracer can be uniquely associated with a particular source type, and the tracer component can be accurately measured both at the source and at the receptor, then the tracer analysis method provides a reliable tool for computing the contribution of the particular source type. The source apportionment is accomplished with a minimum of data and the errors are only associated with the reliability of the two measurements (C_{tk} and A_{tk}) (and the veracity of the uniqueness of the tracer component).

An additional strength of the tracer analysis method is its ability to compute upper bounds for source contributions, even if Assumption 4 is somewhat incorrect. In other words, even in cases where it is known that other source types may emit some amount of the tracer component, the tracer analysis can be used to provide an upper bound to the contribution of the source type. For example, if one has measured the PM composition of local soil dust emissions and found it to contain 20 percent silicon, and the silicon concentration observed at a receptor is 2 $\mu g/m^3$, then the tracer analysis would estimate that soil dust contributes 10 $\mu g/m^3$ (2/0.2) to the total PM concentration at the receptor. However, since silicon is not unique to soil dust (there are non-zero silicon fractions in some other source type compositions), the 10 $\mu g/m^3$ must be taken as an upper limit on the soil dust contribution.

The tracer analysis method is limited in its application, however, because very few source types have their own unique tracer components. A few techniques for overcoming this limitation have been explored, including "correcting" tracer element concentrations to account for other sources of the tracer element. As an example, if a tracer element is known to be associated with two source types, and a second tracer element is associated with only one of those two source types, then the contribution from the second source type may be subtracted, and the resulting "corrected" tracer concentration can then be used to determine the contribution of the first source type. Lewis et al. (1988) applied this technique, creating a "soil-corrected" potassium concentration that was then used as a tracer for woodburning emissions.

Another technique that has been applied to overcome this limitation (for a limited number of sources) is the deliberate release of minute amounts of tracers, of unique chemical composition, along with existing emissions. Measurement at a receptor of the unique tracer definitively indicates a non-zero contribution from the affected source. If the proportion of the tracer to the existing emission rate is known and constant, then estimating the contribution of the source type to the receptor concentration is simply a matter of dividing the tracer concentration at the receptor by the ratio of tracer to total emissions at the source. Unfortunately, such tracer studies are difficult to accomplish. The ability to measure the concentration of tracer material at very low concentrations demands that large amounts of tracer be used, which can get very costly. In addition, tracer studies are typically only carried out for source types consisting of a few individual sources. For source types with many individual sources (such as motor vehicle exhaust or residential heating emissions) it would be nearly impossible to inject tracer material at every source location.

Chemical Mass Balance (CMB) Model

A more sophisticated receptor modeling approach is the Chemical Mass Balance (CMB) model, which is based on the premise that the observed concentration chemical profile (or species "fingerprint," C_{ik}) is made up of a linear combination of individual unique source profiles (A_{ij}). In this context, a source (or ambient) profile consists of the relative composition of numerous chemical species measured at the source (or in the ambient air). This method has been found to be a particularly effective tool in determining source apportionment of atmospheric pollutants, especially aerosols and inert gases.

The application of CMB requires that two data sets be developed. First, chemically speciated air quality measurements (C_{ik}) must be taken. Second, chemically speciated source profiles (A_{ij}) must be compiled, in the form of normalized chemical compositions representing each specific source type. The chemical speciation performed for the ambient measurements should coincide with the species identified in the source profiles. In this context, "speciation" refers to the quantification of specific individual components that make up the mass being examined. For example, speciated PM data typically consist of measurements of the various components in the PM, such as elemental carbon, sulfate, nitrate, iron, lead, and other trace metals.

In the CMB model, the source contributions (S_{jk}) are determined by solving the set of N equations (Eq. 2) using multiple linear regression (least squares) techniques. The application of multiple linear regression to determine source contributions requires two additional assumptions (in addition to Assumptions 1, 2 and 3):

> **Assumption 5.** The number of source types, M, is less than or equal to the number of components, N.

> **Assumption 6.** The compositions of all M source types (the set of A_{ij} for each source type j) are linearly independent of each other.

The least-squares solution of the N equations (each equation is a "mass balance" for component i) for M unknowns ($M \leq N$) requires that exact values of A_{ij} and C_{ik} be obtained. Measurements of component concentrations both at the receptor (C_{ik}) and at the source (A_{ij}) are not exact. In addition, the source profiles (A_{ij}) often exhibit some variation between the individual sources that make up each source type. These uncertainties are accounted for by weighting the variables in the least-squares regression so that less precise measurements have less influence than more precise measurements. The latest EPA version of the CMB model (CMB version 7.0) uses the effective variance weighting scheme (Watson 1979), in which the error term in each equation is divided by the variance of the measurements before the least-squares solution is computed. To produce a CMB solution free from statistical bias, an additional assumption is required:

> **Assumption 7.** Measurement errors (for A_{ij} and C_{ik}) are random, uncorrelated, and normally distributed.

At the outset, there may be more source types than components (i.e., Assumption 5 is untrue), or several source types may have the same (or very similar) composition (i.e.

Assumption 6 is untrue). Two solutions exist to remedy these problems. The first is to measure more components and make sure that they have different concentrations in different source emissions such that Assumptions 5 and 6 are valid. A second, more typical solution is to group sources with similar compositions into composite source types so that $M < N$. However, when sources are grouped, the model can no longer distinguish between individual contributors within a composite source type.

The strength of the CMB modeling approach is that it produces definitive quantitative estimates of the contributions from a number of source types. Successful application of the CMB model generally requires that:

- a deliberate effort is made to collect an adequate speciated ambient air quality data set,

- a limited number of source types are known to contribute to the majority of the components measured at the receptor,

- source profile data (with speciation corresponding to the ambient data) are collected that are representative of the source types, and

- the source profiles are linearly independent of one another (no one source profile can be made up of any possible addition of multiples of the others).

It is no simple task to satisfy these requirements. The CMB technique was described as a viable tool for use in air quality modeling in the early 1970's but it wasn't widely used until the early 1980's, and then with few exceptions, for PM applications. It is a costly and time-consuming undertaking to gather the necessary data and to demonstrate that all important sources of each measured component are considered in the list of source profiles. If it is discovered that a large portion of a component cannot be accounted for with the measured source types, or that the component measurements are unreliable either at the source or at the receptor, then that component must be removed from the regression fit. Recent advances in measurement techniques (X-ray fluorescence, ion chromatography, optical-thermal carbon analysis, etc.) have allowed numerous PM components to be reliably obtained for both sources and ambient samples.

There have been some attempts to use CMB for pollutants other than particulate matter, including VOCs. However, early attempts using CMB for gaseous hydrocarbon species proved largely futile, either because there were not enough inert species measured reliably (relative to the number of source types) or, as was often the case, the source type characterization was not representative of the mix of sources in the air basin being modeled. The studies being examined for this work assignment demonstrate that in the last decade progress has been made to develop reliable source profile data to support the application of CMB for VOC components.

In practice, the linear (or near-linear) dependence of a small number of source types may not completely limit the CMB model from computing source contributions. More recent versions of the CMB model include an approach for combining similar sources into a "source cluster" for which the CMB model can accurately compute the contribution from

the sum of the clustered source types. A less accurate estimate is also made of the individual source type contributions.

Most air quality models compute the contributions of sources to atmospheric concentrations without any estimate of the uncertainty of those contribution estimates. An advantage of the CMB model is that the uncertainties of the source type contributions are computed. The model output also indicates whether each source type contribution is statistically significant from zero. In addition, various diagnostic statistics can be examined to determine the degree to which the model is able to reliably account for the component concentrations with a linear combination of the provided source profiles.

The limitations of the CMB model relate almost entirely to the degree to which the various assumptions are violated. Examination of Assumption 1 (requiring that source compositions are constant) presents two possible problems. First, source compositions are not constant among individual sources within a source type. However, this is only a problem if the variation in actual source profiles within a source type is large relative to the linear independence of the source type from other source types. If there are significant variations in actual profiles within a source type, the CMB model may have difficulty determining the source type contribution. The second problem occurs when source compositions are not constant in the atmosphere (due to reactivity of some components during transport between emission point and receptor). Friedlander (1973) suggested an approach to modify the CMB model for the case of a linear reduction of the A_{ij} with time (requiring additional assumptions); however, this approach has been rarely employed successfully.

Usually the most difficult part of developing a CMB application is constructing a usable set of source profile data. Either there exist source profiles that are (or are nearly) linearly codependent, or one or more of the source type profiles is inadequate in properly representing the sources within the source type to which it is assigned. In addition, unless many different species can be measured reliably, it is often the case that the smallest number of source types that can be used to represent the mix of sources in an air basin is greater than the number of species measured. As the numbers of sources approaches the number of species, the CMB modeling approach becomes much less reliable, and it is likely that one or more source type contributions will be computed as negative which is physically meaningless (in the special case when $N = M$, the CMB model becomes a solution to a linear algebra problem in N unknowns, and will often exhibit negative values of source contributions, S_{jk}).

One of the most significant weaknesses of the CMB model is that, despite its ability to definitively predict source contributions for various source types, the model has absolutely no ability to reveal anything about the relative contributions of individual sources within the source types. Hence the CMB model is often combined with emission inventory information to determine relative source strengths within source types (the use of which requires additional assumptions about the dispersion of sources within source types).

The CMB model is often combined with other modeling tools to complete an air quality assessment for a region. For example, trajectory analysis is often used to segregate the CMB results from numerous ambient samples, depending on general patterns of

transport. Examination of transport patterns and emission densities can be used to confirm the findings of CMB results.

FACTOR ANALYSIS METHODS

Often it is not possible or too costly to reliably measure the source compositions. If the compositions of sources significantly affecting a receptor are unknown, then two possibilities exist: (1) If unique tracer compounds can be identified for some sources, then the tracer analysis method (described above) may be used to estimate source contributions for those sources. (2) If either unique tracer compounds aren't available or the number of source types are unknown, then factor analysis models may be employed (Hopke 1981).

For factor analysis methods, it is necessary to have numerous ambient speciated samples (C_{ik}, $k=1,P$) representing multiple sampling periods. This modeling approach is designed to infer the number of important source types, M, and the source compositions (A_{ij}) from the variations (between sampling periods) in the ambient component concentrations (C_{jk}). The method relies on a statistical examination of the sample variation of the multiple compounds (hence it is called a multivariate method) to determine common causal factors that contribute to the observed ambient compound concentrations. The factor analysis model requires the following assumptions (in addition to Assumptions 1, 2, and 7):

> **Assumption 8.** The relative source contributions at the receptor vary between sampling periods.

> **Assumption 9.** The number of sources significantly affecting the receptor is less than the number of components measured (similar to Assumption 5).

If Assumption 8 is violated, then the factor analysis method will not be able to perform adequately. If Assumption 9 isn't true, then the factor analysis method will only determine a subset of the significant source types. Most factor analysis tools determine the number of source types and their probable compositions, and generally must be used in combination with the CMB model to obtain source contributions.

The basic premise behind factor analysis is that a number (less than N) of "factors" can be found that can be linearly added together to explain the sample-to-sample variation in the set of ambient data. The factors can be used to identify possible emission source profiles or combinations of profiles for the region being examined.

There are a number of different factor analysis models available corresponding to various methods for obtaining a mathematical solution to the problem. These include principal component analysis (PCA), empirical orthogonal function analysis (EOF), target transformation factor analysis (TTFA), and others. Henry (1987) demonstrated that these factor analysis methods suffer from fundamental flaws which limit their ultimate application. He showed that the physical constraints on the system are insufficient to guarantee a unique solution (or to put it another way, that these models have an arbitrary and undetermined systematic error, the magnitude of which could be

large enough to invalidate the model predictions). Henry and Kim (1989) developed a new factor analysis model that incorporates explicit physical constraints (with linear programming) to overcome these problems. Their model, the Source Apportionment by Factors with Explicit Restrictions (SAFER), has been applied to PM air quality data in the Los Angeles air basin (Kim 1991) as well as for other applications (including one of the VOC receptor modeling studies evaluated in Section 3).

The greatest strength of factor analysis methods is that they require no a priori knowledge of the number or composition of sources. In addition, the methods often are able to provide source composition data that are more representative of the local mix of sources than "imported" data collected from other regions. The factor analysis tool is most useful as an independent method of confirming the compositions of representative source types used in the CMB analysis. The method may also suggest emission sources not previously inventoried or considered. For regions where little information exists regarding sources, factor analysis is an indispensable receptor modeling tool.

While factor analysis indicates the importance of each factor, or "source," the identifying and labeling of these sources must be based on previous knowledge concerning emission source characteristics. The greatest weakness of factor analysis methods is that the solutions are not unique. However, the development and application of newer factor analysis tools, such as SAFER, may eliminate much of this problem.

SUMMARY

Receptor models offer an alternative to dispersion models when attempting to determine source contributions to observed receptor concentrations. As has been shown, if the basic assumptions are valid (the components are nonreactive in the atmosphere, etc.) and adequate air quality and emissions databases have been developed, then the application of receptor models yield meaningful results.

The strengths and limitations of receptor modeling methods are related to the validity of the underlying assumptions. If data are collected carefully to ensure that the assumptions are maintained, then the resulting source apportionment is very reliable and is generally a superior tool to most dispersion models. A strength of the receptor modeling methods, especially CMB, is that small deviations of the assumptions may be tolerated, although large deviations cause the method to fail.

When examining the results of a receptor modeling application, one must pay careful attention to the degree to which each assumption is valid. For CMB, this requires examination of the air quality and source composition data sets, and the diagnostic statistics that are produced by the model. An advantage of the CMB model is that, in most cases, if the model cannot produce reliable results, this fact is clearly indicated by examination of the results. The most common reasons for the CMB method not to produce reliable results are that (1) source type profiles are not measured properly or do not adequately represent the sources within the source types, (2) not enough (nonreactive) components are measured reliably relative to the number of important source types, (3) all important sources are not being considered, or (4) a number of source types are collinear (or are nearly collinear). Factor analysis tools may be used to

overcome many of these problems (those related to the inadequacies of source profile data).

The CMB model, in particular, has gained wide popularity in recent years, and is a recommended tool for use in determining the sources of PM concentrations in most air basins. Even though the development and most of the applications of CMB (and other receptor models) have been for PM, it has been shown that nothing precludes using CMB for other compounds such as VOCs. The reason CMB has not until recently been applied (successfully) for VOCs is related to the difficulties in obtaining reliable data, both for receptor concentrations and for source profiles of nonreactive VOC species.

The general weakness of the tracer analysis method relative to the CMB model is that the tracer analysis utilizes only two measurements per source type, whereas the CMB model makes use of multiple component measurements, often including the tracer component. CMB is more robust statistically than is tracer analysis and is a more powerful predictive tool. The CMB is less sensitive to measurement error than tracer analysis. If there is some measurement error in the tracer compound measurement at the source and receptor, the estimate of the source type contribution is uncertain. Applying CMB with numerous components (of similar relative accuracy) necessarily reduces the uncertainty in the source type contribution estimate, relative to the tracer analysis approach (if Assumption 7 is valid).

The tracer analysis solves the set of receptor modeling equations (Eq. 2) by assuming a special case, that in which each equation can be solved independently (one equation with one unknown); however, the solution depends upon the assumptions that (1) the tracer element is unique to the source and (2) the measurements of the tracer at the source and receptor are reliable.

The CMB model uses multiple linear regression to solve an overdetermined system of N equations with M unknowns (it is overdetermined because $N > M$). The use of more species (equations) combined with the least-squares approach of multiple linear regression generally provides a much more reliable tool than tracer analysis.

Factor analysis is an attractive approach when source composition data are inadequate or unknown, and when multiple samples are available. One problem with the approach is that the solution of the general method isn't unique; however, this problem has been largely overcome by restricting the solution by adding explicit physical constraints (i.e., the SAFER model). Generally, factor analysis has been shown to be extremely useful in assisting the determination of source profiles to be used in CMB modeling analyses, or to confirm the results of CMB.

3   CRITICAL REVIEW OF STUDIES

INTRODUCTION

The studies under review can be divided into four basic types: receptor modeling studies, source fingerprint studies, ratio studies, and mass balance studies. Of the 25 studies, 13 are receptor modeling studies, 6 deal primarily with source fingerprints, 5 are ambient ratio studies, and one is a mass balance study. These groupings are used throughout this review.

For each study, a brief review is given first, followed by a summary of strengths and weaknesses of the study. Then comes a review from the viewpoint of an objective reader. Finally, the study is reviewed from the viewpoint of a skeptic. The complete review package for each study starts at the top of a new page. The objective and skeptical reviews were written independently: reviewers did not see the opposing viewpoint until after their review was complete.

Two points about the critical reviews are emphasized:

- The critical reviews are preceded by a brief synopsis of the study intended to help orient readers. However, it was impossible for us to completely summarize each study either in the brief synopsis or the critical reviews. In many cases a complete understanding of both the study and the reviewers comments will require that the original work be consulted. *We strongly advocate that readers do obtain and consult copies of the original work since this is the appropriate context in which to read the critical reviews.* The most balanced view of each study will come from consideration of the author's viewpoint alongside both the objective and skeptical reviews.

- Understand that reviews were written from predetermined viewpoints, which is a departure from the normal peer-review process. In particular, the skeptic "wants to support the opinion that the study proves nothing that will have broad implications" (to quote from the work assignment). *Thus, viewpoints taken in reviews do not necessarily reflect the natural disposition of the reviewer toward the study.*

RECEPTOR MODELING STUDIES

1. **Sources of Atmospheric Hydrocarbons in Sydney: A Quantitative Determination using a Source Reconciliation Technique**, P.F. Nelson, S.M. Quigley, and M.Y. Smith, CSIRO (Australia), *Atmos. Environ.*, 17:439-449 (1983).

This paper presents a VOC source attribution for Sydney, Australia. Six sources were considered, although the composition of one source (refinery process emissions) was determined by what the authors term a "mass balance" technique, in which all material left over was allocated to that source. The average contribution of vehicle exhaust was 36 percent, with 16 percent allocated to both gasoline and gasoline vapor. The exhaust contribution was in good agreement with the inventory, but the total evaporative contribution, defined by the authors as gasoline plus gasoline vapor, exceeded the inventory contribution. The sensitivity of the model results with respect to uncertainties in source composition and atmospheric concentration was examined. The effect of photochemical reactivity, determined by the xylene:ethylbenzene ratio, was also assessed.

Strengths of this paper include the inclusion of the whole gasoline profile for a typical gasoline used in Sydney, and the sensitivity analysis, which provides a quantitative estimate of the uncertainty in the results. Weaknesses include the lack of an actual source profile for the refinery.

Objective Review

This paper represents one of the first successful applications of the CMB technique for determining contributions to atmospheric hydrocarbons (the Australian authors refer to the method as a "source reconciliation" method, but it is identical to CMB). Five profiles (vehicle exhaust, whole gasoline, gasoline vapor, natural gas, and solvents) were used in the CMB analysis to determine contributions to total hydrocarbon concentration, and then the contributions from petrochemical activity was estimated using a mass balance technique on remaining C_2-C_4 alkanes and olefins.

The CMB results appear to be particularly robust. The authors presented evidence that the CMB model results are credible: (1) Using the five source types, CMB was able to produce very small relative errors for all 15 of the fitting species equations, indicating an excellent fit of the ambient data. (2) Sensitivity analysis on source profile uncertainty showed that the results were fairly insensitive to typical uncertainties in source profiles. (3) They examined the effect of hydrocarbon reactivity and found that it was also small. (4) Comparison between CMB results and a local emission inventory showed reasonable agreement. (5) For a subset of the urban samples, the estimated contributions from vehicle exhaust and gasoline evaporation (sum of whole gasoline and gasoline vapor) were highly correlated. These results demonstrate the usefulness of the CMB technique for atmospheric hydrocarbons.

The CMB-estimated contributions of vehicle exhaust and solvents were in reasonably good agreement with local emission inventory estimates. Process emissions (determined by the mass balance technique) were also in good agreement with the inventory. The total gasoline evaporation (sum of whole gasoline and gasoline vapor) contribution was somewhat greater than the inventory, suggesting a possible underestimation of evaporative emissions in the inventory.

The paper does not include regression statistics, but the results for the average (n=137) ambient concentration show excellent agreement for all fitting species. The average contributions computed for individual samples (using additional hydrocarbons in the fit to account for solvent variation) is very close to those obtained for the average data. The sensitivity analysis on source profile uncertainty and reactivity also provide some indication that the results are meaningful. However, it is not indicated in the paper in what season(s) the morning samples were taken.

Skeptical Review

This study presents one of the early uses of multivariate regression analysis for source reconciliation between emissions and ambient profiles of hydrocarbon species. There appears to be some controversy over the originators of this type of source-receptor analysis. Harley et al. (1992) claimed that Friedlander and co-workers deserve credit from two studies published in the early 1970's (Miller, Friedlandler and Hidy, 1972, *J.Colloid Interface Sci.*, 39:165-176 and Friedlander, 1973, *Environ. Sci. Technol.*, 7:235-240). Nelson et al. claimed that Mayrsohn and Crabtree developed the technique in 1976 (*Atmos. Environ.*, 10:137-143). Mayrsohn and Crabtree made no mention of Friedlander's work.

It is curious that this Nelson et al. study makes the same claim for Sydney in 1983 as the Harley et al. (1992) study done nearly a decade later and in Los Angeles, namely that the inventory and the ambient atmosphere seem to be most at odds regarding an appearance of excess unburned gasoline in the atmosphere. Therefore, many of the critical remarks made for the Harley et al. study apply to the Nelson et al. study. Three important remarks are first that the technique itself tends to minimize the importance of the highly reactive species which arguably need to be known most accurately, and second, the unburned gasoline result is questionable on the grounds that the more volatile compounds of petroleum are used so ubiquitously in populated areas that statistically unique profiles specific to individual source categories are not easy to establish. Third, since gasoline is a fuel and volatile solvents are meant to wholly evaporate, there is a vast difference between the fraction of gasoline emitted relative to the amount of gasoline consumed compared to the fraction of solvents emitted to the amount consumed.

It is noteworthy that the earlier Nelson et al. study, contrary to the newer Harley et al. study, did test their results for the significance of reactivity and identified and tested the sensitivity of a potential spatial nonuniformity in solvent uses. Unfortunately, the sensitivity techniques developed by Nelson et al. have apparently not been recognized and utilized extensively in more recent U.S. studies.

2. **Source Discrimination of Short-Term Hydrocarbon Samples Measured Aloft**, R.A. Wadden, Univ. of Ill., I. Uno and S. Wakamatsu, National Institute for Environmental Studies (Japan) *Environ. Sci. Technol.*, 20:473-483 (1986).

This paper presents the results of a CMB analysis in Tokyo for 17 hydrocarbons. The ambient database consists of 192 aircraft samples taken at 300 to 1500 m throughout two days in June 1981. Five source profiles were developed (vehicle exhaust, gasoline vapor, petroleum refinery, paint solvent, and polyethylene plant). The vehicle exhaust, refinery, and polyethylene plant source profiles were taken from ambient monitoring in areas impacted by each particular source. The study apportioned 7 percent of the sum of the measured VOC to vehicle exhaust, 26 percent to the refinery, 27 percent to paint solvents, and 10 percent to gasoline vapor. This was compared to the emission inventory for Tokyo, which showed motor vehicles contributing 32 percent, refineries 9 percent, and paint solvents 37 percent. The authors did not draw any general conclusions from this comparison, but used trajectory analysis to argue that air parcels sampled on those days are likely to have passed over the refinery.

The strengths of this work are the source fingerprint information provided, the demonstration of the receptor modeling technique for VOC, and the checking of CMB results with trajectory analyses. Weaknesses are that source contributions were determined as a percentage of fitting compounds rather than total NMOC, uncertainties in the source profiles, and the lack of consideration of reactivity for species such as propene.

Objective Review

This paper was one of the earlier published attempts to use CMB to apportion ambient volatile organic carbon. Its focus was on demonstrating that the technique can be used to accurately determine receptor contributions. There are some limitations of the data developed in this study which may restrict the ability of the model to provide sound results; however, the research represents a building block for the application of the CMB technique for VOCs.

The paper does not indicate whether the computed source contribution coefficients are statistically significant (i.e., different from zero). It also does not indicate what the computed error estimates are. The average CMB regression coefficient, r^2 (displayed in the context of a sensitivity analysis on the number of species to be used in the fit), for the 192 samples was 0.584.

A particular strength of this work is that the study employed trajectory modeling to confirm both the identification of sources and the quantification of the contributions estimated by CMB (they were not, however, able to completely validate the automotive coefficient). This physical evidence provides direct support for the CMB results and may also provide an indication of the level of uncertainty of the CMB results.

Only four of the five source profiles (representing vehicle exhaust, gasoline vapor, refineries, and paint solvent) were used in the CMB analysis presented in the paper. When all five sources were used, collinearity was observed between the refinery and vehicle source profiles. An additional weakness of this work, and a probable factor in the collinearity problems, is that the source profiles were obtained from air quality measurements rather than from direct source tests.

The CMB model solves an overdetermined set of mass balance equations for numerous species, under a couple of specific rules (e.g., minimize the weighted error term). A puzzling aspect of the statistical analysis in this study is that, for each species mass balance equation, both an intercept and an "unexplained" source category were reported in the CMB results. It is not explained in the paper how (mathematically) the "unexplained" source coefficient was determined. The "unexplained" contribution, when added to the other source contributions, totals 100 percent of the mass. The intercept terms for the majority of runs were negative and particularly large; often exceeding (in absolute value) 100 percent of the mass. The physical (or statistical) meaning of these negative (and large) intercepts was not explained.

Skeptical Review

Ambient Data

Samples were collected in pyrex vessels rather than stainless steel canisters, and it is uncertain how stable different NMOCs are in pyrex. Little information is given on how the gas chromatograph (GC) analysis of speciated NMOCs was performed: how long samples remained in the pyrex vessels, how (if) samples were preconcentrated, how (if) water was removed from the samples, how the GC was calibrated. Samples were also analyzed for total NMHC using a continuous NMHC instrument rather than the PD-FID method. Baugues (1986) has shown that continuous NMHC measurements are unreliable. However, it is not clear how the total NMHC measurement was used in this study, if at all.

Source Profiles

Source profiles were developed for this study. Weight percents were given relative to the sum of 17 fitting compounds, not total NMOC. The vehicle profile was based on 36 ambient measurements made up to two years prior to the study in part of the study area. No more details are presented on where the profiles were obtained (e.g., roadside). Since the vehicle profile contains 25% butane plus isopentane it effectively contains some evaporative emissions. It also contains significant propane attributed to the LPG-fueled taxi fleet. The gasoline vapor profiles were based on storage tank headspace for three brands of unleaded gasoline. Notably, the butane/isopentane ratios in the vehicle and gasoline vapor profiles are reversed, which probably helps avoid collinearity between the profiles. However, it is not clear how this difference can be reconciled since in both cases the butane and isopentane must be from gasoline vapor. The petroleum refinery profile is an average of 36 monthly samples collected near (not necessarily downwind of) a Japanese refinery with no correction for background. The

major compounds identified in the profile are propane (20%), butane (16%) and isopentane (14%). Some collinearity was found between the refinery profile and the vehicle profile. A paint solvent profile was generated by applying national average sales weights to unspecified composition data for several paint types. A profile from a polyethylene plant was also derived (50% ethylene) but not used because of collinearity with vehicles.

In general, a reasonable attempt was made to derive study specific profiles, but significant uncertainties must be recognized in all of the profiles.

Source Contributions

Source contributions are calculated as the percent contribution to the sum of the fitting compounds. This is a reasonable way to treat the data, but is of little relevance to the atmosphere because the 14 or 17 fitting compounds chosen are an arbitrary subset of ambient NMOCs. Calculations are performed with both 14 and 17 fitting compounds, but changes in the estimated source contributions are hard to interpret because this changes "the size of the pie." For example, when benzene, ethane, and acetylene are excluded as a sensitivity test, the vehicle and unexplained contributions are most sensitive: vehicles increase from 7 to 13 percent, unexplained decreases from 29 to 20 percent (average over all runs). But removing these compounds excludes about 14 percent of the mass of total fitting compounds (also overall average), so what happened? Did the vehicle "slice" get larger, or did the "slice" stay the same while the overall "pie" shrank. I find the results of this sensitivity test hard to interpret; maybe the main conclusion is that source contributions expressed as a percent of fitting compounds can depend strongly on the number of compounds, which is arbitrary. The exclusion of these three compounds was intended to be a test for the effects of reactivity on source contributions, but I do not believe it can be interpreted this simply. The authors excluded the three lowest reactivity species, but it would make more sense to exclude highly reactive species such as propene which could have undergone significant losses late in the day.

The vehicle contribution determined in this study (about 10 percent) is low relative to the estimated Tokyo inventory contribution of 32 percent. This may be because samples were taken aloft (mostly at 350-700 m) and thus were not always strongly influenced by surface sources. Inspection of the run-by-run results shows the vehicle contribution peaking in the middle of both study days when vertical mixing in the atmosphere is strongest. The authors estimated that 39 out of 170 samples were collected above the inversion layer (and thus would not see local surface sources), but they do not indicate which runs these were. Back-trajectory analyses also suggested that many of the air parcels sampled had come from over Tokyo Bay.

A complicated back-trajectory analysis is used to compare refinery contributions estimated by CMB and airmass origin. Tokyo is situated on a coastline and thus likely has complicated land-sea breeze windflow patterns that may result in wind convergences and wind shears. Thus, trajectories may trace back to multiple locations and have a large "footprint." The authors did have an extensive network of vertical wind profiles to rely on, but the analysis must have been challenging. The Gaussian treatment of

dispersion used also relies on many assumptions. The results are only credible because Figure 4 shows an apparently reasonable correlation between refinery contribution estimated by the CMB and back-trajectory methods. The authors further use Figure 4 to support the contention that atmospheric losses due to photochemistry (reactivity) did not much impact the CMB results. However, the refinery contribution probably hinges on propane which is one of the less reactive fitting compounds with an atmospheric lifetime of many days. Thus, this is not a very powerful test for the effects of reactivity on source contributions.

Emission Inventory Comparisons

Some comparisons are made to a 1978 annual average inventory for the Tokyo metropolitan area. The main limitations with this comparison are the mismatch between summer day measurements and annual average totals, the fact that CMB estimated contributions are only for a subset of NMOCs, and the potential that many of the aloft samples were not reflective of surface emissions.

Study Conclusions

The authors do not place much emphasis on the source contributions determined in this study, and no values are given in the conclusions. Four applications for the CMB method are given at the end of the paper. The first two effectively say that the CMB method provides a valuable independent check on highly uncertain emission inventories. However, the usefulness of this check does depend on the reliability of the CMB results. The authors make several resourceful attempts to get at elements of the uncertainties in their CMB source contributions, but do not knit them together into an overall assessment. The third suggested application is that source contributions determined for a subset of fitting compounds be extrapolated to a complete inventory by using source profiles that account for all NMOCs. Significant uncertainties would be involved in determining source profiles that are representative of categories as general as vehicles. The fourth application states that it is reasonable to use the CMB method with short-term (1-hour) sampling data provided that trajectory, diurnal use, and appropriate source profiles are available. The most challenging requirement here may be the need for specific source profiles. For large sources that can have significant variation in emissions speciation, such as refineries, hour or day specific profiles may well be needed for this type of application.

3. A Chemical Mass Balance for Volatile Organics in Chicago, W.J. O'Shea and
P.A. Scheff, Ill. Inst. of Tech., *JAPCA* 38:1020-1026 (1988).

This paper describes the use of the CMB model to determine the contribution of three
sources (vehicle exhaust, gasoline vapor, and refinery) to ambient levels of nine VOC
constituents at an urban site in Chicago. The model apportioned 61 percent of the
measured VOC to the vehicle exhaust profile, 10 percent to refineries, and 11 percent to
gasoline vapor. Trajectory analyses were used to validate the refinery contributions.
Some collinearity between the gasoline vapor and refinery fingerprints was noted. The
source apportionments were not compared to emission inventory values.

Strengths of this work include the collinearity analysis. Weaknesses include the limited
number of source profiles and fitting species, and lack of comparison to the inventory.

Objective Review

Because there were only three sources used in this analysis, the researchers were able to
try all possible combinations of source types in the CMB analysis. One of the objectives
in performing this sensitivity test was to show that only the "other" (unknown) category
would increase as sources were removed from the fit (this would be the "ideal" result).
In fact, the results of this analysis demonstrate that there is some uncertainty in the
source contribution estimates produced by the CMB model, especially for the gas vapor
and refinery contribution estimates. The vehicle exhaust contribution estimates were
supported by this analysis.

The researchers observed that many of the standard errors of the source contribution
estimates were large. This was found to be due, in part, to some collinearities between
the gas vapor and refinery source profiles. These source types were both expected to be
important contributors in the Chicago area, and they only started with three source types,
so it was not possible to remove either of the profiles from consideration. For 7 out of
the 20 total samples, the CMB analysis was conducted repeatedly with only two source
profiles (once with vehicle and gas vapor, and once with vehicle and refinery), and the
results were considered as averages of the CMB runs. For the majority of the other runs
(CMB conducted with all three profiles), the standard error for these two sources was
high. These results should be interpreted such that the estimated sum of gas vapor and
refinery contributions is considered to be meaningful, but that the split between these
two source types is less certain.

Skeptical Review

The authors of this paper used only eight NMOC species (plus one group of species) and
only three profiles in this study. With that few species, the results have little value.
The CMB analysis gives the fraction of the sum of these nine species that is due to
motor vehicles, gasoline vapor, and petroleum refining. This tells nothing about the

fraction of total NMOC due to these sources, since the species selected do not make up a large portion of total NMOC.

No comparisons are made with the emission inventory. The authors conclude simply that the results are "reasonable" without any further explanation of why they are reasonable.

Although it is true that this paper was the first attempt at VOC receptor modeling by this group, the 1983 Australian study (Nelson et al., 1983) was available in the literature. The Australian study utilized many more species and profiles, and included comparisons with the inventory. This suggests that information was available to do a more detailed analysis than that attempted by O'Shea and Scheff at the time this work was done.

One positive aspect of this study is the sensitivity analysis, in which each of the three sources was removed individually and its effect on the source apportionment of the other two sources was examined. When the vehicle exhaust profile was removed, that portion of the mass was assigned to the unexplained category. However, when either the gasoline vapor or refinery profiles were removed, the model assigned that portion of the mass to the remaining one of those two profiles. This points to potential collinearity problems between gasoline vapor and refinery profiles.

In summary, this study represents only a tentative first step in attempting to perform receptor modeling for VOC. It does not draw any conclusions regarding emission inventory validity, and is of limited use in understanding VOC source contributions because of the limited number of species and profiles examined.

4. Wintertime Source-Reconciliation of Ambient Organics, P.F. Aronian, P.A. Scheff, and R.A. Wadden, *Atmos. Environ.*, 23:911-920 (1989).

This paper presents the results of a wintertime CMB application for the Chicago area. Eight source profiles, 23 compounds, and 3 sites were utilized. Vehicles accounted for 35 percent of the species measured, gasoline vapor 8 percent, and refineries 18 percent. The vehicle and gasoline vapor contributions were found to agree well with inventory values, although the inventory values were for a typical summer day, not winter. The refinery contribution was found to be much larger than the inventory value. Thirty percent of the measured concentration was not explained by the eight sources examined.

Strengths of this work include the concept of minimizing reactivity effects through the use of winter data. Weaknesses include the lack of discussion of seasonal effects on emissions, the fact that source contributions are expressed as a percentage of fitting compounds, inappropriate averaging of data, and reporting separate source contributions for categories with collinear profiles.

Objective Review

In this CMB analysis, eight source types were considered, but essentially only five source types were used in the fit. Due to collinearities between two groups of source profiles, it was not possible to use all source types simultaneously. The mass balance equations were solved once with the graphic arts profile and once with the architectural coatings profiles and the results were averaged. The same procedure was used for the trio of wastewater treatment, vapor degreasing, and dry cleaning profiles. Hence, only five profiles were used at a time, and the results should be interpreted so that the sum of the two source groups' individual contributions is considered to represent their combined impact. The exact split between graphic arts and architectural coatings, or between wastewater treatment, vapor degreasing, and dry cleaning is less certain.

This report improved upon previous work in Chicago (O'Shea and Scheff 1988) by including additional species; in particular, chlorinated organics. This allowed the dry cleaning, wastewater, and degreasing source types to be included in the analysis since chlorinated organics are emitted in significant quantities from these sources.

A higher than expected gas vapor contribution was predicted at the suburban site. This was possibly explained by the location of a gasoline pump and storage tank in the vicinity of the monitoring site.

The researchers observed good agreement between the CMB results and the emission inventory estimates with the exception of refineries, which are suspected to be underestimated in the emission inventory. The inventory was prepared in 1987, and therefore does not include the most recent EPA estimates for on-road and nonroad mobile emissions.

The researchers also found very close agreement between the average CMB-estimated residual mass (from "unknown" sources) and the "other" category in the emission inventory. Although this observation certainly supports the CMB result, this fact alone cannot provide justification for the conclusion, made by the researchers, that CMB can therefore be used to evaluate and validate an emission inventory. (Of course this statement may be valid, but the fact that the other categories agree is hardly proof.)

Skeptical Review

Site Location

The suburban site is described as being adjacent to the parking lot of a fire station with a gasoline pump and a bulk storage site, and the authors speculate that this may have given rise to a high contribution from gasoline vapor. No information is given about the location of the other sites and any potential biases associated with their locations.

Ambient Sampling

Two independent sampling methods were used in this study: Tenax cartridges for aromatic and chlorinated compounds, canisters for other NMOCs. The separate measurements were combined into a single ambient profile for each sample. This introduces the possibility for biases or random variations between components determined by each method. This might have been addressed by comparing some of the aromatics that could be determined in each method (e.g., benzene, toluene). The total NMOC in each sample was not determined so there is no way to place concentrations on a percent NMOC basis, which is essential to estimating source contributions to total ambient NMOC. Species are expressed as percent THC, where THC is the sum of the fitting compounds, but this contribution depends arbitrarily on the number of fitting compounds selected and therefore has little relevance to the atmosphere.

Source Profiles

The source profiles are described in some detail, and by reference to other papers, but there is no discussion of how relevant they are to the ambient measurements in this study: i.e., 6-9 a.m. wintertime samples in Chicago. Eight profiles are used: vehicles (VEH), gasoline vapor (GV), refinery (REF), wastewater treatment (WAS), vapor degreasing (VDG), dry cleaning (DC), graphic arts (GA), and architectural coatings (AC).

Source Contributions

The authors noted two sets of collinear profiles: GA and AC, and WAS, VDG and DC. Because of this they were generally unable to solve simultaneously for the collinear sources and therefore note that only the total for the sources is meaningful.

Nevertheless, separate source contributions are reported (to several significant figures) and discussed in the paper.

The absolute source coefficients (i.e., in μg m^{-3}) are summarized in Table 4 of the paper for all samples at each site. For example, for the vehicle contribution in 4-hour samples at the urban site, values ranged from 16.2 to 141.6 with a mean of 70.2 and a standard deviation of 48.6 μg m^{-3}. To get the overall average vehicle contribution for the study, shown in Table 5, the authors average the four values for different sample sets given in Table 4. To get percent contributions of different sources to total NMOC in Table 5 they ratio the averages, i.e., they take ratios of averages, not averages of ratios. This is not a statistically sound approach, especially when the raw data span wide ranges of values (e.g., 16.2 to 141.6, above), and is likely to result in significant biases in the source contributions derived. The appropriate statistical approach would be to average percent contributions determined for each sample. However, this approach is not possible for this study because total NMOC was not measured with each sample.

The conversion of average absolute source strengths (μg m^{-3}) to percent THC (shown in Table 5 of the paper) has little relevance to the atmosphere because THC (sum of fitting compounds) is an arbitrary subset of NMOC, and the conversion to percent NMOC involves a major assumption about the relationship between THC and NMOC for each source category.

Comparison with Emission Inventories

The estimated source contributions are compared to typical summer day values from a 1986 inventory prepared by Illinois EPA. It is inappropriate to compare winter measurements to typical summer day inventories. The authors do not attempt to estimate uncertainty ranges for the CMB source contributions, but they would certainly be large because of the variability in the ambient data, uncertainties in the source profiles (fingerprints), and assumptions involved in converting measured concentrations to percent NMOC. The separate estimates for graphic arts and architectural coatings should be combined because of fingerprint collinearity, as should wastewater treatment, vapor degreasing, and dry cleaning.

5. Source Reconciliation of Ambient Volatile Organic Compounds Measured in the Atlanta 1990 Summer Study: The Mobile Source Component, C.W. Lewis and T.L. Conner, EPA AREAL. In *Emission Inventory Issues in the 1990's*, pp. 514-523 (1991).

This paper describes the application of CMB, with a single motor vehicle source profile, for Atlanta. The source profile, described as motor vehicle exhaust, was obtained from tunnel sampling in the Atlanta area. Ten species were selected as fitting compounds. The average calculated motor vehicle exhaust contribution ranged from a low of 50 percent, for weekend afternoons, to a high of greater than 100 percent.

The main strength of this study is the use of a locally generated source profile. The main weakness is the reliance on a single source profile, which only provides an upper-bound estimate of the motor vehicle contribution.

Objective Review

This paper appears to be a preliminary exploration of the use of CMB for the summer 1990 Atlanta field study VOC data. Only one source profile was used, despite the availability in previous literature (e.g., Aronian et al. 1989) of additional source profiles that would be appropriate for an urban area. In fact, as part of the discussion concerning the selection of species to be used in the CMB analysis, the authors even present a vehicle evaporative source profile that may have proven useful in this CMB study.

The single source profile, supposedly representing vehicle exhaust, was obtained from ambient sampling in a tunnel-like underpass. The results of other researchers have indicated that ambient measurements in a tunnel likely include contributions from sources other than tailpipe exhaust, such as running losses. Many other stationary area sources also contribute significant amounts of gasoline vapors to a region's air quality. However, the measured tunnel profile can certainly be considered to be associated with vehicular activity. Hence, the CMB estimate of "vehicle exhaust" should be interpreted as representing "vehicles in motion."

In addition, when using only one profile, it is quite possible that other sources may contribute some amounts to each of the fitted species, thereby causing the predicted source contribution to be overestimated. The authors attempted to minimize this problem by including only species for which no other source was known to contribute a significant quantity of the species. Unfortunately, there are no real VOC "tracers" for vehicle exhaust. Therefore, the results of this analysis (vehicle exhaust was responsible for 40-100 percent of the VOC mass, nearly always greater than 50 percent) must be interpreted as being an upper bound estimate for the vehicle exhaust contribution.

Measurement uncertainties were estimated (somewhat arbitrarily) as a function of concentration, while the source profile uncertainty is based on the sample variation of the (nine) tunnel samples. The CMB model was used to estimate the vehicle exhaust contribution to 139 ambient samples, using 10 fitting species. Examination of the

vehicle exhaust contribution of many of the VOC compounds not included in the fit indicated the presence of additional sources. As would be expected, the vehicle exhaust contributions were temporally correlated with measured CO concentrations; however, the CO concentration generated using the ratio of emissions of CO to NMOC was over twice as high as the CO concentration that was inferred by the correlation.

The paper concludes by discussing the use of a simple box model, similar to that used by other researchers (which is essentially a method for properly weighing portions of an emission inventory for comparison with CMB results); however, the technique was not applied. The use of a multivariate approach (SITEOF) is also discussed for possible future application.

Skeptical Review

This is a preliminary and less refined analysis than later work by the authors of the same Atlanta data. In this study the CMB model is used with a locally derived roadway source profile. This profile is identified as "vehicle exhaust" in this 1992 text but is based on tunnel-like measurements, so running losses should also be present. In the later study (Henry et al., 1994) this profile was more correctly identified as the roadway profile. Tunnel driving conditions are not representative of typical urban driving, tending to have more steady-state operation and certainly no cold starts.

The present text notes that the CMB model often gives greater than 100 percent contribution to the roadway profile. The later studies use the SAFER upgrade with constraints to help ensure more plausible results.

At least one apparently worthy aspect of this early work should survive, however. The authors provide some measure of validation to their results by showing that their estimated "exhaust" results show a fairly linear relationship to CO measurements. Perhaps this measure of validation could become more common across other receptor modeling studies.

In summary, this use of older CMB techniques with only a single profile sometimes gives results greater than 100 percent for the mobile source contribution, which is not plausible. The same authors have now helped develop and implement at least two upgrades to the CMB methodology to eliminate such implausible results. Therefore, this paper is obsolete.

6. **Toxic Volatile Organic Compounds in Urban Air in Illinois**, C.W. Sweet and S.J. Vermette, Ill. State Water Survey, *Environ. Sci. Technol.*, 26:165-173 (1992).

In this study, factor analysis and CMB analysis were applied to 13 toxic VOC compounds in Chicago and East St. Louis. Thirteen source profiles were considered, but only three to six of these were used in the source apportionment. In Chicago, vehicle exhaust was found to account for nearly all the measured toxics on average, but other sources including coke ovens contributed significantly on polluted days. No refinery contribution was found, in contrast to other Chicago CMB studies. In East St. Louis, the motor vehicle contribution was large for toluene and xylenes, but other sources contributed significantly to benzene concentrations.

Strengths of this work include the separate analyses for average and polluted days. Weaknesses include the limited number of species used and lack of discussion of total NMHC.

Objective Review

The objective in this paper was to account for the sources of toxic VOCs at two urban/industrial locations. A number of approaches were attempted, including the examination of ambient data, wind trajectory analysis, factor analysis, and CMB.

The factor analysis provided some indication of source contributions, but not much information was obtained beyond what was known either from results of the wind trajectory analysis or from other physical evidence. For the Southeast Chicago data, the largest factor was associated with a combination of vehicle, evaporative, and solvent emissions. The individual source contributions were too correlated to be separated with the factor analysis technique. For the East St. Louis data, the nearby chemical complex, which had been implicated by wind trajectory analysis, was identified as the major factor. The remaining factors were not explained well with local source information.

The CMB analysis used source profiles mostly from Scheff et al. (1989), with the addition of coke ovens and the nearby chemical complex (for the East St. Louis data) obtained from air monitoring data. Three nontoxic species were added to nine toxic VOC species for a total of 12 species used in the CMB analysis. However, it is not entirely clear how many species were actually used in each CMB analysis. Examination of the degrees of freedom reported for each CMB result, and the number of source profiles used, indicates that the number of species may have been less than 12 for some CMB runs (unless additional sources were used in the fit, but not reported). The contributions to only eight toxic species are reported in the paper because the others were considered to be associated with background air quality.

CMB was conducted on average ambient data from the two cities. For Chicago, the contributions from only three source types are reported, which is (most likely) an indication that only these three (of the 13 possible) source profiles produced a statistically significant contribution coefficient. The CMB regression statistics for the

average East St. Louis data indicated a poor fit of the ambient data, probably due to the fact that source profiles specific to many of the local sources were not included.

CMB results indicated that area sources such as vehicle exhaust, evaporation of petroleum products, and solvent evaporation, were responsible for the majority of ambient toxic VOCs. Industrial sources had, on average, less of an impact than might be expected due to the proximity of these receptors from industrial activity.

In addition, a few CMB results are reported for individual samples during specific meteorological conditions (when the receptor was downwind of a major point source). Not surprisingly, a significant amount of observed VOC concentrations could be attributed to specific industrial sources during these conditions.

Skeptical Review

One of the fundamental rules of CMB application is that there cannot be more source profiles than there are fitting species. Yet this paper presents 13 profiles for only 12 species. Obviously not all were used, but there is no discussion of how the number of source profiles was reduced for CMB application. The focus on toxic components is the main reason for the small number of fitting species. However, better results would be obtained if a more comprehensive list of VOCs had been used to achieve good model fits, even if interpretation of the results focused on the toxics.

One positive aspect of this paper is the use of factor analysis as an initial method for understanding which species may have common sources. For Chicago, four sources accounted for 78 percent of the variance in the data. The largest (45 percent of the variance) was described as "urban sources" and includes motor vehicles and other area sources. For East St. Louis, four factors accounted for 86 percent of the variance. None of the four were identifiable as including motor vehicle emissions; the authors speculated that the presence of a chemical plant masked the motor vehicle signature.

Given these factor analysis results, the CMB results appear somewhat contradictory. The average day source apportionment for Chicago attributes 100 percent of the aromatic compounds to vehicle exhaust, with no contribution of gasoline vapor, solvents, or any other category. This rather unlikely result again points to the need for more fitting compounds.

Because of the small number of fitting species, the results of this study are not amenable to drawing conclusions regarding VOC source attribution. However, an interesting feature of this analysis is the calculation of source contributions on average and polluted days. Motor vehicles are the largest contributors on average days, whereas point sources are the largest contributors on high-concentration days. This makes good intuitive sense, since motor vehicles are always present throughout the urban area, whereas point source emissions can impact different areas depending upon wind direction and other meteorological factors.

7. **Receptor Modeling of VOCs in Atlanta, Georgia**, D.M. Kenski, R.A. Wadden, and P.A. Scheff, Univ. of Illinois, and W.A. Lonneman, EPA AREAL, A&WMA Paper 92-104.06 (1992).

This paper reports the results of CMB application for Atlanta. The data were collected from 6 to 9 a.m. at two sites during the summers of 1984, 1986, and 1987. Source profiles were those used in previous CMB studies by these authors. "Vehicle" emissions were found to account for 53 percent and gasoline vapor 16 percent. About 20 percent remained unaccounted for. These values were compared to two emission inventories, and the "vehicle" contribution was found to be lower than the EI values. The gasoline vapor contribution was higher, but the gasoline vapor total in the inventory was for point sources only. Despite this mismatch, the authors conclude that gasoline vapor may be underestimated in the inventory.

Strengths of this study include the extensive database used. Weaknesses include the lack of effort to place inventory and CMB estimates on a common basis, and failure to consider uncertainties/biases in the CMB-estimated source contributions.

Objective Review

In this CMB analysis, four source types were considered, but essentially only three source types were used in the fit. Due to collinearities between graphic arts and architectural coatings source profiles, it was not possible to use both source types simultaneously. The mass balance equations were solved once with the graphic arts profile and once with the architectural coatings profiles and the results were averaged. Hence, only three profiles were used at a time, and the results should be interpreted so that the sum of the graphic arts and architectural coatings contributions is considered to represent their combined impact. The exact split between graphic arts and architectural coatings is less certain. It was shown that the agreement is much better between the sum of the CMB-derived contributions and the sum of the emission estimates, than for the same comparisons with the two separate source types.

Vehicle exhaust accounted for about 70 percent of the inventory VOC emissions, but the inventory did not include biogenics. With biogenics included, vehicles were reported to account for 46 percent of VOC emissions, which is close to the CMB estimate of 53 percent. The inventory used in the comparison was a NEDS inventory generated in 1990. Thus, it does not include the most recent EPA estimates for on-road and nonroad mobile emissions.

The inventory estimate for gasoline vapor was deficient in that it only included point sources. As expected, the inventory fraction was much lower than the CMB-estimated source contribution coefficient. The researchers relied on previous study results to conclude (despite the fact that there was no new strong supporting evidence) that gasoline vapor is underestimated in the emission inventory.

The ambient data for this study were collected during the summers of 1984, 1986, and 1987. The CMB results for the train station produced somewhat different results for 1987 than for the previous years. For example, the vehicle contribution was computed to be between 48 and 73 percent in 1984 (n=7) and between 56 and 74 percent in 1986 (n=14). The unexplained source contribution was low (less than 10 percent) for almost all these CMB model runs. In 1987, however, the contribution from vehicle exhaust was generally much lower than in previous years, ranging from 26 to 73 percent (n=19 including four replicate samples), and the unexplained source coefficient was much higher (less than 10 percent on only one day). On two occasions, the unexplained sources accounted for over 90 percent of the total mass. This curious shift in source attribution is not addressed in the paper. The use of overall (three year) averages (such as for comparison with emission inventories) must be viewed with some caution, given these unexplained annual variations.

The CMB results from this paper are contained in the five-city study (Kenski et al. 1993) that was also included in these reviews.

Skeptical Review

Source Profiles

The source profiles (fingerprints) used in this work are only referenced via other publications from this group. There is no discussion of how relevant these profiles are to Atlanta. The authors interpret the vehicle profile as being representative of exhaust only: thus when they refer to vehicle contribution they mean only vehicle exhaust. This apparently neglects evaporative emissions. However, since the vehicle profile contains some butane and isopentane, an unknown fraction of evaporative emissions may get included with the vehicle contribution, depending on how representative the vehicle profile is for Atlanta. The gas vapor profile looks like gasoline headspace and likely picks up most of the remaining evaporative emissions. The authors compare this contribution only to emissions associated with gasoline marketing, which certainly underestimates sources of gasoline vapor included in the inventory.

The authors found that the graphic arts and architectural coating profiles were highly collinear: this is not surprising since toluene dominates both profiles with 93 and 73 percent of the fitting compounds, respectively. In other words, the sum of these two sources is likely determined almost entirely by toluene with the percent of total NMOC being effectively based on the assumed toluene/NMOC ratio for the profiles (9 and 4, respectively). This is most easy to see for graphic arts where toluene is 93 percent of the fitting compounds, but only 9 percent of total NMOC, thus the NMOC due to graphic arts is essentially 10 times the fitted toluene value.

Ambient Data

Information is given on the location of the two monitors for this study, but few details are given for the measurement methodology. In particular, it would be useful to know how total NMOC was determined, and whether biogenic hydrocarbons were included in

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the total. The samples were part of a 39-city study by EPA and are referenced to a 1988 paper by Lonneman. This is a well-known database that is widely respected.

Estimated Source Contributions

The summary states that vehicles are "the principal source of VOCs," and the discussion elaborates that "vehicles usually account for slightly more than half (mean = 53%) of the hydrocarbon" in this study of Atlanta. For 1987, vehicles contributed more than 50 percent of NMOC for only 14 of 32 samples at the Train Station and DeKalb.

There is no discussion of uncertainties in the estimated vehicle contribution, but the source contributions for individual runs are given in Table 3. Data for all three years were obtained only at the Train Station and are considered here. Two 1987 samples had unexplained contributions greater than 90 percent, which the authors do not discuss, and are excluded here. A very simple analysis (means, ranges, and population standard deviations, by year) of the vehicle contributions from Table 3 follows:

Analysis of estimated percent contributions of vehicles to total NMOC (% NMOC) at the Train Station site, by year.

Year	Number of Samples	Mean (%NMOC)	Population Standard Deviation (%NMOC)	Range of Values (%NMOC)
1985	7	56	8	48–73
1986	14	65	6	56–75
1987	17	49	15	26–73

Clearly there is considerable run-to-run variability in the vehicle contribution, particularly for 1987. There is no clear trend across years. This summary gives some feel for the variability in the data, but cannot reveal biases, e.g., from uncertainties in the source profile, effects of atmospheric transformations.

The authors note that because of collinearities between the source profiles assumed for graphic arts and architectural coatings only the total for the two categories has any meaning, nevertheless source contributions for both are reported to three significant figures. The split between graphic arts and architectural coatings is clearly highly uncertain and is probably an artifact of the analysis method.

Biogenic emissions are not discussed, which is surprising for Atlanta. It is likely that both isoprene and alpha-pinene were included in Lonneman's NMOC measurements and their contribution to NMOC could have been reported. It is unclear whether biogenics are included in the measured total NMOC. Even though the samples were taken from 6-9 a.m., biogenic emissions (which depend strongly on sunlight and temperature) might be significant by 9 a.m. in Atlanta during the summer.

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Inventory Comparisons

Comparisons are made with two inventories: a 1990 point source inventory from EPA's
National Emissions Data System (NEDS), and an inventory for the Atlanta MSA from
EPA Region 4. No information is given on how these inventories were derived:
whether they are annual or summer average, whether they were corrected to match the
6-9 a.m. monitoring period, what version of MOBILE was used. In any case, the
specific comparisons made seem unrealistic because of:

1. The apparent statistical uncertainties in the source contributions derived from the
   CMB analysis which are not addressed.

2. The uncertainty about whether evaporative emissions would show up in the vehicle
   or gasoline vapor contributions, or both.

3. The inability to resolve graphic arts and architectural coatings, and the likelihood
   that the total NMOC for these categories combined is basically an extrapolation
   from the measured toluene via the assumed toluene/NMOC ratios.

4. The uncertainty in how biogenic emissions were accounted for in calculating percent
   NMOC.

8. **Respeciation of Organic Gas Emissions and the Detection of Excess Unburned Gasoline in the Atmosphere**, R.A. Harley, M.P. Hannigan, and G.R. Cass, California Institute of Technology, *Environ. Sci. Technol.*, 26:2395-2408 (1992).

This paper presents the results of a detailed review of the VOC emission inventory for the Los Angeles area, and application of the CMB model. The authors make numerous revisions to the CARB default VOC speciation profiles, based upon a literature review and evaluation of available data. The authors then use the revised emission inventory to make qualitative comparisons of ambient and inventory profiles, and find generally good agreement. Finally, CMB modeling was performed for nine sites for a set of 13 low-reactivity species, using five source profiles. The authors did not use surface coating as a source profile because insufficient low-reactivity tracers were available for that profile. The model apportioned an average of 35 percent of NMOG to vehicle exhaust, compared to 55 percent in the inventory. However, the CMB technique also allocated 35 percent of the ambient NMOC to raw gasoline, compared to 10 percent for the inventory. The total of all three motor vehicle/gasoline sources was in good agreement with the revised inventory values. The authors estimate that raw gasoline emissions in the basin may be underestimated by 400 tons per day.

Strengths of this study include the detailed evaluation and improvement of the speciated inventory and source fingerprints, and the exclusion of reactive species from the CMB analysis. Weaknesses include the inability to include potentially important sources in the source apportionment.

Objective Review

The reactivity for a number of source profiles (especially for surface coating and solvent use categories) was markedly different for the revised profiles than for the "official" source profiles. The hydroxyl reactivity of the overall organic gas emission inventory increased by 4 percent after respeciation. In addition, the revisions lead to significant changes in the emission inventory estimates of several individual components. For example, emissions of 1,3-butadiene, a toxic air contaminant, were 14 times greater using the revised speciation profiles.

The revised inventory for the individual hydrocarbon components compared well with ambient data, indicating that the source profile revisions are justified (although the improvement is not quantified; i.e., the same comparison with the "official" inventory is not shown).

Both source profile uncertainty and ambient concentration uncertainty were considered in the CMB analysis. Ambient data from eight SCAQS (1987) monitoring sites (1-hour samples) and one previous (1986) study site (Glendora; 4- and 8-hour samples) were fit with five source profiles in the CMB analysis. The number of species used in the CMB analysis is not clearly stated in the paper; 14 organic species are shown that meet specific criteria for inclusion in the analysis. The paper also indicates that the performance of the CMB model can be improved by including other tracer species, such

as CO (a tracer for vehicle exhaust); however, it is not clearly stated whether this was done. The text on page 2405 suggests that CO was used, but no results are presented for CO. The only regression statistics reported in the paper are the computed standard errors of the source type contribution estimates.

The CMB analysis was not able to determine contributions for some potentially important sources such as biogenics, surface coating and solvent use, due to limitations in the species data available from ambient monitoring and the exclusion criteria for reactive species. The authors identify some key species that are recommended for addition to future ambient sampling programs.

The conclusion is reached that the current emission inventory for the Los Angeles area significantly underestimates the emissions of unburned gasoline. The authors indicate that possible sources of this excess are tailpipe exhaust (under driving conditions not represented by the FTP-based driving cycle or for vehicles not adequately represented in source tests), hot soak evaporative emissions, and fuel spillage. The emission inventory used in this comparison was generated in 1990, using the mobile emission model EMFAC7E. This inventory does not include the most recent EPA data for nonroad mobile emissions, which show increases in VOC emissions. In particular, the increased emissions from 2-stroke engines may account for part of the "missing" whole gasoline emissions.

Skeptical Review

Although the authors apparently respeciated an emissions inventory for the Los Angeles area, they failed to properly justify or verify that the new speciation is superior to what they call the "official" inventory that was developed according to standard California Air Resources Board procedures. The authors then use a rather truncated set of information and the CMB7 model to claim that their new inventory leads to a conclusion that a large quantity of unburned gasoline is still not accounted for.

At best, given the meager justification given in this paper, the new inventory should be called an "alternative" inventory. Unfortunately, such an approach was not taken, and the paper fails to provide a convincing case for either the new inventory or the implication for the "missing" unburned gasoline from using the CMB7 model. Had such an approach been taken, then comparisons of agreement between ambient distributions of species between the two inventories might have been provided. Instead the reader is often left with only faith that the choices taken by the authors to use different data sources than the "official" are justified. A noteworthy example concerns the general category of "Industrial Surface Coatings and Adhesives." The official inventory uses the study of Oliver and Peoples (1985) but the new speciation is based on the study by Rogozen et al. Both of these studies were done the same year, both were done for the CARB, and both have nearly identical titles claiming "improved" emission inventory for organics. Thus, it appears that CARB sponsored both studies and chose the Oliver and Peoples work over the Rogozen et al. study, yet the present authors seem to believe that the latter is better. This particular change, according to the authors of this paper, gives an increase of 37 percent in reactivity from this category.

The authors may have been concerned about reactivity, but they did not focus their CBM7 study on reactivity. In fact, they defocused their choices away from reactivity for the sets of species profiles needed to characterize various source categories in their source-receptor reconciliation work. This, of course, is a major short-coming inherent in the use of the CMB7 model. As noted in the review of the Lonneman et al. (1989) study a case can be made from ambient data that the sum of olefins and multi-alkyl benzenes (i.e., xylenes and trimethyl benzenes, etc.) may account for two-thirds of the ozone-forming capacity of the organic compounds in the atmosphere near sources of fresh emissions even though the mass sum of these species constitute only about 20 percent of the total organic hydrocarbon mass. This simple reactivity "rule-of-thumb" implies that a ton of either of these type of species is more than seven times more important to categorize properly than a ton of virtually anything else. Of all the species used by Harley et al. in this study, ethene in their auto exhaust profile is the only species which might be considered important under this reactivity "rule-of-thumb." What is missing from this Harley et al. study is an emphasis on reactivity at each step of their reconciliation work. For example, auto exhaust and whole gasoline both have copious amounts of multi-alkyl benzenes, and auto exhaust is known to have plenty of olefins. Development and verification is needed of reliable fresh emissions ratios for these highly reactive components to the key species to be used in the CMB7 model for all categories. Then the final results of a CMB7 study might be reevaluated (including uncertainty factors) to include some estimate of the ozone-forming importance of the result. The study by Nelson et al. (1983) did include some evaluation of reactivity effects for olefins, xylenes, and trimethyl benzenes.

The result that whole gasoline is the "missing" category by itself seems difficult to justify, as the authors do note. Since whole gasoline is, in reality, the more volatile spectrum of hydrocarbons derived from petroleum, many uses for this general class of compounds exist besides just gasoline. That is, these compounds are used for solvents in many products like surface coatings, consumer products, and degreasing. To be sure, some moderately expensive changes from crude petroleum are done at refineries to improve octane over the natural straight-run gasoline fraction of crude oil, but Harley et al. do not clearly appear to earmark their choices of species in their receptor model to be highly refined species for gasoline. One such choice might have been to focus on the branched to normal ratio of paraffins, since gasoline refining increases this ratio, especially for C6 and greater alkanes. A big and maybe (as the newer and more controlled vehicles dominate the fleet) growing problem separating the highly volatile gasoline-range hydrocarbons into recognizable source profiles, is that only a very small fraction of gasoline is actually emitted (compared to the amount burned as fuel) while at least some solvents are designed to be entirely emitted into the atmosphere (solvent recovery is an important and, hopefully, growing, exception). From an economics point of view, this implies that the volume sold from a refinery for solvent use may be so small compared to gasoline, and the per gallon profits high enough for solvents (compared to gasoline), that merely selling high octane gasoline components for solvent use (even though octane is typically not related to solvent specifications) may be cheaper than the costs of making attempts to further enhance the profit margin by earmarking the cheaper unrefined material to solvents.

9. **Receptor Modeling of SCAQS Volatile Organic Compounds**, A.W. Gertler, D.H. Lowenthal, J.C. Chow, and J.G. Watson, in AWMA conference proceedings, Southern California Air Quality Study (SCAQS): Data Analysis (1992).

This paper describes the application of CMB for eight sources and 19 species for two sites in the Los Angeles area (Long Beach and Claremont). Ambient samples included both morning and afternoon samples from the SCAQS database. Source profiles were taken from Aronian et al. (1989). Vehicle exhaust was found to account for 60 percent of NMOC at Long Beach and 70 percent at Claremont. The refinery and evaporative profiles could not be distinguished; the composite of refinery and evaporative peaked at 40 percent at Long Beach in the morning and 42 percent in Claremont in the afternoon. No comparisons with the inventory were made.

Strengths of this study include the extensive database used. Weaknesses include the lack of consideration of reactivity for afternoon samples, and lack of comparison to the inventory.

Objective Review

Eight source profiles were assembled, including six from Aronian et al. (1989), and two additional single-species profiles (representing propane and biogenics). Profile uncertainties of 10 percent were assumed. Between 15 and 17 species were used in the CMB analysis. Architectural coatings, graphic arts, and wastewater treatment were observed to contribute negligible amounts. The gasoline vapor and refinery contributions could not be distinguished by the CMB model, hence there were only four source types for which CMB was used to quantify source contributions: (1) vehicle exhaust, (2) the sum of evaporative and refinery, (3) biogenics (which used isoprene as a tracer), and (4) propane (which accounted for all excess propane).

CMB results were stratified by time of sample (sample collection starting times were between 5 a.m. and 4 p.m.; sample duration was not indicated in the paper, but samples collected during SCAQS are known to have been obtained over 1-hour sampling intervals) and location (Long Beach and Claremont). Vehicle exhaust was estimated by CMB to contribute much higher concentrations of organics in the morning hours, which is consistent with traffic patterns. Biogenics were a very small contributor for all cases. The average evaporative/refinery contribution (represented by the evaporative profile) was estimated to be 31 and 24 percent, at Long Beach and Claremont, respectively (with peaks as indicated above). The average propane contribution was 9 and 6 percent, at Long Beach and Claremont, respectively. Three profiles (vehicle exhaust, evaporative/refinery, and propane) accounted for close to 94 percent of the average measured organics concentration at both sites.

Skeptical Review

This group of authors have a long history with receptor modeling. Therefore, it is disappointing to see such an overly brief report with such conclusions. The authors claim that their results support a conclusion that over 90 percent of the ambient NMOC can be accounted for from mobile sources. At least two other recent studies have found far less contributions from the mobile source at the same Long Beach and Claremont sites studied by Gertler et al. (and presumably using the same SCAQS data). Harley et al. (1992), using their own alternative emissions inventory and using receptor modeling found about an 80 percent contribution from mobile (counting their profile of whole gasoline as mobile-related). The Harley et al. study did not determine if some of the excess "whole gasoline" found might have been from non-mobile sources such as paints, solvents, and degreasing. Fujita et al. (1992) used inventories where the mobile contribution is between 52 and 72 percent depending on the hour of the day. However, Fujita et al. did suggest that the inventory may be low for mobile sources.

The receptor modeling done by Gertler et al. does not account for several factors that other groups are now using. For example, the Fujita et al. group used day-specific, gridded and hourly emissions inventories. The only emissions information needed for the Gertler et al. approach are emissions speciation profiles. However, the time-of-day can be an important factor for using the CMB model as noted by the authors, because many of the species chemically react at different rates. Little discussion is provided to assure that the differences in chemical reaction rate were adequately accounted for.

The CMB technique can apparently provide results based on the information it uses. That is to say, if only a few profiles are used, the source apportionment gives the best fit result for the profiles provided. If the profiles used are not very accurate, a best fit is given regardless. The Gertler et al. profiles used are not well balanced in the number of species used to characterize each of their sources. The three sources of vehicle exhaust, evaporative, and refinery each provide a large number of species while all the other sources used in their model have very few species, all of which overlap with species found in the three largest sources.

It appears that non-mobile uses of gasoline-range species are not accounted for in this study. These uses often are aimed at full evaporation (e.g., paint thinner) which contrasts sharply with the combustion use of gasoline. Hence, the fraction of gasoline-range compounds used may be very much less than for fuel, but the percentage emitted of the total used is much higher. Also, the combustion use of gasoline is split between on- and off-road sources, which cannot be distinguished by this CMB analysis.

10. A Receptor Modeling Approach to VOC Emission Inventory Validation in Five
U.S. Cities, D.M. Kenski, R.A. Wadden, and P.A. Scheff, Univ. of Ill., and W.A.
Lonneman, EPA, AWMA Paper 93-WP-100.04 (1993).

This paper summarizes the results of CMB modeling for five cities: Detroit, Chicago,
Beaumont, Atlanta, and Washington, D.C. The ambient databases for each city were
collected during the summer in various years ranging from 1984 to 1988. With the
exception of Detroit, the samples were all collected for the 6-9 a.m. period. Source
profiles were the same as used by the authors in other studies, except for the addition of
a coke oven profile. Motor vehicle exhaust was calculated to account for 14 percent of
ambient NMOC in Beaumont, 28 percent in Detroit, 41 percent in Chicago, 53 percent
in Atlanta, and 56 percent in Washington. These results agreed fairly well with reported
emission inventory values. For Detroit, the model showed a peak in the motor vehicle
exhaust contribution at 8 a.m. and a peak in the gasoline vapor contribution at 2 p.m.
Unidentified components accounted for 20 to 50 percent of the ambient NMOC.

Strengths of this paper are the number of sources included and the number of cities
investigated. Weaknesses include the use of an out-of-date profile for vehicle exhaust,
the large amount of mass unaccounted for, and the use of outdated or inappropriate
inventories in the comparison.

Objective Review

One of stated objectives of this work was to use the CMB model to validate the emission
inventories for each of these cities. Average CMB predictions agreed well with the
emission inventories, with the exception of the refinery estimates, which are suspected of
being underpredicted in the Detroit and Chicago emission inventories. In Beaumont, the
CMB estimate of refinery contribution was lower than the inventory and the gas vapor
estimate was much higher than the inventory. However, the sum of the two CMB
estimates (gasoline vapor plus refinery) compares well with the inventory sum. The
presence of storage tanks at refineries is discussed as a possible explanation for this
discrepancy. The agreements between CMB predictions of vehicle exhaust contributions
and emission inventory estimates are noted by the authors as being particularly solid
evidence that the CMB model can be used as an independent method of evaluating the
accuracy of emission inventories.

The report indicates that trajectory analysis was conducted for the Detroit and Beaumont
data, but results of the trajectory model are only presented for Detroit.

In this CMB analysis, between four and six source types were considered for each
location, but essentially one less source type was used in the fit. Due to collinearities
between graphic arts and architectural coatings source profiles, it was not possible to use
both source types simultaneously. The mass balance equations were solved once with
the graphic arts profile and once with the architectural coatings profiles and the results
were averaged. Hence, from three to five profiles (depending on location) were used at
a time, and the results should be interpreted so that the sum of the graphic arts and

architectural coatings contributions is considered to represent their combined impact. The exact split between graphic arts and architectural coatings is less certain.

This report improved upon previous studies by the Illinois research group by increasing the number of species in the ambient and source profile data from 23 to 29. Also, a source profile for coke ovens was used (for the first time) in Detroit and Washington D.C. (The researchers claim that the polyethylene source profile is also used for the first time; however, it was employed in the Wadden et al. [1986] Tokyo study, which was cited in this report.)

This report included the CMB analysis that was conducted for Atlanta and reported in Kenski et al. (1992). As in that paper, the researchers conclude that gas vapor emissions may be underestimated in the Atlanta inventory (although the data don't particularly provide strong evidence for that conclusion; see review of Kenski et al. 1992).

Skeptical Review

This study combines some results already presented by the authors (e.g., Kenski et al., 1992) with similar analyses for other cities. Although the presentation of all five cities in one paper is helpful for comparison purposes, it provides little opportunity within the allotted page limit for discussion of each city individually. The progression of motor vehicle contribution from 14 percent in Beaumont to 28 percent in Detroit, 41 percent in Chicago, 53 percent in Atlanta, and 56 percent in Washington, is consistent with expectations, given the greater amount of industrial activity in Beaumont and Detroit relative to Atlanta and Washington.

There are several shortcomings of the Kenski et al. analysis. A major concern is that the refinery fingerprint is the only one to contain appreciable amounts of propane. Since propane is a major component of ambient NMOC in virtually all cities, application of these profiles would likely result in assignment of nonzero refinery contributions even in cities where no refineries are located. Thus, the conclusion that refinery contributions are higher than inventory values may be questionable. To validate their conclusions regarding refineries, the authors would need to:

- include a composite profile for natural gas/LPG leakage for the area under study (as done by Mukund et al., 1994) to provide an alternative source of the observed propane

- demonstrate that zero refinery contribution is predicted by the model in areas with no refinery activity (such as Atlanta)

- apply the alternative refinery profile developed by Doskey et al. (1992) that is specific to the Illinois area, and determine the sensitivity of the modeled refinery contribution to the profile used.

If a large refinery contribution is still predicted by the model for a given city under these conditions, then the conclusion would be much more believable.

The vehicle fingerprint includes only exhaust and neglects all other important vehicle emissions. However, it is not at all clear whether the inventory comparison is based on exhaust only or total motor vehicle emissions. If the inventory includes all vehicle emissions, and the CMB results include only exhaust, then agreement between the inventory and the CMB results actually suggests that if the comparison were limited to the exhaust, the inventory would be low with respect to the CMB. Conversely, since the CMB vehicle contribution almost certainly includes nonroad mobile sources as well as motor vehicles, the opposite conclusion may be equally plausible.

The origin of the emission inventories is documented only for Atlanta, Chicago, and Washington. None of the inventories were prepared using the latest EPA data for mobile emissions, and the Washington inventory is particularly outdated.

In general, it is nearly impossible to have confidence in the inventory comparison since no efforts were made to spatially or temporally allocate the emissions. The emission inventory values for motor vehicle emissions are seasonal, daily average values, not values for the particular hours during which sampling was conducted. Since an average vehicle contribution of 30 percent may translate to a 6-9 a.m. vehicle contribution of 50 or 60 percent, failure to adjust the inventory essentially invalidates the comparison.

Also of concern is the large unidentified portion of the NMOC. Unidentified sources constituted 35 percent of total NMOC in Detroit and nearly 50 percent in Beaumont. It's difficult to interpret results that include such a large unidentified component. Possibly, the non-exhaust vehicle emissions constitute a large portion of the unidentified material. The authors should include a whole gasoline profile in their analysis.

The results for Detroit are of particular interest because samples were taken at several times throughout the day, rather than just in the morning. This provides the opportunity to check that the results match known source activity patterns. Indeed, the motor vehicle exhaust contribution peaks at 30 percent of the total in the 8 a.m. sample, but the difference between the highest and lowest motor vehicle contribution is only 8 percent. Also, the gasoline vapor contribution peaks in the 2 p.m. sample, but again the range is not as large as might be expected. For the afternoon samples, reactive losses of some of the fitting species are a concern (especially propene, xylenes, and C_3-benzenes). The authors do not address reactivity and do not discuss the possible effects of reactivity on their calculated apportionments.

In summary, this study provides some useful information regarding the range of vehicle contributions to NMOC in different cities. However, the comparison to the inventory is done so poorly that no conclusions can be drawn regarding the accuracy of motor vehicle emission estimates.

11. **Receptor Modeling of Volatile Hydrocarbons Measured in the 1990 Atlanta Ozone Precursor Study**, C.W. Lewis, T.L. Conner, and R.K. Stevens, EPA, J.F. Collins, and R.C. Henry, USC, AWMA Paper 93-TP-58.04 (1993).

This paper reports the results of CMB analysis for Atlanta. The authors note that these results supersede those given in the 1992 Lewis and Conner paper. The analysis is somewhat unique in that source profiles are not taken from the literature or source measurements, but instead are derived from the ambient data, using the GRACE/SAFER method. The method is described by Henry et al. (1994) and is not discussed in this paper. This method apportioned 50 percent of NMOC and 62 percent of NMHC to the "road" source profile (intended to represent vehicle exhaust plus running losses). The sum of the three vehicle-related profiles was 63 percent of NMOC and 80 percent of NMHC. Other profiles were identified as "propane-rich," "toluene-rich," etc. without assigning them to actual source categories. The importance of the definition of NMOC in emission inventory comparisons was emphasized.

The strengths of this paper include the discussion of alternate NMOC definitions and their effect upon the inventory comparison. Weaknesses include the inability to assign many of the profiles to actual source categories.

Objective Review

The researchers used the GRACE/SAFER technique to obtain seven source profiles. Three source profiles were associated with vehicular activity ("road," gasoline, and vapor). The other four SAFER-produced profiles were not necessarily associated with definite source types. An eighth source profile was developed for natural gas from local source test measurements. The contribution computed by CMB for the toluene-rich source profile was not statistically meaningful, so it was dropped from consideration. Thus, there were seven source profiles used in the CMB analysis.

The uncertainties used in the CMB analysis were estimated similarly to those used in the earlier paper (Lewis and Conner, 1991). The CMB analysis was conducted with the seven source profiles, each consisting of 16 species, used to fit 24 hourly (combined) weekday samples, an overall average weekday sample (average of 111 samples), and an overall study average sample (average of 628 samples). The regression statistics demonstrated an excellent fit of the ambient data.

As would be expected, the vehicle exhaust contributions were temporally correlated with measured CO concentrations. The CO concentration that was generated using the ratio of emissions of CO to NMOC, agreed well with the CO concentration that was inferred by the correlation (which was not the case in the earlier paper).

For the weekday average, CMB apportioned 50 percent of NMOC and 62 percent of NMHC to the "road" source profile (intended to represent vehicle exhaust plus running losses). The sum of the contributions for the three vehicle-related profiles was 63 percent of NMOC and 80 percent of NMHC. For the overall study average, the "road"

source type was responsible for 44 percent of NMOC, and the sum of the contributions for the three vehicle-related profiles was 62 percent. The inventory for Fulton County shows an on-road mobile contribution of 56 percent. The inventory was prepared with MOBILE4.1; the on-road mobile emissions increase by 30 percent in the more recent model, MOBILE5a.

The authors demonstrate that the definition of the "total" organics concentration has a significant effect on the interpretation of comparisons between CMB results and emission inventory estimates.

Skeptical Review

The unique feature of this paper is the use of source profiles developed by the GRACE/SAFER technique in the CMB analysis. It is important to realize that there is an extreme reliance upon the ambient database when this technique is used. Not only are the ambient receptor concentrations used in the analysis, but the ambient data are also used to derive the profiles. This method may succeed if the ambient data are of excellent quality, but fails if there are problems with the ambient data. Reports describing the 1990 Atlanta data set detail numerous problems with data quality (Purdue et al., 1992). For the receptor modeling, data from only a single site, Georgia Tech, were used because data quality was considered best for that site. However, the problems with the data at the other sites do not inspire complete confidence in the Georgia Tech data. Also, several species were deleted from the species list because of data quality problems. One of these species is isopentane, which is generally one of the largest NMOC constituents and is a tracer for gasoline vapor. Its exclusion from the analysis may lead to problems.

This is only the second recent paper to include the "whole gasoline" source category, and it is in qualitative agreement with the Harley et al. study that whole gasoline appears to be a larger contributor than gasoline vapor to ambient VOC concentrations. Both studies identify potential sources of whole gasoline, but do not quantify the extent to which these sources are sufficient to account for the modeled whole gasoline contribution. Thus, it is unclear to what extent the whole gasoline component should be lumped in with motor vehicle emissions, nonroad mobile emissions, such as 2-stroke engines, or area source emissions such as service stations. Most likely there are contributions from all three. However, the authors assume all whole gasoline emissions are motor vehicle-related.

One of the main difficulties with this paper is that none of the profiles, other than the vehicle-related profiles, are specifically related to a given source category. Profiles are identified only as "propane-rich," "toluene-rich," etc. Thus, there is no way to compare the apportionments for these categories to an emission inventory. This limits the usefulness of the paper.

This study addresses the question of the contribution of biogenic emissions, although unfortunately isoprene was the only biogenic species measured. Many of the other receptor modeling studies neglect biogenic emissions entirely. The finding that the biogenic contribution to total NMOC is small is not surprising, but is possibly

misleading. Isoprene is so much more reactive than the other NMOC that even a 2 percent contribution to NMOC might translate to a 10 to 20 percent contribution towards ozone formation. The CMB/inventory comparison presented for biogenics shows a much lower biogenic contribution from the CMB analysis (2 percent) than from the inventory (17 percent). The authors note that the CMB estimate is a lower bound because of the reactivity of isoprene. The short atmospheric lifetime of isoprene means that ambient concentrations reflect emissions only in the immediate vicinity of the monitor. Comparisons of inventory and ambient isoprene should be limited to a small region surrounding the monitor.

A key point brought out by the authors is that the source apportionment results are sensitive to the definition of NMOC used. The Atlanta ambient data set contains a large proportion of unidentified compounds (indeed, it is somewhat unique among U.S. cities in that respect). The authors show that the source contribution for motor vehicles is 63 percent for total NMOC but is 80 percent for total identified NMOC (termed NMHC in the paper). However, they do not take the next step and normalize the emission inventory the same way. If they had done so, they would have found that the motor vehicle contribution in the inventory increases for the subset of measured species as well. This is because the species that are the largest contributors to MV exhaust are generally those measured in NMOC monitoring programs. Other VOC sources can include large amounts of alcohols, ethers, and ketones that are generally not measured. Thus, they compare the total mobile contribution of 80 percent (expressed as NMHC) to the inventory value of 56 percent (expressed as NMOC) and conclude that the inventory could be underestimating motor vehicle emissions by a factor of four. This conclusion is almost certainly in error, and adjustment of the inventory is needed to assess the degree of agreement.

This paper raises some valid points, such as the discussion of definition of NMOC, and provides the first application of the GRACE/SAFER technique. Given the untested nature of their approach, it is somewhat reassuring that their results for motor vehicle contribution are similar to those of Kenski et al. (1992) for Atlanta. Further investigation of the GRACE/SAFER technique is needed.

12. **Receptor Modeling of Volatile Organic Compounds. 1. Emission Inventory and Validation**, P.A. Scheff and R.A. Wadden, Univ. of Ill., *Environ. Sci. Technol.*, 27:617-625 (1993).

This paper presents the results of CMB analysis for three sites in Chicago. Ambient 4-hour samples were collected in the summer of 1987. Eight source categories were included; source profiles were those developed and used by the authors previously (Scheff et al., 1989). The vehicle exhaust profile was based on the 1987 Sigsby study. The model apportioned 33 percent of the NMOC to motor vehicle exhaust, in good agreement with the Illinois emission inventory. Refineries were apportioned 6 to 17 percent, approximately five times the inventory value. Gaussian plume modeling was used to evaluate the predictions for the refinery contribution for individual samples.

Strengths of this paper include the use of the Gaussian model for evaluation. Weaknesses include the lack of effort to place inventory values on a common basis with CMB values, and the use of a questionable profile for vehicle exhaust.

Objective Review

One stated objective of this work was to use the CMB model to validate the emission inventory. Average CMB predictions for the 55 analyzed samples agreed well with the region's emission inventory, except for the refinery estimates, which are suspected of being underpredicted in the inventory. The study used trajectory model results to support this conclusion. These results corroborate earlier results, such as those reported by Aronian et al. (1989), which were generated using a similar set of source profiles.

This CMB analysis, like the Aronian et al. (1989) study, considered eight source types, but essentially only five source types were used in the fit. Collinearities between two groups of source profiles made it impossible to use all source types simultaneously. The mass balance equations were solved once with the graphic arts profile and once with the architectural coatings profiles and the results were averaged. The same procedure was used for the trio of wastewater treatment, vapor degreasing, and dry cleaning profiles. Hence, only five profiles were used at a time, and the results should be interpreted so that the sum of each of the two source groups' contributions is considered to represent their combined impact. The exact split between the components of the two groups is less certain. Despite the collinearities of these source profiles, good agreement was found between the CMB-derived source type contributions and the emission inventory for these five source types. However, the emission inventory is a 1986 Illinois EPA inventory which is outdated and does not include the latest estimates for on-road (MOBILE5a) or off-road mobile emissions.

Skeptical Review

Although the subtitle of this paper is "Emission Inventory and Validation," the comparisons to the emission inventory in this paper and other studies by these authors is

cursory at best. No adjustments to the inventory are made for time of day, temperature, or spatial location of the monitor, and the inventory is not normalized to include only the chemical species measured in the ambient program. It is also not clear whether or not the non-exhaust motor vehicle emissions are included in the inventory totals for "vehicles." Given these limitations, it is difficult to assess whether the agreement with the inventory is good for motor vehicles, as the authors conclude, or not.

The authors use a motor vehicle exhaust profile that is known to have problems, most notably that it overstates propane emissions (profile 1203 from SPECIATE Version 1.4 which is based on Sigsby et al., 1987 and is discussed in our review of the EPA SPECIATE database, below). The exhaust profile is based on winter-blend gasoline with an RVP of 12 psi; the gasoline vapor profile is based on summer-blend gasoline with an RVP of 9 psi. The authors do not justify this mismatch or discuss the RVP typical of gasoline in use in Chicago during the period sampled. (Fuel survey data for 1987 are available and show an average RVP of 11 psi for the state of Illinois). The profiles also exclude all non-exhaust motor vehicle emissions, which probably accounted for a major portion of the total summertime motor vehicle NMOC emissions, especially given the high RVP levels. Some non-exhaust emissions are allocated to the "gasoline vapor" category, which the authors interpret as including stationary sources only.

In the case of graphic arts, the authors state that much of the emissions consist of "non-fitting compounds" such as naphtha and petroleum distillate. They do not appear to understand that naphtha and petroleum distillate are just names for mixed refinery streams that contain many of the chemical species used as fitting compounds. Excluding these species from the graphic arts profile largely invalidates the results for that profile, since only a small fraction of the total NMOC emissions are represented in the profile.

One positive development in this paper is the use of NO_x emissions in conjunction with NMOC emissions to further distinguish between profiles. However, the only profile with significant NO_x emissions is the vehicle exhaust profile; other major NO_x sources are not included. The vehicle exhaust profile is intended to represent gasoline vehicles only, but the value used for the NO_x emissions (257 percent of NMOC) is far too high for gasoline vehicles and the source of that value is not documented.

Another area of concern is the large amount of unexplained NMOC mass. More than 50 percent of the NMOC is not accounted for by any of the eight sources. It is not clear whether this suggests that there are other, unidentified major sources, or whether it merely suggests that the profiles used to describe the eight source categories are inadequate. At the very least, the authors should have identified the chemical compounds responsible for the unexplained mass, and include a principal component analysis (PCA) to identify species that are correlated and might give some clue as to the source categories responsible for the unexplained mass.

In summary, this study raises more questions than it answers. The conclusion that motor vehicle emissions are in agreement with the inventory has little value given the remaining questions regarding the unexplained mass, the temporal adjustments, and the non-exhaust contribution.

13. **Source Attribution of Toxic and Other VOCs in Columbus, Ohio**, R. Mukund, T.J. Kelly, and C. W. Spicer, Battelle, submitted to *Environ. Sci. Technol.*, January 1994.

In this study, the CMB technique was applied for six sites in Columbus. The focus was on toxic air pollutants, but additional VOCs such as light hydrocarbons were included in order to improve the model fit. Formaldehyde and acetaldehyde were also included. Five source profiles were used (vehicle exhaust, gasoline vapor, natural gas, industrial solvents, and degreasing/wastewater). Vehicle exhaust accounted for 34 percent of the sum of the measured species, with gasoline vapor accounting for 19 percent. Only 6 percent was unidentified. A box model was used to estimate emission totals; these totals were compared to the NEDS inventory and were found to be considerably higher.

The strengths of this study include the spatial and temporal resolution and the application of the CMB technique to an urban area that had not been studied previously. Weaknesses include the questionable approach used to compare results to the emission inventory.

Objective Review

One of the central objectives of this research was to include the temporal and spatial resolution necessary to assess the variability of source contributions in urban areas. Columbus, Ohio does not contain any large point sources such as refineries or chemical plants, which was expected to improve the ability to determine the contributions from important mobile and area sources.

CMB was used to determine contributions of five source types to the sum of 19 VOC species (and to each individual species). Although 19 species were considered for this sum, only 14 of these species were used for the CMB analysis. Five source profiles were selected for use in the CMB analysis after trying various combinations of profiles available in the literature. These profiles represented the following source types: vehicle exhaust, gasoline vapor, natural gas, industrial solvents (surface coating), and chlorinated solvents (a degreasing composite used to represent dry cleaning, degreasing, and wastewater treatment).

The uncertainties associated with ambient measurements was assumed to be 10 percent for all species; the uncertainty for the source profiles was assumed to be 20 percent.

Examination of the diurnal patterns of the CMB source attributions for various species (including the sum of fitted species) provided a number of observations. For example, natural gas emission levels appear to be constant between day and night (relative to other source types such as vehicle exhaust and gas vapor), and the contributions of natural gas increase in the night when lower inversion heights are present.

The authors indicate that this was the first study to identify natural gas as a contributor to ambient VOCs in an urban area; however, Nelson et al. (1983) also showed that

excess propane could be accounted for by considering natural gas as a source in the CMB analysis. This paper uses a more accurate profile for natural gas, however.

Vehicle exhaust was found to be most important as a contributor in the morning and evening hours, consistent with traffic patterns. Gasoline vapor contributed most in urban/industrial areas during the day, and in residential areas in the evening and at night. This observation was interpreted to mean that gasoline vapor is associated more with running losses and evaporative emissions from vehicles, rather than with emissions from fixed sites such as service stations.

The CMB model results were compared with emission inventory estimates for the region. The results of this comparison provide similar conclusions to those found by previous researchers, specifically that substantial VOC emissions from mobile and area sources (especially vehicle exhaust and gasoline vapor) are not included in current emission inventories (or that emission inventories underestimate VOC emissions for these categories). However, in this case comparisons were with the Toxic Release inventory, which is not any way representative of overall VOC emissions.

Skeptical Review

This study makes some new contributions to understanding VOC and toxic source contributions, but not quite as many as the authors claim it does. The authors state that their work is the first to identify natural gas as a significant source of light hydrocarbons. If they were familiar with the literature they would know that, on the contrary, this contribution has been documented for nearly two decades (Mayersohn and Crabtree, 1976; Nelson et al., 1983). However, the Mukund study does make a significant contribution in that it demonstrates the diurnal pattern of the natural gas contribution, showing that it tends to peak around 3 a.m., when other source categories are largely inactive.

The vehicle exhaust profile was taken from a roadway study by Zweidinger et al. (1988). The Zweidinger data were acquired in 1983 and may not be representative of the 1989 vehicle fleet and gasoline. In particular, acetylene fractions from 1983 are expected to be much higher than those from 1989. In addition, the acetaldehyde fraction of this profile (2.9 percent) is incorrect based upon the Zweidinger data and is a factor of five or more higher than typical acetaldehyde values for motor vehicle exhaust.

The authors present statistical fit parameters demonstrating that the sources modeled provided good fits to the data. This type of information should be routinely included in receptor modeling papers. In addition, 94 percent of their measured species were accounted for by the sources modeled. These features lend credibility to the work.

The study focused on apportionment of toxics rather than total VOC. It is an improvement over the earlier toxics apportionment study (Sweet and Vermette, 1992) in that it includes enough nontoxic species to achieve reasonable model fits. The total VOC parameter used, called TMVOC by the authors, is a sum of 19 modeled species that includes 14 NMHCs, 3 chlorinated species, and 2 aldehydes. The use of the two aldehydes was somewhat a waste of time since it is well documented that the majority of

ambient aldehydes are secondary products of atmospheric reactions rather than direct emissions. Not surprisingly, the authors found that less than 20 percent of the ambient aldehydes could be attributed to the sources modeled.

It is important to bear in mind that the apportionment of a species to a source profile does not demonstrate conclusively that that source is responsible for that species, only that of the source profiles used, that profile gave the best mathematical fit. CMB studies often find that the motor vehicle exhaust profile accounts for a large fraction of combustion products such as acetylene, propene, or benzene. However, in this and most studies, the vehicle exhaust profile is the only combustion-related profile used. Other combustion sources, particularly if their emission speciation is similar to that of vehicle exhaust, end up lumped in with vehicle exhaust. In particular, the vehicle exhaust contribution in this and other studies almost certainly includes emissions from nonroad mobile sources. Indeed, although nearly all of the ambient benzene in this study is apportioned to the vehicle exhaust profile, the ambient benzene data do not show the morning peak expected for motor vehicle emissions.

The authors correctly point out that since total VOC was not apportioned, comparisons with the emission inventory would not be appropriate. Instead, they attempt to derive VOC emissions estimates using a box-modeling approach in conjunction with the receptor modeling results. Their purpose was to demonstrate that toxic emissions reported in the Toxic Release Inventory (TRIS) are a small percentage of total emissions. The emission estimates are order-of-magnitude estimates at best and should not be used for any other purpose.

SOURCE FINGERPRINT STUDIES

14. Source Fingerprints for Receptor Modeling of Volatile Organics, P.A. Scheff, Ill. Inst. of Tech., R.A. Wadden and B.A. Bates, Univ. of Ill., and P.F. Aronian, UOP Inc., *JAPCA*, 39:469-478 (1989).

This paper presents a literature review and evaluation of VOC source composition data for 10 source categories and 23 compounds. The sources are "vehicles," gasoline vapor, refinery, architectural coatings, wastewater treatment, graphic arts, automotive painting, ethylene production, degreasing, and drycleaning. These profiles are used by the authors in their later CMB studies. The "vehicle" profile is based on the 1987 Sigsby study. The gasoline vapor fingerprint is from an unleaded winter blend. The architectural coating composite fingerprint is derived from three profiles in the SPECIATE database, combined with product usage data for southern California.

The study also briefly presents a comparison of CMB and emission inventory estimates for Chicago, and shows good agreement for vehicle emissions (35 percent of both CMB and inventory) but poor agreement for refineries (CMB estimate 11 percent, inventory 2 percent).

The strengths of this paper are the compilations of source fingerprints, particularly for source categories such as architectural coatings and wastewater treatment. Weaknesses include the lack of discussion of variability of source profiles, and the use of a winter gasoline vapor profile for summer applications.

Objective Review

This paper was a valuable addition to the literature at the time it was published. It provided a fairly comprehensive review of speciation data available at that time, including some data from outside the U.S. that was not widely known. Source categories covering a range of source types that are large contributors to VOC inventories were included. This paper is also important because the profiles developed in it were used for all subsequent CMB analyses conducted by this group.

For the vehicle profile, dynamometer (exhaust only) results from Sigsby et al. (1987) are compared to roadway and tunnel results, which presumably include running losses, and also to a composite profile from the then current SPECIATE database, which includes hot soak and diurnal emissions as well as exhaust. The agreement between the dynamometer, roadway, and tunnel profiles is reasonably good. The composite profile, with its large contribution of evaporative emissions, looks very different. The authors select the dynamometer profile as the most representative vehicle profile. Thus, apportionments conducted using this profile represent exhaust only.

For gasoline vapor, the authors compared values for several summer and winter blend gasolines. They selected a winter blend unleaded gasoline profile as the best available,

since the available summer blend profiles were composites that included some leaded gasoline. However, it is not clear that the differences between leaded and unleaded summer blend gasoline vapor profiles are as great as the differences between summer and winter blend profiles.

Profiles for refinery operations included profiles for specific processes within a refinery, along with profiles for a "refinery plume" collected from downwind ambient sampling. Creating a composite refinery plume is a difficult task because emissions can occur from a variety of release points, representing different processes with different feedstocks. Thus, the downwind plume approach is probably the best way to create a refinery fingerprint for receptor modeling purposes. However, the authors' statement that the various profiles are in good agreement is somewhat questionable based upon the data presented. Also, the authors do not discuss the variability in the data originally used to construct the profiles. For the profile selected as the best refinery profile, the original data show enormous variability (see Doskey et al., 1992).

The authors created a composite surface coating profile from the solvent-based paint profile, a water-based paint profile and a thinning solvents profile from SPECIATE, combined according to usage fractions for the New York area. This appears to be the correct approach, but unfortunately the resulting profile contains only a few fitting species, with the majority of the VOC mass composed of non-fitting species. The graphic arts profile has the same difficulties. In both cases, toluene is essentially used as a tracer for these processes. It is no wonder that collinearities between the two profiles prevent them from being resolved in receptor modeling applications.

The authors conclude, on the basis of the similarity between various profiles for a given process, that VOC emission composition is governed by the process rather than by location-specific factors. Indeed, subsequent work and common sense show that this type of generalization has limited validity. It has since been demonstrated that characteristics of the fuel, the fleet, and the operating mode can significantly affect the composition of a vehicle exhaust profile, for example. Small changes in fuel RVP can have large changes on a gasoline vapor profile. Refinery profiles can vary significantly with time as well as spatially. Thus, the applicability of these profiles is not likely to be quite as universal as the authors imply.

Skeptical Review

Source and Species Selection

A number of reasons are given for selecting the 23 species. One of these is that the 23 compounds make up the majority of the NMOC emissions from most of the sources studied. The data show that the 23 fitting species represent only 33 percent of architectural coating NMHC emissions, 26 percent of wastewater treatment NMOC emissions, 12 percent of graphic arts NMOC emissions, and 41 percent of automotive painting NMOC emissions. However, it is not really important if significant other NMOCs are emitted along with the 23 identified. In fact, it was not necessary to include this provision as one of the reasons. It is more important, when selecting the sources, to demonstrate that the identified sources (actually the set of sources used in a

particular CMB analysis) must account for the majority of emissions of these species. This is one of the important CMB assumptions, and it is not clearly satisfied in this paper (although it is really the responsibility of those conducting specific CMB applications using these profiles to verify that this assumption is valid).

Upon examination of subsequent CMB analyses that were conducted using these source profiles (including those of the authors, and others), it can be observed that CMB was often applied with only a few of these sources in the fit. In these cases, typically only a fraction of the mass was accounted for (i.e., the "unexplained" source contribution was large). However, if the unknown sources that are contributing to the ambient air quality are made of sufficient quantities of the fitting species, these species are not well fitted. If there are enough of these species, the entire fit may be jeopardized. If there are a significant number of important sources not considered in the CMB fit, then (as is often the case), it is quite possible that certain of the source type contributions are overestimated. For this reason, if there is evidence that there may be important additional sources (for example, if the estimated "unknown" contribution is high), then CMB source contribution estimates should be considered as upper bounds.

Motor vehicles

In the discussion on the vehicle emission profile, the range of weight fractions (among the various sampling methodologies) for some species are presented. Ethane is stated to range "from 1.52 to 1.77 percent"; from the data in Table I, this should be "from 1.57 to 1.77 percent" presumably a typo). The fitting compound total is stated to range "from 45.67 to 52.43 percent"; this should be "from 45.67 to 53.77 percent."

No chlorinated hydrocarbons were measured in any of the fingerprints examined. While these compounds are not expected to be large fractions of vehicular emissions, no evidence is presented (including reference to any measurements) to confirm or justify the assumption that these compound fractions are zero. Since vehicle emissions are often responsible for a large portion of the VOC air quality, even small amounts of these compounds may obscure the quantification of sources associated with these compounds (e.g., wastewater treatment).

Gasoline vapor

The normalized profile presented for this source type (Table VIII) is from the unleaded winter fingerprint (Table II). However, the actual measurements of this fuel indicated zero amounts of ethane (propane was not measured). The authors used the average of summer blend, winter blend, and service station fractions for propane, and the average of summer blend and winter blend for ethane (not measured in service station). No discussion of this assumption or justification for its use is presented. These two species are small fractions of this source type, so this assumption is probably reasonable; however, the decision to use these averages should be addressed.

The unleaded winter fingerprint was selected to represent this source category because it is "the most appropriate for CMB modeling during the cold months of the year." Future

CMB applications using these profiles will not always be for winter ambient data and may also not be for cold weather locations (such as Chicago). The authors should make it clear that the summary presented in Table VIII is for cold winter locations, and that one of the alternative profiles presented in Table II may be more representative for other areas.

Chlorinated hydrocarbons were not measured in any of these source tests. The authors should present some confirmation that the assumption of zero fraction for these species is reasonable.

In addition to gasoline vapor, the set of source profiles should have also included evaporation of whole gasoline.

Petroleum refineries

The consistency between the various petroleum emission profiles is discussed. The fitting compound total is stated to range from 71.96 to 80.47 percent, presumably for all measurements. From Table III, this range should be from 54.60 to 80.47 percent.

The refinery plume profile was selected to represent this source category because the data from those tests were more complete, and because there was general similarity observed among the various source test data. Is may be more appropriate to use a weighted composite which includes some amounts of the fugitive emissions. Because gasoline is often stored at refinery locations, it can become difficult for CMB to distinguish between gasoline vapor, evaporation of whole gasoline (not accounted for in the set of source profiles developed in this study), and refinery emissions.

Chlorinated hydrocarbons were not measured in any of these source tests. The authors should present some confirmation that the assumption of zero fraction for these species is reasonable.

Architectural coatings

The composite profile was based on relative emission levels for solvent-based coating, thinning and clean-up solvents, and water-based coating for the New York City area and the state of New Jersey. There was considerable variation in speciation between these three profiles. In addition, the three profiles are composites taken from usage patterns in California. Therefore, the use of this composite for other locations assumes that the activity levels for these three main coating types are similar to those in New York City and New Jersey, and that the relative sales and usage levels within the coating types are similar to those in California.

Chlorinated hydrocarbons were not measured in any of these source tests. The authors should present some confirmation that the assumption of zero fraction for these species is reasonable.

Wastewater treatment

The average of four profiles is used to represent this source category. The authors state that "despite the very limited air concentration data available, the five fingerprints in Table V are quite similar." The four profiles used in the average shows some striking differences, however. Almost an order of magnitude range is evident for some of the compounds. For example, the benzene fraction ranges from 0.11 to 1.15 percent, the chloroform fraction ranges from 1.52 to 9.73 percent, the 1,1,1-trichloroethane fraction ranges from 3.1 to 17.5 percent, and the methylene chloride fraction ranges from 0.43 to 8.65 percent. The averaging technique may be reasonable, but it is clear that the resulting profile has a fair amount of uncertainty associated with it.

Many of the 23 fitting compounds were not measured in any of these profiles. The authors note that the fractions of these species may not be zero, but that the studies cited did not measure them. However, the summary profile table (Table VIII) includes zero values for many of the lighter hydrocarbon compounds. The authors should present some confirmation that the assumption of zero fraction for these species is reasonable.

Graphic Arts

Similarly to the architectural coatings profile, the composite profile for graphic arts was based on relative emission levels for four different printing types. It is not stated in the paper whether the emission estimates are for a particular region (or the entire U.S.). There was considerable variation in speciation between these three profiles. Therefore, the use of this composite for a specific location assumes that the relative activity levels for these four printing types in the region of interest are adequately represented by these emission estimates.

Results

The authors contend that the VOC source profiles are controlled by the physical and chemical processes involved, and are therefore representative for all locations. However, it has been seen that site-specific factors, such as fuel composition or solvent and coating usage patterns, may vary considerably by location. These variations may have a significant effect on the actual source profiles that would be most representative for each region.

Source profile uncertainties are not required as CMB inputs; however, it is desirable to include the source profile uncertainties in the CMB weighting scheme. For example, the effective variance-weighted least squares method, currently used in EPA CMB version 7, requires estimates of source profile uncertainty. During the assembly of various source tests and related data for this study, it was observed that the profiles for some of the source types are much more uncertain than for others. It would have been very helpful if an estimate of the level of uncertainty for each source profile had also been presented along with the source profile estimates.

15. **Volatile Organic Compound (VOC)/Particulate Matter (PM) Speciation Data System, Version 1.4**, EPA OAQPS, EPA-450/4-91-027 (1991).

This report and the accompanying database provide VOC and PM speciation profiles for a wide range of mobile and stationary source types. Each profile is assigned a data quality rating based on the number and quality of the data sources used to generate the profile. The profiles are from a wide range of data sources and vary in completeness; some are based only on engineering judgment.

This database has been updated since 1991. Version 1.5, released in late 1992, contains updated profiles for gasoline vehicle exhaust and evaporative emissions. Most other profiles remain unchanged.

Strengths of this database are the comprehensive coverage of source types. Weaknesses arise primarily from the variation in the quality of the data from which profiles were derived.

Objective Review

An objective review of the profiles in the SPECIATE database is beyond the scope of this study. However, we include here the general information and references given in SPECIATE for the profiles specifically mentioned in the skeptical review. No data sources or references are available for profile #1305, 1306, 1307, 1308, or 1313 from SPECIATE version 1.5.

Profile Data Quality

A ranking scheme is employed to assign data quality indicators to each profile in the SPECIATE database. The following criteria were used in assigning data quality indicators:

Data Quality A: Data set based on a composite of several tests using analytical techniques such as GC/MS and can be considered representative of the total population.

Data Quality B: Data set based on a composite of several tests using analytical techniques such as GC/MS and can be considered representative of a large percentage of the total population. Profiles from the VOC field sampling program are assigned data quality "B."

Data Quality C: Data set based on a small number of tests using analytical techniques such as GC/MS and can be considered reasonably representative of the total population.

Data Quality D: Data set based on a single source using analytical techniques such as GC/MS; or data set from a number of sources where data are based on engineering calculations.

Data Quality E: Data set based on engineering calculations from one source; data set(s) based on engineering judgment; data set(s) with no documentation provided; may not be considered representative of the total population.

Summary of Profiles

Profile Number:	1003 (SPECIATE version 1.5)
Data Quality:	B
Profile Name:	Surface Coating Operations - Coating Application -Solvent-base Paint
Control Device:	Uncontrolled
Reference(s):	Oliver and Peoples (1985)
Data Source:	Composite of profiles 1017 (lacquer), 1019 (primer), and 1018 (enamel) in proportion to individual emission totals for the South Coast Air Basin.

Profile Number:	1014 (SPECIATE version 1.5)
Data Quality:	B
Profile Name:	Gasoline - Summer Blend
Control Device:	Uncontrolled
Reference(s):	Oliver and Peoples (1985)
Data Source:	A composite of four product types combined in proportion to 1979 sales figures for California was used to develop vapor samples which were analyzed using a dual detector FID/PID GC.

Profile Number:	1015 (SPECIATE version 1.5)
Data Quality:	B
Profile Name:	Gasoline - Winter Blend
Control Device:	Uncontrolled
Reference(s):	Oliver and Peoples (1985)
Data Source:	Four product types combined in proportion to 1979 sales figures for California was used to develop vapor samples that were analyzed using a dual detector FID/PID GC.

Profile Number:	1190 (SPECIATE version 1.5)
Data Quality:	B
Profile Name:	Gasoline Marketed
Control Device:	Uncontrolled
Reference(s):	Radian (1987)
Data Source:	Fourteen samples of leaded, unleaded and unleaded premium grades from five oil companies composite based on 1984 national sales data. Headspace analyzed by GC/MS. Profile represents summer blend gasoline from one bulk terminal distribution region.

Profile Number: 1203 (SPECIATE version 1.4)
Data Quality: B
Profile Name: Light-Duty Gasoline Vehicles - Exhaust
Control Device: Catalyst
Reference(s):   Sigsby et al. (1987, Black and High (1980)
Data Source: Composition data collected using GC/FID and DNPH methods
                      for exhaust and evaporative (hot soak) emissions from 45 cars
                      were composited. Based on AP-42 (4th edition), data were
                      weighted according to travel fractions (see Appendix A for
                      details).

Profile Number: 1204 (SPECIATE version 1.4)
Data Quality: B
Profile Name: Light-Duty Gasoline Vehicles - Evaporative
Control Device:
Reference(s):   Sigsby et al. (1987), Black and High (1980)
Data Source: Composition data collected using GC/FID and DNPH methods
                      for exhaust and evaporative (hot soak) emissions from 45 cars
                      were composited. Based on AP-42 (4th edition), data were
                      weighted according to travel fractions (see Appendix A for
                      details).

Profile Number: 9021 (SPECIATE version 1.5)
Data Quality: E
Profile Name: Surface Coating Operations - Average
Control Device: Not Applicable
Reference(s):   Shareef (1987)
Data Source: Average profile developed from original profiles representing the
                      source category 402XXXXX.

Skeptical Review

The purpose of this review is to examine selected profiles from the SPECIATE database,
versions 1.4 (1991) and 1.5 (1992) that have been used in receptor modeling or
ambient/emission inventory comparisons, or have been criticized in those contexts.
These include profiles for motor vehicle exhaust and evaporative emissions, gasoline
vapor, and surface coating processes.

Motor vehicle exhaust

The profile for gasoline vehicle exhaust in SPECIATE version 1.4 (profile #1203) is
derived from the data of Sigsby et al. (1987). Sigsby tested 46 in-use vehicles of model
year 1975-1982; most were tested on winter-blend gasoline with an RVP of 12 psi.
Several pairs of VOC species were not resolved in the chemical analysis; propane and
propene, benzene and cyclohexane, butadiene and butane, etc. SPECIATE v. 1.4
divides the benzene/cyclohexane peak evenly between the two compounds. Subsequent

testing programs have shown that essentially all of this peak is benzene.
Several CMB studies have used the Sigsby exhaust profiles (Scheff et al., 1989; Kenski et al., 1993; Scheff and Wadden, 1993); however, the SPECIATE version was not used. In these studies, the benzene fraction was specified correctly but the split between propane and propene was specified incorrectly, resulting in unrealistically high propane fractions for motor vehicle exhaust.

In SPECIATE version 1.5, the Sigsby profile has been replaced by a profile (#1313) derived from data from the Auto/Oil Air Quality Improvement Research Program (AQIRP) and other recent studies, as processed by SAI (Fieber and Cohen, 1992). Separate profiles were developed by Fieber and Cohen for each catalyst technology type. However, only the profile for three-way catalyst vehicles was selected by EPA for inclusion into the SPECIATE database. The inclusion of only the three-way catalyst profile means that this profile may not be representative of in-use fleets from the late 1980s and early 1990s, in which emissions may still be dominated by oxidation catalyst and noncatalyst vehicles.

EPA modified this profile by replacing the mass fractions for four toxic compounds with values obtained from an independent EPA analysis. Although the toxics values were obtained from a larger database and may be more accurate than those in the original profile, the arbitrary substitution of a subset of values within a profile decreases the value of the profile for receptor modeling purposes. For example, changing the mass fraction of benzene while leaving toluene intact changes the benzene:toluene ratio, and the resulting profile may have a benzene:toluene ratio that is not typical of motor vehicle exhaust.

Motor vehicle evaporative

There is a single profile for gasoline vehicle evaporative (diurnal plus hot soak) emissions in SPECIATE version 1.4 (profile #1204). It is also derived from Sigsby et al. (1987) data, and suffers from the same problems as the exhaust data. Most relevant to the evaporative emissions is the fact that most vehicles were tested on winter-blend gasoline with an RVP of 12 psi; the resulting profile is not likely to be representative of summer gasoline.

SPECIATE version 1.5 contains separate profiles for hot soak, diurnal, and running loss emissions (profiles #1307, 1306, and 1308) and also contains a composite evaporative profile (#1305) obtained from a 70:30 weighting of the hot soak and diurnal profiles. The addition of individual profiles for each of these emission categories is an improvement. Also, the fuel used was industry-average summer-blend gasoline with an RVP of 8.4 psi, an improvement over the Sigsby study. However, the profiles themselves are very questionable. These profiles are derived from EPA/ATL data for a single vehicle, from which the gas cap had been removed, resulting in unrealistically high diurnal and running loss emissions (Lindhjem and Somers, 1992). EPA contends that, despite the high mass emissions, the speciation profiles derived from this vehicle are representative of the in-use fleet. This claim is somewhat supported by the general similarity between these profiles and the older Sigsby evaporative profiles. However,

the credibility of these profiles is not up to EPA standards; EPA should test additional vehicles with realistic evaporative emission levels and replace these profiles.

An additional problem with these profiles is that two species with very different reactivities were not resolved in the chemical analysis. These species are 4-methyl-c-2-pentene and 2-methylpentane. The sum of these two components is large (5-7 percent of the total). In the process of incorporating these profiles into SPECIATE version 1.5, the entire combined fraction for these two compounds was assigned to the more reactive component, 4-methyl-c-2-pentene. In fact, based on emission data from studies in which these two compounds were resolved, about 90 percent of the total should be assigned to the less reactive compound, 2-methylpentane. As a result of this incorrect assignment, the reactivity of the evaporative profiles is too high. This error can be seen in the inventory/ambient NMOC comparison described by Korc et al. (1993). In that study, "internal C_6 olefins" (a category which includes 4-methyl-c-2-pentene) were found to be grossly overestimated in an inventory generated using the EPA evaporative profiles.

Gasoline Marketing

SPECIATE profile #1190 was derived from headspace measurements from a composite of summer-blend gasolines. Yet the profile contains no butane, very little C_4 and C_5 compounds, and very high aromatic fractions (15 percent toluene and 21 percent xylene). This is completely unrepresentative of a gasoline headspace sample, as can be seen by comparing this profile with other gasoline headspace profiles (#1014 and 1015, for example).

This profile was developed by Radian for the 1988 version of SPECIATE. According to their description of the analytical method (Appendix G of Shareef, 1988), it seems clear that the volatile components of the sample were lost in their analysis. Thus, this profile is worthless as a gasoline headspace profile; profiles 1014 and 1015 should be used instead. Interestingly, however, the profile is somewhat reminiscent of a profile for whole gasoline. Its inclusion in emission inventories may inadvertently supply the whole gasoline component that some studies have suggested is missing (e.g., Harley et al., 1992). (Note that this profile is used widely in emission inventories prepared under EPA guidance but is not used in inventories prepared under CARB guidance). However, it would be much preferable if this profile were discarded, a new profile representing whole gasoline were included in SPECIATE, and composite profiles were developed for the various gasoline marketing processes that included weighted averages of the headspace and whole gasoline components.

Surface Coating Processes

Another category of SPECIATE profiles that has been used in receptor modeling (Scheff et al., 1989) and ambient/inventory comparison studies (Korc and Chinkin, 1993) is surface coating. This category includes application of paints, lacquers, and varnishes, and also includes clean-up and thinning solvents associated with such processes. SPECIATE includes numerous profiles for surface coating processes. The most widely used may be profile 1003, described as "surface coating - solvent based paint." This

profile is a composite of profiles for lacquer, primer, and enamel originally developed for the CARB by SAI and Radian (Oliver and Peoples, 1985). Scheff et al. (1989) created a composite surface coating profile by combining this profile with profiles for water-based paint and thinning solvents. Harley et al. (1992) presented an alternative to this profile. Korc and Chinkin (1993) argued that this profile should be replaced with the Harley profile because it contained too much toluene.

According to the Oliver and Peoples (1985) report weighting fractions of 64 percent enamel, 13 percent lacquer, and 23 percent primer were used to develop the composite. However, application of these fractions to the individual profiles does not give the values in the composite profile (e.g., for toluene, the weighted average is 26 percent, the profile value is 38 percent). This is relevant because the enamel profile shows much lower toluene and higher xylenes than do the other two profiles. Thus, the distribution between toluene and xylenes in profile 1003 should be considered very uncertain. Ideally, users of these profiles should determine the usage of lacquer, enamel, and primer in their particular geographic location, and create their own composite surface coating profiles.

There is another composite surface coating profile in SPECIATE called "surface coating - average" (profile 9021). This profile is an average of all profiles for all processes related to surface coating. The profiles are averaged using equal weightings for each, rather than weighted by the relative emissions from each process. Some of the profiles contain only a single component (e.g., "Thinning solvents - acetone"). Although this profile is only intended to be used for "miscellaneous" source categories where the inventory gives no hint as to what type of surface coating process is involved, in fact it is probably not representative of any actual surface coating process. This profile should not be used for receptor modeling applications. Korc and Chinkin (1993) recommended replacing this profile with the profile developed by Harley et al.

16. Source Fingerprints for Volatile Non-Methane Hydrocarbons, P.V. Doskey, J.A. Porter, and P.A. Scheff, *J. Air Waste Manage. Assoc.*, 42:1437-1445 (1992).

This paper presents the results of a source and ambient sampling program designed to develop source fingerprints for evaporative emissions as a function of gasoline grade, vehicle hot soak, cold start, and roadway emissions, and refinery emissions. Evaporative profiles for three gasoline grades were obtained from headspace analysis. Cold start and hot soak profiles were obtained from ambient sampling in a parking garage. Refinery emissions were obtained from ambient sampling downwind of a refinery; the presence of the refinery plume was detected by odor. The study points out the variability of butane and toluene content among gasoline grades and between summer and winter blends. Significant temporal variability in the refinery profile was noted.

Strengths of this paper are the identification of season and gasoline grade as key variables that affect the composition of evaporative emissions, which had been neglected in many of the CMB studies. Weaknesses include the assumption that refueling emissions are equivalent to headspace vapors (i.e., no spillage contribution), and recovery problems with the analytical method.

Objective Review

One of the unique features of this paper is the presentation of gasoline headspace vapor profiles for all three grades of unleaded gasoline. Much recent motor vehicle speciation data has focused on "industry average" gasoline, which is a weighted blend of gasoline grades. However, it is useful to see the data for the individual grades in order to understand the potential variability in the species profiles. The results showed higher butane and toluene in the premium gasoline, consistent with expectations since these are high octane components. No olefins were included in the species profiles; olefin levels would be expected to be higher in the regular grade profile. One limitation of these profiles is that only a single sample from each gasoline grade was analyzed. Significant variation might be expected among brands of gasoline even within a given gasoline grade, and a composite sample would be more representative than a single sample.

The authors created a composite summer refueling profile by weighting the headspace profiles according to national sales fractions for the three grades. Thus, the refueling profile is purely a vapor displacement profile, without any contribution from spillage. Yet refueling emissions are generally considered to be a mixture of both vapor displacement and spillage. Where vapor recovery systems (Stage II refueling controls) are in place, refueling emissions may consist almost entirely of spillage. The contribution of spillage was not addressed by the authors.

Although the authors discuss the importance of fuel volatility on the evaporative profile composition, particularly the butane:isopentane ratio, and show differences between summer-grade and winter-grade gasoline profiles, the RVP of the gasoline samples used to construct the profiles is not presented. This is a potentially serious omission since summer fuel RVP has varied widely over the past decade and from region to region.

The authors also developed hot soak and cold start profiles by conducting measurements in a parking garage. The hot soak measurements were taken following the morning rush hour; the cold start measurements were taken during the onset of the evening rush hour. In both cases, the samples were corrected for background by subtracting concentrations from outside the parking garage. The authors argue that this method provides an integrated measurement of actual in-use vehicle emissions and may thus be superior to data obtained from dynamometer and SHED testing of limited numbers of vehicles. This argument has some merit, but there may be other problems with this approach. For instance, it is virtually impossible to obtain a pure hot soak sample without any contribution of exhaust.

The cold start profile developed in this manner is most notable for its high acetylene content. Acetylene accounts for 10 percent of NMHC, twice as much as ethylene. Dynamometer tests for Bag 1, containing the cold start and the first 3 miles of the FTP cycle, generally do not show acetylene at higher concentrations than ethylene. Thus, this cold start profile provides some new information, and suggests that the sensitivity of ambient acetylene fractions to operating mode distributions may be even greater than previously understood.

Two additional profiles developed in this study are roadway and refinery. The roadway profile was derived from measurements taken along a street that was described as "essentially a tunnel because it is enclosed on three sides." The authors do not describe whether vehicles traveling along this roadway were accelerating, decelerating, or cruising, or whether traffic was congested or free-flowing, or what fraction of the vehicles were diesels. All of these factors can affect the composition of a roadway profile. The authors also note that recoveries of xylenes and C_3-benzenes in the chemical analysis were only about 50 percent. Thus, the roadway profile is of questionable applicability.

The refinery profile discussion is interesting because it emphasizes the temporal variability of refinery emissions. The profile derived from the Illinois refinery is significantly different than the profile used in many CMB applications (e.g., Kenski et al., 1993; Scheff and Wadden, 1993). It contains much less propane, higher benzene and xylenes, and lower toluene.

In summary, this paper presents some useful new data regarding VOC profiles from various emission sources. The paper explores potential sources of variability in source profiles to a greater degree than some previous studies, although still neglects basic concepts such as fuel RVP. Some of the profiles derived in this study are likely to be an improvement over existing profiles, particularly for the Chicago area.

Skeptical Review

<u>GC Methodology</u>

The authors show that the method used to dry ambient samples before GC analysis results in significant losses of aromatics and olefins. They say that a correction for recovery should be applied before the ambient profiles are used.

All of the results in the paper are presented as weight percentages, but is unclear how weight percent was determined. This issue seems particularly important since some of the ambient profiles would apparently total more that 100 percent if a recovery correction were applied for aromatics (e.g. Cold Start). It is also surprising that the headspace profile for premium gasoline totals 100 percent with the limited number of compounds quantified (e.g., no olefins greater than C_3). It appears likely that the species quantified that were not subject to recovery losses may have been overestimated.

Gasohol (10 percent ethanol splash blended with gasoline) has a significant market penetration in the Chicago area. It is not stated whether the gasoline samples obtained for headspace were known to contain ethanol or not. Ethanol is not reported as one of the compounds detected by the GC methodology, and since it is unclear how the GC concentrations were converted to weight percent, it is impossible to tell whether a shortfall in the profiles due to nondetection of ethanol would show up.

Refueling Emissions (Fuel Headspace)

Fuel was obtained at a single gas station and therefore presumably represents a single producer. Doskey et al. found the headspace composition (in particular, the ratio of n-butane to 2-methylbutane) varied substantially between grades, but they do not account for the likelihood that composition also varies significantly between producers because of differences in refinery configurations and feedstocks. The headspace profiles total 93 to 100 weight percent, but contain no light olefins and low (2 to 5%) aromatics. Fuels for 1991 would likely have contained at least 5 percent light (C_4 to C_6) olefins that are volatile and would be expected to show up in headspace vapors, and the authors note that toluene was much lower than observed previously by Lonneman et al. (1986). It appears very likely that both olefins and aromatics are underestimated in the headspace profiles for some reason. For these reasons, conclusions about the ratios of n-butane to 2-methylbutane, saturates to unsaturates, and saturates to aromatics based on these data seem suspect.

The authors equate headspace vapor to refueling emissions which neglects the contribution of fuel spillage (whole gasoline) to refueling emissions. The temperature at which headspace was measured is not stated. Potential effects of fuel weathering (i.e., selective loss of the most volatile components of the fuel such as butane) on headspace composition are not considered for either the fuel samples or real world emissions.

Ambient Profiles

A general weakness for the ambient profiles is that only weight percents are reported, which obscures the ambient concentrations sampled. This deficiency denies the reader the opportunity of gauging how likely it is that the ambient profiles are representative of the emissions category in question, e.g., how high the measured concentrations are above background.

Cold Start, Hot Soak and Roadway

The methodologies used to obtain representative profiles in a parking structure and an "urban canyon" appear reasonable: the best way to gauge how successful were the approaches used would be from the profiles obtained. Unfortunately, I believe the deficiencies with the analytical methods described above make any such comparisons suspect. In particular, I do not believe that the ratios of saturates to unsaturates, and saturates to aromatics are meaningful. Interestingly, the ratios of n-Butane to 2-Methylbutane determined for Cold Start (1.46) and Hot Soak (1.88) in the parking structure over the same time period are different, but the authors do not discuss this.

Refinery

Samples downwind of the refinery were taken on six occasions in March and May of 1990 and the authors note that composition was highly variable. They further show that this is consistent with previous studies. That being the case, it is not clear that six samples collected with no knowledge of refinery operations will be adequate to characterize an average profile. The profiles are subject to the limitations of the analytical methodology discussed above, but in addition the authors noted a complex mixture of unidentified compounds eluting in region of C_3 and C_4 substituted benzenes suggesting that aromatics may have been underestimated even more for the refinery profile than in other ambient profiles. A background correction was made to the refinery profiles, but little information is provided on how this was done or what effect it had.

Overall Conclusions

The stated objective of the study is to determine fingerprints for vehicle and refinery emissions in the Chicago area. However, the fingerprints based on ambient data are suspect because of documented problems with underestimation of olefins and aromatics, and possible overestimation of the remaining compounds. The authors say that the ambient profiles should not be used without a correction for recovery. The fuel headspace profiles are unlikely to be representative because all the fuels were from a single source. Furthermore, equating headspace with refueling neglects fuel spillage.

The temporal variability of the refinery plume composition has important implications for receptor modeling studies since it suggests that day specific ambient data cannot be analyzed for refinery contribution using an averaged refinery source profile.

17. **The Observation of a C$_5$ Alcohol Emission in a North American Pine Forest**, P.D. Goldan, W.C. Kuster, F.C. Fehsenfeld, and S.A. Montzka, NOAA, *Geophys. Res. Lett.*, 20:1039-1042 (1993).

This paper reports evidence for biogenic emissions of a reactive alcohol (2-methyl-3-buten-2-ol). Concentrations of the alcohol at Niwot Ridge, CO, were five to eight times those of isoprene, and showed a similar diurnal profile. Because the alcohol is expected to be somewhat less reactive than isoprene, the authors conclude that biogenic emissions of this species are roughly equal to those of isoprene. If so, this represents a major un-inventoried biogenic hydrocarbon component. The authors note significant measurement uncertainty due to the polar nature of the alcohol.

Strengths of this paper include the potential identification of an important new reactive species emitted by vegetation. This finding should not be extrapolated to biogenic inventories in general without independent confirmation by other groups for different locations. Weaknesses include the measurement uncertainties.

Objective Review

Biogenic emissions are one of the most uncertain VOC emission categories. The finding of a new biogenic species with emissions roughly equal to isoprene would likely have a major impact on modeling results for ozone. However, there are certainly some questions to be addressed before these results can be accepted. First, has it been demonstrated that the substance measured is 2-methylbutenol? The authors state that the identification was made on the basis of the GC/MS spectrum, but do not say whether the reference 2-methylbutenol mass spectrum came from analysis of the pure compound, or from a library of mass spectra. Most likely, the latter is true. Identifications based on computer matches of library spectra can be uncertain, especially in identifying specific isomers. However, even if the exact structure of the compound is not correct as reported, the conclusions regarding its potential importance would still hold.

The second question is why this compound has not been identified previously. The authors state that it has, but was attributed to insect activity rather than the vegetation itself. They further state that in their own previous measurements the methylbutenol was lost in the cold trap used to remove water from the sample. This is plausible for a polar compound such as methylbutenol. Still, it seems peculiar that a compound with emissions equal to those of isoprene would remain undetected for so long.

The next question is whether it is possible for the observed methylbutenol to be an artifact or isoprene reaction product, formed either in the atmosphere or during sampling. The structure of methylbutenol is similar to that of isoprene, with the addition of a molecule of water across one of the double bonds. Atmospheric reactions of alkenes generally produce aldehydes and ketones rather than alcohols. The products of isoprene photooxidation have been fairly well characterized, and do not include methylbutenol. It is less clear what type of products could be formed from isoprene during sample collection and analysis, but it seems unlikely that any sampling artifact

would result in concentrations five times as high as isoprene itself. Any sampling artifact not related to isoprene would not produce such high correlations with isoprene.

The final question is whether the results, if proven correct for this specific location, are generally applicable. This paper describes the mix of vegetation at the sampling location, but does not provide information on whether the methylbutenol was emitted generally or from one particular species. Measurements in other locations are needed to confirm these results. In addition, the recovery of methylbutenol in their analysis procedure was reported to be only 50 percent. Essentially, this means that they multiplied their measured values for methylbutenol by two. Better techniques should be developed that provide higher recoveries.

It seems clear that these results, while interesting, need further confirmation before they can be generally accepted.

Skeptical Review

The authors claim to have identified methylbutenol as a new biogenically emitted compound and quantified its abundance relative to isoprene at a site in the Rocky Mountains near Boulder, CO. Before this finding is fully accepted the following issues must be considered:

1. Is the compound correctly identified? No information is given on how the GC-MS identification was made. Ideally, an authentic sample should be synthesized to confirm the GC/FID retention time and response factor, and the GC/MS spectrum. The authors do not say how the GC/FID response factor was calibrated bearing in mind that the molecule contains oxygen which inhibits the FID response.

2. Is the observed compound of biogenic origin? The similarity between the observed diurnal patterns of methylbutenol and isoprene supports a common source for these compounds (biogenic), but it would be reassuring to confirm this finding for more than one site.

3. Why has the compound not been seen before? The authors explain that they did not previously observe methylbutenol because it was retained by the dry ice trap used to remove water from the ambient samples. However, other research groups have used different drying methods (Nafion tubing, chemical drying, cold traps at different temperatures) but not reported this compound. The observation of methylbutenol should be confirmed by other groups and at different sites.

4. Could the observation be an artifact of the sampling protocol? Methylbutenol is isoprene with water added across one of the double bonds and might have been formed from isoprene during the sample pre-concentration. However, the results shown in Figure 2 suggest that the methylbutenol/isoprene ratio is very stable with time, whereas for a sampling artifact the ratio might be expected to be variable because of slight differences in the handling of successive samples.

If the observation of methylbutenol at Niwot Ridge is accepted, before the finding is interpreted as representing a major increase in national biogenic emissions, the following issues must be considered:

5. Is methylbutenol a ubiquitous biogenic species (as is isoprene), or is it peculiar to one of the tree species surrounding Niwot Ridge (mainly lodgepole pine and aspen).

6. Are the emissions of significant magnitude? This paper estimates emissions from ambient concentrations relative to isoprene. By considering two limits (sources in equilibrium with losses and sources much greater than losses), the authors reasonably estimate that methylbutenol emissions are 1 to 8 times larger than isoprene at Niwot Ridge. However, this ratio may not apply to other species such as oak that are high isoprene emitters and make major contributions to biogenic inventories in the Eastern U.S. At Niwot Ridge, aspen is an isoprene emitter, but lodgepole pine is not.

If methylbutenol does represent a significant source of biogenic emissions nationally on a mass basis, it will be necessary to quantify its reactivity toward ozone formation which is presently unknown.

The results presented in this paper could potentially have an important impact on national biogenic emission inventories; however, the results must be confirmed by other research groups and for different sites. Since methylbutenol emissions are only estimated relative to isoprene, the potential impact of methylbutenol on emission inventories should be viewed in the context of the reliability of current estimates of biogenic emissions, which are highly uncertain.

18. **Improvement of the Speciation Profiles Used in the Development of the 1991 LMOS Emission Inventory**, M.E. Korc and L.R. Chinkin, Sonoma Technology, Draft Final Report prepared for LADCO, STI-92324-1394-DFR (1993).

This report reviews several speciation profiles used in the development of the LMOS modeling inventory and alternative profiles from the CARB and Harley et al. (1992). Both mobile and stationary source profiles are reviewed. The main focus of the review is on those species for which poor agreement was found between the ambient and inventory mass fractions, particularly butane, C_6 olefins, and toluene. The authors recommend substituting profiles from the Harley et al. study for the EPA profiles for several gasoline-related evaporative and surface coating emission categories. They also provide medium and long-term recommendations for further improvement of speciation profiles.

The strengths of this study are the review and comparison of available profiles, and the use of the ambient database to provide feedback. Weaknesses include the lack of discussion of reasons for variations in source profiles and minimal justification for replacement of profiles.

Objective Review

As discussed in the review of Korc et al. (1993), there were two phases of work done in between which the emissions inventory was adjusted. This Korc and Chinkin report came as part of the work that went into the inventory adjustment. Apart from any mass discrepancies implied by the initial Korc et al. study, there appeared to be problems with speciation profiles in the inventory especially involving apparent overpredictions of butane, C_6-olefins, and toluene. Xylenes also appeared to be high in some comparisons.

Korc and Chinkin do not offer extensive explanations of why particular alternate profiles should be used in place of the original EPA profiles. However, the profiles of Harley et al. (1992) were always recommended (with only one exception). Since the original Korc et al. report identified apparent high emissions inventory levels for butane, toluene and C_6-olefins, the Harley et al. profiles seemed to be chosen because these particular species were not so highly weighted. However, the type of analysis done originally by Harley et al. and by Korc et al. is least accurate for comparisons between emissions and ambient for highly reactive species. Although butane and toluene are relatively low in reactivity, olefins and xylenes are high in reactivity. According to the Harley et al. report the xylene fraction in their profiles can be expected to increase. Hence, the expected result of comparing the new inventory with ambient data is worse agreement for xylenes if the Harley et al. profiles are used. Nevertheless, this xylene enhancement actually may be more "correct," but the lower olefins may not since both xylenes and olefins could be reacted out of the ambient data more than other compounds. Continuing on, this in turn might imply that more carryover of aged pollutants might have been in the ambient data than previously implied in the Korc et al. report.

Butane in speciation profiles can vary greatly with the Reid vapor pressure (RVP) of gasoline used in the local area. There may also be a temperature component in that more butane would be lost proportionately as the temperature increases. Another issue concerning butane may come from the widespread use of ethanol blends in the Chicago area (approximately 40 percent in 1991). Ethanol increases the RVP and can lead to higher butane emissions. Hence, it is confusing why the butane emissions were overpredicted in the original inventory and why a Harley et al. profile was recommended to replace the EPA headspace profile.

Another curious recommendation in this Korc and Chinkin report concerns surface coating and thinning solvents. Korc and Chinkin recommend using Harley et al. profiles to replace EPA profiles 1003 and 1016 because the Harley et al. profiles will help reduce the emissions of toluene which, according to the Korc et al. study were too high in the inventory. However, for EPA profile 9021 Korc and Chinkin also recommend using a Harley et al. profile (PN #5) even though Figure 4-10 clearly shows that toluene is increased by this substitution. For this recommendation Korc and Chinkin claim that the original EPA profile "is based on engineering judgment" while the Harley et al profile "is based on manufacturer-supplied data in California." More and clearer reasons are needed here.

Skeptical Review

This study and its companion study (Korc et al., 1993) are one of the few studies to attempt to use speciated ambient data in a "top-down" inventory evaluation. Unfortunately, the authors have taken a somewhat superficial approach to reviewing the EPA profiles used in the construction of the LMOS inventory. Rather than investigating possible reasons for differences between profiles, they rely on the results of the ambient/inventory speciation comparison (Korc et al., 1993) to guide their recommendations on replacement of default profiles. However, discrepancies between ambient and inventory profiles can arise from other problems, such as incorrect spatial or temporal allocation of emissions and measurement errors, and should not be used as the sole reasoning behind replacement of speciation profiles.

STI limited its review to profiles for which alternatives were available in the literature. These included motor vehicle (MV) exhaust and evaporative emissions, gasoline vapor, and surface coating. The LMOS inventory had correctly taken into account the fact that ethanol blends make up a sizeable market share of gasoline sold in the Chicago area, and developed a composite exhaust profile based on the EPA profiles for gasoline and ethanol blends. STI did not recommend any changes to the EPA default MV exhaust profiles. Its focus was on MV evaporative emissions and surface coating processes.

There is a factual error on page 2-5 of the STI report. EPA profile number 1305, the composite MV evaporative profile, is not derived from data obtained from the Auto/Oil Air Quality Improvement Research Program (AQIRP). Instead, it is derived from testing performed for EPA by ATL. This testing was performed on a single vehicle, from which the gas cap had been removed in order to simulate emissions from a high-emitting vehicle. EPA used this profile in preference to the profile developed from the AQIRP data because they felt that, since the vehicles in the AQIRP program all had very

low evaporative emissions, they were not representative of the in-use fleet, which includes and may be dominated by emissions from high-emitting vehicles. There are legitimate issues regarding the applicability of this profile that STI could have addressed, but it did not.

The main reason used by STI in recommending the replacement of the EPA default MV evaporative profile is the disagreement between the ambient and inventory C_6 olefins. As discussed in the reviews of the SPECIATE database and the Korc et al., 1993 study, the origin of this error in the EPA profiles is understood. It arose from the fact that 2-methylpentane and 4-methyl-2-pentene could not be resolved in the ATL analysis. In SPECIATE version 1.5, the sum of the two species was incorrectly reported as 4-methyl-2-pentene, when in fact the vast majority of it is 2-methylpentane. The error could easily be corrected, has been corrected for all emission inventory work performed at SAI, and would not require replacing the entire profile.

STI recommends replacing this profile with a profile from Harley et al. (1992). The Harley et al. profile is not actually a MV evaporative emissions profile, but is derived from gasoline headspace profiles from 1979 for various gasoline grades, adjusted for transition to unleaded fuels and RVP levels in southern California in 1987. STI does not discuss the importance of RVP in determining the composition of evaporative profiles, and does not compare RVP levels used in the derivation of the profile with those existing in the LMOS region in 1991. Once the EPA profile values for 2-methylpentane and 4-methyl-2-pentene are corrected, the EPA and Harley et al. profiles become virtually identical, and the decision of whether to replace one with the other becomes moot.

The other profiles recommended by STI for replacement are surface coating profiles 1003 and 9021. As discussed in the SPECIATE database review, profile 9021 is essentially a "miscellaneous" surface coating profile that should not be used widely in the generation of inventories. If it is used extensively in the LMOS inventory, an effort needs to be made to update the cross-reference files to direct emissions from specific activities to more appropriate profiles. STI somewhat misleadingly states that this profile was derived from "engineering judgment," implying that no actual data were used. In fact, the profile is a composite of actual profiles. Engineering judgment was used to determine which profiles to average together to obtain profile 9021.

Profile 1003 is the composite profile for solvent-based paint. As discussed in the SPECIATE review, the toluene value in this profile appears to be too high, based on the constituent profiles and the stated weighting factor for the composite. Thus, there is a reasonable basis for questioning this profile. It would have been nice if the authors had investigated further into the types of surface coating activities that take place in the Lake Michigan region. Instead, they simply recommend substituting the surface coating profile from Harley et al. Since there are significant differences in California and Federal regulations concerning solvent-based paints and surface coating processes in general, it is not at all clear that the Los Angeles profile is appropriate for the LMOS region. The STI report concludes that the Harley et al. profile is better purely because it contains less toluene. As discussed in the review of the Korc et al. report, other factors may have lead to the high toluene emissions in the LMOS inventory.

There is no question that the profiles in the SPECIATE database are default profiles, to be used when no locally derived data are available. If STI had used information specific to the LMOS region as a basis for modifying or replacing profiles, this would have been a more valuable study.

In summary, the STI report identifies some potential problems with default profiles for gasoline vapor and surface coating processes, and is valuable in that regard. The use of the ambient/inventory comparison for speciated NMOC to guide review of the profiles is a new and potential useful technique. Although the replacement of the EPA profiles with the Harley et al. profiles as recommended by STI is not likely to cause any major problems in the LMOS inventory, insufficient discussion and justification were used by STI in its analysis.

19. Vehicle-Related Hydrocarbon Source Compositions from Ambient Data: The GRACE/SAFER Method, R.C. Henry, USC, C.W. Lewis, EPA, and J.F. Collins, USC, *Environ. Sci. Technol.*, 28:823-832 (1994).

This paper describes a new methodology for deriving vehicle-related source profiles directly from ambient data. The Source Apportionment by Factors with Explicit Restrictions (SAFER) technique is relatively well-known multivariate method for obtaining "factors" that correspond to particular source categories. The SAFER technique allows for the use of physical constraints to help ensure that a physically valid solution is obtained. The Graphical Ratio Analysis for Composition Estimates (GRACE) method is a new technique that is described for the first time in this paper. The GRACE technique is used to identify appropriate physical constraints for input into SAFER.

The ambient database is from the Atlanta 1990 summer study. Three sources are considered: "roadway", whole gasoline, and gasoline vapor. The GRACE analysis is first conducted for the roadway source, assumed to be the dominant source. Acetylene is assumed to be a tracer for the roadway profile. Scatter plots of each species to acetylene frequently showed a distinct minimum slope. The authors propose that this minimum slope corresponds to the source ratio for the roadway source, and use it to develop maximum and minimum ratios to acetylene for input to SAFER. The roadway contribution is then subtracted from the ambient data, and the process is repeated for whole gasoline, using 2,3-dimethylpentane as a tracer. Finally, the process is repeated for gasoline vapor, using butane as a tracer. The results of this analysis are the same as those presented by Lewis et al. (1993): 50 percent roadway, 10 percent whole gasoline, 4 percent vapor.

The strength of this paper is the description of the new technique, which potentially provides a means of using city-specific source profiles for source apportionment, for databases similar to those that will be generated in the PAMS program. The weaknesses are remaining questions regarding the fundamental assumptions, uncertainties, and applicability of the technique.

Objective Review

Source compositions for the three sources are determined using 550 ambient hourly concentration measurements of 37 VOC compounds.

Factor analysis methods are mathematically ill-posed, in that a unique solution cannot be obtained. By adding a few physical constraints, however, the SAFER technique overcomes this problem. Previous uses of the SAFER techniques for aerosols have considered physical constraints obtained from a priori knowledge of specific characteristics of various source types. In this new GRACE approach, a systematic method for determining the constraints has been developed.

Comparisons between source-derived compositions (typically from source tests) and GRACE/SAFER-derived compositions showed very good agreement for all three source

types. This research was able to reveal a number of interesting findings, such as a clear presence of unburned whole gasoline in the ambient air that is not associated with tailpipe emissions. For the 1990 Atlanta data (for which these profiles were derived), whole gasoline was shown to contribute to ambient VOC concentrations to a much greater extent than gasoline headspace vapor.

This technique is demonstrated to be a valuable new tool for determining certain source profiles (given a large enough ambient data set), possibly eliminating the need for expensive source testing. This is potentially very important, considering the uncertainties that exist with many source profiles (e.g., due to variability in fuel composition). At a minimum, the method provides a means for evaluating source profiles that are being considered for use in CMB analyses.

The only apparent weakness with the method is the need for a large ambient data set representing a reasonably stable group of emission sources. The small biases introduced by the explicit constraints can be minimized, as demonstrated in the paper. The model results were shown to be fairly insensitive to these small biases.

Skeptical Review

This very recent article appears to provide one more step in mutivariate analysis methodology for reconciling ambient measurements to emissions inventories. In particular this latest step offers the potential to "boot-strap" source profiles directly from ambient data once a suitable surrogate species is selected. The new step is a graphical ratio analysis (for composition estimates or GRACE) that is sequential in a fashion similar to computer techniques used for some time in FTIR analysis. A known spectrum (i.e., source profile) is subtracted from the observed spectrum to provide the starting point to develop the next profile. Eventually, all "knowns" can be subtracted to give a previously unknown spectrum.

In this paper the method is applied to data for the Atlanta area and surprisingly reaches a similar conclusion to that of an earlier study of Los Angeles air by different workers using older techniques. This conclusion is that whole gasoline is present in these urban atmospheres at levels unaccounted for by the latest emissions inventories. The earlier study is Harley et al. (1992), reviewed elsewhere in this report. A key critical comment to both these studies comes from the rather ubiquitous use in urban society of the spectrum of petroleum hydrocarbons between C_3 and C_8. Not only are these hydrocarbons used in whole gasoline, they are common in paint and other solvents and degreasing agents as well. Therefore, the potential exists to put "missing" emissions into this convenient designation of whole gasoline.

The GRACE technique, as shown in Figure 1 of the Henry et al. paper, appears most impressive for the compounds that do not correlate well with the surrogate. In the gasoline case (using acetylene as the sole surrogate) isoprene and a mixture of cyclopentene with 4-methyl-1-pentene show very poor correlation (i.e., high scatter) for the ratios to acetylene. For isoprene, at least, this is to be expected due to the biogenics source of isoprene. Conversely, the ethene and propene scatter plots show exceptionally high correlations to acetylene, which is consistent with these olefins being highly

associated with exhaust emissions. There may be further steps or enhancements to this GRACE method. For example, other single surrogates (such as ethene or propene for gasoline) might be used, or some specific combinations of surrogates (ethene, in fact, is noted for such by the authors).

A potential problem with the present use of the new GRACE technique may be the choice of acetylene as a surrogate for automobile exhaust. At noted in the Lonneman et al. (1989) study reviewed in this report, the use of catalysts has significantly reduced the emissions of acetylene. Olefins such as ethene and propene are also known to be very low when the catalyst system is functioning well. Hence, the surrogate used by Henry et al. here may really be for older cars and high emitters rather than the entire automobile fleet. Unfortunately, a suitable single compound as good as acetylene but representative of newer cars has not yet been established.

There are at least two confusing issues (or unanswered questions) from this review. First the tunnel data lead to a 2,3-dimethyl pentane (DMP) to acetylene ratio of 0.24 while the ambient data show a value of 0.15 (when constrained to be within 0.10 to 0.19). The authors use 2,3-DMP as the basis for the whole gasoline profile. So this seems to imply that the tunnel data have higher whole gasoline/(exhaust + running loss) ratio than ambient data. Although the authors dismiss the tunnel data as "not representative of the average emissions in the region," due partially to its restricted morning rush hour conditions, the extra whole gasoline implications of the high 2,3-DMP ratio seems contrary to the expectation of less raw gasoline in a tunnel, where the dominant sources are expected to be exhaust and running losses.

The second question concerns the approach of taking minimum slopes for species concentrations versus the acetylene roadway tracer to determine the roadway profile. In this way, only a minimum amount of each species is allocated to the roadway profile. This is clearly shown in Figure 2 for 2,3-DMP versus acetylene, where constraining the slope to the range 0.1 to 0.19 allocates the minimum plausible amount of 2,3-DMP to the roadway profile. Hence, the next profile determined (whole gasoline), derived from an analysis of the remaining data, may still have some residual roadway information in it. If more "whole gasoline" were included in the roadway profile, then the estimate for the whole gasoline component would be smaller.

The authors clearly state that "tailpipe emissions are *not* [emphasis in original] the source of the whole gasoline source profile developed in the present article" and that their "method clearly shows that there are additional source(s) of whole gasoline that are unconnected with vehicles in motion." However, given the uncertainties raised by the two issues discussed above it seems possible that many of the emissions identified as whole gasoline may really be associated with vehicles in motion and that the "whole gasoline" contribution may be overestimated.

RATIO STUDIES

20. **A Review of NMOC, NO$_x$, and NMOC/NO$_x$ Ratios Measured in 1984 and 1985**, K. Baugues, EPA, EPA-450/4-86-015 (1986).

This report summarizes 6-9 a.m. NMOC and NO$_x$ data obtained in 1984 and 1985 in 30 U.S. cities, and presents median NMOC:NO$_x$ ratios and carbon fractions for use in EKMA modeling. Although detailed speciated NMOC data were collected, they are not presented in this report. City-specific ambient ratios of NMOC:acetylene were used to calculate the mobile source fraction of the ambient concentrations. A NMOC:acetylene ratio of 27 was assumed for mobile sources, based upon data from the Lincoln Tunnel (Lonneman et al., 1986). Using this method, mobile source contributions of 18 to 88 percent were calculated for 1984; for 1985 the range was 7 to 96 percent. Excluding cities in the Houston area, the range of mobile source contribution was 31 to 96 percent. The calculated mobile source contributions were compared to 1980 inventory values for seven cities, and were higher. However, the inventory values were not specific to the 6-9 a.m. period.

The main strength of this work is the broad geographic coverage of the NMOC data. The main weakness is the reliance on acetylene as an absolute tracer for mobile sources.

Objective Review

The first part of this report discusses methodologies for measuring 6-9 a.m. NMOC and calculating representative NMOC/NO$_x$ ratios for urban areas. Important conclusions from this part of the report are (1) that 6-9 a.m. NMOC, NO$_x$ and NMOC/NO$_x$ ratios are variable from day to day at a given site, and therefore that a single site is probably inadequate to characterize an urban area, and (2) that measurements with continuous NMHC analyzers agree poorly with NMOC measured by PDFID, but PDFID agrees well with GC speciated NMOC measurements, therefore the continuous NMHC measurements are suspect. These conclusions are based on extensive data for 1984 and 1985 and the organic compound measurements are convincing. However, no consideration is given to the validity of NO$_x$ measurements even though they enter equally into the calculated NMOC/NO$_x$ ratios. The paper goes on to discuss changes in median NMOC, NO$_x$ and NMOC/NO$_x$ ratios between 1984 and 1985. These discussions are probably suspect because no account is taken of potentially significant differences in meteorology between 1984 and 1985. Observed data are handled well in this paper: representative values for the NMOC/NO$_x$ ratio are correctly given as the average (median) ratio, rather than the ratio of the averages (i.e., average NMOC/average NO$_x$), and a nonparametric test (U-test) is used to look for differences between sets of data for which the parent distribution is unknown.

The report goes on to discuss, briefly, relationships between observed NMOC/NO$_x$ ratio and maximum ozone for Dallas in 1984, and between observed NMOC and maximum

ozone for Kansas City in 1984 and 1985. No account is taken of meteorology in either analysis, leading Baugues to conclude for Dallas that the analysis is too simple to support conclusions. For Kansas City, Baugues finds some correlations between 6-9 a.m. NMOC and maximum hourly ozone, but, because meteorology is neglected, it is impossible to conclude whether this is cause and effect, or whether (for example) both NMOC and maximum ozone are responding to changes in meteorology and therefore appear to be correlated.

The sections of the report most relevant to this report are those discussing the estimated contributions of mobile sources and biogenics to ambient NMOCs. The analyses were based on the GC speciated NMOC data: 22 sites in 1984, 19 sites in 1985, with 11 sites common to both years.

Estimated Mobile Source Contribution

Acetylene was used as a tracer for the mobile source contribution by assuming acetylene contributes 3.7 percent of mobile source NMOC. Thus, the estimated mobile source contribution depends completely on the validity of the assumption that ambient acetylene comes solely from local mobile sources, and on the assumed acetylene/NMOC ratio. The first assumption is probably reliable for analyzing 6-9 a.m. urban NMOC data given that (1) the observed acetylene concentration is probably much higher than the regional background, and (2) mobile sources are probably the dominant local source of acetylene assuming reasonable site location.

The assumption that the mobile source NMOC/acetylene ratio is 27 (100/3.7) was based on 1982 measurements in New York's Lincoln Tunnel (Lonneman et al., *Environ. Sci. Technol.*, pp 790-796, 1986). Lonneman et al. (1986) say that this ratio was 26.0 $\pm$ 2.10 in 1982, down from 15.7 $\pm$ 1.87 in 1970. The 1970 to 1982 change is consistent with the known effectiveness of catalytic converters in removing acetylene. For example, Jackson (SAE Paper 780624, 1978) found that catalysts reduced acetylene from 7.9 percent to 2.2 percent of exhaust hydrocarbons, which corresponds to a change in ratio from 13 to 45. Thus, while the tunnel study data suggest that the acetylene/NMOC ratio was quite stable (26 $\pm$ 2) for the 1982 database, this ratio clearly depends strongly on the fraction of functioning catalyst-equipped vehicles in the fleet. The acetylene/NMOC ratio also differs between start (catalyst cold) and hot stabilized (catalyst hot) modes of vehicle operation. Since the tunnel study data include no cold starts, the acetylene/NMOC ratio is biased low relative to ambient data. It is difficult to estimate the impacts of these opposing effects on Baugues' estimates of mobile source contribution. A likely lower limit to the ambient acetylene/NMOC ratio is the 1970 Lincoln Tunnel value of 16 measured before the introduction of catalysts. Thus, Baugues may have overestimated the mobile source contribution by up to a factor of 1.7 (27/16). This would decrease the median 1984 and 1985 mobile source contributions across cities from 57 and 66 percent, to 34 and 39 percent, respectively. If the acetylene/NMOC ratio is much higher than 27, median mobile source contributions would become more than 100 percent for some cities (e.g., Washington, D.C.).

Baugues compared estimated mobile source contributions for 1984 and 1985 to 1982 SIP inventories. The 1982 inventories are so outdated (e.g., mobile sources from MOBILE 2) that these comparisons no longer have much credibility or relevance.

Estimated Contribution of Biogenics

The measured concentrations for isoprene plus alpha-pinene constituted between 0.1 and 1.5 percent of 6-9 a.m. NMOC, excluding data for Beaumont, TX which appeared invalid. This includes data for several southern cities in North Carolina, Alabama, and Tennessee expected to have high biogenic emissions. However, these are certainly underestimates because (1) compounds other than isoprene and alpha-pinene are emitted biogenically, and (2) biogenic emissions peak in the middle of the day when temperatures and solar radiation are higher.

Skeptical Review

It is a pity that this report did not present complete ambient speciation data, since such data were collected and analyzed in the study. Instead, for the motor vehicle source attribution, acetylene was used as a single motor vehicle tracer. It would have been very interesting to see whether the motor vehicle fraction calculated by this method was consistent with other species concentrations. The results are at least qualitatively consistent with expectations in the sense that the Gulf Coast sites showed the lowest motor vehicle fraction and cities with relatively little industry, such as Washington, D.C., showed the highest mobile source fraction.

Acetylene has traditionally been used as a motor vehicle tracer. It is more correctly thought of as a combustion tracer, since it is produced in most combustion processes. The assumption that the vast majority of acetylene comes from motor vehicles may have been reasonable prior to the introduction of catalytic convertors. Since that time, however, acetylene has become a less ideal choice as a motor vehicle tracer because the acetylene fraction of NMOC is highly sensitive to fleet composition and operating mode. Acetylene fractions are higher for noncatalyst vehicles than for catalyst vehicles (see Lonneman et al., 1986); for catalyst vehicles, acetylene fractions are much higher for the cold start than for hot stabilized operation (Doskey et al., 1992). Because of this, acetylene fractions of NMOC may vary considerably from one site to another because of variations in fleet composition and operating mode, and this variation would be incorrectly interpreted as variations in mobile source contribution.

The study assumed an NMOC:acetylene ratio of 27, based on 1982 tunnel data (Lonneman et al., 1986). By comparison, this ratio is on the order of 17 for a roadway study conducted in 1983, but in a different part of the country than the tunnel study (Zweidinger et al., ES&T, pp. 956-962, 1988). This ratio is higher in dynamometer testing: around 40 for the Sigsby exhaust data in SPECIATE version 1.4, and around 50 for the most recently developed vehicle exhaust speciation profiles (Fieber et al., 1993; final report prepared for EPA, SYSAPP-93/189). Thus, the acetylene fraction of motor vehicle exhaust can range over a factor of two to three. This large variability makes acetylene a poor tracer species.

Indeed, the report describes this method as an approximation. However, it implies a fairly high degree of confidence in the results. The reported mobile source contributions should have been referred to as upper-bound estimates, since they are based on the assumption that 100 percent of ambient acetylene is from mobile sources. In particular, the fact that a mobile source contribution of 96 percent was found for Washington seems to demonstrate that this method overestimates the mobile source contribution. It is simply implausible that the mobile source contribution could be this high, especially considering that this amount does not include any evaporative emissions except running losses. The report did not present the variability of the estimated mobile source contribution for each city; that would have been a useful piece of information.

The mobile source contribution is compared with the emission inventory value for highway vehicles for seven cities, and is found to be higher in all cases. However, the inventories used are 1980 SIP inventories developed in 1982, most probably using the emissions model MOBILE2. These emission estimates for motor vehicles are relatively primitive by current standards; the mobile source fractions in these inventories would be much higher if they were backcast with MOBILE5. In addition, as the report correctly points out, the inventory fractions are daily averages. The ambient data are 6-9 a.m. averages, which would be expected to have a larger motor vehicle component. A point that is not brought out in the report is that the mobile source fraction calculated from acetylene includes at least some portion of the nonroad mobile emissions as well; those emissions, if included at all in the 1980 inventories, would be in the area source category. Finally, the inventories are for the entire urban area, not just for the area in the vicinity of the monitor. Thus, the comparisons to the inventories presented in this report provide no information that could be used to determine whether current inventories underestimate motor vehicle emissions.

Another piece of information presented in this report is the biogenic contribution, measured as the sum of isoprene and α-pinene. Even though measurements were conducted in several southeast cities that would be expected to have significant biogenic emissions, the sum of isoprene and α-pinene was only about 1 percent of NMOC. However, the 6-9 a.m. contribution of biogenics is not really a pertinent piece of information, since isoprene emissions peak in the early afternoon and are low during the 6-9 a.m. period.

21. **Speciated Hydrocarbon and NO$_x$ Comparisons at SCAQS and Receptor Sites**, W.A. Lonneman and R.L. Seila, EPA, and W. Ellenson, AWMA Paper 89-152.5 (1989).

This paper examines the NMOC:NO$_x$ ratios at source and receptor sites in the Los Angeles area. At the receptor site, total nitrogen compounds (NO$_y$) are measured rather than NO$_x$, in recognition of the potential for chemical transformation of NO$_x$. Morning (6-9 a.m.) NMOC:NO$_x$ ratios are lower at the receptor site (Claremont) than at either of the source sites (Long Beach and downtown L.A.). Afternoon NMOC:NO$_y$ ratios are similar to the morning ratios. The authors note the large contribution of ethane and propane to the ambient concentrations, and attribute them to petroleum extraction and refining activities. The 1987 speciated VOC data are also compared with 1968 concentrations. Concentrations of most compounds decreased 50 percent or more from 1968 to 1987, with the greatest decreases for acetylene and the smallest decreases for propane.

The strengths of this paper are the NO$_y$ measurements and the use of NMOC:NO$_y$ ratios. The weaknesses are the general lack of conclusions and interpretation of the findings.

Objective Review

W.A. Lonneman has a long history of careful speciation analysis work at EPA. This particular paper contains some very important information on the ambient atmosphere of the nation's most polluted city. However, the paper is very brief and the authors do not interpret much of their data. One interpretation that is provided by Lonneman is a comparison with some 1968 data taken under similar circumstances. (It is curious that the earlier paper cited for the 1968 data does not actually provide such data. The earlier study focused on acetylene and carbon monoxide (CO) to help identify the vehicular contribution to the NMOC burden.) It is unfortunate that the new study provides no information on CO and the importance of acetylene is minimized according to the new text because of the use of catalysts. Hence, the new 1987 data presented in this paper apparently cannot be analyzed using the techniques developed earlier for the 1968 data. One very simple interpretation provided by this review is the use of reactivity weighting the speciated information provided by Lonneman et al. in their Table VI of the 25 most abundant HC compounds.

Figure 1 is created by simply grouping the 25 molecules from their Table VI into the classes similar to those used by several photochemical smog mechanisms such as the Carbon Bond Mechanism, namely paraffins, olefins, multi-alkyl benzenes (called xylenes in Figure 1), mono-alkyl benzenes (called toluenes in Figure 1), and other (everything else). The reactivity MIR weighting factors were generated by Carter in November 1991 for the CBM-IV mechanism. The simple "rule-of-thumb" result based on Figure 1 suggests that the sum of xylenes and olefins accounts for nearly two-thirds of the total ozone-forming potential of this atmosphere even though these two classes account for less than 20 percent of the mass of the HC represented. Conversely, paraffins account

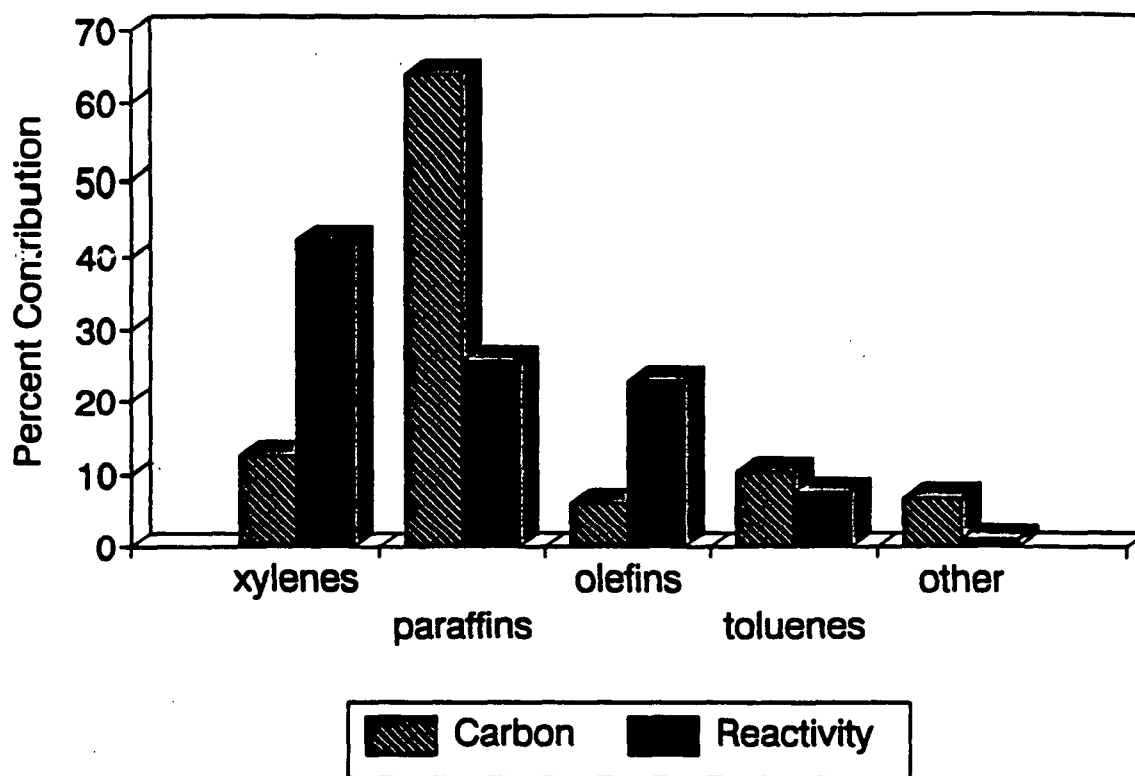# Los Angeles Air
Downtown, 06-09, August 28, 1987 (Lonneman)

FIGURE 1. Percent contributions of different classes of NMOC's to total carbon (i.e., ppmC) and reactivity (i.e., g potential O_3/g NMOC). Data of Lonneman et al., 1989.

for about two-thirds of the mass but little more than 20 percent of the ozone-forming potential of these ambient HCs. This "rule-of-thumb" result can be compared to emissions inventories. Due to the potential of carryover from aged HC, this ambient reactivity estimate should be considered a lower limit. That is, inventories of fresh emissions should be more reactive than what was shown here. The earlier Lonneman study of 1968 data does have an interesting interpretation of vehicular contribution for olefins and aromatics in that they indicate that morning samples at the downtown LA site have a 92 percent vehicle contribution for olefins but only a 59 percent contribution for aromatics. This indicates that further analysis of the new data should look for such a discrepancy between the olefin and xylene contribution, because the importance of xylenes noted in our Figure 1 may have a large stationary source component.

Some important information not provided in the paper itself but readily available concerns the nature of the smog episodes on the days reported. A curious statement in the paper is that the measurements were stopped on 4 September because they were only interested in the highest ozone episodes. Yet four days later on 8 September 1987, the highest ozone in the region was observed at the Glendora site, and on 2 October the second highest ozone was seen at the same site. That is, the two worst ozone episodes unfortunately occurred between the "summer" and "fall" intensive measurement periods of the SCAQS program. This is further a mystery because the 1968 data were all collected during the fall.

Another "missing" piece of useful information in this paper is the lack of information on the weekday of the data shown. This is curious, since the earlier Lonneman study of 1968 data cited in this new study provides some interesting comparisons between weekday and weekend precursor concentrations and diurnal profiles. We looked up the day-of-the-week information for this new study and with the exception of Table IV the data are for working days. Table IV shows data from a Saturday, 29 August 1987. The Friday/Saturday data shown between Tables III and IV are interesting in that the morning precursor concentrations are significantly reduced by Saturday at the Long Beach and Downtown LA sites but not at the Claremont site, although the NO_y distribution is shifted at Claremont consistent with carryover of PAN and aerosol nitrate from the episode the day before. It would be interesting to obtain and analyze the speciated NMOC for this Saturday morning in Claremont as well to see if there is evidence of carryover in the NMOC.

Skeptical Review

This paper presents ambient NMOC, NO_x and NO_y data, but really draws few conclusions from these data. My comments are divided between the data obtained and the limited conclusions that are presented.

Data Issues

What Lonneman et al. call TNMHC is really NMOC since it includes both NMHC (by GC/FID) and carbonyls (by HPLC). Also, what they call NO_x in Tables I-V and in TNMHC/NO_x ratios is actually the sum of all nitrogen compounds, now commonly

called NO_y. The conventional definition of NO_x is NO plus NO_2, although it is often recognized that a "NO_x" analyzer can measure additional nitrogen compounds in total or part. Thus, the $TNMHC/NO_x$ ratios given in this paper are highly unconventional and should not be compared directly with any other reported values. Conventional values for $NMOC/NO_x$ can be calculated from the data given in Tables I-V as $TNMHC/(NO+NO_2+PAN)$. PAN probably should be included for consistency with generally reported $NMOC/NO_x$ ratios. The PAN measurements reported are difficult to perform, primarily because of calibration difficulties. The calibration method used here (relative to an infrared absorption spectrometer) is probably the best available at the time, but the calibration was done in the lab before field trip, which introduces the potential for drift in calibration. The denuder measurements of nitric acid and organic nitrates are probably even more difficult than the PAN measurements.

Study Conclusions

An objective of the study was to compare morning $NMOC/NO_x$ ratios in source regions, Downtown Los Angeles (DOLA) and Long Beach (LB), with afternoon $NMOC/NO_y$ ratios in downwind receptor areas with high ozone (Claremont) on individual days. The hypothesis to be tested is that the afternoon $NMOC/NO_y$ ratios should relate to the morning $NMOC/NO_x$ ratio because NMOC is not significantly depleted during transport and the NO_x is transformed to NO_y. In other words, the afternoon $NMOC/NO_y$ ratio at Claremont is expected to be similar to the morning $NMOC/NO_x$ ratio at DOLA and LB. The authors find that the $NMOC/NO_y$ ratio at Claremont (generally 4-7) is lower than the morning $NMOC/NO_x$ at DOLA and LB (generally 7-11) and they conclude that the air picked up more NO_x than NMOC during transport. In other words, they imply that the $NMOC/NO_x$ ratio of emissions received during transport was lower than the morning $NMOC/NO_x$ ratio: a ratio somewhere around 4-6 would be consistent with this suggestion. While this observation provides a novel way of estimating the $NMOC/NO_x$ ratio of emissions, the small number of observations combined with the measurement uncertainties would not support any statistically sound analysis of this nature.

Ethane and propane were found to contribute a large fraction of NMOC at the sites studied: petroleum fields or refining are suggested as the likely source of high ethane and propane, but no supporting evidence is provided, and no there is no discussion of potential alternative sources such as LPG usage and natural gas leakage.

The observed drop in abundance rank for acetylene at Downtown Los Angeles between 8-10 September 1968 and 28 August 1987 (shown in Table VI) is attributed to the introduction of catalytic converters, which is reasonable. The concentrations of all the species listed in Table VI are lower in 1987 than 1968, but no conclusions can be based on this observation without comparing the meteorology (dilution) for the two data sets: note that the 1987 SCAQS data (Fujita et al., 1992) show higher surface concentrations (less dilution) in the fall than in summer. Lonneman et al. avoid this problem by comparing abundance ranks.

22. **Reconciling Differences Between Ambient and Emission Inventory Derived NMOC/NO$_x$ Ratios: Implications for Emission Inventories**, K. Baugues, EPA, AWMA Paper 91-67.5 (1991).

This paper describes adjustments to emission inventories coupled with comparisons of inventory and ambient NMOC:NO$_x$ ratios. Three inventory enhancements are investigated: addition of biogenic VOCs, rule effectiveness assumptions, and mobile source assumptions. Mobile emissions were from MOBILE4. On average, inventory-derived NMOC:NO$_x$ ratios from 16 cities were found to be 23 percent lower than ambient ratios without any enhancements. With the enhancements to the inventory, the ratios are within 2 percent (excluding Beaumont). Rule effectiveness assumptions were found to have a large effect on the inventory NMOC:NO$_x$ ratios.

The strengths of this paper are the large ambient database used, the investigation of sensitivity of results to key assumptions such as rule effectiveness, and the efforts to place inventory and ambient ratios on a common basis. One weakness is the use of emission inventories for the entire urban area rather than gridded inventories specific to the vicinity of the ambient monitor.

Objective Review

Keith Baugues at EPA has written a series of reports and papers on the subject of NMOC/NO$_x$ ratios. This particular paper must be recognized for aspects that can withstand the rapid developments in this field as new data become available. In particular this is evident in inventory preparation. This paper compares NAPAP inventories using MOBILE4 with ambient measurements. Since the paper was published the EPA has released the Interim 1990 inventory database and MOBILE4 has been replaced by MOBILE5a. The newer mobile model generates significantly more NMOC than previously, while the EPA and others continue to suggest that future versions of MOBILE may provide even higher emissions estimates as previously unaccounted for effects like exhaust enrichment from rapid acceleration are considered. Hence, the important and lasting parts of this paper become not the results, but the techniques used and the insights presented on finding ways to reconcile ambient versus inventory differences.

This paper focuses on the VOC inventories from the popular standpoint that they are low and in need of "enhancement." Three main enhancements are explored here: biogenics, rule effectiveness, and mobile source assumptions. The most unique to this particular study is the area of rule effectiveness. Here the paper is notable for showing the large net effects on emissions from specific categories that can stem from assuming that some controls are less effective in practice than on paper. The mathematics that results from such an assumption is clearly shown in the paper's Figure 1. For controls that are intended to reduce the emissions by 80 percent or more, the lack of full effectiveness leads to gross underestimation of source strength. For example, a control intended to reduce emissions by 95 percent but, in reality, is only 80 percent effective results in an underestimate by a factor of four. Not only can this be very important to inventory

estimates, but it should also be cause to carefully consider enforcement costs along with control costs when evaluating the benefits of many controls. A point the paper fails to make is the mobile source history of controls and I/M enforcement programs that also are subject to the mathematical implications of effectiveness assumptions.

Another important and lasting contribution that this paper does make is its analysis across several cities. Baugues argues that there appears to be no consistent enhancement of inventory emissions that improves agreement with ambient data across the group of cities studied, even though the overall average may be improved. A suggestion not made by Baugues, but stemming from this result of no universal solution, is to select surrogate cities (perhaps from the list used by Baugues here) to be routinely reevaluated as many inventory improvements become universally adapted. Of course, some of the surrogate cities might also need improved ambient measurements.

Some suggestions for future work provided by Baugues in this paper have indeed been adapted by others. For example, Baugues notes three improvements that have been used by works also reviewed here like Korc et al. (1993): (1) use gridded emissions to compared with a monitor in a given grid cell, (2) use several monitoring sites per county, and (3) use day-specific inventories compared with the ambient data for the same day.

Skeptical Review

The ambient data used in this study are from Baugues (1986), which is reviewed elsewhere in this report. Emission inventories are based on 1985 NAPAP data, MOBILE4, and PC-BEIS. These inventories are now outdated by the release of MOBILE5a and the EPA 1990 Interim inventory. Inventory $NMOC/NO_x$ ratios were converted from a mass to molar basis using average molecular weights and carbon numbers from city-specific ambient data. This approach is reasonable, but no details are given for the factors used, or of the sensitivity of $NMOC/NO_x$ ratios to these assumptions. Point source NO_x emissions were excluded from the inventories, which is probably the most reasonable course of action. Baugues finds that on average the inventory ratios are 23 percent lower than ambient measurements. But the ambient measurements vary from 6.5 to 48.3 and the inventory ratios vary from 4.4 to 36.5, and one wonders if a 23 percent difference is significant. The two sites for Philadelphia differed by 15 percent.

Biogenic emissions were calculated using seasonal average meteorological parameters, but no information on how land-use data (i.e., vegetation type) were determined and whether estimates were city-specific. Apparently estimated NMOC emissions changed by 5 percent on average (since the average $NMOC/NO_x$ ratio changed from 11.1 to 11.7). The biogenic contribution estimated from the ambient data in Baugues (1986) was much smaller than this, 0.1 to 1.5 percent for isoprene plus alpha-pinene. Thus it appears that the biogenic emission inventories may have been overestimated on average.

Baugues demonstrates very effectively that assumptions for rule effectiveness make a big difference when the inventory contains large, highly controlled point sources (e.g.,

Houston and Beaumont, TX), but there is no justification given for the 80 percent rule effectiveness tried in this study.

Mobile source inventories are calculated with three distributions of speed by road class, one from NAPAP and two simple alternatives proposed by Baugues as sensitivity tests. Neither alternative improved the inventory comparison, and the most plausible conclusion is that a single speed distribution cannot represent 16 different cities.

Baugues did find that a combination of these adjustments improved agreement in 11 of 16 cases and eliminated the bias between ambient and inventory ratios with Beaumont excluded. But this is hardly proof that the proposed package of changes is correct since many alternatives inventory changes could likely have similar impacts. This is reflected in Baugues' first conclusion that "there is no consistent bias indicating a flaw in the inventories"—in other words, none of the inventory changes investigated consistently improved agreement with ambient data across all, or even most, of the cities, and thus no consistent bias was discovered.

23. **Comparison of Emission Inventory and Ambient Concentration Ratios of CO, NMOG, and NO$_x$ in California's South Coast Air Basin**, E.M. Fujita, B.E. Croes, C.L. Bennett, D.L. Lawson, F.W. Lurmann, and H.H. Main, *J. Air Waste Manage. Assoc.*, 42:264-276 (1992).

This paper presents the results of an analysis and comparison of emission and ambient NMOG:NO$_x$ and CO:NO$_x$ ratios for the Los Angeles area during the SCAQS study in the summer and fall of 1987. Ambient 7-8 a.m. data from eight sites were used to calculate ambient ratios for summer and fall. Emission inventories used in the comparison were developed with the EMFAC7E model and were gridded and temporally adjusted to represent the 6-8 a.m. PDT period. The inventories were day-specific for one of the days in each season. Inventory ratios were calculated for various combinations of grid cells surrounding each site, and for back-trajectories. Emissions were also adjusted for NMOC compounds present in the inventory but not measured in the ambient samples. Ambient NMOC:NO$_x$ and CO:NO$_x$ ratios were found to be higher than corresponding emission inventory ratios by factors of 2-2.5 and 1.5, respectively. NMOC composition was also compared qualitatively to vehicle exhaust composition.

Strengths of this paper include the development of the approach for this type of analysis, the extensive database utilized, and the efforts to place inventory and ambient values on a common basis. Weaknesses include use of an inventory from a single day in comparison to ambient data from several days, and only qualitative use of speciated VOC data.

Objective Review

This paper presents a very detailed and thoughtful evaluation of ambient ratio data and comparisons to emissions inventories. The information is so extensive that it can be difficult to see the forest for the trees, so I start by summarizing the main findings. From the analysis of ambient data, representative basinwide average 7-8 a.m. NMOG/NO$_x$ and CO/NO$_x$ ratios of 8.8 and 20 were derived for the summer, and 6.9 and 18.4 for the fall (Table II). The ambient ratios were compared to several different inventory ratios (1-cell, 9-cell average, back trajectory, basinwide average; 6-8 a.m., overnight; motor vehicle, total) in Tables III-V. The most appropriate inventory comparisons were determined to be basinwide average motor vehicle, 6-8 a.m. for the summer, overnight for the fall. Based on the assumption that the NO$_x$ inventory is reliable, these comparisons suggest that "motor vehicle CO and ROG emissions are about 1.5 and 2 to 2.5 times higher, respectively, than emissions inventory estimates." ROG means the same thing as NMOG or NMOC in this context. The authors add that "the uncertainty in these estimates due to variability in the ambient data is about 10 percent (1 sigma)."

Emission Inventories

The emission inventories used in this work were prepared by the California Air Resources Board Technical Support Division and were current through March 1991.

This probably means that the point, area, and biogenic emissions are from the 1991 Air Quality Management Plan for the South Coast Air Basin. However, in mid-1991 the area source inventories were revised with a change to off-road emissions that resulted in an increase in area source NMOG and NO_x emissions. Mobile source inventories were prepared with the EMFAC7E emission factor model coupled with the Direct Travel Impact Model using activity estimates derived via transportation modeling. Mobile NMOG emissions would be higher if calculated with the more recent EMFAC7F model.

Effect of Different Inventory Comparisons

The inventory pollutant ratios, averaged over all sites, do not vary much with spatial method used as the basis for the estimate at each site: 1-cell, 9-cell average, back trajectory, basinwide average. The inventory ratios do vary with time period used: the overnight ratios are different than the 6-8 a.m. ratios generally resulting in larger discrepancies with the ambient data when overnight values are used. Since the discrepancies with the inventories are generally larger in the summer than the fall, comparison with overnight ratios in the fall and 6-8 a.m. ratios in the summer results in consistent estimates of the discrepancies for summer and fall. Comparisons with the total inventory instead of motor vehicles would make little difference for $NMOG/NO_x$, but for CO/NO_x would result in larger discrepancies. The overall ranges for the ambient/inventory ratios across all comparisons are 1.1 to 2.7 for CO/NO_x and 1.7 to 3.0 for $NMOG/NO_x$. The data underlying this synopsis are all presented in Table III of the paper.

Variability in the Ambient Data

The authors estimate this at 10 percent (1 sigma). Statistically, their estimate comes from taking means of pollutant ratios across sites (which is reasonable) and estimating the standard deviation of the mean. This assumes that the measurements at each site are independent estimates of the mean. However, different sites may be correlated by large scale effects such as meteorology. For instance, pollutant emission ratios may be temperature dependent causing cooler coastal sites to be grouped around a different ratio than inland sites, or pollutant recirculation patterns may impact certain groups of sites but not others. An alternative estimate of the variability would be the population standard deviation which is the square root of n times the standard deviation of the mean, where n is the number of sites (8 for summer, 6 for fall). This would increase the 1 sigma estimate of the variability in the ambient data to about 25 percent.

Correction for Background

No corrections to ambient concentrations to account for background are described in this study; however, this is probably a very minor omission. The most appropriate background concentrations would be for clean Pacific air. Moore et al. (1991) found that clean air off the southern California coast typically contained less than 20 ppbC NMHC and 150 ppb CO. These values are only a few percent of the mean 7-8 a.m. concentrations at all sites in the fall and most sites in the summer. A background

correction for CO could be about a 10 percent effect for coastal sites (Hawthorne and Long Beach) in the summer. Subtracting a background for CO would decrease the ambient CO/NO_x ratio, slightly reducing the discrepancy with inventory values.

Discrepancy due to Mobile Sources

The authors strongly suggest that the discrepancy between ambient and inventory pollutant ratios results from underestimation of mobile source NMOG and CO in the inventory. This appears to be based on (1) the high contribution of mobile sources to 7-8 a.m. pollutant concentrations based on inventory estimates, (2) the similarity between 7-8 a.m. ambient NMOG speciation and gasoline vehicle tailpipe emissions (Figure 7), and (3) evidence for the underestimation of motor vehicle NMOG and CO emissions from the SCAQS tunnel study. The first reason is valid if the discrepancy is due to mobile sources, but invalid if it is due to some other reason, and thus is not a powerful argument. The third reason is external to this study and therefore should not be counted here. When viewing the comparisons of ambient NMOG profiles with gasoline vehicle exhaust shown in Figure 7, the eye sees mainly the good agreements for some large peaks (butane, isopentane, toluene, xylene and maybe benzene). These compounds are likely indicators of gasoline related emissions, but not necessarily of mobile sources. Fujita et al. also note that the similarity in CO/NO_x and $NMOG/NO_x$ ratios between sites and the high correlation between CO, NMHC, benzene, and NO_x across all sites suggests a common, basinwide source for these pollutants. This is consistent with motor vehicles being the source, but cannot distinguish contributions from any other widespread source, such as nonroad equipment. Some results from photochemical grid modeling with the UAM are also presented, although few details on the methodology are given. The UAM results confirm the discrepancies between inventory and ambient ratios that were identified by direct comparison. Showing that the discrepancy between ambient and inventory ratios is due to underestimation of mobile source NMOG and CO is the most difficult piece of the argument presented by Fujita et al.

Conclusions

Overall, the analyses presented in this paper are very thorough and provide solid evidence for a discrepancy between the ambient and inventory pollutant ratios. The uncertainties in the analysis are likely larger than the 10 percent estimate of variability in the ambient data. The weakest link in the argument for underestimation of mobile source NMOG and CO emissions may be the difficulty in showing that discrepancies in the ambient/inventory ratios are due to mobile sources (discussed above).

Skeptical Review

Since its publication in early 1992, this paper has received considerable attention with numerous citations in recent publications. In particular, it is cited as evidence that mobile source inventories are low for NMOG and CO estimates, but not so for NO_x. The work reported in this paper also represents a rather comprehensive accumulation of analysis techniques across what might be argued as some of the best ambient and

emissions data available. However, the paper suffers from a lack of balance between the enormous effort put into analyzing the organic and CO data on the one hand and the rather limited attention given to the NO_x data on the other hand.

Some contrast in NO_x data accuracy and attention given to NO_x problems can be seen between this paper of Fujita et al. (1992) for South Coast data and a similar analysis done by Korc et al. (1993) on the Lake Michigan data. The NO_x data for the South Coast study listed in Table I of this paper have, for the most part, detection limits of 10 ppb and 15 percent precision. The Lake Michigan data (taken 4 years later) listed in Table 2-2 of Korc et al. (1993) have detection limits of 1 ppb (or better) and precision of 10 percent. Furthermore, Korc et al. (1993) made a careful screening of all data comparisons so that NO_x is at least 8 ppb (i.e., a factor of 8 or more above the detection limits of the instruments), whereas the Fujita et al. study rarely discusses the implications of low NO_x comparisons. The presentation of information on data precision and detection limits in Table I of Fugita et al. is commendable, but unfortunately the information is not propagated beyond Table II. Table II shows pooled estimates of measurement errors of 5 to 10 percent for $NMOG/NO_x$ and CO/NO_x ratios at most sites in summer and fall. The estimated error is highest (16 percent) for the summer $NMOG/NO_x$ at Long Beach, where the mean NO_x was only 76 ppb.

This Fujita et al. paper does note that one site (Hawthorne) shows a potential problem from nearby elevated sources. When the elevated emissions are ignored the emissions estimates agree much better with ambient ratio measurements. The difference is approximately a factor of two between the ratio with and without the elevated NO_x emissions. Such a large effect suggests that other sites throughout the basin, not so clearly influenced by a nearby elevated source, may also at least be affected to the 10 percent range, which could influence the results of the overall study. The acceptability and accuracy of the NO_x data is the cornerstone of this Fujita et al. study, the foundation on which their conclusions are built, so the lack of attention given to the potential problems with the NO_x data (both ambient and inventory) make the NO_x data a weak link in their conclusions on the NMOG and CO inventories.

Focusing on early morning and nighttime hours as is done in this study is a two-edged sword: mixing heights and photochemical action are low, which helps alleviate detection uncertainties and biases due to divergent atmospheric chemical loss rates for NMOG, NO_x and CO, but horizontal mixing and vertical mixing are also low, which compounds inhomogeneous emissions problems in both the vertical and the horizontal. Moreover, a clearly defined vertical mixing height is not normally present during nighttime and early morning hours. Using ratios of precursors instead of absolute concentrations helps to reduce this vertical mixing problem if the precursors are emitted with similar vertical distributions. However, this may not be the case because NO_x is associated with combustion sources that often have some thermal buoyancy, whereas NMOG and CO are more often emitted at ground level. Light-duty vehicles may have hot exhausts but typically have small diameter tailpipes close to the ground, so that exhaust gases cool rapidly. Light-duty vehicle evaporative NMOG emissions are also likely to remain near the surface. On the other hand, diesel exhaust from large trucks and stationary engines (a significant source of NO_x) is much more likely to have some plume rise. These arguably often have taller and larger diameter "stacks" which might penetrate nocturnal inversions in many areas. Thus, the nighttime and early morning emissions of NMOG,

CO, and especially NO_x may not be well mixed vertically. Also, horizontal inhomogeneities can create problems even though this was addressed quite well in this study. As noted above, the authors' use of gridded inventories and back trajectories represents a noteworthy improvement over past studies. However, it should be noted that the authors rejected comparisons of ambient data to the gridded inventories even though the spatially averaged, single cell, and back trajectory results differed in some cases, yet they then concluded that the remaining results being similar for single cell, spatially averaged, and back trajectory cases meant that such detail need not be considered in the rest of the paper, so only the basinwide comparisons were used. As shown in Table III of Fujita et al., the inventory basis for comparison can affect the apparent discrepancy in pollutant ratios. Although comparisons to overnight inventories were deemed most appropriate for the fall, the 1-cell, 9-cell, back trajectory, and basinwide inventories were compared only for 6-8 a.m. in Table III.

If a significant fraction of the NO_x emissions are stored just above the nocturnal inversion, then an expected result is a downmixing of NO_x as the mixing height rises during the mid-morning to noon hours. With only initial precursors present, smog chamber experiments typically show rapid increases in both the CO/NO_x and the $NMOG/NO_x$ ratios during the course of a day. This occurs because NO_x reacts faster than the average NMOG species or CO. In the ambient atmosphere, the presence of enhanced NO_x just above the early morning mixing height (with nearly all the emitted NMOG at the surface) might result in more nearly constant $NMOG/NO_x$ ratios due to a compensation effect between the expected increase in $NMOG/NO_x$ ratios due to reaction of NO_x and any potential decrease from downmixing of NO_x from just above the surface mixed layer. Figure 5 in the Fujita et al paper shows a rather constant $NMOG/NO_x$ ratio at downtown Los Angeles during the summer midmorning to noon timeframe that is consistent with this compensation effect. However, Figure 5 also shows that both the summer and fall CO/NO_x ratios increase significantly during these hours and that the fall $NMOG/NO_x$ ratios also increase similar to the fall CO/NO_x ratios. The difference between summer and fall may be explained by less active photochemistry on the fall days. At any rate, the near-constant $NMOG/NO_x$ ratios during summer mornings are curious and need further explanation.

Fujita et al. present a comparison of the ambient NMOG speciation profile averaged over all sites with an ARB profile for motor vehicle exhaust. They state that the two profiles are very similar, and use that perceived similarity to back up their claim that vehicle exhaust is the main component of morning ambient NMOG, and therefore that vehicle exhaust is underestimated in the inventory. In fact, the agreement between the ambient and vehicle exhaust profiles is not particularly good for several species, most notably ethene. Furthermore, the ARB vehicle exhaust profile (which is derived from the Sigsby data - see the SPECIATE database review) is in error regarding the relative predominance of propane and propene in vehicle exhaust. When this error is corrected, the agreement between the ambient and exhaust profiles worsens, and it becomes clear that a major non-mobile source of propane is present in the ambient samples. The poor agreement for the combustion products ethene (and propene in the revised comparison) supports the contention that the perceived shortfall in NMOG emissions may be more similar in composition to unburned gasoline than it is to vehicle exhaust (see Harley et al., 1992).

A better approach than that used by Fujita is to develop site and time-specific inventory profiles for the total NMOG inventory and compare those profiles to the ambient profiles. This approach was used in the later study by Korc et al. (1993). Without this information, it is impossible to determine what fraction of the postulated inventory shortfall is due simply to a lack of propane in the inventory, and whether any other species are systematically under- or overestimated.

Finally, the uncertainties in the proposed factors for underestimation of CO and NMOG emissions (1.4 and 2 to 2.5, respectively), referred to in the conclusions seem optimistic: The authors refer only to a 1 sigma estimate of uncertainties in the ambient data of 10 percent. This estimate results from their adopted approach of taking means of ambient ratios across days and then sites, and calculating the uncertainty in the average as the standard deviation of the mean. This assumes all measurements are independent estimates of a constant underlying property, which is an optimistic error analysis. A more conservative approach that recognizes that all the data may not be independent would result in higher uncertainties. As noted above, the measurement errors estimated in Table II of Fujita et al. of 5 to 15 percent apparently are not included in the overall uncertainty estimation of 10 percent derived by Fujita et al.

24. **Comparison of Emission Inventory and Ambient Concentration Ratios of NMOC, NO_x, and CO in the Lake Michigan Air Quality Region**, M.E. Korc, P.T. Roberts, L.R. Chinkin, and H.H. Main, Sonoma Technology, Draft Final Report prepared for Lake Michigan Air Directors Consortium (LADCO), STI-90218-1357-DFR (1993). Also, LADCO memorandum **Revised comparison of emission inventory and ambient concentration ratios of NMOC, NO_x, and CO**, April 15, 1994.

This report presents the results of an analysis of ambient NMOC:NO_x and CO:NO_x ratios for three cities in the Lake Michigan area (Chicago, Gary, and Milwaukee) for two episodes in the summer of 1991. The 7-9 a.m. ambient ratios were compared to emission inventory ratios for the same time period, for grid cells surrounding and upwind of the ambient sites. The ambient ratios were generally higher than the inventory ratios, with the best agreement observed for the Gary site, identified as an industrial site. In addition, ambient VOC profiles were compared to profiles obtained from the speciated VOC inventory, and discrepancies were identified for butane, C_6 olefins, and toluene. The general similarity between ambient VOC speciation profiles and motor vehicle exhaust profiles led the authors to conclude that motor vehicle exhaust was responsible for the discrepancy between the ambient and inventory ratios.

In response to this study, LADCO reevaluated and revised the modeling inventory, and recomputed the inventory NMOC:NO_x and CO:NO_x ratios. LADCO also revised the ambient ratios to incorporate estimates of background NMOC, NO_x, and CO based on measurements at rural upwind sites. The revised ambient:inventory ratios are lower than those reported by STI. The revised NMOC:NO_x ratios agree to within 20 percent for Gary and Chicago, but ambient ratios are still 40 percent higher than inventory ratios for Milwaukee. For CO:NO_x, the agreement is within 20 percent for Chicago and Milwaukee, but the ambient ratios are 50 percent higher than inventory ratios for Gary.

The strengths of this study are the detailed enumeration of potential sources of uncertainty in the analysis, efforts to place inventory and ambient NMOC on a common basis, and comparison of ambient VOC profiles to the speciated inventory. Weaknesses include the lack of statistical support for the conclusions of "significant" differences.

Objective Review

This analysis includes a thorough treatment of the emission inventory adjustments needed to compare inventory and ambient NMOC:NO_x and CO:NO_x ratios. The use of day- and time-specific gridded inventories and the adjustments to the inventory to exclude species that were not measured lends credibility to this work. It is also the only study to use inventories generated with MOBILE5a. The study also enumerates potential sources of uncertainty in the comparison. One shortcoming is that in the conclusion section the overall uncertainty in the ambient/inventory comparison is given as 20 percent, yet that value is never derived in the report. Indeed, after reading the discussion of the potential sources of uncertainty, one might conclude that the overall uncertainty could be considerably greater than 20 percent.

The authors use three different gridded areas to compare inventory to ambient ratios. These were a 9-cell block centered on the cell containing the ambient monitor; an 81-cell block centered on the cell containing the ambient monitor; and the upwind quadrant of the 81-cell block. The authors stated that the upwind quadrant comparison was likely to be the most valid, since wind speeds were relatively high and steady from a given direction. However, the comparisons were not particularly sensitive to which of the three gridded areas were used for the comparison, except in Gary.

Based upon STI's conclusion that NMOC and CO emissions were underestimated, the Lake Michigan Air Directors Consortium (LADCO), with the assistance of the states, reevaluated the LMOS inventory. They made several changes to the inventory. Thus, the STI analysis was successful in achieving its goal, which was essentially to provide an additional quality assurance tool to be used in verifying modeling inventories.

STI used a screening criterion in which ambient samples with NMOC less than 200 ppbC, CO less than 1000 ppbC, or NO_x less than 8 ppbC were not included in the analysis. This was done to minimize the contribution of background NMOC, CO, and NO_x to the ambient concentrations. In the reanalysis conducted by LADCO, they chose a different method of correcting for background: all samples were retained, and concentrations of NMOC and NO_x at upwind background sites were used to adjust the measured concentrations. This was not done for CO, because CO was not measured at the background sites.

Inspection of the data for the background sites shows that these sites have NMOC and NO_x concentrations considerably higher than those characteristic of a remote site. The value recommended for CO boundary concentrations in UAM modeling is 350 ppb (EPA, 1991); this value may be representative of CO concentrations at the upwind background sites. The ambient CO concentrations in STI's Table 2-3 show that this value represents over half of the average measured CO at the Milwaukee site, half of the average measured CO at the Gary site, and 20 percent of the average measured CO at the Chicago site. This high potential background CO contribution for Milwaukee and Gary suggests that $CO:NO_x$ ratio comparisons that do not account for background CO will show high ambient ratios at those sites. Thus, the Chicago site is the best site for comparing ambient and inventory $CO:NO_x$ ratios.

In the STI report (Table 5-8) the ambient $CO:NO_x$ ratio for Chicago is found to average 2.3 times higher than the inventory $CO:NO_x$ ratio. However, in the LADCO reanalysis, the average ambient and inventory $CO:NO_x$ ratios for Chicago agree to within 10 percent. The LADCO reanalysis found that ambient $CO:NO_x$ ratios at Gary were 50 percent higher than inventory values; however, subtraction of background CO would very likely reduce this value to within the 20 percent uncertainty.

The emission inventory changes responsible for the large differences between the STI ratio comparisons and those calculated by LADCO were not enumerated in the LADCO memorandum, and thus cannot be reviewed. Inventory updates are described in another LADCO memorandum "Third Round Update to the LMOS Regional Modeling Inventory" (March 18, 1994). Assuming that all changes made to the inventory represent valid corrections of error, there does not appear to be any evidence to support

the conclusion that ambient $CO:NO_x$ ratios are higher than inventory ratios in the revised inventory.

For the $NMOC:NO_x$ ratios, the STI analysis shows ambient ratios exceeding inventory ratios by 20 percent in Gary, 60 percent in Milwaukee, and 90 percent in Chicago. The LADCO reanalysis shows ambient ratios 20 percent lower than inventory ratios for Gary, values agreeing to within 20 percent for Chicago, and ambient ratios exceeding inventory ratios by 40 percent for Milwaukee. Thus, in the LADCO reanalysis, Milwaukee appears to be the only city for which there is the potential for underestimation of the NMOC inventory. It is also important to recall that a low inventory $NMOC:NO_x$ ratio does not necessarily imply that NMOC emissions are low; the other potential cause is that NO_x emissions are high.

STI also compared ambient NMOC profiles with profiles derived from the inventory. This is the only study to have performed this analysis, and it adds to the value of the work. If a particular source category is under- or overestimated, it should show up in the comparison for species characteristic of that source. The comparison of inventory and ambient speciation is shown in STI's Figure 5-3 for Milwaukee. Species that might be used as tracers for motor vehicle exhaust in the 7-9 a.m. time period include acetylene, ethene, propene, and benzene. STI's Figure 5-3 shows that the agreement between the inventory and ambient profiles is excellent for propene and benzene, and good for ethene. The inventory value for acetylene is about half of the ambient value. Acetylene emissions are very sensitive to operating mode, and represent a higher fraction of NMOC emissions during the cold start than during stabilized operation (e.g., see Doskey et al., 1992). If the mix of operating modes at the monitoring site differed from the FTP conditions used to derive the profile, the acetylene fraction could be quite different. Given the high variability in the acetylene fraction, combined with the good agreement for the other three species, the disagreement for acetylene does not appear to be sufficient to support the conclusion that motor vehicle exhaust emissions are responsible for the majority of the underestimate.

STI's Figure 5-3 shows that the largest apparent underestimates in the inventory are for ethane and propane. These two species are not associated with motor vehicle emissions. They are quite unreactive, and are likely to have a significant background and day-to-day carryover contribution. They are also associated with leakage from natural gas and LPG systems. These fugitive emissions are not likely to be accurately represented in the inventory. However, these species also are very small contributors to ozone formation, and their potential omission from the inventory would not be expected to affect modeling results.

The other major discrepancies between the inventory and ambient profiles are that the inventory butane is high, the inventory isopentane is low, and the inventory toluene is high. The butane and isopentane emissions are primarily due to gasoline evaporative emissions, including those from motor vehicles and stationary sources. These emissions are extremely sensitive to the ratio of butane to isopentane in the gasoline. It is perfectly plausible that the butane:isopentane ratios differed between the gasoline used in Milwaukee and the gasoline used to develop the profiles. Since the inventory overestimate of butane is nearly balanced by the underestimate of isopentane, and since these two species have similar reactivities and are treated identically in modeling, this

discrepancy does not appear to be important. There are also compensating errors in the inventory fraction of branched C_6 compounds and C_6 internal olefins. As discussed in the review of the SPECIATE database, the profiles for motor vehicle evaporative emissions in version 1.5 incorrectly assign emissions of 2-methylpentane (a branched C_6 compound) to 4-methyl-2-pentene (a C_6 internal olefin). This probably accounts for the observed discrepancies. The result of this is that the inventory NMOC emissions for motor vehicle evaporative emissions are likely to be somewhat too reactive.

The high inventory toluene appears to be due to surface coating (solvent-based paint, thinners, lacquers, etc.) emissions, for which the SPECIATE profiles contain very high fractions of toluene. STI concluded that the toluene fractions in the surface coating profiles were too high. This is certainly a possibility; as discussed in the review of the SPECIATE database, the toluene fraction appears to be higher than that calculated from the component profiles and their relative weightings. However, SAI has produced numerous modeling inventories using these same profiles and they generally do not show such large toluene fractions in the 7-9 a.m. period. It is possible that the temporal profile used to construct the LMOS inventory allocated too much of the daily surface coating emissions to the 7-9 a.m. period.

In summary, STI has developed a credible methodology for providing an independent check of emission inventories. This analysis apparently assisted LADCO in identifying problems with the LMOS inventory. In particular, the comparison of the inventory and ambient NMOC speciation profiles provided a dimension to this study that had been lacking in previous NMOC:NO_x ratio comparison studies. The more limited of STI's conclusions, which were that there were some discrepancies between the ambient data and the inventory, appear to be valid. However, the specific conclusion that MV NMOC and CO emissions were underestimated was not fully justified in STI's analysis. Based on the LADCO reanalysis and the comparison of the ambient and inventory NMOC profiles, there appears to be little evidence that motor vehicle NMOC and CO emissions are underestimated in the revised LMOS inventory. Ethane and propane appear to account for much of the apparent underestimate of NMOC emissions.

Skeptical Review

This study involves two important phases: the first phase is described in the title report while the second is described only in summary. The results of the first phase suggested that several updates were needed in the emissions inventory. Many of these updates were implemented, and the second phase consisted of a reevaluation comparison using the revised emissions data. The new inventory appears to provide closer agreement with ambient data. However, the basic conclusion still remains that the emissions inventory and ambient data are not yet in agreement in that the CO and NMOC ratios to NO_x appear to be low in the inventory. The study, like others before it, tends to focus the errors in the inventory on low estimates for the CO and NMOC while deemphasizing potential errors in the NO_x inventory. The revised inventories appear to give ratios within 20 percent of observed ratios for the Chicago and Milwaukee areas but still are as far as 40 to 50 percent high for the Gary area.

While much credit must be given to the overall care taken in this analysis, there are some points which detract from a conclusive finding that the NMOC and CO inventories are low and that the NO_x inventory (or the interpretations of ambient data) might be influencing the conclusion. As noted in the review of Fujita et al. (1992), the use of early morning ambient data has its good points and its problems. A key problem is the potential for NO_x and NMOC to have somewhat different vertical profiles because NO_x is always associated with at least some thermal buoyancy (or vertical stack velocity) while most of the NMOC emissions have neither buoyancy nor a vertical velocity. The atmosphere during the 0700-0900 morning hours is undergoing a transition as the nocturnal inversion layer is being eroded towards a higher midday subsidence inversion layer. The report cites an earlier study by Roberts et al. (1993) that supports an early morning mixed layer of 150 to 300 meters in depth. This was cited to imply that elevated point sources above 50 m could be downmixed to the surface. However, a study by Ziman, Viezee, and Pederson saw an early morning plume rise to 500 m in the California San Joaquin Valley from emissions estimated to have a plume rise of only 75 m, illustrating the potential difficulties in estimating plume rise. The definition of a mixed layer is very important in this context. There may not be a full inversion between the surface and 300 m, but the mixing rate might be slow enough compared to the emissions rates so that NO_x (having a different vertical emissions profile than NMOC) and the other pollutants are not *well mixed* vertically.

However, the EPA mobile emissions are known to still ignore the enrichment emissions associated with high acceleration. These emissions will increase the CO and NMOC ratios to NO_x because enriched operation can be expected to show more NMOC and CO and maybe less NO_x (although sustained acceleration on a long grade may eventually show high NO_x emissions). In California one recent estimate of including enrichment showed mobile CO emissions to be 67 percent higher; however, current estimates of enrichment emissions are highly uncertain. Hence, the conclusions of Korc et al. may yet be even closer when enrichment is accounted for, but agreement between inventories and ambient ratios does not prove that emissions inventories themselves are correct. That is, both the NO_x portion and the NMOC could be off by similar percentages.

Another critical problem with the Korc et al. study involves the use of mobile emissions that are not separated into operational modes. The ratios of CO and NMOC to NO_x for mobile emissions are not constant across operating mode. Indeed, the evaporative modes all have zero NO_x emissions, and even within the FTP bags the ratio can be significantly different between cold starts and hot stabilized driving; there are temperature and speed effects as well. However, the influence of high emitting vehicles may be the most uncertain; the ratios of CO and NMOC to NO_x are much higher than for normal emitting vehicles. There has been some evidence that, in addition to an overall uncertainty on high emitting vehicles, there can also be spatial differences within the gridded region.

MASS BALANCE (URBAN FLUX) STUDY

25. Evaluation of the Mass-Balance Approach for Estimating Urban Emissions of NO$_x$ and VOC, N.V. Gillani and W.H. White, Washington University, Final Report prepared for EPA AREAL, Research Triangle Park, NC (1989).

Note: The EPA project officer notes that this report has not been finalized and should be considered a preliminary draft.

This study investigates the possibility of using mass balance, or ambient flux measurement techniques, to provide independent emission inventory verification. The concept proposed is to measure total flux of NO$_x$ (and/or VOC) from an urban area and back-calculate the total mass of emissions. The authors report that existing VOC databases were not adequate to demonstrate the method. Using aircraft NO$_x$ measurements from project MISTT/RAPS, conducted in St. Louis in 1975-76, the authors conclude that emissions estimates derived from the mass balance calculations are roughly consistent with inventory estimates. They also analyze data from project NEROS II, conducted in the Baltimore area in 1980. They conclude that this method is best applied to an isolated urban area with relatively simple meteorology, such as St. Louis, rather than an area potentially affected by upwind sources and complex meteorology, such as Baltimore.

The strength of this study is the concept of the mass balance method. Unlike the receptor modeling studies, the mass balance method, if successful, could provide an absolute calibration of emission inventories. The weaknesses of the study are the lack of success in applying the methodology, the failure to account for NO$_x$ reactivity, and the likelihood of high uncertainty even if a targeted study were carried out for this purpose.

Objective Review

The authors set out to assess the feasibility of conducting a mass balance inventory assessment by analyzing two existing databases. They have performed a fairly thoughtful and thorough examination of the problem, and their report highlights all too clearly the challenging nature of the problem. They conclude that the approach can only work under the most favorable conditions, i.e., an isolated city to minimize upwind boundary concentrations and a geographical location which promotes smooth and homogeneous airflow patterns. As the authors state: "The mass-balance estimation of emissions is just not feasible for all cities; it should not be viewed as a replacement for the emissions inventory."

Of the two cases considered in the report, St. Louis comes closest to meeting the requirements outlined above. The authors analyzed only the NO$_x$ data because the hydrocarbon data were found to be too unreliable. The method basically requires that the concentrations and winds be characterized across a slice through the urban plume to

determine the mass flux through that slice. It proved to be impossible to analyze morning data because NO_x was concentrated too close to the ground (because of low mixing heights) and was inaccessible to the aircraft measurements. Thus, it was impossible to characterize NO_x concentrations across the plume section. It was much easier to characterize concentrations across the plume in the middle of the day when strong vertical mixing produced a more homogeneous plume, but in an urban plume under episodic conditions the atmospheric lifetime of NO_x may get short enough in the middle of the day (a few hours) to introduce significant uncertainties into the analysis. The authors make a good point in observing that the most favorable conditions for a mass balance analysis may be on cloudy days with steady synoptic winds. These are the sorts of days that are normally rejected during an intensive ozone field study, in favor of stagnation days with clear skies, thus the two approaches might mesh together fairly well in the overall context of a field study.

Skeptical Review

This mass balance approach reminds one of the classic problem of fitting mathematical models to the physical world: they tend to be either too good to be true or too true to be good. Mass balance is apparently a powerful and true concept but appears to be of little good considering all the problems in gathering the needed data and accounting for all the loss mechanisms.

It can be argued that one good application of this technique would go a long way towards validating (or not) present inventory techniques. The authors claim to be optimistic about this technique, but they are also quick to point out that even an adequate application requires a long list of special circumstances and expensive data. For example, most modern major field programs focus on ozone episode days, yet the high photochemical activity, stagnation or recirculative meteorology, and high temperatures that characterize smog episodes all are not so favorable to this technique. Hence, the authors' claim that it should be inexpensive to collect data earmarked for this technique during a major field study is weak. Some extra and expensive focus would be needed on non-episode days which have clouds and well-defined windflow patterns. The presence of clouds would reduce not only the photochemical activity but the temperature and emissions associated with higher temperatures (evaporation and higher power plant operation). Other important criteria needed to optimize the data for this technique eliminate many cities and regions known to have high ozone and that could be expected to support the major field (mainly aircraft sampling) program needed for the mass-balance estimate. That is, the South Coast Air Basin and the Northeast would not be good sites due to complex terrain features or the lack of an isolated city. St. Louis may have the flat terrain and isolation needed, but St. Louis no longer has a major ozone problem and will not likely have any more large field programs funded there.

A key problem with this technique is that the requirements for good data are all too often in conflict. Minimal photochemistry suggests morning hours, but this time of day is bad because of flight restrictions on altitude and the uncertain mixing heights and emissions heights (NO_x sources tend to have more buoyancy than VOC sources).

Two potential ideas that this report seems to miss are the use of CO data and grid model results. CO data can be obtained in aircraft and CO is rather inert. One problem with CO, however, is that it is a product of smog photochemistry. Grid models provide information in the upper cells and in the downwind boundary that can be related to mass balance analysis. Thus, aircraft data could be compared to grid model results for upwind and downwind cells to help provide some mass balance-like verification of inventories as they are "processed" by the grid models.

4 SYNTHESIS OF CRITICAL REVIEWS

RECEPTOR MODELING STUDIES AND SPECIES PROFILES

This section begins with a review of the assumptions underlying the receptor modeling method discussed in Section 2 and then discusses specific issues raised by the critical reviews in Section 3. Finally, the results obtained in multiple studies of Atlanta, Chicago, and Los Angeles are compared.

Review of Assumptions

In the receptor modeling overview (Section 2), a number of assumptions associated with the CMB analysis technique were identified. In practice, strict compliance with these assumptions is rarely found. However, for most of the assumptions, the CMB model can still perform well and provide useful results even if there is some deviation. The extent to which the CMB analysis provides meaningful results depends on the level of deviation from these assumptions.

Assumption 1 requires that the relative composition of source emissions are constant, or that the removal by reaction or deposition is constant between the various species within the fingerprint. This is an important assumption to examine in the context of CMB analysis for organic gases where species present in source profiles can span a wide range of atmospheric reactivities (lifetimes ranging from hours to weeks). Most researchers seemed to be aware of this point and set out to use only less reactive species in their analyses; that is, they tried to avoid the problem. A few groups performed analyses including reactive species in an attempt to quantify the potential effects of reactivity on their CMB analysis; that is, they embraced the problem. Attempts to deal with the issue of reactivity generally increased the credibility of the CMB results.

Assumption 2 requires that components do not react with one another (i.e., they add linearly). This assumption is violated if secondary organic compounds (e.g., carbonyls, CO) are included in the CMB analysis.

Assumption 3 indicates that the number of sources (or source types) contributing to a receptor must be known. For many of the CMB analyses conducted in these papers, the violation of this assumption may have caused problems. A large unidentified fraction in the CMB analysis is a clear indication that important sources are missing. A majority of the analyses did not consider potentially important sources of organic material, for example, evaporation of whole gasoline. Additionally, many of the studies were not able to properly define the mix of solvent uses that may have contributed to the ambient

air. These shortcomings have the potential to result in overprediction of the source types that were included.

The GRACE/SAFER technique (Henry et al., 1994) appears to be a promising method for overcoming this weakness. If enough ambient air quality data are available, the method can be used to examine the ambient data to accurately determine a composite source profile representing the average solvent evaporation sources contributing to a receptor. In addition, if additional sources are contributing that were not included in the original CMB analysis, this method can potentially identify those sources (although it is still up to the researcher to "name" the source or sources represented by the identified source profile).

It is necessary that the majority of the ambient species concentrations be accounted for by the set of sources used in the CMB analysis. In a number of the papers, this was not the case; the CMB model did not adequately account for a majority of the observed species concentrations, and hence, for these analyses, the source contributions must be considered to be highly uncertain.

Assumption 5 (assumption 4 was for tracer analysis only) requires that the number of source types be less than or equal to the number of components. While this was generally always the case, it is further necessary that the difference (degrees of freedom) be as large as possible to provide statistically meaningful results. The number of degrees of freedom has a direct bearing on the statistical interpretation of the results. When the degrees of freedom are small (i.e., the number of species is not much greater than the number of sources), there is a good chance that the uncertainties of the source contributions are high and that some source contributions may not be statistically different from zero. In addition, a number of the source contributions may be computed as negative (not physically meaningful) values and are therefore usually removed from the CMB analysis. This results in problems concerning assumption 3 (not all important source types are considered in the model). If there are a large number of actual source types contributing to a receptor, then it is imperative that the number of species be large or else CMB cannot perform effectively.

Assumption 6 requires that the composition of all source types are linearly independent. Some linear dependence can be tolerated by the CMB model; however, when two (or more) source types are nearly collinear (i.e., they have a high degree of correlation) the CMB model is unable to distinguish the two sources. It is important for the researchers to recognize this occurrence and to make attempts to remove this collinearity, either by increasing the number of species (e.g., adding species to the analysis for which the relative proportions in the collinear sources are different, effectively removing the collinearity), or by preparing a composite profile to represent the total contribution of the collinear sources.

Assumption 7 requires that the measurement errors are random, uncorrelated, and normally distributed. If this assumption holds, then the CMB results are unbiased, and the estimated uncertainties for each source contribution are meaningful. There has been little demonstrated evidence either supporting or negating this assumption. It is generally considered to be reasonably valid as evidenced by the widespread use of receptor models. Even though it is nearly impossible for researchers to demonstrate the

validity of this assumption study by study, at the very least they should seriously consider and report the statistical properties of their CMB analysis.

Issues Raised by the Critical Reviews

Source Profiles

Source profiles must be appropriate. It is critical that the source profiles reflect conditions in the region during the time of ambient sampling. It is necessary to use source profiles that correspond with the actual emission sources in the region, and for the time periods for which the ambient air quality data were collected. For example, sources related to gasoline use (gasoline vapor, exhaust, whole gasoline) exhibit different chemical profiles depending on the composition of the gasoline, which varies between geographical areas, between winter and summer, between grades and between refiners within a given area.

Source profiles must be correctly identified (labeled) or the study results may be interpreted improperly. The CMB model estimates the contribution for each source profile given. However, the source profile may, in fact, be representative of multiple similar sources in addition to the one for which it is named. For example, motor vehicle exhaust profiles assembled from either tunnel measurements or dynamometer tests are likely representative of emissions from all combustion of motor-vehicle type fuels. In other words, a CMB result for "motor vehicle exhaust" contribution should be interpreted as the total of many other sources in addition to on-road mobile sources, such as off-road mobile, stationary industrial internal combustion engines, construction/farm equipment, etc. This is an important point to consider when comparing the CMB results to emission inventories. The problem of misinterpretation of CMB results is very common in all applications of CMB. Often, a profile is developed for a particular source (or source type) in one study and then used in many other CMB analyses. Often the researcher developing the profile is aware of the range of sources that may be captured by the profile, but subsequent researchers basing CMB source contribution results on the profile lose sight of this limitation.

Source profiles can not be collinear. When collinearities exist between two (or more) source profiles, the CMB model has difficulty distinguishing between the source types, and the resulting estimated source contributions are highly uncertain. The optimal approach is to prepare a composite profile which reflects the emission strengths of each of the individual source types. For example, a composite profile for a combination of graphic arts and architectural coating (painting) could be constructed from a weighted average of the two individual source type profiles, with the weights equal to the estimated relative NMOC emission rates of these two sources in the region being considered. Using the resulting composite profile in the CMB analysis results in an accurate estimate of only the sum of the two source types. In many papers by the University of Illinois group (e.g., Kenski et al., 1992) the graphic arts and architectural coatings profiles were found to be collinear. The approach to overcoming this problem was to use each individual profile in a separate CMB analysis, and then to average the two results. The averaged results are then reported as the individual contribution from each source type, which is meaningless; only the total of the two contributions has any

significance. However, there are likely additional biases introduced by this averaging technique so that even the total contribution is less accurate than would be the case if a composite profile had been used.

Statistical Performance Measures

Several researchers indicate either implicitly or explicitly that the statistical performance of the CMB analysis is not important. In many papers there is little demonstrated evidence of the statistical significance of the CMB results. Kenski et al. (1992) actually stated,

> "One of the model's useful aspects is that the coefficients have an actual physical meaning. Although one can examine the statistical properties of the model, it is not clear whether these can be similarly interpreted in a physical sense."

While agreeing that physical interpretation of CMB results is an essential "reality check," we do not agree that difficulty in physically interpreting established statistical measures such as r-squared, chi-squared or t-tests is reason for ignoring the important model performance information that they convey. There is currently little information on what statistical performance should be expected or required in CMB analyses for organic gases, and so long as the issue is ignored no guidance will emerge. Guidance is available for other CMB applications (e.g., Pace and Watson, 1987) and would seem to be a relevant starting point. The following basic guidance is from Pace and Watson (1987) which contains much more detailed information:

- percent mass accounted for 80 to 120 percent

- r-squared at least 0.8, chi-squared less than 4

- t-statistic greater than 2 for each source profile

Many of the studies reviewed here rely on the use of other physical evidence to support the CMB results, such as comparisons between CMB results and emission inventories, or between CMB and trajectory analyses. However, the statistics are important for assessing the uncertainties in the computed results. One of the particular strengths of the CMB model is its ability to positively identify the presence of source types. In these studies the model is further used to quantify the contributions to ambient concentrations, but without examination of the regression statistics, the significance of the identifications are in doubt and the uncertainties of the computed source type contributions are unknown, and possibly large.

The ability of CMB to identify the presence of sources of a particular type may be important in some applications, but in the case of CMB analyses for organic gases, the few source types generally used in the CMB analysis are usually known to exist in the region of interest. Therefore, it is not a particularly useful result to identify that motor vehicles, for example, contribute a non-zero amount to the ambient air at a particular receptor. The objective of the CMB modeling was to determine with reasonably small uncertainty the absolute amount of that contribution. For many of the studies reviewed,

the quantification of the source contributions cannot be supported with any statistical significance without additional information from the CMB results.

Reactivity

For CMB analysis of organic gases atmospheric reactivity (i.e., different lifetimes for different species) is potentially a major difficulty. All the applications of the CMB model reviewed here recognized this difficulty, but the approaches to dealing with the issue ranged from almost an overreaction to the use of interesting and clever techniques to cope with this limitation. Nelson and Quigley (1983) used source profiles with a large number of species and tested the impact of including or excluding the most reactive species. Surprisingly Nelson and Quigley found that reactivity was not a very severe limitation if a large number of species were used. Yet several recent users of the CMB model have severely reduced the number of species in their profiles so that only the very lowest in reactivity remain. Generally, the capabilities of CMB are likely to be enhanced as the number of species employed is increased. Hence, Nelson and Quigley's approach of using sensitivity tests to determine the optimum number of species seems sensible. Presumably, the optimum number would strike a balance between the problems associated with including species that are too reactive and reduced accuracy from having too few species.

Although not specifically reviewed as part of this project, Li and Kamens (1993) presented some good discussions of the CMB model and an interesting approach to coping with reactive species in particulate analyses. Li and Kamens used a normalization approach based on species ratios to address the reactivity problem. They found several pairs of species within each source profile that maintain stable ratios unique to that source profiles even though individually the species have high reactivity. Hence, profiles of species pair ratios were used instead of actual species profiles.

Receptor Location Biases

If the intent of a receptor modeling study is to characterize urban emission inventories, receptors must be located so that they are impacted by air masses containing a representative sample of the emission inventory. For instance, receptors located near roadways should be expected to show high mobile source contributions. Kenski et al. (1993) analyzed 6-9 a.m. samples for two surface sites in Chicago and from the top of the Sears tower. The vehicle contribution for the Sears tower was half (21 percent) that determined for the surface sites (45 and 48 percent). Similarly, Wadden et al. (1986) analyzed samples collected aloft throughout the day between 300 and 1500 m above Tokyo and found an average vehicle contribution (vehicles plus gasoline vapor) of only 18 percent. Just as the surface samples for Chicago may be biased toward a high motor vehicle contribution relative to the area-wide emission inventory, the loft samples may be biased low. In particular, the Sears tower samples were probably collected above the mixed layer and were therefore decoupled from local emissions. Samples collected aloft, but still within the mixed layer, later in the day when vertical mixing is stronger may be influenced more evenly by emissions from a large area, and thus be more representative of the emission inventory. This approach may lead to problems in coping with reactivity

but, as discussed elsewhere, maybe the problem of reactivity is tractable provided that a large number of species are included in the CMB analysis.

Definitions of Total Organic Gases

The receptor modeling studies reviewed all express source contributions as a relative contribution to some "total organic gas" burden in the atmosphere. However, the definitions of the total vary significantly between studies with the major difference being between "totals of CMB fitting compounds" and totals for all "non-methane organic compounds." There are many acronyms for the "total of non-methane organic compounds" (e.g., NMOC, TNMOC, NMHC, VOC, NMOG, ROG) but any differences in definitions are probably small in this context: the essential point is that all (most) organic gases other than methane are included. In contrast, a CMB study may typically use only about 20 fitting compounds so that "total fitting compounds" is substantially smaller than total NMOC. Since the ratio of total fitting compounds to NMOC can vary widely between source, relative source "contributions to total fitting compounds" is hard to relate to "contribution to NMOC." Since emission inventories are also generally based on NMOC, this difficulty extends to comparisons with inventories. Some studies approach this difficulty by explicitly or implicitly using a ratio of total fitting compounds to NMOC for each source profile, but this extrapolation relies on the assumption that the ratios are valid for the particular study, which is frequently untested. This difficulty is a strong argument for including as many compounds as possible, and especially compounds with high ambient concentrations or high contributions to source profiles, in all CMB analyses. The statistical significance discussion above should also be considered in the context of individual fitting components.

Applicability of CMB to Organic Gases

As discussed above, reliable application of the CMB model to ambient measurements of organic gases requires careful attention to issues such as source profiles, model performance and reactivity. However, some questions remain about the ability of CMB to characterize organic gas emissions for an urban area. Basically, the issue not yet discussed is temporal and spatial variability of source emissions. Considering just total NMOCs, such variability produces changing source contributions at a given receptor, and source contributions which depend on receptor location. This part of the problem can be addressed by careful study design, data analysis and data interpretation. But if the chemical profiles of sources impacting the receptor vary significantly, the CMB analysis becomes unreliable.

Mobile source emissions are likely the most ubiquitous and best suited source for CMB modeling because they come from a large number of widely distributed sources. But even for mobile sources some care is needed to allow for local (receptor specific) influences from mobile source emission subcategories with different source profiles, e.g., start or hot soak emissions from parking areas, or refueling emissions from filling stations. However, spatial and temporal variability in emissions from major non-mobile sources may lead to much greater difficulties that have not always been addressed adequately. Nelson and Quigley (1983), for example, found that solvent use profiles in

Sydney were too spatially diverse to accurately be used with the CMB approach. In other words, a profile for solvent use that is representative on average may not be appropriate for individual samples because the receptors are impacted by a limited number of sources that do not have the average composition. This problem may be most severe for large individual sources such as refineries. Doskey et al. (1992) measured NMOC composition downwind of a refinery on six occasions and found that profiles were highly variable, a result which they report is consistent with previous studies. Doskey et al. developed an average refinery profile, but it seems unlikely that this will be applicable to individual ambient samples which may contain emissions from only a single refinery emitted over a narrow time span.

If the source profiles for sources making significant contributions to individual ambient samples are poorly characterized (e.g., for solvents and refineries), the CMB analysis may be very inaccurate. This is a direct consequence of assumption 3 discussed above. The inaccuracy likely applies to all the sources, not only those that are poorly characterized, because the CMB model attempts to reconcile the ambient sample with the specified source profiles.

Results from Multiple Studies of a Single City

Bearing in mind the limitations discussed above, we compared results obtained by different researchers for the same city, in some cases using the same ambient database.

<u>Atlanta</u>

Receptor modeling for Atlanta was performed by Kenski et al. (1992) and Lewis et al. (1993). In addition, Baugues (1986) estimated the motor vehicle contribution in Atlanta using acetylene as a tracer. The Kenski et al. study utilized 6-9 a.m. data from two locations and the years 1984 to 1987, whereas the Lewis et al. study utilized data collected each hour of the day at a single site in 1990. Kenski et al. allocated 53 percent of NMOC to vehicles, using a profile that only included exhaust. Lewis et al. allocated 50 percent of NMOC (daily average) to a roadway profile that presumably includes running losses in addition to exhaust. For the 6-9 a.m. period, Figure 1 from Lewis et al. shows that the roadway profile accounted for about 57 percent of NMOC. These two results appear quite consistent. Baugues reported a higher 6-9 a.m. motor vehicle contribution for Atlanta (68 percent for 1984) but his method tends to produce an upper bound.

Lewis et al. used a profile for whole gasoline (complete evaporation) in addition to a profile for gasoline vapor. The whole gasoline profile accounted for 10 percent of NMOC, whereas the gasoline vapor profile accounted for 4 percent. Kenski et al. did not use a whole gasoline profile. They found that 16 percent of NMOC was allocated to their gasoline vapor profile. Profiles for whole gasoline and gasoline vapor are sufficiently different that Kenski et al.'s calculated gasoline vapor contribution is not likely to contain much whole gasoline. Instead, the large contribution of gasoline vapor in the Kenski et al. study may be due to the fact that fuel volatility was much higher in 1984-87 than in 1990.

Lewis et al. found a total daily average vehicle-related contribution of 63 percent, assuming all whole gasoline and gasoline vapor was vehicle-related. The results of Kenski et al. lead to a total 6-9 a.m. contribution of 69 percent assuming all gasoline vapor was vehicle-related (although the authors did not ascribe the gasoline vapor to mobile sources). The inventory for Fulton County used by Lewis et al. in their comparison shows 56 percent of NMOC due to onroad vehicles. The onroad vehicle NMOC emissions in that inventory were calculated with MOBILE4.1 and would be 25-30 percent higher with MOBILE5a (i.e., 70-73 percent instead of 56 percent). In addition, the CMB vehicle category includes emissions from nonroad mobile sources and may include stationary combustion of petroleum-based fuels. Since inventory estimates of these contributions were not provided, a direct comparison cannot be made. However, the CMB technique does not appear to show that motor vehicle emissions are underestimated in Atlanta.

Kenski et al. found a large contribution to NMOC (9 percent) from architectural coatings/graphic arts. Lewis et al. identified a similar profile which they called "toluene-rich," but found that it had a negligible contribution to NMOC (probably less than 2 percent). Kenski et al. compared their architectural coatings/graphic arts contribution to the contribution of these sources in the NEDS inventory. They found good agreement, with the inventory assigning 7.7 percent of NMOC to these sources, and the CMB assigning 8.6 percent. The fact that Lewis et al. did not find a similar contribution may reflect differences in site locations between the two studies.

Essentially, this discrepancy between the two studies means that all toluene was accounted for by the three vehicle-related profiles in the Lewis et al. analysis, but that there was "excess" toluene in the Kenski et al. analysis that was not accounted for by the two vehicle/gasoline-related profiles. This may be due in part to Lewis et al.'s use of a whole gasoline profile, since gasoline contains a large fraction of toluene. The surface coating/graphic arts emissions may be buried in the whole gasoline contribution in the Lewis et al. study. Alternatively, toluene emissions related to gasoline may be misidentified as architectural coating/graphic arts emissions in the Kenski et al. study.

Another aspect of this issue is that the reliance of Kenski et al. on toluene as a tracer for architectural coatings/graphic arts may be incorrect. According to Harley et al. (1992), the profile used by Kenski et al. for architectural coatings contained too much toluene and too little xylene. Our review of the SPECIATE database confirmed that the profile labeled as a composite for surface coating (and used by Kenski et al.) was not computed correctly, and that if it were, the toluene fraction would decrease and the xylene fraction would increase. Lewis et al. did find that a "xylene-rich" profile accounted for about 3 percent of NMOC, but that profile contained no toluene at all.

Lewis et al. found a biogenic contribution of 2.4 percent (lower bound), peaking at 6 percent in the late afternoon. The 6-9 a.m. biogenic contribution was about 1 percent. Kenski et al. did not include a profile for biogenics in their CMB analysis. Baugues reported that isoprene accounted for 1 percent of 6-9 a.m. NMHC in Atlanta. Although the inventory shows a much greater biogenic contribution to NMOC (17 percent for Fulton County), it is difficult to compare a contribution derived from a point measurement to a county-level inventory, since spatial variations in isoprene are likely to be large.

Chicago

Several receptor modeling analyses have been conducted by Scheff and co-workers at the University of Illinois at Chicago (UIC) for Chicago (O'Shea and Scheff, 1988; Aronian et al., 1989; Scheff and Wadden, 1993; Kenski et al., 1993). In addition, the toxics receptor modeling study by Sweet and Vermette (1992) included Chicago. The early O'Shea and Scheff study found a vehicle exhaust contribution of 61 percent of a set of 9 VOC constituents. The Aronian et al. study, conducted during the winter, reported a vehicle exhaust contribution of 35 percent of the sum of 23 VOC (including five chlorinated solvents). The Scheff and Wadden study reported two sets of results, obtained from two different ambient databases. In one case, referred to as the UIC study, vehicle exhaust accounted for 34 percent of NMOC (average of three sites); in the other case, referred to as the USEPA study, vehicle exhaust accounted for 39 percent of NMOC (average of two sites). The Kenski et al. study also presented results from the same USEPA study, but reported a slightly different vehicle exhaust contribution to NMOC of 41 percent.

Interestingly, vehicle contributions of 45 to 48 percent were found at two Chicago surface sites, but only 21 percent at the top of the Sears Tower, which was presumably above the mixed layer during the 6-9 a.m. sampling time. This finding was not emphasized by Kenski et al., but has interesting implications regarding the importance of site location on source attribution.

The fact that each of the early studies used a different basis for reporting VOC means that comparisons cannot easily be drawn between them and the later studies. Scheff and Wadden compared their CMB results to a 1986 Illinois inventory. They found excellent agreement between the inventory and the UIC study CMB results for vehicle exhaust (both 34 percent of NMOC). The USEPA study CMB results showed a somewhat greater vehicle contribution of 39 percent. However, as discussed in the reviews of these studies, this apparent good agreement needs further substantiation to be convincing. The CMB results for vehicles in these studies do not include non-exhaust emissions. The authors stated that the inventory was adjusted to be consistent with the CMB categories, but they did not provide any details of how this was done. Unanswered questions are where the nonexhaust vehicle emissions ended up in both the CMB apportionment and the inventory, whether nonroad emissions were included in the inventory "vehicle" category, and what source types were included in the inventory "gasoline vapor" category. In addition, the inventories were not adjusted to match the time periods used in the CMB analysis (8 a.m. to noon in the UIC study and 6-9 a.m. in the USEPA study).

Sweet and Vermette did not apportion total NMOC, focusing instead on 13 toxics. There is no easy way to compare their overall results to those of the UIC group. One interesting difference between the studies is that Sweet and Vermette found no measurable refinery contribution at their Chicago site. This is in direct contrast to the UIC studies, all of which found refinery contributions of 10 percent or more. Sweet and Vermette used the same refinery profiles as the UIC group. Sweet and Vermette used a smaller set of fitting species, but did include propane and other refinery tracers, so it is

not obvious that the smaller number of species would account for the discrepancy. Differences in site locations may also be a factor.

Scheff and co-workers used their CMB results for refineries to conclude that refinery emissions are underestimated by as much as a factor of five in emission inventories. Thus, it is significant that the Sweet and Vermette study failed to confirm this finding. As discussed in the review of Kenski et al. (1993), the UIC group's large refinery contributions may be primarily a result of the model's attempt to fit observed ambient levels of propane. The UIC group does not use a natural gas/fuel gas type of profile such as those used by Nelson et al. (1983), Harley et al. (1992), Lewis et al. (1993), and Mukund et al. (1994). Thus, their refinery profile is the only profile that contains large amounts of propane. The Nelson et al. study was the only study to consider both natural gas and refinery as sources of propane. That study found that natural gas accounted for 27 percent of observed propane in Sydney and vehicle-related sources accounted for 9 percent. They assumed that the remaining propane was due to the refinery.

There may be evidence in some of the studies reviewed that propane is a tracer for refinery emissions. For instance, Lonneman et al. and Gertler et al. presented SCAQS data for Los Angeles that show a large concentration of propane in Long Beach (near the refineries) in the morning. Propane concentrations in Claremont (downwind suburban) are low in the morning but peak in the afternoon. It is not obvious why propane should peak in the morning at Long Beach and in the afternoon at Claremont if the source is leakage from natural gas or LPG usage. For the episodic conditions of the SCAQS study, Claremont is generally downwind of Long Beach such that a buildup of propane overnight from the refineries near Long Beach could impact Claremont later in the day.

Another finding of Sweet and Vermette was that surface coating/graphic arts was not identified as a major contributor to aromatic levels on an average day, but did show up during a pollution episode. This is also in contrast with the UIC results, and illustrates the possible problems with application of CMB for sources that are highly variable in space and/or time.

Los Angeles

Receptor modeling of the Los Angeles area was performed by Harley et al. (1992) and Gertler et al. (1993). Both used the 1987 SCAQS ambient database, although Harley used eight SCAQS sites and Gertler only two. Both used hourly data from various times of the day. The two studies used different source profiles; Gertler et al. used the profiles from Aronian et al. (1989), whereas Harley et al. selected their profiles from a variety of sources. Harley et al. expressed their source apportionments as fractions of the sum of five sources, rather than fractions of total NMOC. Gertler et al. found a vehicle exhaust contribution of 60 percent of NMOC at Long Beach and 70 percent at Claremont. Harley et al. found lower vehicle exhaust contributions of approximately 30 and 35 percent at the same two sites. However, Harley et al. also found a 30 to 35 percent contribution from whole gasoline at each site. Gertler et al. did not include a whole gasoline profile in their analysis.

Gertler et al. found that the refinery and gasoline vapor (head space) profiles were too similar to be resolved, and reported results as the sum of refinery/gasoline vapor (31 percent at Long Beach, 24 percent at Claremont). Harley et al. did not use a refinery profile in their analysis, and found a much smaller gasoline vapor contribution (approximately 15 percent at Long Beach and 10 percent at Claremont). It is interesting to note that Gertler et al. ascribed much of the refinery/gasoline vapor contribution to mobile sources, despite the fact that the Long Beach site is located near several refineries. Gertler et al. also found that propane accounted for 9 percent of NMOC at Long Beach, in addition to the propane accounted for by the refinery profile. They stated that this excess propane is a combination of refinery emissions and LPG, which has relatively high usage in the Los Angeles area. As discussed above, the data suggest the possibility of a refinery plume, characterized by high propane levels, that is present in Long Beach in the morning and moves downwind to Claremont in the afternoon. However, neither CMB study identified this component.

Gertler et al. used a surface coating profile, but did not find any significant contribution from it at either site. However, they used the same profile as the UIC group, which may not be representative of surface coating emissions (see discussion above, as well as the reviews of the SPECIATE database, Harley et al., and Korc and Chinkin (1993)). Harley et al. did not use a surface coating profile in their CMB analysis, although such a profile is presented in their paper. Their reason for not including it was that toluene was the only component of the profile that was measured in the field study and met their criteria for nonreactivity, and that a single component was not adequate to characterize a profile.

The lack of agreement between these two studies, using the same ambient database and conducted by two organizations with long traditions in receptor modeling, is an indication of the potential uncertainties in the receptor modeling method for VOCs. It is possible that the lack of use of a profile for whole gasoline led Gertler et al. to overpredict the vehicle exhaust contribution, whereas Harley et al.'s lack of a refinery profile may have caused one of the other sources (whole gasoline) to be overestimated.

Gertler et al. did not explicitly compare their results to an emission inventory. They concluded that vehicle-related emissions account for more than 90 percent of ambient concentrations, based on the assumption that most of the refinery/gasoline vapor emissions are motor vehicle-related. This conclusion clearly implies that mobile emissions are underestimated in the inventory. Even if the questionable refinery/gasoline vapor contribution is removed from the vehicle category, the vehicle exhaust contribution of 60 to 70 percent is likely to be higher than the inventory estimate (although the motor vehicle contribution to the inventory was not presented in Gertler et al., a value of 52 percent was given by Fujita et al. (1992) for the same time period).

Harley et al. found that the CMB vehicle exhaust contribution of roughly 35 percent was lower than the inventory estimate, but that the whole gasoline contribution of 35 percent was roughly five times the inventory estimate. There are two possible interpretations of this result. One is that the inventory allocates some emissions to vehicle exhaust that the CMB identified as whole gasoline (i.e., that the inventory has the correct total vehicle emissions, but incorrect speciation). The other possible interpretation is that the

inventory emissions for exhaust equate to the CMB exhaust contribution, and that the whole gasoline emissions identified by the CMB are not present in the inventory (i.e., that additional emissions resembling whole gasoline are missing from the inventory). The authors advocated the latter interpretation. Based only on the information presented in the paper, there is no way to choose between the two interpretations. The author's viewpoint is consistent with an independent body of information obtained during the SCAQS, including the results presented by Fujita et al. and the SCAQS tunnel study results.

The inventory used for comparison by both Harley et al. and Fujita et al. was prepared in 1990 using the CARB mobile emissions model EMFAC7E. It is difficult to compare emissions generated with EMFAC to those generated by the EPA MOBILE models because of fundamental differences between the two models. However, basic exhaust NMOC emission rates are fairly similar in EMFAC7E and MOBILE5a. EMFAC7E gives lower running loss emissions than MOBILE5a, and EMFAC7E does not include resting loss emissions at all. (The more recent CARB model EMFAC7F has higher running loss emissions and does include resting losses). Resting loss emissions would be expected to resemble whole gasoline. The inventory also did not include the higher nonroad emissions that are present in current inventories. Emissions from 2-stroke gasoline nonroad engines are expected to resemble whole gasoline. The inventory also did not include exhaust emissions under off-cycle, enrichment conditions, which might resemble whole gasoline. These emissions are not included in current inventories, but are currently under investigation by EPA and other organizations. The relative importance of these known shortcomings of the inventory as compared to other potential, as yet unidentified, emission sources cannot be assessed at this time.

AMBIENT RATIO STUDIES

Studies of ambient ratios (NMOC/NO_x and CO/NO_x) generally focus on early morning measurements for urban areas because it is anticipated that high emission densities combined with low dilution and chemical loss will cause pollutant ratios in the atmosphere to be closely related to the emission inventory. Ratios of pollutants are expected to be more stable from day to day than absolute concentrations because differences in dilution will tend to compensate between pollutants. The earliest study reviewed here (Baugues, 1986) was performed to obtain NMOC/NO_x ratios needed for ozone modeling with EKMA, but in later studies the objective shifts to direct comparisons with emission inventories.

The 1986 study by Baugues provides a good starting point for a consideration of ambient ratio measurements. This study is based on 6-9 a.m. measurements of NMOC and NO_x for 30 U.S. cities in 1984 and 1985. An important conclusions from the study was that 6-9 a.m. NMOC, NO_x, and NMOC/NO_x ratios are variable from day to day at a given site, and therefore that a single site is probably inadequate to characterize an urban area. If accepted, this conclusion places an important limitation on the later studies by Baugues (1991) and Korc et al. (1993) in which only a single site is available for each urban area.

There is good reason to believe that a single receptor cannot characterize pollutant ratios for a whole urban area because under conditions of slow vertical mixing concentrations at a receptor are likely to be strongly influenced by emissions from a small area upwind of the site (the receptor has a small "footprint"). This difficulty may be addressed by comparing the ambient data to a gridded inventory as recommended by Baugues (1991) and done by both Korc et al. (1993) and Fujita et al. (1992). At first sight this approach seems preferable to making comparisons with an area-wide inventory, but there are potential problems (1) it confounds potential errors in total emissions for source categories with errors in the spatial allocation of emissions; (2) gridded inventories generally have a resolution of 4 to 5 km at best, which may be coarser than the footprint of the receptor; and (3) a finding that the gridded inventory has a different pollutant ratio than the area-wide inventory suggests that the receptor is not representative of the urban area, but conversely, a finding that the gridded and area-wide inventories have similar ratios does not guarantee that the receptor is representative. We note that Fujita et al. included comparisons to gridded inventories in their analysis but based the final conclusions on comparisons with area-wide inventories. Overall, it is not clear that measurements of pollutant ratios at a single site in an urban area are meaningless, but it seems likely that measurements for multiple sites in an area are potentially much more reliable.

Among the studies reviewed here, those by Baugues (1986 and 1991) are based on measurements at a single sites in multiple cities, Lonneman et al. (1989) is based on five sites in the Los Angeles area, Fujita et al. (1992) is based on six to eight sites in the Los Angeles area, and Korc et al. (1993) is based on single sites in Chicago, Gary, and Milwaukee. The study by Lonneman et al. is very brief and is superseded by Fujita et al. (1992). The study by Baugues (1991) compares ambient data reported in Baugues (1986) with emission inventories. Baugues' conclusions are briefly summarized below; however, they are based on emission inventories that are now outdated (MOBILE4 and 1985 NAPAP). The discussion below focuses mainly on the studies by Fujita et al. (1992) for Los Angeles and Korc et al. (1993) for Chicago, which were performed (in part) by the same group, using similar ambient data, and with fairly current emission inventories.

Baugues (1991) found that median summer $NMOC/NO_x$ ratios across 15 U.S. cities in 1985 varied from 6.5 to 48.3. The city-wide emission inventory ratios varied from 4.4 to 36.5 and on average were 23 percent lower than the ambient measurements. The increase in estimated mobile source NMOC emissions between MOBILE4 and MOBILE5a alone would likely eliminate much of this bias; however, there are many other changes between the inventories used by Baugues and current estimates making interpretation of Baugues' results uncertain. The study also includes an investigation of the sensitivity of the emission inventories to alternate estimates for mobile source activity data, point source control rule effectiveness, and biogenic emissions. None of the alternate estimates systematically improved agreement between the ambient and inventory $NMOC/NO_x$ ratios, leading Baugues to conclude that there was no evidence for any systematic bias in the base inventories. Baugues did show that NMOC inventories can be very sensitive to assumptions for point source control rule effectiveness, particularly in areas with large, highly controlled point sources of NMOCs.

Los Angeles

Fujita et al. (1992) analyzed 7-8 a.m. NMOC CO and NO_x data collected during the SCAQS field study conducted in the Los Angeles basin in the summer and fall of 1987. Data were available for up to 9 days at eight sites and in the summer and 6 days at six sites in the fall. Fujita et al. calculated mean $NMOC/NO_x$ and CO/NO_x ratios for each site, and then averaged ratios across sites, separately for the summer and fall data. The overall mean $NMOC/NO_x$ ratio was 8.8 in the summer and 6.9 in the fall, which they concluded was 2 to 2.5 times higher than the relevant inventory ratios. The overall mean CO/NO_x ratio was 20 in the summer and 18.4 in the fall, which they concluded was about 1.5 times higher than the relevant inventory ratios. The mean pollutant ratios by site are quite constant across sites: $NMOC/NO_x$ 8.1 to 9.5 (mean 8.8) summer and 5.6 to 9.5 (mean 6.9) fall; CO/NO_x 17.3 to 23.7 (mean 20) summer and 14.5 to 21.6 (mean 18.4) fall.

For Los Angeles, there is evidence for a discrepancy between the ambient and emission inventory ratios of $NMOC/NO_x$ and CO/NO_x. The analyses by Fujita et al. are for multiple sites, and ambient ratios appear consistent across sites, suggesting that the ambient ratios have been characterized. Even if the uncertainties in the final estimates of the discrepancy in ratios are two to three times greater than Fujita's 1 sigma estimate of 10 percent (see the reviews of Fujita et al., 1992), the differences are sufficiently large that there is still a case for a systematic discrepancy. The inventories used by Fujita et al. (1992) were prepared in 1990 and are now outdated, but it seems unlikely that recent changes to the Los Angeles inventory are sufficient to account for the discrepancies found by Fujita et al. Fujita et al. advocated strongly that the discrepancy between ambient and inventory $NMOC/NO_x$ and CO/NO_x ratios is due to under-estimation of NMOC and CO in the inventories rather than overestimation of NO_x, and advocated almost as strongly that this underestimation is attributable to mobile sources. However, other reasons for the discrepancies are possible and should be considered.

The ambient measurements may not be representative of the emission inventories. The ambient concentrations of NMOC, CO, and NO_x were very high, much higher than any likely background (see objective review of Fujita et al.), strongly suggesting that fresh emissions dominated the samples. But the ambient concentrations measured at the surface might not reflect the emissions if NMOC, CO, and NO_x emissions have different vertical profiles in the atmosphere. As discussed in the skeptical review of Fujita et al., surface NO_x emissions may be mixed higher, on average, than either NMOC or CO because a greater fraction of NO_x emissions come from sources with significant plume rise. This would tend to increase ambient $NMOC/NO_x$ and CO/NO_x ratios measured at the surface.

The NO_x inventory may be overestimated. The estimated 1987 mobile and area source NO_x emissions for Los Angeles have changed between the 1991 and 1994 air quality management plans, suggesting that there are uncertainties in the inventories for NO_x as well as for NMOG and CO.

The discrepancies may not be due to mobile sources. Fujita's conclusion that the discrepancy between ambient and inventory ratios is due to mobile sources is mainly based on the argument that mobile sources dominate the morning samples (see the

objective review of Fujita et al., 1992). If the morning samples really are dominated by mobile source emissions, ideally receptor modeling should be able to confirm this from the ambient NMOC data. However, any such conclusion may be subject to the limitations of receptor modeling for NMOCs discussed above, in particular, mobile source emissions may not be distinguished from other combustion emissions. Harley et al. (1992) performed receptor modeling for the SCAQS NMOC data, but unfortunately they did not give results separately for the morning samples. Overall, Harley et al. found that the vehicle exhaust contribution was about 35 percent and that gasoline vapor was about 10 to 15 percent, to give a mobile source contribution of up to about 50 percent, suggesting that mobile sources may not completely dominate the early morning samples. However, Harley et al. also found a contribution of about 35 percent from sources resembling whole gasoline which they concluded were missing from the emission inventory. An obvious conclusion is that this proposed missing "whole gasoline" component is the cause of the discrepancy between ambient and inventory $NMOC/NO_x$ ratios. This would imply a missing NMOC source that resembles whole gasoline and has early morning emissions comparable in magnitude to the mobile source inventory (hundreds of tons of NMOC per day). At present there is really no explanation for what such a source might be. Alternatively, the "whole gasoline" may be a component of identified emission categories such as motor vehicle exhaust implying a mismatch in speciation profiles between the receptor model and the atmosphere.

Chicago

Korc et al. (1993) analyzed 7-9 a.m. NMOC CO and NO_x data collected during the LMOS field study conducted in the Lake Michigan region in the summer of 1991. Data for one site in three separate cities (Chicago, Gary, and Milwaukee) on 6 days were analyzed, thus the ambient database is far smaller than for the study by Fujita et al. Two analyses of the data were reviewed. In the first, by Korc et al., data with CO, NMOC, and NO_x less than 1000 ppb, 200 ppbC, and 8 ppb, respectively, were excluded as being too close to background, levels eliminating half of the $NMOC/NO_x$ data and essentially all of the CO/NO_x data for Gary and Milwaukee. In the second analysis, by the Lake Michigan Air Directors Consortium (LADCO), all data were included in the analysis but background concentrations of 10-15 ppb of NO_x and 60-80 ppbC of NMOC were subtracted. No background concentrations were estimated or subtracted for CO, but a reasonable value would be 200 ppb or more. These background values are often substantial fractions of the measured NMOC, CO, and NO_x concentrations for Gary and Milwaukee. We feel that only for Chicago are the ambient concentrations sufficiently higher than the estimated background to suggest that local emissions really dominated the ambient concentrations. This conclusion is essentially equivalent to the cut-off approach used by Korc et al.

The $NMOC/NO_x$ ratios for Chicago are quite constant across all six days: five of six samples have ratios in the range 3.9 to 4, and the remaining sample has a ratio of about 6, irrespective of whether a background correction is made. The CO/NO_x ratios are much more variable within the range 10.6 to 18.6. When LADCO compared these ratios to a revised gridded inventory (excluding elevated point sources), the ambient $NMOC/NO_x$ ratios without background correction were 1.4 to 1.0 (mean 1.16) times higher than the inventory. With background correction, the ambient $NMOC/NO_x$ ratios

were 1.4 to 0.9 (mean 1.13) times higher than the inventory. The ambient CO/NO_x ratios without background correction were 1.3 to 0.8 (mean 0.95) times higher than the inventory. CO/NO_x ratios were not determined with a background correction. Given the small ambient database (six samples) these differences should not be considered significant. However, because the database is so small and for a single receptor only, neither can much significance be attached to the good agreement (within about 15 percent for $NMOC/NO_x$ and 5 percent for CO/NO_x) between the mean ambient ratios and the inventory ratios.

Comparison of the Chicago and Los Angeles Studies

It is interesting to compare the results for Los Angeles and Chicago discussed above since they were performed in part by the same group (Sonoma Technology Inc.) using similar ambient data. Within the limitations of the small ambient database for Chicago, the ambient $NMOC/NO_x$ ratio for Chicago in the summer of 1991 (about 4 to 5) is significantly lower than the ratio for Los Angeles in the summer of 1987 (about 9), suggesting a real difference in ambient conditions between the two cities. In contrast, the emission inventory $NMOC/NO_x$ ratios are very similar for both cities, about 4. These data lead directly to the conclusion that the ambient $NMOC/NO_x$ ratio is underestimated by a factor of two for Los Angeles, but correctly estimated for Chicago. Potential explanations for the discrepancy between ambient and inventory $NMOC/NO_x$ ratios in Los Angeles should also be considered against the apparent good agreement for Chicago.

EVIDENCE FOR MISSING EMISSIONS

Of the 13 receptor modeling studies reviewed, 9 reported evidence of source underestimation for one or more source categories or missing sources. Only one (Gertler et al., 1993) reported a motor vehicle exhaust contribution that was much higher than the inventory value. One (Wadden et al., 1986) reported a motor vehicle contribution much lower than the inventory value. Two studies (Kenski et al., 1992, 1993) reported higher gasoline vapor contributions than the inventory values. As discussed in the reviews, there are significant problems with these inventory comparisons that may weaken or even invalidate these conclusions. Three studies (Nelson et al., 1983; Harley et al., 1992; Lewis et al., 1993) identified whole gasoline as a significant NMOC source; Nelson et al. reported that the sum of whole gasoline and gasoline vapor contributions was greater than the inventory value, and Harley et al. reported the whole gasoline was five times the inventory estimate.

Although there is no consistent conclusion of motor vehicle exhaust underprediction in the studies reviewed, there is a consistent result of low gasoline vapor contribution. Modeled gasoline vapor contributions ranged from 4 to 16 percent, and were generally less than half the modeled exhaust contributions. When both whole gasoline and gasoline vapor were included in analyses (Nelson et al., 1983; Harley et al., 1992; Lewis et al., 1993), the gasoline vapor contribution was smaller than the whole gasoline contribution in two of the three studies, and equal in the third study.

Current EPA profiles in the SPECIATE database for motor vehicle evaporative (particularly running loss and diurnal, and to a lesser extent hot soak) emissions resemble profiles for gasoline vapor. MOBILE5a generally produces evaporative emission rates that are at least half the modeled exhaust emissions, and can be greater than the exhaust emissions, depending upon the ambient temperature and fuel volatility. Area sources (vehicle refueling vapor displacement) also contribute to gasoline vapor totals in emission inventories. If accepted, the low gasoline vapor contributions found in the receptor modeling studies appear to suggest two possibilities: either MOBILE5a evaporative emissions are too high relative to exhaust estimates, or actual evaporative emissions resemble whole gasoline to a greater extent than represented in current profiles.

Since significant whole gasoline contributions were found in every study that used a whole gasoline profile, and since current inventories contain little or no emissions that are speciated as whole gasoline, the whole gasoline issue is the most important inventory discrepancy identified by the receptor modeling technique. The extent to which the discrepancy implies that emissions resembling whole gasoline are missing from current inventories is unclear since some portion of the discrepancy may simply be due to inadequacies in existing speciation profiles.

Some insight into the sources of the whole gasoline signature can be obtained by comparing the studies by Harley et al. (1992) and Lewis et al. (1993). Harley et al. used a dynamometer exhaust profile and obtained a very large whole gasoline contribution, whereas Lewis et al. used a "vehicles in motion" profile derived from ambient data (Henry et al., 1994) and obtained a smaller whole gasoline contribution. Lewis et al. suggest that their "vehicles in motion" profile incorporates some whole gasoline emissions that are not included in the dynamometer exhaust profiles used by Harley et al. and others. Our review suggests that "vehicles in motion" profiles, whether derived from tunnel measurements or from ambient data (via the GRACE/SAFER technique described by Henry et al., 1994) are consistently different from dynamometer profiles, and that further investigation of these differences is needed to understand what categories in emission inventories should be compared to receptor modeling estimates for sources resembling whole gasoline.

Receptor modeling studies conducted by UIC researchers reported evidence of underpredicted refinery emissions in Chicago and Detroit but not in Beaumont, Texas. However, this finding was not confirmed by Sweet and Vermette (1992) for Chicago. This conclusion rests upon the choice of profiles used in these studies. Propane appears to have been a key species in the estimation of refinery emissions. The composition of refinery emissions is highly variable and therefore particularly difficult to characterize for receptor modeling purposes. Based upon our review, refinery emissions may be underestimated in inventories, but the receptor modeling results require further confirmation.

Two studies (Gertler et al., 1993, Lewis et al., 1993) reported low or negligible contributions of sources related to surface coatings/solvents. Other studies (Nelson et al., 1983, Kenski et al., 1993) found larger contributions for these source categories in good agreement with inventories. Spatial and temporal variability of source composition

may be difficult to characterize for surface coatings and solvent use, which may be responsible for these varied results.

Only one of the ambient ratio studies, that by Fujita et al. (1992) for Los Angeles, provides evidence for a discrepancy between ambient and inventory $NMOC/NO_x$ and CO/NO_x ratios. This study is discussed in detail both above and in the critical reviews. In brief, the evidence for a discrepancy in ratios is substantial for both $NMOC/NO_x$ and CO/NO_x, but the discrepancies need not necessarily reflect biases in the emission inventory. If biases exist, it is difficult to be certain which pollutants are biased, i.e., whether CO and NMOC are underestimated, NO_x is overestimated, or some combination of both. Thus, while this study is an important piece of evidence to consider, it is difficult to conclude that emissions from any particular source category are underestimated based on the evidence of this study alone. Until the source(s) of the discrepancies in ambient ratios found for Los Angeles are fully understood, it is uncertain what implications they have for other areas.

The study by Goldan et al. (1993) reports that methylbutenol is a biogenically emitted compound not considered in current inventories. Golden et al. quantified its abundance relative to isoprene at a site in the Rocky Mountains near Boulder, Colorado, and thereby estimated that methylbutenol emissions were 1 to 8 times larger than isoprene. The major isoprene emitter at the site was aspen. However, this ratio may not apply to other species such as oak that are high isoprene emitters and make major contributions to biogenic inventories in the Eastern U.S. So far, the identification of methylbutenol at concentrations comparable to isoprene has not been confirmed by other research groups. Thus, the potential impact of this study on biogenic emission inventories remains highly uncertain. In general, biogenic emission estimates remain highly uncertain as indicated by a recent paper (not reviewed here) by Geron, Guenther, and Pierce (1994) stating that emission estimates from the current EPA biogenic emission model may soon be revised upward by factors of three to five.

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APPENDIX 1: EPA WORK ASSIGNMENT

STATEMENT OF WORK

WORK ASSIGNMENT 2-03   EPA Contract 68-C1-0059

A. Issuing Office: Environmental Protection Agency
                                           2565 Plymouth Road
                                             Ann Arbor, Michigan 48105

B. Contractor: ICF Incorporated
                                             9300 Lee Highway
                                               Fairfax, VA 22031-1207

C. Statement of Work: Evaluation of Ambient Species Profiles, Ambient
                                           Versus Modeled NMHC:NOx and CO:NOx Ratios,
                                           and Source-Receptor Analyses

BACKGROUND

Over the last few years, Clean Air Act requirements and new EPA guidance have resulted in increased activity in the area of stationary and mobile source emissions estimation. These developments have led to increased scrutiny of the emissions estimates and the methodologies used to derive them.

This scrutiny has included tunnel studies comparing measured concentrations of pollutants to automobile emissions estimated by the MOBILE and EMFAC emission factor models;[1] city-wide studies comparing ratios of ambient pollutant concentrations to emission inventory ratios; source-receptor analyses aimed at using the different chemical fingerprints of the major source categories to identify the relative proportion of total emissions attributable to these source categories; the initiation of cooperative multi-state regional air quality modeling efforts in the Northeastern (Regional Oxidant Modeling), Lake Michigan (Lake Michigan Air Directors Consortium), and Southeastern (Southern Oxidant Study) regions; and city-specific modeling efforts funded by industry groups examining control policy issues of particular interest to them.

At the same time, improvements have been made to the MOBILE model, particularly the addition of running loss emissions and the use of IM240 test data. Highway motor vehicle emissions of hydrocarbons (HC) and carbon monoxide (CO) have increased on a gram per mile basis by approximately 50 percent. The increase for nitrogen oxide (NOx) emissions is up to 30 percent. Also, while fleet turnover and reductions in fuel volatility have had a downward effect on emission ratios, increases in vehicle miles traveled (VMT) combined with these generally higher emission factors have resulted in a net increase in total emissions from motor vehicles. At the same time, point and area source emission controls have changed little.

These developments have influenced the debate over the mobile source contribution to overall pollution levels. Tunnel studies, comparisons of ambient versus modeled NMHC:NOx and CO:NOx ratios, ambient species profiles, and city-wide source-receptor monitoring analyses are being used as the basis for discussing the accuracy of emission inventory methodologies, specifically as they relate to highway mobile sources. Some of the ambient studies include those done for Los Angeles, Atlanta, and the Lake Michigan area. While the preliminary results from recent tunnel studies seem to indicate a closer agreement with the MOBILE model

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[1]   Tunnel study results shall not be discussed by the contractor in this work assignment. Tunnel studies will be addressed by EPA in a forthcoming "White Paper" on the subject.

than was indicated by the original tunnel study, both ambient versus modeled NMHC:NOx and CO:NOx studies and source-receptor analyses continue to suggest that not all hydrocarbon or CO emissions are accounted for using current emission inventory methodologies. There is some suggestion that this shortfall should be attributed to mobile source emissions.

NATURE OF THE WORK ASSIGNMENT

The aim of this work assignment is a thoughtful evaluation of ambient species profiles, ambient versus modeled NMHC:NOx and CO:NOx ratios, and source-receptor analyses. After careful consideration of all issues involved, the contractor shall determine:

- whether the analyses point to one or more missing sources of NMHC and CO not accounted for under current, accepted emission inventory preparation methodologies; potential sources include mobile, biogenic,[2] and stationary;[3]

- the composition of any identified shortfall (i.e., the relative contributions of various source categories);

- if the evidence indicates that one or more source categories are currently being underestimated and the degree of the underestimate;

- whether the modeled ratios were obtained from inventories prepared for the period compared to the ambient data in accordance with EPA guidance, specifically for mobile sources, including motor vehicle emission factors, VMT, and nonroad guidance;

- methodological shortcomings of the various analyses;

- uncertainties contained in the analyses, including the directional and, if possible, the quantifiable effect these uncertainties may have on the emissions estimates.

Task 1   Work Assignment Methodology

The contractor shall prepare and present to the Work Assignment Manager a methodology that identifies how the contractor will proceed with the work assignment. This methodology shall include a discussion of studies to be examined, issues and ideas that will direct the analysis, presentation of the results of the evaluation, and the expected time-frame for completion of individual tasks and the overall work assignment. The contractor shall not expend effort on Task 3 until the Work Assignment Manager approves this deliverable.

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[2] Estimates of biogenic emission factors have fluctuated significantly over the last several years and may continue to do so into the future.

[3] Stationary sources would be underpredicted if control efficiencies, rule effectiveness, and/or rule penetration are overestimated.

Task 2   Compilation and Brief Summary of Studies

The contractor shall obtain copies of the studies listed below and any other relevant studies of which the contractor is aware.

- "A Chemical Mass Balance for Volatile Organics in Chicago." William J. O'Shea and Peter A. Scheff. JAPCA, Vol. 38, 1988.

- "A Method for Separating Volatile Organic Carbon from 0.1 m^3 of Air to Identify Sources of Ozone Precursors via Isotope (^{14}C) Measurements." G. A. Klouda et al. To be published in the Proceedings of the AWMA/EPA Symposium, "Measurement of Air Toxic and Related Air Pollutants," May 3-7, 1993, Durham, North Carolina.

- "A Receptor Modeling Approach to VOC Emission Inventory Validation in Five U.S. Cities." D. M. Kenski, R. A. Wadden, P. A. Scheff, W. A. Lonneman. Paper No. 93-WP-100.04. Presented at the 86th Annual Meeting of the Air and Waste Management Association, Denver, Colorado, June 1993.

- "An Update of the Emission Inventory and Ambient Concentration Data Comparison in Los Angeles." Bart E. Croes, Hector M. Maldonado, and Randy J. Pasek, California Air Resources Board.

- "Application of the Systems Applications International Mesoscale Model to the Atlanta Area Part IV: Preparation of the UAM-IV and UAM-V Meteorological Input Files." Draft Technical Memorandum prepared by SAI for the Atlanta UAM-IV/UAM-V Comparison Technical Work Group. January 14, 1994.

- "Comparison of Emission Inventory and Ambient Concentration Ratios of CO, NMOG, and NOx in California's South Coast Air Basin." Eric M. Fujita, Bart E. Cross, Charles L. Bennett, Douglas R. Lawson, CARB, and Frederick W. Lurmann and Hilary H. Main, Sonoma Technology, Inc. J. Air Waste Manage. Assoc., Volume 42, No. 3, March 1992.

- "Comparison of Emission Inventory and Ambient Concentration Ratios of NMOC, NOx, and CO in the Lake Michigan Air Quality Region." Marcelo E. Korc, Paul T. Roberts, Lyle R. Chinkin, and Hilary H. Main, Sonoma Technology, Inc. Draft Final Report prepared for the Lake Michigan Air Directors Consortium. October 1993.

- "Emissions of Volatile Organic Compounds from Vegetation and the Implications for Atmospheric Chemistry." F. Fehsenfeld et al. Global Biochem. Cycles. 6:389-430. 1992.

- "Evaluation of the Mass-Balance Approach for Estimating Urban Emissions of NOx and VOC." Noor V. Gillani and Warren H. White, Washington University. Prepared for the Atmospheric Research and Exposure Assessment Lab, U.S. EPA, Research Triangle Park, NC. December 1989.

- "Improvement of the Speciation Profiles Used in the Development of the 1991 LMOS Emission Inventory." Marcelo E. Korc and Lyle R. Chinkin, Sonoma Technology, Inc. Draft Final Report prepared for the Lake Michigan Air Directors Consortium. December 1993.

- "Ozone Production in Urban Plumes Transported Over Water: Photochemical Model and Case Studies in the Northeastern and Midwestern United States." Sanford Sillman, Perry J. Samson, and Jeffrey M. Masters. Journal of Geophysical Research, Vol. 98, No. D7, Pages 12,687-12,699, July 20, 1993.

- "Receptor Modeling of VOCs in Atlanta, Georgia." D.M. Kenski, R.A. Wadden, P.A. Scheff et al. Paper No. 92-104.06 in Proceedings of the 85th Annual Meeting of AWMA, 1992.

- "Receptor Modeling of Volatile Hydrocarbons Measured in the 1990 Atlanta Ozone Precursor Study." Charles W. Lewis, Teri L. Conner, Robert K. Stevens, US EPA, and John F. Collins and Ronald C. Henry, University of Southern California. Paper No. 93-TP-58.04. Presented at the 86th Annual Meeting & Exhibition, Air & Waste Management Association, Denver, Colorado, June 1993.

- "Receptor Modeling of Volatile Organic Compounds. 1. Emission Inventory and Validation." P. A. Scheff, R. A. Wadden. Environ. Sci. Technol. 27:617-625, 1993.

- "Receptor Models." G. E. Gordon. Environ. Sci. Technol. 22:1132-1142, 1988.

- "Receptor Model Technical Series, Volume III (1989 Revision) CMB7 User's Manual." J. G. Watson et al. Report No. EPA 450/4-90-004. U.W. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Trinagle Park, NC, 1990.

- "Respeciation of Organic Gas Emissions and the Detection of Excess Unburned Gasoline in the Atmosphere." Robert A. Harley, Michael P. Hannigan, and Glen R. Cass, California Institute of Technology. Environ. Sci. Technol. 26:2395-2408, 1992.

- "Results of Recent Non-Methane Hydrocarbon Measurements." Keith Baugues, U.S. EPA. For presentation at the 79th Annual Meeting of the Air Pollution Control Association, Minneapolis, MN, June 22-27, 1986.

- "Source Discrimination of Short-Term Hydrocarbon Samples Measured Aloft." R. A. Wadden, I. Uno, S. Wakamatsu. Environ. Sci. Technol. 20:473-483. 1986.

- "Source Fingerprints for Receptor Modeling of Volatile Organics." P.A. Scheff, R.A. Wadden, and B.A. Bates, et al. JAPCA 39 (4) : 469-478 (1989).

- "Source Reconciliation of Ambient Volatile Organic Compounds Measured in the Atlanta 1990 Summer Study: The Mobile Source Component." C. W. Lewis, T. L. Conner. Presented at the Air and Waste Management Association Specialty Conference, Emission Inventory Issues in the 1990's, Durham, North Carolina, September, 1991. VIP-22; pp. 514-523.

- "Speciated Hydrocarbon and NOx Comparisons at SCAQS and Receptor Sites." W.A. Lonneman, R.L. Seila, and W. Ellenson. Paper No. 89-152.5 presented at the AWMA 82nd Annual Meeting, Anaheim, CA, 1989.

- "The Observation of a C_5 Alcohol Emission in a North American Pine Forest." P. D. Goldan et al. Geophys. Res. Lett. 20:1039-1042. 1993.

- " Vehicle-Related Hydrocarbon Source Compositions from Ambient Data: The GRACE/SAFER Method." Ronald C. Henry, Charles W. Lewis, and John F. Collins. July 1993.

- "Volatile Organic Compound (VOC)/Particulate Matter (PM) Speciation Data System, Version 1.4." Office of Air Quality Planning and Standards, Research Triangle Park, NC. EPA Report No. EPA-450/4-91-027, 1991.

The contractor shall provide a brief summary of each study, to include the location of the study, the time-frame for the study, the study's sponsor, the study's methodology and assumptions, the study's basic conclusions, and the weaknesses and strengths of the study. In addition, the contractor shall provide an explanation, in lay person's terms, of the source-receptor analysis method itself, its variations, any methodological limitations or weaknesses, and a brief history of the method.

Task 3   Critical Evaluation of the Studies

The contractor shall critically evaluate the methodologies and conclusions of the studies to determine:

- whether the analyses point to one or more missing sources of NMHC and CO not accounted for under current, accepted emission inventory preparation methodologies; potential sources include mobile, biogenic,[2] and stationary;[3]

- the composition of any identified shortfall (i.e., the relative contributions of various source categories);

- if the evidence indicates that one or more source categories are currently being underestimated and the degree of the underestimate;

- whether the modeled ratios were obtained from inventories prepared for the period compared to the ambient data in accordance with EPA guidance, specifically for mobile sources, including motor vehicle emission factors, VMT, and nonroad guidance;

- methodological shortcomings of the various analyses;

- uncertainties contained in the analyses, including the directional and, if possible, the quantifiable effect these uncertainties may have on the emissions estimates.

The contractor shall evaluate each study from the following two perspectives, even if one of them more accurately represents the contractor's view: 1) A skeptic who wants to support the opinion that the study proves nothing that will have broad implications but who has to admit that the study has proven some points (to be identified by the contractor) and 2) An impartial observer for whom the weight of the evidence leads to a particular conclusion (to be identified by the contractor).

The contractor shall compare each study's assumptions about the split between exhaust and various non-exhaust emissions (i.e., diurnal, hot soak, etc.) and assumptions about speciation with the best currently available data and with other studies. The contractor shall also determine whether any inconsistencies found are likely to affect the conclusions of the studies.

If direct comparisons are made to past versions of the MOBILE model or other EPA guidance, the contractor shall assess and discuss whether more recent changes to the model/guidance would be likely to result in different conclusions.

If the various studies differ from one another in their conclusions, the contractor shall assess and explain possible reasons for the differences.

In its evaluation of the studies, the contractor shall consider the validity and technical merit of the approach used and whether that approach is sufficient to identify and quantify any identified shortfall by source category.

In its evaluation, the contractor shall also consider the following specific issues:

- whether alternative emissions "fingerprinting" methodologies would show the same results;

- the effect of different definitions of VOC on comparisons of measured ambient VOC concentrations to emissions inventory estimates of VOC;

- whether all gasoline vapor emissions [headspace vapor (storage tank evaporation, vehicle diurnal evaporation), whole gasoline emissions (spillage, leakage, vehicle hot-soak emissions), refueling emissions, other evaporative emissions from vehicles, and other vapor losses attributed to gasoline production and/or marketing] are correctly accounted for;

- the extent to which excluding whole gasoline from an analysis may tend to overestimate the vehicle exhaust contribution;

- whether gasoline composition is correctly accounted for, since it affects both exhaust and evaporative emissions speciation (e.g., the concentrations of olefins and aromatics within fuel can vary from one brand to the next within the same area);

- whether emissions from nonroad sources were estimated properly;

- whether biogenic emissions have been appropriately accounted for (estimates of biogenic emissions have varied widely over the last few years) and the effects of not using the most current guidance;

- the extent to which errors in assumptions made about control efficiency, rule penetration, and rule effectiveness may impact stationary source emission inventory estimates;

- whether the effect of temperature is appropriately accounted for;

- whether certain factors may have caused systematic offsets in the ratios (e.g., carryover, transport from regional background areas, and photochemical processing);

- the effect atmospheric transformation may have on relative source apportionment; (See Li and Kamens, Atm. Env., v. 27A, n. 4, pp. 523-532, 1993);

- whether emissions from all source categories were estimated in accordance with EPA's latest guidance so that an under-reporting of emissions from one source does not incorrectly suggest an underestimate of another;

- whether specific compounds are attributed correctly to the appropriate source category and whether all possible sources were considered.

The contractor shall consult the attached memorandum, "Conference Call on LADCO Inventories," for additional areas of inquiry.

D.   Deliverables

All deliverables shall be presented in language appropriate for a non-specialist audience that does not necessarily have a technical understanding of the concepts discussed.

All information obtained under this work assignment shall become the property of EPA and shall be conveyed to the Work Assignment Manager at the conclusion of this work assignment.

1.   The contractor shall submit its methodology detailing how it intends to proceed with the work assignment.

2.   The contractor shall submit a brief summary of the ambient species profiles, ambient versus modeled NMHC:NOx and CO:NOx ratios, and source-receptor analyses evaluated as detailed in Task 2 above.

3.   The contractor shall submit the results of its critical analysis, as detailed in Task 3 above, to the Work Assignment Manager prior to delivery of the draft report; the format for the presentation of these results shall be the format intended to be used for the draft and final reports.

4.   The contractor shall submit to the Work Assignment Manager two copies, including one unbound, reproducible master, and one electronic copy on a 3.5-inch IBM disk of a draft report written in Word Perfect Courier format.

5.   The contractor shall submit to the Work Assignment Manager five copies, including one unbound, reproducible master, and one electronic copy on 3.5-inch IBM disk of the final report written in Word Perfect Courier format.

E.   Task Completion

At least once every two weeks, beginning when the contractor has received approval of the work plan, the contractor shall call the Work Assignment Manager to make an informal progress report. The Work Assignment Manager and the contractor shall set up a routine date and time for these calls.

At the end of each month during which the project is underway, the contractor shall submit a progress report in writing, noting progress made to date, any problems that have been encountered, the solutions to those problems, the amount of funds expended to that point, and the funds that remain.

F.   Schedule

Methodology:	1 week after work plan approval
Task 2 completion and brief summary of the ambient species profiles, ambient versus modeled NMHC:NOx and CO:NOx ratios, and source-receptor analyses evaluated:	5 weeks after work plan approval
Task 3 completion and results of critical analysis:	12 weeks after work plan approval
Draft report:	15 weeks after work plan approval
Final report:	2 weeks after receiving comments from the Work Assignment Manager on the draft report

APPENDIX 2: CHANGES TO THE LIST OF STUDIES IN THE WORK ASSIGNMENT

APPENDIX 2

Appendix 2 briefly describes the six studies that were added to the original list of 25 in the work assignment (Appendix 1), followed by the six studies that were removed.

Studies Added

1.   "Sources of Atmospheric Hydrocarbons in Sydney: A Quantitative Determination Using a Source Reconciliation Technique." P.F. Nelson, S.M. Quigley and M.Y. Smith, *Atmos. Environ.* 17:439-449 (1983). This study is one of the earliest attempts at receptor modeling for VOCs. Although it is somewhat dated and does not apply directly to an American city, it is valuable for several reasons. Because it was one of the first studies of its kind, it may have influenced later researchers. It also addressed sensitivity of model results to uncertainties in a more comprehensive way than many more recent studies. Finally, it represents a viewpoint that is independent of the current debate over this issue in the U.S.

2.   "Toxic Volatile Organic Compounds in Urban Air in Illinois." C.W. Sweet and S.J. Vermette, *Environ. Sci. Technol.* 26:165-173 (1992). This paper focuses on mobile, area, and point source contributions for toxic VOCs. However, many of the compounds considered are also important ozone precursors (e.g. xylenes). This study also provides separate source apportionments for average days and polluted days, and the results are quite different. Finally, this study addressed the Chicago area, and can be compared with other studies conducted for that area.

3.   "Receptor Modeling of SCAQS Volatile Organic Compounds". A.W. Gertler, D.H. Lowenthal, J.C. Chow, and J.G. Watson, in *Southern California Air Quality Study—Data Analysis*, pp. 103-109 (1992). Since much of the debate concerning potential underprediction of mobile emissions has focused on the Los Angeles area, this paper, although very brief, is relevant.

4.   "Wintertime Source Reconciliation of Ambient Organics". P.F. Aronian, P.A. Scheff, and R.A. Wadden, *Atmos. Environ.* 23:911-920 (1989). This paper is interesting, despite the fact that it was conducted for winter, because reactive losses of ambient VOCs may be minimized under winter conditions.

5.   "Composition of Volatile Compound Emissions from Spark Ignition and Diesel Vehicles, Coke Ovens, Wastewater Treatment Plants and Wood Combustion." P.A. Scheff, R.A. Wadden, C.B. Keil, J. Graf-Teterycz, and J-Y. Jeng. AWMA Paper 92-66.02. This paper provides some of the VOC source fingerprints that are used by the authors in other receptor modeling papers.

6. "Source Attribution of Toxic and Other VOCs in Columbus, Ohio." R. Mukund, T.J. Kelly, and C. W. Spicer, Battelle, submitted to *Environmental Science and Technology*, January 1994. This paper discusses motor vehicle, area and point source apportionment for toxic VOCs.

Studies Removed

1. "A Method for Separating Volatile Organic Carbon from 0.1 m^3 of Air to Identify Sources of Ozone Precursors via Isotope (^{14}C) Measurements". This paper describes a new methodology that eventually may be used to distinguish the relative contributions of contemporary carbon (e.g. biogenics) and aged carbon (e.g. fossil fuels) in ambient VOC samples. While this is an interesting approach, the method has not advanced to the point where results are available. Thus, review of this paper would not shed any light on the issue of VOC source contributions.

2. "Application of the Systems Applications International Mesoscale Model to the Atlanta Area Part IV: Preparation of UAM-IV and UAM-V Meteorological Input Files". This memorandum describes only the preparation of UAM meteorological input files. Although plans for this modeling study include model performance evaluations for speciated VOC and NO_x that may ultimately provide valuable information on the accuracy of the emission inventory for Atlanta, these analyses will not be completed in the timescale of this work assignment. Furthermore, because this work is being performed by SAI, it would not be appropriate for us to review it.

3. "Ozone Production in Urban Plumes Transported Over Water: Photochemical Model and Case Studies in the Northeastern and Midwestern United States." This paper focuses on a dispersion modeling approach for use over large bodies of water. It does not address emission inventory validation or ambient/inventory comparisons. Therefore, review of this paper would lead us far afield from the primary issue to be addressed in this work assignment.

4. "Receptor Models". This review article focuses on "traditional" receptor modeling using elemental fingerprints from PM sources, and devotes only a paragraph to the application of receptor modeling techniques to VOCs. Although it is valuable as background material on the general subject of receptor modeling, it contains no conclusions related to source attribution of VOCs.

5. "Receptor Model Technical Series, Volume III (1989 Revision) CMB7 Users Manual." This is a reference manual and will be important to this study as background material, but not as a study to be reviewed.

6. "Emissions of Volatile Organic Compounds from Vegetation and the Implications for Atmospheric Chemistry." This article focuses more on the atmospheric chemistry implications of biogenic emissions than on estimated biogenic emission rates.

APPENDIX 3: OTHER RELEVANT STUDIES

After the list of studies to be reviewed had been finalized (see page 1-1), several new studies became available in published or pre-print form, and other relevant studies were recommended to us for inclusion. We were unable to expand the scope of our review to include them, but they are listed here for completeness.

Conner, T. L., W. A. Lonneman, and R. L. Seila. 1993. "Transportation-related volatile hydrocarbon source profiles measured in Atlanta." Submitted to *J. Air Waste Management Association*.

Conner, T. L., W. A. Lonneman, and R. L. Seila. 1994. "Motor Vehicle Volatile Hydrocarbon Source Profiles for Chemical Mass Balance Receptor Modeling." Presented at the Air and Waste Management Association/U.S. Environmental Protection Agency International Symposium, "Measurement of Toxic and Related Air Pollutants," Durham, North Carolina (May 3-6, 1994).

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.*, 28:1633-1649.

Kenski, D. M., R. A. Wadden, and P. A. Scheff. 1994. "Receptor Model Evaluation for Lake Michigan Ozone Study Measurements for VOC." Presented at the Air and Waste Management Association Meeting, San Diego, California (November 1993).

Wadden, R. A., P. A. Scheff, and I. Uno. 1991. "Receptor Model Allocation of Ozone-Forming Potential to NMOC Sources in Northeast Illinois." Presented at the 84th Annual Meeting of the Air and Waste Management Association, Vancouver, British Columbia (June 1991).

APPENDIX 4: COMMENTS ON THE DRAFT OF THIS REPORT

The draft final version of this report (dated August 1994) was reviewed by several scientists internal and external to the EPA. Our ability to respond to comments was limited by available resources: we incorporated many suggestions but were unable to expand the scope of the report. We thank the reviewers for their helpful comments, and for agreeing to the inclusion of their reviews in the final report.

One set of comments could not be reprinted in the report because there was insufficient time for the reviewer to obtain the necessary clearance.

September 15, 1994

Review of August 1994 Draft Final Report "Evaluation of Ambient Species Profiles, ..., and Source-Receptor Analyses" (SAI)

1.   I paid particular attention to Section 4 (Synthesis of Critical Reviews), which is a new section. It seems to me to be generally well-written and acceptable in content. There are a number of typos which a spell checker will pick up.

2.   Every comment that I passed on in the August 12th teleconference has been acted upon in the new draft.

3.   The changes that were made in the last paragraph on pg. 3-57 and the next page have improved the text. However two more simple changes would improve clarity further. In the last paragraph on pg. 3-57 change "roadway" to "ambient", and change "whole gasoline component than roadways" to "whole gasoline/(exhaust + running losses) ratio than ambient data." That is, the GRACE/SAFER analysis was performed on ambient data collected far from the tunnel and not close to a roadway.

4.   I understood that relevant preprints that were not received in time for review would be noted in the report. Why is the Conner, Lonneman, Seila article on vehicle-related source profiles not mentioned?

5.   My comment about R. Mukund's name being incorrect was not valid. I have just learned that he has recently legally changed his name (from Mukund Ramamurthi)! Sorry.

Charles Lewis
Research Physicist
Source Apportionment Research Branch
AREAL, RTP, NC

Additional Comments from Teri L. Conner, U.S. EPA

SYNTHESIS OF CRITICAL REVIEWS
EVIDENCE FOR MISSING EMISSIONS, 3ᵈ paragraph

The hot soak evaporative emissions most strongly resemble the whole gas profiles rather than gasoline vapor profiles. Also, the motor vehicle refueling should be listed as an evaporative emission resembling gasoline vapor.

Comments on the Draft Final Report 'Evaluation of Ambient Species Profiles, Ambient Versus Modeled NMHC:NOx and CO:NOx Source Receptor Analysis'

Christian E. Lindhjem   September 19, 1994
EPA, Office of Air and Radiation, Office of Mobile Sources

The reviews were helpful in summarizing most of the relative work on VOC source\receptor work to date. The synthesis was a good summary of the chemical mass balance method and its limitations.

I was expecting a little more description of the constructed emission inventories used to compare with the source apportionment model results. Have the differences between the inventory and model results been reconciled with updated inventories?

<u>Biggest Concern</u>

I would like to have seen some more thought given to the question of reactivity and its effect on the source apportionment in the discussion on page 4-4. The discussion was limited and disproportionally brief for the importance of the topic.

It seems to me that the primary reason for the apparent success of receptor modelling in apportionment of particulate emissions has been that elements (i.e. Mn for coal, V for oil and so on) could be used for source and ambient characterization. One major advantage of elemental analysis is the absence of reactivity concerns. With VOC source apportionment, reactivity of the species should be the greatest concern.

To circumvent the problems of VOC reactivity, many if not all of the works/reports used ambient data in the morning. Reaction rates are fairly low giving some confidence that the ambient data might be reflective of the inventory. One problem with morning ambient data is that it is not well mixed horizontally or vertically leading to questions whether certain stationary sources should be included. Another problem is that some significant sources, evaporation and biogenics, are emitted primarily in the afternoon. This begs the question whether the source apportionment method(s) could be used with afternoon ambient data, and that requires some discussion of reactivity and its effect on the results.

I also think that SAI missed the point of the Li and Kamens work. They showed that reactivity can have an effect on the estimated source apportionment in contradiction to the conclusions reached on pages 4-4 and 4-5. The Li and Kamens work was interesting to me because it presented a method for correcting the source profiles for the reactive loss of species in the chemical mass balance model. The use of species ratios was used as a verification of the correction method not as a source apportionment method as SAI suggested. The question raised by the Li and Kamens work is 'could the VOC source profiles be corrected using the Li and Kamens method and an average OH reaction rate?' The method described seems to be able to address the VOC reactivity problems encountered with afternoon ambient data. I would liked to have seen a discussion of the Li and Kamens "normalization" method as it might apply to VOC source apportionment.

<u>Minor Point</u>

The Harley, Hannigan, and Cass 'Respeciation of Organic Gas Emissions.................' study was excluded from the list of source apportionment studies in Table 1 on pages 1-4 and 1-5.

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September 15, 1994

SUBJECT: Comments on SAI Report ("Evaluation of Ambient Species Profiles, Ambient Versus Modeled NMHC:NOx and CO:NOx Ratios, and Source-Receptor Analyses")

FROM: Michael Koerber
           Technical Director

TO: Natalie Doble
           USEPA, OMS

Thank you for the opportunity to review the draft SAI report concerning various approaches to evaluate emission inventories. My comments are as follows:

* This report represents a much-needed consolidation of many very interesting research efforts over the past several years. I commend the contractor for bringing this information together.

  I am curious, however, about the sponsoring office. The role of other appropriate USEPA offices (i.e., SRAB, EIB, MRB) should be clarified.

* The "skeptical" review section is troublesome. Its inclusion indicates a clear reluctance to change existing emission estimates and further implies an unwillingness to even evaluate these estimates. Rather, the report should openly acknowledge the problems/deficiencies with emission inventories and should strongly encourage evaluations. I recommend that only the "critical" review be included in the final report; eliminate the skeptical review.

* A few of the studies are quite dated by today's standards. The report should acknowledge that there are problems due to the age of these studies, and should dwell on what the study has to offer in terms of emissions evaluation methods and suggested areas of necessary emission inventory improvements.

* If time and resources permit, then it would be desirable if the primary authors of each study had a chance to respond to SAI's review. This additional collaboration may better define the relevant study findings.

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* The final section is critical on the use of a single monitoring station in several ambient ratio studies. While more sites are certainly preferable, a single well-sited monitor may be sufficient to characterize the impact of motor vehicles - the largest source category in most cities. This concern has implications on USEPA's PAMS program, which only requires a single source-oriented monitoring station in many cases. If one monitor is not enough, then how many are needed? Further discussion of this point is suggested.

* The section entitled "Evidence for Missing Emissions" seems to dismiss the mounting evidence that emission inventories do require improvement and reflects the status quo philosophy alluded to above. If the inventories are so good, then why is there so much effort within USEPA and other groups (e.g., Auto/Oil) to come up with better numbers? Why not just admit that while emission inventories have gotten better, these studies clearly demonstrate that problems remain which must be fixed. The report would be more valuable if it identified the remaining problems and recommeded ways to correct them.

To this end, the contractor (or USEPA) should, at a minimum, include a set of recommendations concerning:

(a) the major problems with today's emissions inventories;

(b) portions of an emissions inventory most in need of local information, quality assurance, and independent evaluation (e.g., particular source categories, emission factors, activity levels, spatial and temporal allocation factors, and speciation profiles)

(c) preferred methods for evaluating emission estimates;

(d) ambient measurements needed to conduct a credible evaluation; and

(e) role of PAMS data in evaluating emission estimates

Miscellaneous

p.1-1 (second paragraph, first sentence): the ratio comparisons are for ambient v. emissions ratios, not ambient v. modeled ratios

p.1-1 (third paragraph, first sentence) and p.1-3 (last sentence): beside the underestimation of NMOC or CO, the overestimation of NOx should be noted

p.1-5 (Table 1): Two additional studies should be addressed:

(1) D. Kenski receptor modeling study using the 1991 LMOS field data (presented at Nov 1993 San Diego AWMA Conference)

(2) P. Scheff receptor modeling using 1987 data for northeast Illinois which assessed the ozone forming potential of various source categories (presented at June 1991 AWMA Meeting)

p.3-74 (last paragraph): Meteorological data for LMOS episode days are presented in Table 2-1 of the STI report.

p.3-75 (fifth paragraph): Emission inventory changes implemented by LADCO are addressed in a memorandum entitled "Third Round Updates to the LMOS Regional Modeling Inventory" (March 18, 1994).

p.3-77 (first paragraph): Please note that OMS has previously rejected LADCO's concern that the motor vehicle NOx emissions are overestimated with MOBILE5. As such, USEPA has directed us to ignore "potential errors in the NOx inventory".

p.3-77 (second paragraph): An early morning mixing height in a big city like Chicago of 150 - 300 m is not unrealistic. The reference to mixing heights in the California San Joaquin Valley is irrelevant given the obvious differences between this rural area and the Chicago urban area.

p.3-76 and 3-78: The suggestions that there may be spatial or temporal allocation problems in the LMOS inventory which contribute to the difference between the ambient and emissions ratios are not justified. If such claims are made, then the evidence for these problems should be presented.

Comments on Draft Final Report:
Bart Croes, California Air Resources Board
**Evaluation of Ambient Species Profiles,
Ambient Versus Modeled NMHC:NO$_x$ and CO:NO$_x$
Ratios, and Source-Receptor Analyses**

September 19, 1994

The authors are to be congratulated on a thorough, well-written review of a large number of studies touching on the issue of emission shortfall. The objective and skeptical reviews were an interesting contrast. The summary of receptor models (Section 2) was excellent, but the synthesis of reviews (Section 4) just restated the earlier sections with little synthesis and few conclusions. Also, the authors should add recommendations of follow-up work to correct the deficiencies they uncovered in their reviews.

There was not enough time to review the entire report in detail, so I focused my critique on the reviews of the Harley *et al.* (1992) and Fujita *et al.* (1992) studies, the two with which I am most familiar. My comments also carryover to Section 4, particularly pages 4-11 to 4-13.

Harley *et al.* (1992)

Both reviewers missed the point that the source-receptor modeling results, and the conclusions on excess unburned gasoline, are very sensitive to the relative amounts of ethene and acetylene assumed in the engine exhaust profile because of the collinearity in the engine exhaust and whole gasoline profiles for other species. A recent study by Watson, *et al.* ("Particulate and Gaseous Organic Receptor Modeling for the Southern California Air Quality Study, report to ARB on Contract No. A832-132, November 1993), using different source profiles, found much better agreement between the emission inventory estimate and the relative source contributions derived from ambient data.

Paragraph 2 - Discussion of possible sources responsible for the excess unburned gasoline are contained in several places on page 2406.

Objective Review

Paragraph 1 - The hydroxyl radical reactivity increased by 4%.

Paragraph 3 - It is very clear from Table VI that 14 organic fitting species (15 at Glendora) were used in the analysis. Also, it is clear from page 2405 that CO was used as a tracer for vehicle exhaust.

Skeptical Review

Paragraph 2 - A list of 35 references (13-47) is hardly meager supporting documentation. The reviewer should have focused their critique on the profiles used in the source-receptor modeling, where the supporting documentation makes a good case for the revised inventory, rather than "Industrial Surface Coatings and Adhesives". Even for the latter category, it is clear that use of solvents, rather than direct chemical analysis of primers, lacquers, enamels, and adhesives (which include non-volatile materials), is an improvement.

Paragraph 3 - The reviewer makes a good point which can easily be addressed by looking at reactive species during the 6-9 a.m. time period when emissions are high and little photochemistry has taken place.

Paragraph 4 - Does the first sentence imply that unburned gasoline has low reactivity? Also, the subsequent speculation on solvents might be more convincing if it included any data or references.

Paragraph 5 - It is clear from page 2405 that CO was used as a tracer for vehicle exhaust. It is difficult to imagine a situation where photochemically produced CO is significant compared to direct emitted CO at an urban monitoring site.

Fujita *et al.* (1992)

Objective Review

Paragraph 2 - EMFAC7F estimates of NMOG emissions are higher than those of EMFAC7E, but so are NO_x emission estimates. The $NMOG/NO_x$ emission ratio with EMFAC7F only reduces the discrepancy from a factor of 2.5 to 2.0.

Paragraph 4 - Why would pollutant ratios (representing fresh emissions) be affected by meteorology or any other basinwide effect? The ratios should be independent.

Paragraph 5 - Background concentrations of CO are closer to 100 ppb, implying that even for Hawthorne and Long Beach in the summer, a background correction for CO would be less than a 10% effect.

Paragraph 6 - The reviewer missed three other reasons discussed in the paper: 1) the similarity in CO/NO_x and $NMHC/NO_x$ ratios among all the sites (Table II) implies a common, basinwide source (e.g., motor vehicles); 2) the strong correlations between CO, NMHC, NO_x, and benzene (Figure 6 and Table VII); and 3) airshed modeling results (Table VIII).

Paragraph 7 - The 10% estimate of variability in the ambient ratios is reasonable (see comment on Paragraph 4 above).

Skeptical Review

Paragraph 1 - The paper carefully states that the ambient ratios disagree with emission inventory estimates, and discusses four reasons why the error is likely to be in the CO and NMHC emissions. Also, all pollutants are given equal attention.

Paragraph 2 - Examination of Figure 6 reveals that all the fall NO_x data, and most of the summer data, are at least a factor of 8 or more above the minimum detection limit. Also, the implications of any values near the detection limit are considered in the error analysis. None of the participants in the Korc *et al.* (1993) study were significant participants in this study.

Paragraph 3 - None of the other sites have nearby elevated NO_x sources.

Paragraph 4 - Use of any other emission averaging scheme does not affect the conclusions of the paper.

Paragraph 5 - The reason the ambient ratios are constant throughout the day at the source sites is not due to a balance between photochemistry and fumigation of elevated NO_x emissions, as indicated by the constant xylene/benzene ratios in Figure 3 and the distribution of NO_x species in Figure 4. The only explanation is that fresh emissions dominate over photochemistry at these sites, but that photochemistry dominates at the downwind sites.

Paragraphs 6 and 7 - The Harley *et al.* (1992) study addresses these concerns.

Paragraph 8 - The 10% estimate of variability in the ambient ratios is reasonable. Why would pollutant ratios (representing fresh emissions) be affected by meteorology or any other basinwide effect? The ratios should be independent.

Paragraph 9 - From Table II, it is obvious that the measurement errors represent less than a 10% effect.